

## CHAPTER 6

### THERMODYNAMICS: THE FIRST LAW

6.1 (a) isolated; (b) closed; (c) isolated; (d) open; (e) closed;  
(f) open

6.3 (a) Work is given by  $w = -P_{\text{ext}}\Delta V$ . The applied external pressure is known, but we must calculate the change in volume given the physical dimensions of the pump and the distance,  $d$ , the piston in the pump moves:

$$\Delta V = -\pi r^2 d = \pi(1.5 \text{ cm})^2(20 \text{ cm})\left(\frac{1 \text{ L}}{1000 \text{ cm}^3}\right) = -0.141 \text{ L}$$

$\Delta V$  is negative because the air in the pump is compressed to a smaller volume work is then:

$$w = -(2 \text{ atm})(-0.141 \text{ L})\frac{101.325 \text{ J}}{\text{L} \cdot \text{atm}} = 28.7 \text{ J}$$

(b) Work on the air is positive by convention as work is done on the air, it is compressed.

6.5 The change in internal energy  $\Delta U$  is given simply by summing the two energy terms involved in this process. We must be careful, however, that the signs on the energy changes are appropriate. In this case, internal energy will be added to the gas sample by heating and the gas gains more energy through compression. Therefore the change in internal energy is:  
 $\Delta U = 524 \text{ kJ} + 340 \text{ kJ} = +864 \text{ kJ}$

6.7 (a) The internal energy increased by more than the amount of heat added. Therefore, the extra energy must have come from work done on the system.

$$(b) w = \Delta U - q = 982 \text{ J} - 492 \text{ J} = +4.90 \times 10^2 \text{ J}.$$

6.9 To get the entire internal energy change, we must sum the changes due to heat and work. In this problem,  $q = +5500 \text{ kJ}$ . Work will be given by

$w = -P_{\text{ext}} \Delta V$  because it is an expansion against a constant opposing pressure:

$$w = -\left(\frac{750 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right) \left(\frac{1846 \text{ mL} - 345 \text{ mL}}{1000 \text{ mL} \cdot \text{L}^{-1}}\right) = -1.48 \text{ L} \cdot \text{atm}$$

To convert to J we use the equivalency of the ideal gas constants:

$$w = -(1.48 \text{ L} \cdot \text{atm}) \left(\frac{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}{0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}\right) = -1.50 \times 10^2 \text{ J}$$

$$\Delta U = q + w = 5500 \text{ kJ} - 0.150 \text{ kJ} = 5500 \text{ kJ}$$

The energy change due to the work term turns out to be negligible in this problem.

6.11 Using  $\Delta U = q + w$  where  $\Delta U = -2573 \text{ kJ}$  and

$$q = -947 \text{ kJ} - 2573 \text{ kJ} = -947 \text{ kJ} + w$$

$$w = -1626 \text{ kJ}$$

1626 kJ of work can be done by the system on its surroundings.

6.13 (a) true if no work is done; (b) always true; (c) always false; (d) true only if  $w = 0$  (in which case  $\Delta U = q = 0$ ); (e) always true

6.15 (a) The heat change will be made up of two terms: one term to raise the temperature of the copper and the other to raise the temperature of the water:

$$\begin{aligned}
 q &= (750.0 \text{ g})(4.18 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(100.0\text{°C} - 23.0\text{°C}) \\
 &\quad + (500.0 \text{ g})(0.38 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(100\text{°C} - 23\text{°C}) \\
 &= 242 \text{ kJ} + 14 \text{ kJ} = 256 \text{ kJ}
 \end{aligned}$$

