

CHAPTER 7

THERMODYNAMICS: THE SECOND AND THIRD LAWS

7.2 (a) rate of entropy generation = $\frac{\Delta S_{\text{surroundings}}}{\text{time}} = -\frac{q_{\text{rev}}}{\text{time} \cdot T}$

$$= -\frac{\text{rate of heat generation}}{T} = \frac{-(1.8 \times 10^3 \text{ J} \cdot \text{s}^{-1})}{298 \text{ K}} = -6.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{s}^{-1}$$

(b) $\Delta S_{\text{day}} = (7 \text{ J} \cdot \text{K}^{-1} \cdot \text{s}^{-1})(60 \text{ sec} \cdot \text{min}^{-1})(60 \text{ min} \cdot \text{hr}^{-1})(24 \text{ hr} \cdot \text{day}^{-1})$

$$= 5.2 \times 10^5 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{day}^{-1}$$

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

7.4 (a) $\Delta S = \frac{\Delta H}{T} = \frac{235}{273 \text{ K}} = 0.861 \text{ J} \cdot \text{K}^{-1}$

(b) $\Delta S = \frac{235 \text{ J}}{372 \text{ K}} = 0.632 \text{ J} \cdot \text{K}^{-1}$

(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.

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

substitute

$$dq = nC_p dT :$$

$$dS = \frac{nC_p dT}{T}$$

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

simply plugging in the known quantities. Remember that for an ideal monatomic gas $C_p = \frac{5}{2}R$:

$$\Delta S = (2.92 \text{ mol})\left(\frac{5}{2} \times 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\right) \ln \frac{220.76 \text{ K}}{380.50 \text{ K}} = -33.0 \text{ J} \cdot \text{K}^{-1}$$

(b) A similar analysis using C_v gives $\Delta S = nC_v \ln \frac{T_2}{T_1}$, where C_v for a

monatomic ideal gas is $\frac{3}{2}R$:

$$\Delta S = (2.92 \text{ mol})\left(\frac{3}{2} \times 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\right) \ln \frac{220.76 \text{ K}}{380.50 \text{ K}} = -19.8 \text{ J} \cdot \text{K}^{-1}$$

7.8 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

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

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

but because $P_1V_1 = P_2V_2$, we can also write $\frac{P_1}{P_2} = \frac{V_2}{V_1}$

$$\Delta S = nR \ln \frac{P_1}{P_2}$$

Substituting the known quantities, we obtain

$$\begin{aligned} \Delta S &= (6.32 \text{ mol})(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \ln \frac{6.72 \text{ atm}}{13.44 \text{ atm}} \\ &= -36.4 \text{ J} \cdot \text{K}^{-1} \end{aligned}$$

7.10 In order for this process to occur spontaneously, entropy cannot decrease. However, to get as much work out of the transfer of energy as possible, we do not want to waste energy increasing entropy unnecessarily. Therefore,

the most work will be done when ΔS for the process is infinitesimally greater than zero, just enough to make the process spontaneous. This will ensure as little energy is lost to entropy as possible, but enough energy is lost to make the process spontaneous. The change in entropy due to the extraction of 100 J of energy from the hot energy source is:

$$\Delta S_{hot} = \frac{q}{T} = \frac{-100 \text{ J}}{573 \text{ K}} = -0.1745 \text{ J} \cdot \text{K}^{-1}. \text{ In order for the net change in}$$

entropy to be greater than zero, a slightly greater increase in entropy must be realized at the cold energy sink. The minimum energy needed to affect an offsetting increase in entropy is given by:

$$\Delta S_{cold} = \frac{q}{T} = \frac{q}{293 \text{ K}} = +0.1745 \text{ J} \cdot \text{K}^{-1}$$

$$q = 51 \text{ J}$$

Therefore, of the 100 J extracted from the heat source, slightly more than 51 J must be deposited into the cold energy sink to make the ΔS positive and the transfer spontaneous. Slightly less than 49 J is therefore available to do work.

- 7.12** (a) Using Table 6.2, the entropy for the vaporization of 1.00 mol of water at the boiling point under a constant pressure of 1.00 atm is found by:

$$\Delta S = \frac{q}{T} = \frac{\Delta H}{T} = \frac{40700 \text{ J} \cdot \text{mol}^{-1}}{373.2 \text{ K}} = 109 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

- (b) As in part (a) the molar change in entropy is:

$$\Delta S = \frac{q}{T} = \frac{\Delta H}{T} = \frac{-4600 \text{ J} \cdot \text{mol}^{-1}}{158.7 \text{ K}} = -109 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

the change in entropy for freezing 3.33g of $\text{C}_2\text{H}_5\text{OH}$ is:

$$\left(-109 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\right) \left(\frac{3.33 \text{ g}}{46.069 \text{ g} \cdot \text{mol}^{-1}}\right) = 7.88 \text{ J} \cdot \text{K}^{-1}$$

- 7.14** (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 $\Delta H^{\circ}_{\text{vap}}$ or $\Delta S^{\circ}_{\text{vap}}$, using the enthalpy and entropy differences between the gas and liquid forms at 298 K, will give a good approximation of these quantities but the values will not be exact. For $\text{Br}_2(\text{l}) \longrightarrow \text{Br}_2(\text{g})$, the data in the appendix give

$$\Delta H_{\text{vap}} \cong 30.91 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S_{\text{vap}} \cong 245.46 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - 152.23 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 93.23 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T_{\text{B}} = \frac{30.91 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{93.23 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} = 331.5 \text{ K}$$

(b) The boiling point of bromine is 58.4°C or 332 K.

(c) These numbers are in excellent agreement.

- 7.16** (a) Trouton's rule indicates that the entropy of vaporization for a number of organic liquids is approximately $85 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. From this information we can calculate T_{B} :

$$T_{\text{B}} = \frac{\Delta H^{\circ}_{\text{vap}}}{\Delta S^{\circ}_{\text{vap}}} = \frac{25.76 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{85 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} = 303 \text{ K}. \quad (\text{b) The experimental}$$

boiling point of ethanal, 294 K, agrees reasonably although not perfectly with the calculated value.

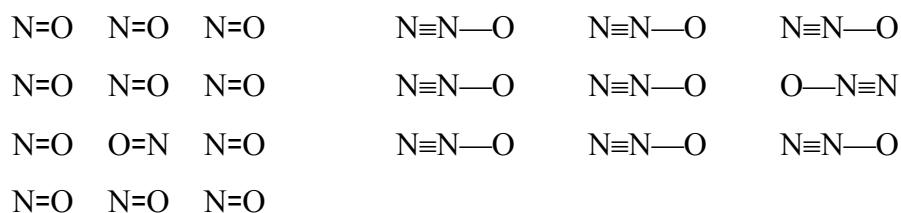
- 7.18** (a) The value can be estimated from:

$$\begin{aligned} \Delta H^{\circ}_{\text{vap}} &= T \Delta S^{\circ}_{\text{vap}} \\ &= (329.4 \text{ K})(85 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \\ &= 28.0 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

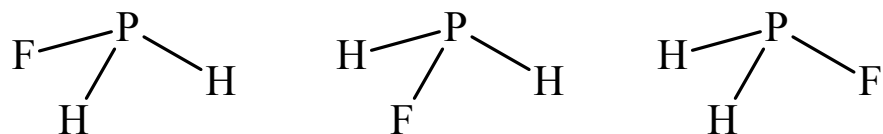
$$(\text{b}) \quad \Delta S^{\circ}_{\text{surr}} = -\frac{\Delta H^{\circ}_{\text{system}}}{T}$$

$$\Delta S_{\text{surr}}^{\circ} = - \left(\frac{10 \text{ g}}{58.08 \text{ g} \cdot \text{mol}^{-1}} \right) \times 85 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -15 \text{ J} \cdot \text{K}^{-1}$$

- 7.20** We would expect NO and N₂O to be the most likely to have a residual entropy at 0 K. This is because the structures are set up so that the O and N atoms, which are of similar size, could be oriented in one of two ways without perturbing the lattice of the solid, as shown below. Because CO₂ and Cl₂ are symmetrical, switching ends of the molecule does not result in increased disorder.



- 7.22** There are three orientations that PH₂F could adopt in the solid state.



The Boltzmann entropy calculation then becomes:

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

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

- 7.24** (a) C₂H₆(g), because it has a greater molecular complexity; (b) KCl(aq) because ions distributed in solution will be arranged more randomly than ions localized in a crystal lattice; (c) Kr(g), because Kr is more massive and has more elementary particles; (d) O₂(g) at 450 K, because of increased molecular randomness (1 mol of O₂ at 1.00 atm pressure will occupy a larger volume at 450 K than at 273 K).
- 7.26** Gases will have a higher entropy than liquids so we expect H₂O(l) to have the lowest molar entropy. The gases will increase in entropy in the order

$\text{Ne(g)} < \text{Ar(g)} < \text{CO}_2\text{(g)}$. Ne and Ar are both atoms so they should have less entropy than a molecular substance, which will have more complexity. Ar will have a higher entropy than Ne because it has a larger mass and more fundamental particles. The final order is $\text{H}_2\text{O(l)} < \text{Ne(g)} < \text{Ar(g)} < \text{CO}_2\text{(g)}$.

- 7.28** Benzene is a rigid molecule in which the carbon and hydrogen atoms are all constrained to lie in a plane. Benzene has some added entropy due to the delocalization of electrons caused by resonance. However, this effect does not outweigh the added flexibility in cyclohexane, in which the C—C bonds can twist and turn. The additional H atoms also add to the molecular complexity, giving more possibilities for bond vibrations.
- 7.30** (a) increases. Generally, entropy increases when a solid is dissolved because the molecules or ions are dispersed in the solvent, giving them more locations over which to arrange themselves. (b) decreases. In this example, twelve moles of reactants form seven moles of products, so we might expect immediately that entropy would decrease; however, we must also consider the states of the various reactants and products. There are six moles of gas on each side of the equation so this might roughly balance; however, we still expect a decrease in entropy for the gases because $\text{CO}_2\text{(g)}$ (a triatomic molecule) is more complex than O_2 (a diatomic molecule). The remainder of the reaction is six moles of liquid going to one mole of solid, which again would predict a decrease in overall entropy. (c) In the evaporation of water, a liquid is converted to a gas, which should be accompanied by an increase in entropy.

- 7.32** The total change in entropy is given by:

$$\Delta S = \Delta S_{\text{Ne}} + \Delta S_{\text{F}_2} = n_{\text{Ne}} \cdot C_{V,\text{Ne}} \cdot \ln \frac{T_2}{T_1} + n_{\text{F}_2} \cdot C_{V,\text{F}_2} \cdot \ln \frac{T_2}{T_1}$$

where the heat capacities of the monatomic gas Ne and diatomic gas F₂ are $3/2 R$ and $5/2 R$, respectively. This equation can be reduced to one unknown by the fact that the sum $n_{\text{Ne}} + n_{\text{F}_2}$ is equal to the total number of moles of gas present, n_{tot} calculated using the ideal gas law:

$$n_{\text{tot}} = \frac{P \cdot V}{R \cdot T} = \frac{3.32 \text{ atm} \cdot 2.5 \text{ L}}{(0.0820574 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \cdot 273.2 \text{ K}} = 0.370 \text{ mol}.$$

Therefore,

$$\begin{aligned} \Delta S &= 0.345 \text{ J} \cdot \text{K}^{-1} = n_{\text{Ne}} \cdot C_{V,\text{Ne}} \cdot \ln \frac{T_2}{T_1} + (0.370 \text{ mol} - n_{\text{Ne}}) \cdot C_{V,\text{F}_2} \cdot \ln \frac{T_2}{T_1} \\ 0.345 \text{ J} \cdot \text{K}^{-1} &= n_{\text{Ne}} \cdot \frac{3}{2} R \cdot \ln \frac{288.15 \text{ K}}{273.15 \text{ K}} \\ &\quad + (0.370 \text{ mol} - n_{\text{Ne}}) \cdot \frac{5}{2} R \cdot \ln \frac{288.15 \text{ K}}{273.15 \text{ K}} \\ 0.345 &= n_{\text{Ne}} \cdot 0.667 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &\quad + (0.370 \text{ mol} - n_{\text{Ne}}) 1.111 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ n_{\text{Ne}} &= 0.150 \text{ mol} \end{aligned}$$

and

$$n_{\text{F}_2} = 0.370 \text{ mol} - 0.15 \text{ mol} = 0.22 \text{ mol}$$

7.34 (a) $\Delta S^\circ_r = S^\circ_m(\text{CS}_2, \text{l}) + 2S^\circ_m(\text{H}_2\text{S}, \text{g})$
 $- [S^\circ_m(\text{CH}_4, \text{g}) + 4S^\circ_m(\text{S(s), rhombic})]$
 $= 151.34 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 2(205.79 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
 $- [186.26 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 4(31.80 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})]$
 $= +249.46 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

The entropy change is positive because there are two more moles of gas in the products than in the reactants. In addition, the molecular structure of the products indicates more disorder.

(b) $\Delta S^\circ_r = S^\circ_m(\text{Ca(OH)}_2, \text{s}) + S^\circ_m(\text{C}_2\text{H}_2, \text{g})$
 $- [S^\circ_m(\text{CaC}_2, \text{s}) + 2S^\circ_m(\text{H}_2\text{O}, \text{l})]$
 $= 83.39 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 200.94 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
 $- [69.96 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 2(69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})]$
 $= 74.55 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

The entropy change is positive because the reaction produces one mole of gas. Originally there were no gases.

(c)

$$\begin{aligned}\Delta S^\circ_r &= 4S^\circ_m(\text{NO}, \text{g}) + 6S^\circ_m(\text{H}_2\text{O}, \text{l}) - [4S^\circ_m(\text{NH}_3, \text{g}) + 5S^\circ_m(\text{O}_2, \text{g})] \\ &= 4(210.76 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + 6(69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\ &\quad - [4(192.45 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + 5(205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -533.00 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

The entropy change is large and negative because the number of moles of gas has decreased by five.

(d)

$$\begin{aligned}\Delta S^\circ_r &= S^\circ_m(\text{CO}(\text{NH}_2)_2, \text{s}) + S^\circ_m(\text{H}_2\text{O}, \text{l}) - [S^\circ_m(\text{CO}_2, \text{g}) + 2S^\circ_m(\text{NH}_3, \text{g})] \\ &= 104.60 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &\quad - [213.74 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 2(192.45 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -424.13 \text{ J} \cdot \text{K}^{-1}\end{aligned}$$

The change in entropy is negative because there are no moles of gas in the products, but there are three moles of gas in the reactants.

- 7.36** The standard molar entropy of a substance at temperature T_i may be found by plotting C_p/T vs. T for that substance and finding the area under the curve from $T = 0$ to $T = T_i$. If at low temperatures $C_p \propto T^3$, the standard molar entropy of the substance is:

$$S(T) = \int_{0 \text{ K}}^T \frac{C_p}{T} dT = \int_{0 \text{ K}}^T \frac{T^3}{T} dT = \frac{1}{3}T^3$$

- 7.38** For $\text{C}_2\text{H}_5\text{O}$, the molar enthalpy of vaporization is found by dividing the amount of energy supplied to cause the phase transition by the number of moles of $\text{C}_2\text{H}_5\text{O}$ that underwent the transition:

$$\Delta H_{\text{vap}} = \frac{(500 \text{ J} \cdot \text{s}^{-1})(4.0 \text{ min})(60 \text{ s} \cdot \text{min}^{-1})}{\left(\frac{400.15 \text{ g} - 271.15 \text{ g}}{46.688 \text{ g} \cdot \text{mol}^{-1}} \right)} = 43 \text{ kJ} \cdot \text{mol}^{-1}$$

The associated change in entropy is then found using:

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{43 \text{ kJ} \cdot \text{mol}^{-1}}{351.5 \text{ K}} = 120 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