(b) The percentage of heat attributable to raising the temperature of water will be

$$\left( \frac{241 \text{ kJ}}{256 \text{ kJ}} \right) (100) = 94.3\%$$

**6.17** heat lost by metal = 2 heat gained by water

$$\begin{aligned}
 (20.0 \text{ g})(T_{\text{final}} - 100.0\text{°C})(0.38 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1}) \\
 &= -(50.7 \text{ g})(4.18 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(T_{\text{final}} - 22.0\text{°C}) \\
 (T_{\text{final}} - 100.0\text{°C})(7.6 \text{ J} \cdot (\text{°C})^{-1}) &= -(212 \text{ J} \cdot (\text{°C})^{-1})(T_{\text{final}} - 22.0\text{°C}) \\
 T_{\text{final}} - 100.0\text{°C} &= -28(T_{\text{final}} - 22.0\text{°C}) \\
 T_{\text{final}} + 28 T_{\text{final}} &= 100.0\text{°C} + 616\text{°C} \\
 29 T_{\text{final}} &= 716\text{°C} \\
 T_{\text{final}} &= 25\text{°C}
 \end{aligned}$$

$$\mathbf{6.19} \quad C_{\text{cal}} = \frac{22.5 \text{ kJ}}{23.97\text{°C} - 22.45\text{°C}} = 14.8 \text{ kJ} \cdot (\text{°C})^{-1}$$

**6.21** (a) The irreversible work of expansion against a constant opposing pressure is given by

$$\begin{aligned}
 w &= -P_{\text{ex}} \Delta V \\
 w &= -(1.00 \text{ atm})(6.52 \text{ L} - 4.29 \text{ L}) \\
 &= -2.23 \text{ L} \cdot \text{atm} \\
 &= -2.23 \text{ L} \cdot \text{atm} \times 101.325 \text{ J} \cdot \text{L}^{-1} \cdot \text{atm}^{-1} = -226 \text{ J}
 \end{aligned}$$

(b) An isothermal expansion will be given by

$$w = -nRT \frac{V_2}{V_1}$$

$n$  is calculated from the ideal gas law:

$$n = \frac{PV}{RT} = \frac{(1.79 \text{ atm})(4.29 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(305 \text{ K})} = 0.307 \text{ mol}$$

$$w = -(0.307 \text{ mol})(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(305 \text{ K}) \ln \frac{6.52}{4.29}$$

$$= -326 \text{ J}$$

Note that the work done is greater when the process is carried out reversibly.

**6.23**  $\text{NO}_2$ . The heat capacity increases with molecular complexity—as more atoms are present in the molecule, there are more possible bond vibrations that can absorb added energy.

**6.25** (a) The molar heat capacity of a monatomic ideal gas at constant pressure is  $C_{p,m} = \frac{5}{2}R$ . The heat released will be given by

$$q = \left( \frac{5.025 \text{ g}}{83.80 \text{ g} \cdot \text{mol}^{-1}} \right) (25.0^\circ\text{C} - 97.6^\circ\text{C}) (20.8 \text{ J} \cdot \text{mol}^{-1} \cdot (^\circ\text{C})^{-1}) = -90.6 \text{ J}$$

(b) Similarly, the molar heat capacity of a monatomic ideal gas at constant volume is  $C_{v,m} = \frac{3}{2}R$ . The heat released will be given by

$$q = \left( \frac{5.025 \text{ g}}{83.80 \text{ g} \cdot \text{mol}^{-1}} \right) (25.0^\circ\text{C} - 97.6^\circ\text{C}) (12.5 \text{ J} \cdot \text{mol}^{-1} \cdot (^\circ\text{C})^{-1}) = -54.4 \text{ J}$$

**6.33** (a)  $\Delta H_{\text{vap}} = \frac{4.76 \text{ kJ}}{0.579 \text{ mol}} = 8.22 \text{ kJ} \cdot \text{mol}^{-1}$

(b)  $\Delta H_{\text{vap}} = \frac{21.2 \text{ kJ}}{\left( \frac{22.45 \text{ g}}{46.07 \text{ g} \cdot \text{mol}^{-1}} \right)} = 43.5 \text{ kJ} \cdot \text{mol}^{-1}$

6.39 (a)  $\Delta H = (1.25 \text{ mol})(+358.8 \text{ kJ} \cdot \text{mol}^{-1}) = 448 \text{ kJ}$