For C_4H_{10} the enthalpy and entropy of vaporization are:

$$\Delta H_{\text{vap}} = \frac{(500 \text{ J} \cdot \text{s}^{-1})(4.0 \text{ min})(60 \text{ s} \cdot \text{min}^{-1})}{\left(\frac{398.05 \text{ g} - 74.95 \text{ g}}{58.123 \text{ g} \cdot \text{mol}^{-1}} \right)} = 22 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{22 \text{ kJ} \cdot \text{mol}^{-1}}{273.2 \text{ K}} = 81 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

For CH_4O the enthalpy and entropy of vaporization are:

$$\Delta H_{\text{vap}} = \frac{(500 \text{ J} \cdot \text{s}^{-1})(4.0 \text{ min})(60 \text{ s} \cdot \text{min}^{-1})}{\left(\frac{395.15 \text{ g} - 294.25 \text{ g}}{32.042 \text{ g} \cdot \text{mol}^{-1}} \right)} = 38 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{38 \text{ kJ} \cdot \text{mol}^{-1}}{337.7 \text{ K}} = 110 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

7.40 For this problem we can treat the two different samples of ethanol as different systems, and find the total change in entropy by addition. The change in entropy for both samples of ethanol is found using:

$$\Delta S = C \ln \frac{T_2}{T_1} \text{ so our first job is to determine the final equilibrium}$$

temperature after the two samples mix:

$$\begin{aligned} T_F &= \frac{m_1 \cdot T_1 + m_2 \cdot T_2}{m_1 + m_2} = \frac{250.0 \text{ g} \cdot 329.2 \text{ K} + 150.0 \text{ g} \cdot 295.15 \text{ K}}{250.0 \text{ g} + 150.0 \text{ g}} \\ &= 316.4 \text{ K} \end{aligned}$$

The change in enthalpy for the ethanol initially at 22°C is:

$$\Delta S_{\text{sys}} = (150.0 \text{ g}) \cdot (2.42 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}) \ln \frac{316.4 \text{ K}}{295.2 \text{ K}} = 25.2 \text{ J} \cdot \text{K}^{-1}$$

and the change in enthalpy for the ethanol initially at 56°C is:

$$\Delta S_{\text{sys}} = (250.0 \text{ g}) \cdot (2.42 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}) \ln \frac{316.4 \text{ K}}{329.2 \text{ K}} = -23.9 \text{ J} \cdot \text{K}^{-1}.$$

The total change in entropy is that of the entire system (there is no change in entropy of the surroundings as the vessel isolates the system from the surroundings):

$$\Delta S_{tot} = 25.2 \text{ J} \cdot \text{K}^{-1} - 23.9 \text{ J} \cdot \text{K}^{-1} = +1.3 \text{ J} \cdot \text{K}^{-1}$$

7.42 (a) The change in entropy will be given by

$$\Delta S_{surr} = \frac{-\Delta H_{system}}{T} = \frac{1.00 \text{ mol} \times -5.65 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{195.4 \text{ K}} = -28.9 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta S_{system} = \frac{\Delta H_{system}}{T} = \frac{1.00 \text{ mol} \times 5.65 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{195.4 \text{ K}} = +28.9 \text{ J} \cdot \text{K}^{-1}$$

(b)

$$\Delta S_{surr} = \frac{-\Delta H_{system}}{T} = \frac{-(1.00 \text{ mol} \times -3.16 \times 10^3 \text{ J} \cdot \text{mol}^{-1})}{175.2 \text{ K}} = +18.0 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta S_{system} = \frac{\Delta H_{system}}{T} = \frac{1.00 \text{ mol} \times -3.16 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{175.2 \text{ K}} = -18.0 \text{ J} \cdot \text{K}^{-1}$$

(c)

$$\Delta S_{surr} = \frac{-\Delta H_{system}}{T} = \frac{-(1.00 \text{ mol} \times 40.7 \times 10^3 \text{ J} \cdot \text{mol}^{-1})}{373.2 \text{ K}} = -109 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta S_{system} = \frac{\Delta H_{system}}{T} = \frac{1.00 \text{ mol} \times 40.7 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{373.2 \text{ K}} = +109 \text{ J} \cdot \text{K}^{-1}$$

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

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

we need the value of n , which is obtained by use of the ideal gas law:
 $(0.6789 \text{ atm})(12.62 \text{ L}) = n(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(412 \text{ K})$; $n = 0.253 \text{ mol}$.

$$\Delta S = (0.253 \text{ mol})(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln \frac{19.44 \text{ L}}{12.62 \text{ L}} = +0.909 \text{ J} \cdot \text{K}^{-1}.$$

Because the process is reversible,

$\Delta S_{\text{tot}} = 0$, so $\Delta S_{\text{surr}} = -\Delta S = -0.909 \text{ J} \cdot \text{K}^{-1}$. (b) For the irreversible process, ΔS also $= +0.909 \text{ J} \cdot \text{K}^{-1}$. 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 $\Delta S_{\text{tot}} = +0.909 \text{ J} \cdot \text{K}^{-1}$.

7.46 Under constant temperature and pressure conditions, it is the sign of ΔG_r that determines whether or not a process is spontaneous. If $\Delta G_r < 0$, (ΔG_r is negative); the process is spontaneous. ΔG_r is related by the equation $\Delta G_r = \Delta H_r - T\Delta S_r$ to the enthalpy and entropy changes in a reaction. If a reaction is endothermic (ΔH_r is positive), then the reaction will be spontaneous only if $-T\Delta S_r$ is larger than ΔH_r . So, effectively, a reaction that is endothermic can be spontaneous only if the entropy change in the system outweighs the enthalpy change's effect on the entropy of the surroundings.

7.48 (a)

$$\begin{aligned}\Delta H_r^\circ &= -2279.7 \text{ kJ} \cdot \text{mol}^{-1} - [-771.36 \text{ kJ} \cdot \text{mol}^{-1} + 5(-285.83 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -79.19 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

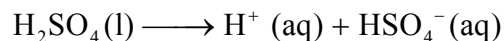
$$\begin{aligned}\Delta S_r^\circ &= 300.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [109 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 5(69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -158 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G_r^\circ &= -1879.7 \text{ kJ} \cdot \text{mol}^{-1} - [-661.8 \text{ kJ} \cdot \text{mol}^{-1} + 5(-237.13 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -32.3 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

ΔG_r° may also be calculated from ΔH_r° and ΔS_r° (the numbers calculated differ slightly from the two methods due to rounding differences):

$$\begin{aligned}
\Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r \\
&= -79.19 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-158 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
&= -32.1 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

(b) The major process occurring upon dissolution of H_2SO_4 in water is



This ionization is complete.

The second ionization occurs to a much smaller extent:



Using the first equation:

$$\begin{aligned}
\Delta H^\circ_r &= -887.34 \text{ kJ} \cdot \text{mol}^{-1} - [-813.99 \text{ kJ} \cdot \text{mol}^{-1}] \\
&= -74.35 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= +131.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - (156.90 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\
&= -25.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
\Delta G^\circ_r &= -755.91 \text{ kJ} \cdot \text{mol}^{-1} - (-690.00 \text{ kJ} \cdot \text{mol}^{-1}) \\
&= -65.91 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

or

$$\begin{aligned}
\Delta G^\circ_r &= -74.35 \text{ kJ} \cdot \text{mol}^{-1} - \frac{(298 \text{ K})(-25.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})}{1000 \text{ J} \cdot \text{kJ}^{-1}} \\
&= -66.87 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

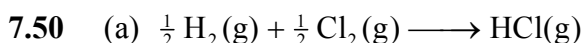
(c)

$$\begin{aligned}
\Delta H^\circ_r &= -986.09 \text{ kJ} \cdot \text{mol}^{-1} - [(-635.09 \text{ kJ} \cdot \text{mol}^{-1}) + (-285.83 \text{ kJ} \cdot \text{mol}^{-1})] \\
&= -65.17 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= 83.39 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [39.75 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\
&= -26.27 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
\Delta G^\circ_r &= -898.49 \text{ kJ} \cdot \text{mol}^{-1} - [(-604.03 \text{ kJ} \cdot \text{mol}^{-1}) + (-237.13 \text{ kJ} \cdot \text{mol}^{-1})] \\
&= -57.33 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

or

$$\begin{aligned}
\Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r \\
&= -65.17 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-26.27 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
&= -57.34 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

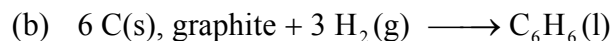
(d) In order to rank the ability of these compounds to remove water, we can examine the free energies for the reactions involved. The one with the greatest driving force (most negative ΔG°_r) is the hydration of calcium oxide, followed closely by that of sulfuric acid, with the hydration of copper sulfate falling somewhat further behind. In practice, both sulfuric acid and calcium oxide are used as water-scavenging agents; copper sulfate is ineffective.



$$\Delta H^\circ_r = \Delta H^\circ_f(\text{HCl}, \text{g}) = -92.31 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\begin{aligned} \Delta S^\circ_r &= S^\circ_m(\text{HCl}, \text{g}) - \left[\frac{1}{2} S^\circ_m(\text{H}_2, \text{g}) + \frac{1}{2} S^\circ_m(\text{Cl}_2, \text{g}) \right] \\ &= 186.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - \left[\frac{1}{2} (130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \right. \\ &\quad \left. + \frac{1}{2} (223.07 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \right] \\ &= 10.04 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ_r &= -92.31 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(10.04 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) / (1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= -95 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

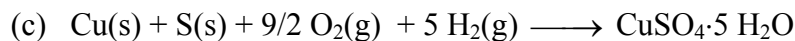


$$\Delta H^\circ_r = \Delta H^\circ_f(\text{C}_6\text{H}_6, \text{l}) = 49.0 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\begin{aligned} \Delta S^\circ_r &= S^\circ_m(\text{C}_6\text{H}_6, \text{l}) - [6S^\circ_m(\text{C}, \text{s}) + 3S^\circ_m(\text{H}_2, \text{g})] \\ &= 173.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [6(5.740 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\ &\quad + 3(130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -253.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

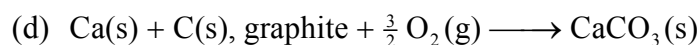
$$\begin{aligned} \Delta G^\circ_r &= 49.0 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-253.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) / (1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= 124.5 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$S^\circ_m(\text{C}_6\text{H}_6, \text{l}) = 173.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$



$$\begin{aligned}
\Delta H^\circ_r &= \Delta H^\circ_f (\text{Cu}_6\text{SO}_4 \cdot 5 \text{H}_2\text{O}, \text{s}) = -2279.7 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= S^\circ_m (\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}, \text{s}) - [S^\circ_m (\text{Cu}, \text{s}) + S^\circ_m (\text{S}, \text{s}) \\
&\quad + \frac{9}{2} S^\circ_m (\text{O}_2, \text{g}) + 5 S^\circ_m (\text{H}_2, \text{g})] \\
&= 300.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [(33.15 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\
&\quad + (31.80 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + \frac{9}{2} (205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\
&\quad + 5 (130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\
&= -1341.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
\Delta G^\circ_r &= -2279.7 \text{ kJ} \cdot \text{mol}^{-1} \\
&\quad - (298 \text{ K})(-1341.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
&= -1880.0 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

$$S^\circ_m (\text{C}_2\text{H}_5\text{OH}, \text{l}) = 160.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$



$$\begin{aligned}
\Delta H^\circ_r &= \Delta H^\circ_f (\text{CaCO}_3, \text{s}) = -1206.9 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= S^\circ_m (\text{CaCO}_3, \text{s}) - [S^\circ_m (\text{Ca}(\text{s}) + S^\circ_m (\text{C}, \text{s}) + \frac{3}{2} S^\circ_m (\text{O}_2, \text{g})] \\
&= 92.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [41.42 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 5.740 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
&\quad + \frac{3}{2} (205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\
&= -262.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
\Delta G^\circ_r &= -1206.9 \text{ kJ} \cdot \text{mol}^{-1} \\
&\quad - (298 \text{ K})(-262.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
&= -1.1288 \times 10^3 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

$$S^\circ_m (\text{CaCO}_3, \text{s}) = 92.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The ΔS°_f value is negative because of the reduction of the number of moles of gas during the reaction. For all of these, the important point to gain is that the S°_m value of a compound is not the same as the ΔS°_f for the formation of that compound. ΔS°_f is often negative because one is bringing together a number of elements to form that compound.

7.52 Use the relationship $\Delta G^\circ_r = \Sigma \Delta G^\circ_f (\text{products}) - \Sigma \Delta G^\circ_f (\text{reactants})$:

$$\begin{aligned}
 \text{(a)} \quad \Delta G^\circ_r &= 2\Delta G^\circ_f(\text{NH}_3, \text{g}) + \Delta G^\circ_f(\text{HCl}, \text{g}) - [\Delta G^\circ_f(\text{NH}_4\text{Cl}, \text{s})] \\
 &= (-16.45 \text{ kJ} \cdot \text{mol}^{-1}) + (-95.30 \text{ kJ} \cdot \text{mol}^{-1}) - [-202.87 \text{ kJ} \cdot \text{mol}^{-1}] \\
 &= +91.12 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

The reaction is not spontaneous.

$$\begin{aligned}
 \text{(b)} \quad \Delta G^\circ_r &= \Delta G^\circ_f(\text{H}_2\text{O}, \text{l}) - [\Delta G^\circ_f(\text{D}_2\text{O}, \text{l})] \\
 &= (-237.13 \text{ kJ} \cdot \text{mol}^{-1}) - [-243.44 \text{ kJ} \cdot \text{mol}^{-1}] \\
 &= +6.31 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

The reaction is not spontaneous.

$$\begin{aligned}
 \text{(c)} \quad \Delta G^\circ_r &= \Delta G^\circ_f(\text{N}_2\text{O}, \text{g}) + \Delta G^\circ_f(\text{NO}, \text{g}) - [\Delta G^\circ_f(\text{NO}_2, \text{g})] \\
 &= 104.20 \text{ kJ} \cdot \text{mol}^{-1} + 86.55 \text{ kJ} \cdot \text{mol}^{-1} - 51.31 \text{ kJ} \cdot \text{mol}^{-1} \\
 &= +139.44 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

The reaction is not spontaneous.

$$\begin{aligned}
 \text{(d)} \quad \Delta G^\circ_r &= 2\Delta G^\circ_f(\text{CO}_2, \text{g}) + 4\Delta G^\circ_f(\text{H}_2\text{O}, \text{l}) - [2\Delta G^\circ_f(\text{CH}_3\text{OH}, \text{g})] \\
 &= 2(-394.36 \text{ kJ} \cdot \text{mol}^{-1}) + 4(-237.13 \text{ kJ} \cdot \text{mol}^{-1}) \\
 &\quad - [2(-161.96 \text{ kJ} \cdot \text{mol}^{-1})] \\
 &= -1413.32 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

7.54 To answer this question, we examine the standard free energies of formation of the compounds. These values from the Appendix are:

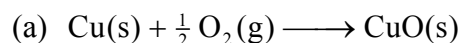
(a) $\text{CuO}(\text{s})$, $-129.7 \text{ kJ} \cdot \text{mol}^{-1}$;

(b) $\text{C}_6\text{H}_{12}(\text{l})$, cyclohexane, $26.7 \text{ kJ} \cdot \text{mol}^{-1}$;

(c) $\text{PCl}_3(\text{g})$, $-267.8 \text{ kJ} \cdot \text{mol}^{-1}$;

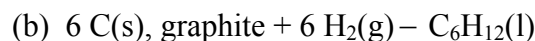
(d) $\text{N}_2\text{H}_4(\text{l})$, $149.34 \text{ kJ} \cdot \text{mol}^{-1}$. Those compounds with a negative free energy of formation are stable, whereas those with a positive free energy of formation are unstable with respect to the elements that compose them. Accordingly, compounds (b) and (d) are thermodynamically unstable, whereas (a) and (c) are thermodynamically stable.