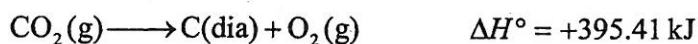
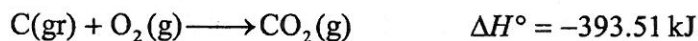
(b)  $\Delta H = \left( \frac{197 \text{ g C}}{12.01 \text{ g} \cdot \text{mol}^{-1} \text{C}} \right) \left( \frac{358.8 \text{ kJ}}{4 \text{ mol C}} \right) = 1.47 \times 10^3 \text{ kJ}$

(c)  $\Delta H = 415 \text{ kJ} = (n_{\text{CS}_2}) \left( \frac{358.8 \text{ kJ} \cdot \text{mol}^{-1}}{4 \text{ mol CS}_2} \right)$

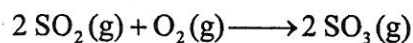
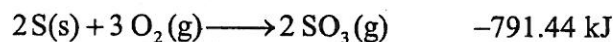
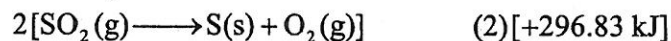
$n_{\text{CS}_2} = 4.63 \text{ mol CS}_2$  or  $(4.63 \text{ mol})(76.13 \text{ g} \cdot \text{mol}^{-1}) = 352 \text{ g CS}_2$

6.45 From  $\Delta H = \Delta U + P\Delta V$  at constant pressure, or  $\Delta U = \Delta H - P\Delta V$ .  
Because  $w = -P\Delta V = +22 \text{ kJ}$ , we get  $-15 \text{ kJ} + 22 \text{ kJ} = \Delta U = +7 \text{ kJ}$ .

6.51 The combustion reaction of diamond is reversed and added to the combustion reaction of graphite to give the desired reaction:

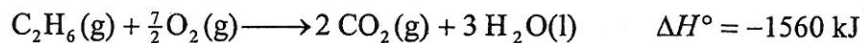
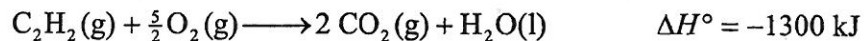


6.53 The first reaction is doubled, reversed, and added to the second to give the desired total reaction:

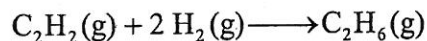
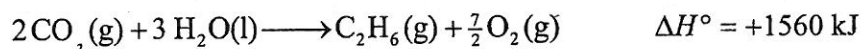
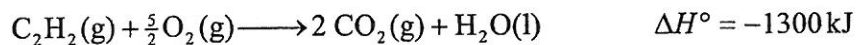


$$\Delta H^\circ = (2)(+296.83 \text{ kJ} \cdot \text{mol}^{-1}) - (791.44 \text{ kJ} \cdot \text{mol}^{-1}) = -197.78 \text{ kJ}$$

6.55 First, write the balanced equations for the reaction given:

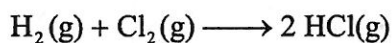
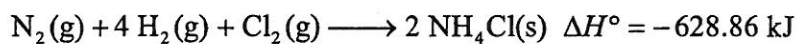
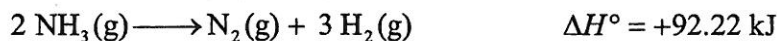
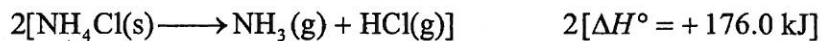


The second equation is reversed and added to the first, plus two times the third:



$$\Delta H^\circ = -1300 \text{ kJ} + 1560 \text{ kJ} + 2(-286 \text{ kJ}) = -312 \text{ kJ}$$

6.59 The desired reaction may be obtained by reversing the first reaction and multiplying it by 2, reversing the second reaction, and adding these to the third:



$$\Delta H^\circ = 2(+176.0 \text{ kJ}) + 92.22 \text{ kJ} - 628.86 \text{ kJ} = -184.6 \text{ kJ}$$

|                 |                 |                                |
|-----------------|-----------------|--------------------------------|
| 6.71 (a) break: | 3 mol C=C bonds | 3(612) kJ · mol <sup>-1</sup>  |
| form:           | 6 mol C=C bonds | -6(518) kJ · mol <sup>-1</sup> |