7.56 To understand what happens to ΔG°_r as the 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 ΔS°_r is a negative number. Therefore, we only have to find out whether the standard entropy of formation of the compound is a negative number. This is calculated for each compound as follows:



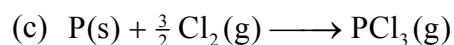
$$\begin{aligned}\Delta S^\circ_r &= S^\circ_m(\text{CuO, s}) - [S^\circ_m(\text{Cu, s}) + \frac{1}{2}S^\circ_m(\text{O}_2, \text{g})] \\ &= 42.63 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [33.15 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &\quad + \frac{1}{2}(205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -93.09 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

The compound is less stable at higher temperatures.



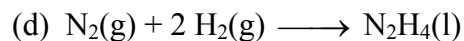
$$\begin{aligned}\Delta S^\circ_r &= S^\circ_m(\text{C}_6\text{H}_{12}, \text{l}) - [6S^\circ_m(\text{C, s}) + 6S^\circ_m(\text{H}_2, \text{g})] \\ &= 204.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [6(5.740 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\ &\quad + 6(130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -614.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

The compound is less stable at higher temperatures.



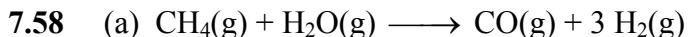
$$\begin{aligned}\Delta S^\circ_r &= S^\circ_m(\text{PCl}_3, \text{g}) - [S^\circ_m(\text{P, s}) + \frac{3}{2}S^\circ_m(\text{Cl}_2, \text{g})] \\ &= 311.78 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [41.09 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &\quad + \frac{3}{2}(223.07 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -63.92 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

The compound is less stable at higher temperatures.



$$\begin{aligned}\Delta S^\circ_r &= S^\circ_m(\text{N}_2\text{H}_4, \text{l}) - [S^\circ_m(\text{N}_2, \text{g}) + 2S^\circ_m(\text{H}_2, \text{g})] \\ &= 121.21 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [191.61 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &\quad + 2(130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -331.76 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

The compound is less stable at higher temperatures.



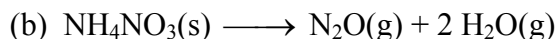
$$\begin{aligned}\Delta S^\circ_r &= S^\circ_m(\text{CO}, \text{g}) + 2S^\circ_m(\text{H}_2, \text{g}) - [S^\circ_m(\text{CH}_4, \text{g}) + S^\circ_m(\text{H}_2\text{O}, \text{g})] \\ &= 197.67 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 3(130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\ &\quad - [186.26 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 188.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\ &= +214.62 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_r &= \Delta H^\circ_f(\text{CO}, \text{g}) - [\Delta H^\circ_f(\text{CH}_4, \text{g}) + \Delta H^\circ_f(\text{H}_2\text{O}, \text{g})] \\ &= (-110.53 \text{ kJ} \cdot \text{mol}^{-1}) - [(-74.81 \text{ kJ} \cdot \text{mol}^{-1}) + (-241.82 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= +206.10 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ_r &= \Delta G^\circ_f(\text{CO}, \text{g}) - [\Delta G^\circ_f(\text{CH}_4, \text{g}) + \Delta G^\circ_f(\text{H}_2\text{O}, \text{g})] \\ &= (-137.17 \text{ kJ} \cdot \text{mol}^{-1}) - [(-50.72 \text{ kJ} \cdot \text{mol}^{-1}) \\ &\quad + (-228.57 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= +142.12 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

ΔG°_r can also be calculated from ΔS°_r and ΔH°_r using the relationship:

$$\begin{aligned}\Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r = +206.1 \text{ kJ} \cdot \text{mol}^{-1} \\ &\quad - (298 \text{ K})(+214.62 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\ &= +142.1 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$



$$\begin{aligned}\Delta S^\circ_r &= S^\circ_m(\text{N}_2\text{O}, \text{g}) + 2S^\circ_m(\text{H}_2\text{O}, \text{g}) - S^\circ_m(\text{NH}_4\text{NO}_3, \text{s}) \\ &= 219.85 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 2(188.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\ &\quad - 151.08 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= +446.43 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_r &= \Delta H^\circ_f(\text{N}_2\text{O}, \text{g}) + 2\Delta H^\circ_f(\text{H}_2\text{O}, \text{g}) - [\Delta H^\circ_f(\text{NH}_4\text{NO}_3, \text{s})] \\ &= 82.05 \text{ kJ} \cdot \text{mol}^{-1} + 2(-241.82 \text{ kJ} \cdot \text{mol}^{-1}) - [-365.56 \text{ kJ} \cdot \text{mol}^{-1}] \\ &= -36.03 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ_r &= \Delta G^\circ_f(\text{N}_2\text{O}, \text{g}) + 2\Delta G^\circ_f(\text{H}_2\text{O}, \text{g}) - [\Delta G^\circ_f(\text{NH}_4\text{NO}_3, \text{s})] \\ &= 104.20 \text{ kJ} \cdot \text{mol}^{-1} + 2(-228.57 \text{ kJ} \cdot \text{mol}^{-1}) - [-183.87 \text{ kJ} \cdot \text{mol}^{-1}] \\ &= -169.07 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

ΔG°_r can also be calculated from ΔS°_r and ΔH°_r using the relationship:

$$\begin{aligned}
 \Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r \\
 &= -36.03 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(446.43 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
 &= -169.07 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

7.60 In order to find ΔG°_r at a temperature other than 298 K, we must first calculate ΔH°_r and ΔS°_r and then use the relationship

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

$$\begin{aligned}
 \text{(a) } \Delta H^\circ_r &= \Delta H^\circ_f(\text{CH}_3\text{NH}_2, \text{g}) - [\Delta H^\circ_f(\text{HCN}, \text{g}) \\
 &= -22.97 \text{ kJ} \cdot \text{mol}^{-1} - [135.1 \text{ kJ} \cdot \text{mol}^{-1}] \\
 &= -158.1 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \Delta S^\circ_r &= S^\circ_m(\text{CH}_3\text{NH}_2, \text{g}) - [S^\circ_m(\text{HCN}, \text{g}) + 2S^\circ_m(\text{H}_2, \text{g})] \\
 &= 243.41 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
 &\quad - [201.78 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 2(130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\
 &= -219.73 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \Delta G^\circ_r &= -158.1 \text{ kJ} \cdot \text{mol}^{-1} \\
 &\quad - (223 \text{ K})(-219.73 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
 &= -109.1 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

In order to determine over what range the reaction will be spontaneous, we consider the relative signs of ΔH°_r and ΔS°_r and their effect on ΔG°_r .

Because ΔH°_r is negative and ΔS°_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 ΔH°_r . To find the temperature of the cutoff, we calculate the temperature at which $\Delta G^\circ_r = 0$. For this reaction, this temperature is

$$\Delta G^\circ_r = 0 = -158.1 \text{ kJ} \cdot \text{mol}^{-1} - (T)(-219.73 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$$

$T = 719.4 \text{ K}$ The reaction should be spontaneous below 719.4 K.

(Although the number of significant figures here is calculated according to the numbers given, the actual number of figures is less, because the values of reaction enthalpy and entropy are not exactly constant with temperature, especially over a larger temperature range such as this.)

$$\begin{aligned}
 \text{(b) } \Delta H^\circ_r &= \Delta H^\circ_f(\text{Cu}^{2+}, \text{aq}) - [2\Delta H^\circ_f(\text{Cu}^+, \text{aq})] \\
 &= 64.77 \text{ kJ} \cdot \text{mol}^{-1} - [2(71.67 \text{ kJ} \cdot \text{mol}^{-1})] \\
 &= -78.57 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \Delta S^\circ_r &= S^\circ_m(\text{Cu}, \text{s}) + S^\circ_m(\text{Cu}^{2+}, \text{aq}) - [2S^\circ_m(\text{Cu}^+, \text{aq})] \\
 &= 33.15 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + (-99.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\
 &\quad - [2(40.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\
 &= -147.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \Delta G^\circ_r &= -78.57 \text{ kJ} \cdot \text{mol}^{-1} - (223 \text{ K})(-146.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
 &= -45.9 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

Because ΔH°_r is negative and ΔS°_r is negative, the reaction will be spontaneous at lower temperatures as in (a).

$$\begin{aligned}
 \Delta G^\circ_r = 0 &= -78.57 \text{ kJ} \cdot \text{mol}^{-1} - (T)(-147.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
 T &= 532 \text{ K}
 \end{aligned}$$

The reaction is spontaneous at temperatures below 532 K.

$$\begin{aligned}
 \text{(c) } \Delta H^\circ_r &= \Delta H^\circ_f(\text{CaF}_2, \text{s}) + 2\Delta H^\circ_f(\text{HCl}, \text{g}) \\
 &\quad - [\Delta H^\circ_f(\text{CaCl}_2, \text{s}) + 2\Delta H^\circ_f(\text{HF}, \text{g})] \\
 &= (-1219.6 \text{ kJ} \cdot \text{mol}) + 2(-92.31 \text{ kJ} \cdot \text{mol}^{-1}) \\
 &\quad - [(-795.8 \text{ kJ} \cdot \text{mol}^{-1}) + 2(-271.1 \text{ kJ} \cdot \text{mol}^{-1})] \\
 &= -66.2 \text{ kJ} \cdot \text{mol}^{-1} \\
 \Delta S^\circ_r &= S^\circ_m(\text{CaF}_2, \text{s}) + 2S^\circ_m(\text{HCl}, \text{g}) - [S^\circ_m(\text{CaCl}_2, \text{s}) + 2S^\circ_m(\text{HF}, \text{g})] \\
 &= 68.87 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 2(186.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\
 &\quad - [104.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 2(173.78 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\
 &= -9.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
 \end{aligned}$$

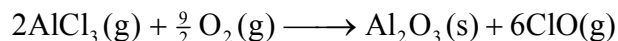
$$\begin{aligned}
 \Delta G^\circ_r &= -66.2 \text{ kJ} \cdot \text{mol}^{-1} - (223 \text{ K})(-9.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
 &= -64.1 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

Because ΔH°_r is negative and ΔS°_r is negative, the reaction will be spontaneous at lower temperatures as in (a).

$$\begin{aligned}
 \Delta G^\circ_r = 0 &= -66.2 \text{ kJ} \cdot \text{mol}^{-1} - (T)(-9.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
 T &= 6.97 \times 10^3 \text{ K}
 \end{aligned}$$

The reaction is spontaneous at temperatures below $6.97 \times 10^3 \text{ K}$, which essentially covers the entire accessible temperature range.

7.62 The balanced chemical reaction is:



and ΔG°_r for the reaction at 2000 K is:

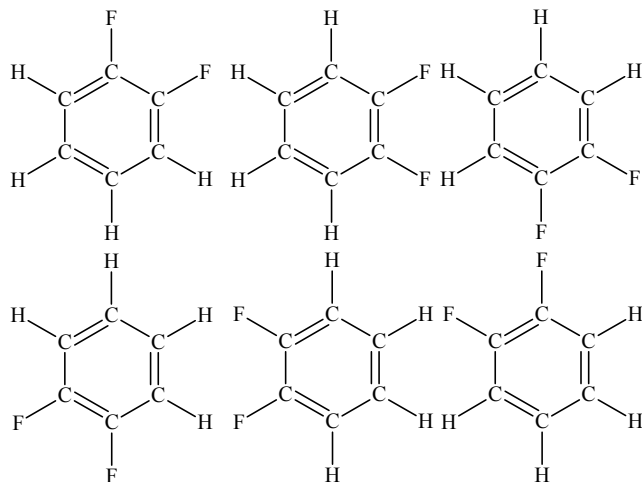
$$\Delta G^\circ_r = -1034 \text{ kJ} \cdot \text{mol}^{-1} + 6(75 \text{ kJ} \cdot \text{mol}^{-1}) - 2(-467 \text{ kJ} \cdot \text{mol}^{-1})$$

$$\Delta G^\circ_r = 350 \text{ kJ} \cdot \text{mol}^{-1}$$

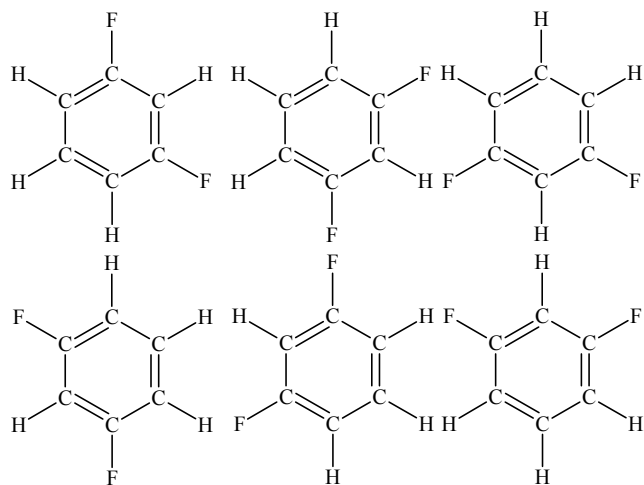
Given the sign of ΔG°_r , it does not appear that the reaction will be spontaneous and, therefore, this reaction does not appear to be a good candidate for rocket propulsion.

7.64 (a) and (b) Normally one would expect dissolution of a substance in another to increase the entropy of the substance. The ability of acetic acid to hydrogen bond to water molecules makes the solution more ordered than in the pure liquid in spite of the mixing.

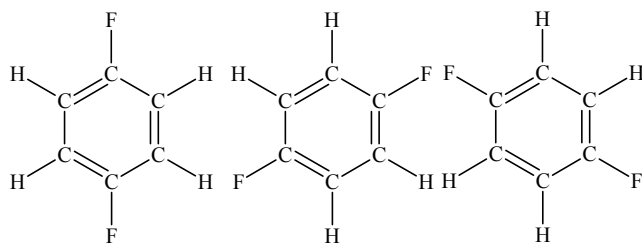
7.66 1,2-difluorobenzene has six possible orientations:



1,3-difluorobenzene also has six possible orientations:



1,4-difluorobenzene has only three possible orientations:



The least residual molar entropy will be exhibited for the compound that has the fewest possible orientations, in this case 1,4-difluorobenzene. The 1,2- and 1,3- isomers should have a higher residual entropy (assuming that all three are disordered) and the residual entropies should be about the same for these two compounds.

7.68 First, calculate the ΔG°_r for both reactions:

$$\begin{aligned} \text{(a)} \quad \Delta G^\circ_r &= 2\Delta G^\circ_f(\text{CO}, \text{g}) - [\Delta G^\circ_r(\text{TiO}_2, \text{s})] \\ &= 2(-200 \text{ kJ} \cdot \text{mol}^{-1}) - [-762 \text{ kJ} \cdot \text{mol}^{-1}] \\ &= +362 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \Delta G^\circ_r &= \Delta G^\circ_f(\text{CO}_2, \text{g}) - [\Delta G^\circ_r(\text{TiO}_2, \text{s})] \\ &= (-396 \text{ kJ} \cdot \text{mol}^{-1}) - [-762 \text{ kJ} \cdot \text{mol}^{-1}] \\ &= +362 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Neither reaction is spontaneous, so TiO_2 cannot be reduced by carbon at 1000 K.

7.70 (a) $\Delta H^\circ_r = \Delta H^\circ_f(\text{C}_2\text{H}_6, \text{g}) - [\Delta H^\circ_f(\text{C}_2\text{H}_2, \text{g})]$

$$= (-84.68 \text{ kJ} \cdot \text{mol}^{-1}) - [226.73 \text{ kJ} \cdot \text{mol}^{-1}]$$

$$= -311.41 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S^\circ_r = S^\circ_m(\text{C}_2\text{H}_6, \text{g}) - [S^\circ_m(\text{C}_2\text{H}_2, \text{g}) + 2 S^\circ_m(\text{H}_2, \text{g})]$$

$$= 229.60 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$- [200.94 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 2(130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})]$$

$$= -232.70 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

(b) $\Delta G^\circ_r = \Delta H^\circ_r - T\Delta S^\circ_r$

$$= -311.41 \text{ kJ} \cdot \text{mol}^{-1}$$

$$- (298 \text{ K})(-232.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) / (1000 \text{ J} \cdot \text{kJ}^{-1})$$

$$= -242.07 \text{ kJ} \cdot \text{mol}^{-1}$$

(c) The entropy change of the reaction is negative, because there are fewer moles of gas on the reactant side of the equation than on the product side. The reaction enthalpy is exothermic, because one obtains more energy in the formation of four C—H bonds than one gives up to break 2 H—H bonds.