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|       |                              |
|-------|------------------------------|
| Total | -1272 kJ · mol <sup>-1</sup> |
|-------|------------------------------|

|            |                   |                                |
|------------|-------------------|--------------------------------|
| (b) break: | 4 mol C—H bonds   | 4(412) kJ · mol <sup>-1</sup>  |
|            | 4 mol Cl—Cl bonds | 4(242) kJ · mol <sup>-1</sup>  |
| form:      | 4 mol C—Cl bonds  | -4(338) kJ · mol <sup>-1</sup> |
|            | 4 mol H—Cl bonds  | -4(431) kJ · mol <sup>-1</sup> |

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|       |                             |
|-------|-----------------------------|
| Total | -460 kJ · mol <sup>-1</sup> |
|-------|-----------------------------|

(c) The number and types of bonds on both sides of the equations are equal, so we expect the enthalpy of the reaction to be essentially 0.

|                 |                        |                                       |
|-----------------|------------------------|---------------------------------------|
| 6.73 (a) break: | 1 mol N—N triple bonds | (1 mol)(944 kJ · mol <sup>-1</sup> )  |
|                 | 3 mol F—F bonds        | (3 mol)(158 kJ · mol <sup>-1</sup> )  |
| form:           | 6 mol N—F bonds        | (6 mol)(-195 kJ · mol <sup>-1</sup> ) |

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|       |         |
|-------|---------|
| Total | +248 kJ |
|-------|---------|

|            |                 |                                       |
|------------|-----------------|---------------------------------------|
| (b) break: | 1 mol C=C bonds | (1 mol)(612 kJ · mol <sup>-1</sup> )  |
|            | 1 mol O—H bonds | (1 mol)(463 kJ · mol <sup>-1</sup> )  |
| form:      | 1 mol C—C bonds | -(1 mol)(348 kJ · mol <sup>-1</sup> ) |
|            | 1 mol C—O bonds | -(1 mol)(360 kJ · mol <sup>-1</sup> ) |
|            | 1 mol C—H bonds | -(1 mol)(412 kJ · mol <sup>-1</sup> ) |

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|       |        |
|-------|--------|
| Total | -45 kJ |
|-------|--------|

|            |                   |                                       |
|------------|-------------------|---------------------------------------|
| (c) break: | 1 mol C—H bonds   | (1 mol)(412 kJ · mol <sup>-1</sup> )  |
|            | 1 mol Cl—Cl bonds | (1 mol)(242 kJ · mol <sup>-1</sup> )  |
| form:      | 1 mol C—Cl bonds  |                                       |
|            | 1 mol H—Cl bonds  | -(1 mol)(431 kJ · mol <sup>-1</sup> ) |

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|       |         |
|-------|---------|
| Total | -115 kJ |
|-------|---------|

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

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

- 7.17 (a) The value can be estimated from

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

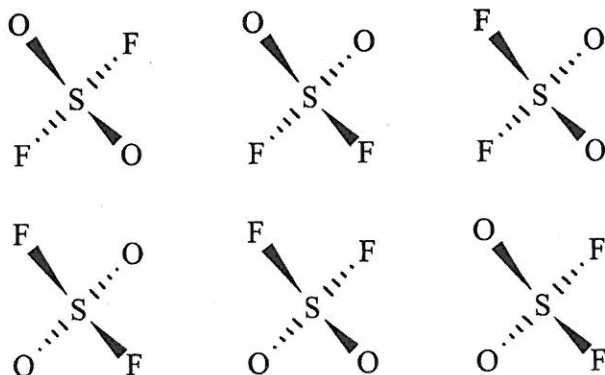
$$\begin{aligned} \Delta H^\circ_{\text{vap}} &= (353 \text{ K})(85 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \\ &= +30. \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

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

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

- 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.  $\text{C}(\text{s}) < \text{H}_2\text{O}(\text{s}) < \text{H}_2\text{O}(\text{l}) < \text{H}_2\text{O}(\text{g})$

7.29 (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.