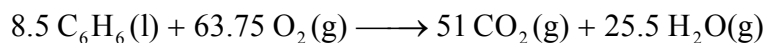
(d) $\Delta G^\circ_r = \Delta H^\circ_r - T\Delta S^\circ_r$

$$= -311.41 \text{ kJ} \cdot \text{mol}^{-1} - (T)(-232.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) / (1000 \text{ J} \cdot \text{kJ}^{-1}) = 0$$

$$T = 1338 \text{ K}$$

(e) This is the temperature at which the reaction switches from being spontaneous to becoming nonspontaneous.

7.72 (a) First, balance the equation for the combustion of 8.50 mol of $\text{C}_6\text{H}_6(\text{l})$ to give carbon dioxide and water vapor:



The work term will be dominated by the change in the number of moles of gas, which in this case is 76.5 moles – 63.75 moles = 12.75 moles. Work will be given by

$$w = -P\Delta V$$

$$\Delta V = \frac{RT}{P} \Delta n$$

$$w = -P \frac{RT}{P} \Delta n$$

$$= -RT\Delta n$$

$$= -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})(12.76 \text{ mol})$$

$$= -31.6 \text{ kJ}$$

$$\begin{aligned} \text{(b)} \quad \Delta H^\circ &= 51(-393.51 \text{ kJ} \cdot \text{mol}^{-1}) + 25.5(-241.82 \text{ kJ} \cdot \text{mol}^{-1}) \\ &\quad - 8.5(49.0 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -26651 \text{ kJ} \end{aligned}$$

$$\text{(c)} \quad \Delta U^\circ = \Delta H^\circ + w = -26650 \text{ kJ} - 31.6 \text{ kJ} = -26680 \text{ kJ}$$

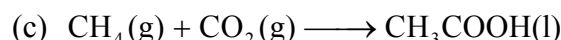
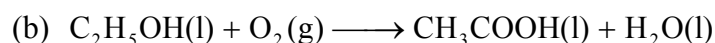
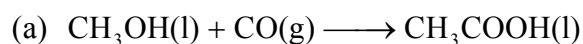
7.74 (a) Reactions with negative reaction free energies are thermodynamically favored, but the thermodynamics will not tell us how fast a process takes place. For example, some reactions with large negative free energies do not happen unless initiated, as in the case of the reaction of hydrogen gas with oxygen gas to produce water.

(b) This statement is false because the sample of the element must be in its standard state. Not all forms of the element at a given temperature have the same energy; the one chosen as the standard state will have the lowest energy.

(c) False. For this process, ΔH°_r is a negative number, ΔS°_r will be positive because the number of moles of gas increases. According to the relationship $\Delta G^\circ_r = \Delta H^\circ_r - T\Delta S^\circ_r$, if ΔH°_r is negative and ΔS°_r is positive, ΔG°_r must be negative.

7.76 According to the second law of thermodynamics, the formation of complex molecules from simpler precursors would not be spontaneous, because such processes create order from disorder. If there is an external input of energy, however, a more ordered system could be created. One of the challenges remaining to evolutionary biology is to explain how the exceedingly complex and highly organized biological structures were created from randomly occurring chemical reactions.

7.78 The reactions are



To understand these three reactions completely, we must calculate

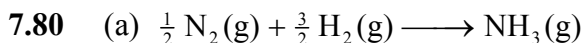
ΔH°_r , ΔS°_r , and ΔG°_r for each reaction:

$$\begin{aligned}
 \text{(a)} \quad \Delta H^\circ_r &= \Delta H^\circ_f(\text{CH}_3\text{COOH}, \text{l}) \\
 &\quad - [\Delta H^\circ_f(\text{CH}_3\text{OH}, \text{l}) + \Delta H^\circ_f(\text{CO}, \text{g})] \\
 &= (-484.5 \text{ kJ} \cdot \text{mol}^{-1}) - [(-238.86 \text{ kJ} \cdot \text{mol}^{-1}) \\
 &\quad + (-110.53 \text{ kJ} \cdot \text{mol}^{-1})] \\
 &= -135.1 \text{ kJ} \cdot \text{mol}^{-1} \\
 \Delta S^\circ_r &= S^\circ_m(\text{CH}_3\text{COOH}, \text{l}) - [S^\circ_m(\text{CH}_3\text{OH}, \text{l}) + S^\circ_m(\text{CO}, \text{g})] \\
 &= 159.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [126.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
 &\quad + 197.67 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\
 &= -164.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
 \Delta G^\circ_r &= \Delta G^\circ_f(\text{CH}_3\text{COOH}, \text{l}) - [\Delta G^\circ_f(\text{CH}_3\text{OH}, \text{l}) + \Delta G^\circ_f(\text{CO}, \text{g})] \\
 &= (-389.9 \text{ kJ} \cdot \text{mol}^{-1}) - [(-166.27 \text{ kJ} \cdot \text{mol}^{-1}) \\
 &\quad + (-137.17 \text{ kJ} \cdot \text{mol}^{-1})] \\
 &= -86.5 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
\text{(b) } \Delta H^\circ_r &= \Delta H^\circ_f(\text{CH}_3\text{COOH}, \text{l}) \\
&\quad + \Delta H^\circ_f(\text{H}_2\text{O}, \text{l}) - [\Delta H^\circ_f(\text{C}_2\text{H}_5\text{OH}, \text{l})] \\
&= (-484.5 \text{ kJ} \cdot \text{mol}^{-1}) + (-285.83 \text{ kJ} \cdot \text{mol}^{-1}) \\
&\quad - [-277.69 \text{ kJ} \cdot \text{mol}^{-1}] \\
&= -492.6 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= S^\circ_m(\text{CH}_3\text{COOH}, \text{l}) + S^\circ_m(\text{H}_2\text{O}(\text{l})) \\
&\quad - [S^\circ_m(\text{C}_2\text{H}_5\text{OH}, \text{l}) + S^\circ_m(\text{O}_2, \text{g})] \\
&= 159.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
&\quad - [160.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\
&= -136.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
\Delta G^\circ_r &= \Delta G^\circ_f(\text{CH}_3\text{COOH}, \text{l}) + \Delta G^\circ_f(\text{H}_2\text{O}, \text{l}) - [\Delta G^\circ_f(\text{C}_2\text{H}_5\text{OH}, \text{l})] \\
&= (-389.9 \text{ kJ} \cdot \text{mol}^{-1}) + (-237.13 \text{ kJ} \cdot \text{mol}^{-1}) - [-174.78 \text{ kJ} \cdot \text{mol}^{-1}] \\
&= -452.3 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

$$\begin{aligned}
\text{(c) } \Delta H^\circ_r &= \Delta H^\circ_f(\text{CH}_3\text{COOH}, \text{l}) \\
&\quad - [\Delta H^\circ_f(\text{CH}_4, \text{g}) + \Delta H^\circ_f(\text{CO}_2, \text{g})] \\
&= (-484.5 \text{ kJ} \cdot \text{mol}^{-1}) - [(-74.81 \text{ kJ} \cdot \text{mol}^{-1}) + (-393.51 \text{ kJ} \cdot \text{mol}^{-1})] \\
&= -16.2 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= S^\circ_m(\text{CH}_3\text{COOH}, \text{l}) - [S^\circ_m(\text{CH}_4, \text{g}) + S^\circ_m(\text{CO}_2, \text{g})] \\
&= 159.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [186.26 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 213.74 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\
&= -240.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
\Delta G^\circ_r &= \Delta G^\circ_f(\text{CH}_3\text{COOH}, \text{l}) - [\Delta G^\circ_f(\text{CH}_4, \text{g}) + \Delta G^\circ_f(\text{CO}_2, \text{g})] \\
&= (-389.9 \text{ kJ} \cdot \text{mol}^{-1}) - [(-50.72 \text{ kJ} \cdot \text{mol}^{-1}) + (-394.36 \text{ kJ} \cdot \text{mol}^{-1})] \\
&= +55.2 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

It is clear from these numbers that the second reaction, the oxidation of ethanol, is by far the most favorable thermodynamically. The addition of CO to methanol is favorable but less so than the oxidation of ethanol. The addition of carbon dioxide to methane is not thermodynamically favored.



(b) The ΔH°_r of this reaction is simply the standard heat of formation of ammonia gas, which is $-46.11 \text{ kJ} \cdot \text{mol}^{-1}$.

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

(c) These values are calculated using the relationship

$\Delta G^\circ_r = \Delta H^\circ_r - T\Delta S^\circ_r$. The following values of ΔG°_r are calculated at the different temperatures:

150 K -31.20 kJ

298 K -16.49 kJ

350 K -11.33 kJ

(d) The thermodynamics of this process show that as the temperature is raised, the reaction becomes less favorable. Raising the temperature will increase the rate but will also reduce the amount of products present at equilibrium. The actual reaction conditions employed are a compromise between the rate and thermodynamic considerations.

7.82 For any reaction, $\Delta G^\circ_r = \Delta H^\circ_r - T\Delta S^\circ_r$. If a liquid boils above room temperature, ΔG°_r for this phase change must be positive at room temperature. ΔS°_r for a vaporization reaction will generally be positive due to the increase in disorder leading to a negative $-T\Delta S^\circ_r$ term.

Therefore, for ΔG°_r to be positive, ΔH°_r must be greater than $T\Delta S^\circ_r$ or:

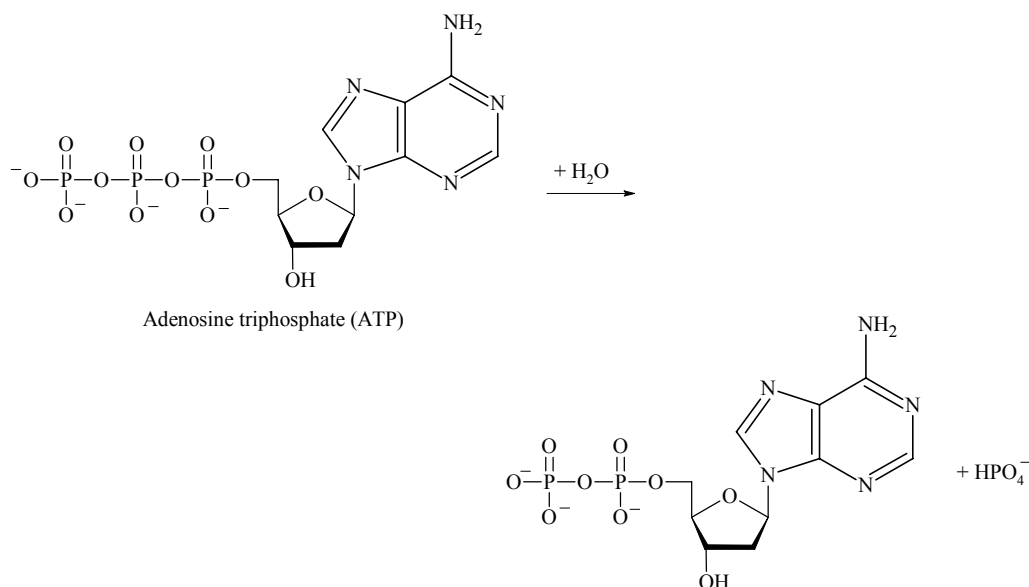
$$\begin{aligned}
\Delta H^\circ_r \left(\text{kJ} \cdot \text{mol}^{-1} \right) &> (298 \text{ K}) \left(\Delta S^\circ_r \left(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \right) \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \\
&\cong 0.3 \cdot \Delta S^\circ_r \left(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \right)
\end{aligned}$$

Therefore, for the liquid to have a boiling point above room temperature,

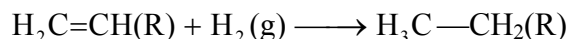
ΔH°_r in kJ mol^{-1} must be greater than ΔS°_r in $\text{J mol}^{-1} \text{ K}^{-1}$.

7.84 Adenosine triphosphate is a nucleotide that can be viewed as being composed of three subunits: the base adenine, the sugar ribose, and the triphosphate group, as shown below. The conversion of ATP to ADP

involves the removal of one of the phosphate groups by hydrolysis. The ΔG° of this reaction is -30 kJ . In some parts of the cell where energy-producing reactions occur (such as the oxidation of glucose), ADP is converted into ATP (the energy produced is used to drive the hydrolysis reaction in the reverse direction). ATP can then be transferred to other parts of the cell where it can undergo hydrolysis, thereby releasing the energy stored in the bonding of the phosphate to the diphosphate group. These reactions are catalyzed by enzymes that bring the necessary molecules together in order to cause the overall desired reaction.



7.86 The hydrogenation reaction corresponds to the general reaction:



where R is H, CH_3 , CH_2CH_3 , $\text{CH}_2\text{CH}_2\text{CH}_3$, or C_6H_5 for this problem. The calculations of ΔG°_r and ΔH°_r are based on the general equations:

$$\Delta G^\circ_r = \Delta G^\circ_f(\text{H}_3\text{C}-\text{CH}_2(\text{R})) - \Delta G^\circ_f(\text{H}_2\text{C}=\text{CH}(\text{R}))$$

$$\text{and } \Delta H^\circ_r = \Delta H^\circ_f(\text{H}_3\text{C}-\text{CH}_2(\text{R})) - \Delta H^\circ_f(\text{H}_2\text{C}=\text{CH}(\text{R}))$$

Using these equations and numbers obtained from the literature, we can calculate the following values:

Compound	$\Delta G^\circ_f (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta H^\circ_f (\text{kJ} \cdot \text{mol}^{-1})$
ethene	68.15	52.26
ethane	-32.82	-84.68
propene	62.78	20.42
propane	-23.49	-103.85
1-butene	71.30	-0.13
butane	-17.03	-126.15
1-pentene	79.12	-20.92
pentane	-8.20	-146.44
styrene	213.8	147.8
ethyl benzene	130.6	29.8

ΔS°_r is calculated from $\Delta G^\circ_f = \Delta H^\circ_f (\text{kJ} \cdot \text{mol}^{-1}) - T\Delta S^\circ_r$

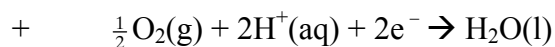
Hydrogenation reaction	ΔG°_f ($\text{kJ} \cdot \text{mol}^{-1}$)	ΔH°_f ($\text{kJ} \cdot \text{mol}^{-1}$)	ΔS°_r ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)
ethene	-100.97	-136.94	-121
propene	-86.27	-124.27	-127
1-butene	-88.33	-126.02	-126
1-pentene	-87.32	-125.52	-128
styrene	-83.80	-118.0	-115

The data are reasonably consistent but there are some differences. The molecules that are most similar in structure give the closest agreement (R = H vs. R = alkyl group vs. R = aromatic ring). According to bond enthalpy calculations, we would have expected all of these numbers to be the same, because the same number and type of bonds are broken and formed in each case. It is not unusual to find an error of 10 to 15 percent in bond enthalpy calculations. Note also, that the entropy changes are all negative as expected, based on the loss of one mole of gas as a result of going from reactants to products.

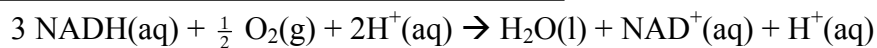
7.88 The reactions (2) and (3) in this problem are used to drive the regeneration of ATP. For every three molecules of NADH that undergo reaction:



$$\Delta G^\circ_r = 3(-158.2 \text{ kJ})$$



$$\Delta G^\circ_r = 3(-61.9 \text{ kJ})$$



$$\Delta G^\circ_r = -660.3 \text{ kJ}$$

Therefore, for every three NADH molecules, $660.3 \text{ kJ} / 30.5 \text{ kJ} = 21.6$ ATP molecules would be regenerated if all of the free energy released were used to drive reaction (1).