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

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

$$\begin{aligned}
\Delta G_r^\circ &= \Delta H_r^\circ - T\Delta S_r^\circ \\
&= -235.8 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-133.17 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(100 \text{ J} \cdot \text{kJ}^{-1}) \\
&= -196.1 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

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

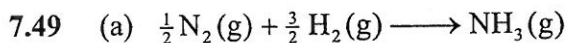
or

$$\begin{aligned}
\Delta G_r^\circ &= \Delta H_r^\circ - T\Delta S_r^\circ \\
&= 11.5 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-149.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
&= 56.1 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

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

or

$$\begin{aligned}
\Delta G_r^\circ &= \Delta H_r^\circ - T\Delta S_r^\circ \\
&= -57.2 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-175.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
&= -4.80 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$



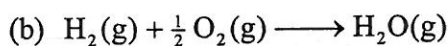
$$\Delta H_r^\circ = \Delta H_f^\circ(\text{NH}_3) = -46.11 \text{ kJ} \cdot \text{mol}^{-1}$$

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

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

$$S_m^\circ(\text{NH}_3) = 192.45 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

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



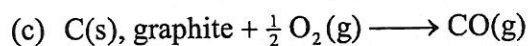
$$\Delta H_r^\circ = \Delta H_f^\circ(\text{H}_2\text{O}, \text{g}) = -241.82 \text{ kJ} \cdot \text{mol}^{-1}$$

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

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

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

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



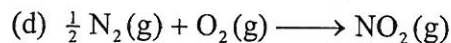
$$\Delta H_r^\circ = \Delta H_f^\circ(\text{CO}, \text{g}) = -110.53 \text{ kJ} \cdot \text{mol}^{-1}$$

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

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

$$S_m^\circ(\text{CO}, \text{g}) = 197.67 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

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



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

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

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

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

The  $\Delta S^\circ_f(\text{NO}_2, \text{g})$  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  $S^\circ_m$  value of a compound is not the same as the  $\Delta S^\circ_f$  for the formation of that compound.  $\Delta S^\circ_f$  is often negative because one is bringing together a number of elements to form that compound.

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

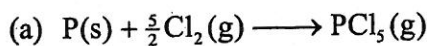
$$\begin{aligned} (a) \Delta G^\circ_r &= 2\Delta G^\circ_f(\text{SO}_3, \text{g}) - [2\Delta G^\circ_f(\text{SO}_2, \text{g})] \\ &= 2(-371.06 \text{ kJ} \cdot \text{mol}^{-1}) - [2(-300.19 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -141.74 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

The reaction is spontaneous.

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

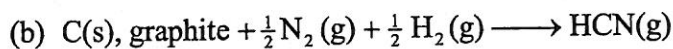
The reaction is not spontaneous.

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 find out whether the standard entropy of formation of the compound is a negative number. This is calculated for each compound as follows:



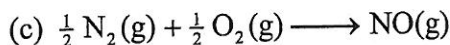
$$\begin{aligned}\Delta S^\circ_r &= S^\circ_m(\text{PCl}_5, \text{g}) - [S^\circ_m(\text{P, s}) + \frac{5}{2}S^\circ_m(\text{Cl}_2, \text{g})] \\ &= 364.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [41.09 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + \frac{5}{2}(223.07 \text{ J} \cdot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

The compound is less stable at higher temperatures.



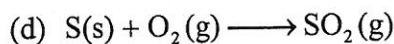
$$\begin{aligned}\Delta S^\circ_r &= S^\circ_m(\text{HCN, g}) - [S^\circ_m(\text{C, s}) + \frac{1}{2}S^\circ_m(\text{N}_2, \text{g}) + \frac{1}{2}S^\circ_m(\text{H}_2, \text{g})] \\ &= 201.78 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [5.740 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}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

HCN(g) is more stable at higher  $T$ .



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

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



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

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