

CHAPTER 6

THERMODYNAMICS: THE FIRST LAW

6.2 (a) The internal energy of an open system could be increased by (1) adding matter to the system, (2) doing work on the system, and (3) adding heat to the system. (b) Matter cannot be added to a closed system, so only (2) doing work on the system and (3) adding heat to the system could be used to increase the internal energy. (c) The internal energy of an isolated system cannot be changed.

6.4 (a) Given four cylinders operating at 60 cycles per minute and displacing 2.5 L each under a constant pressure of 1400 bar, the work done is given by:

$$\begin{aligned} & (4 \text{ cylinders}) \cdot \left(60 \frac{\text{cycles}}{\text{min}} \right) \cdot \left(-1400 \text{ bar} \cdot 10^5 \frac{\text{Pa}}{\text{bar}} \right) \cdot \left(2.5 \text{ L} \cdot \frac{0.001 \text{ m}^3}{\text{L}} \right) \\ & = -8.4 \times 10^7 \text{ J} \end{aligned}$$

(b) The expanding gas in the cylinder does work on the pistons (and to the load connected to the pistons by the crankshaft of the engine). Therefore, work done by the gas is negative.

6.6 (a) The change in internal energy ΔU 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, but the expansion will remove internal energy from the sample so it will be a negative number:

$$\Delta U = 325 \text{ kJ} - 515 \text{ kJ} = -190 \text{ kJ}$$

(b) If the heat added had exactly matched the amount of energy lost due to the work of the gas (i.e., if q had been 235 kJ), then ΔU would have been 0 and the temperature of the gas would not have changed. Because less heat was added, however, and the gas was allowed to expand further, the temperature of the gas would have had to decrease, and consequently the pressure of the gas would be lower at the end.

6.8 To calculate this, we use the relationship $\Delta U = q + w$, which arises from the first law of thermodynamics. Because the system releases heat, q will be a negative number as will ΔU , because it is a decrease in internal energy:

$$-125 \text{ kJ} = -346 \text{ kJ} + w$$

$$w = +221 \text{ kJ}$$

Because work is positive, the surroundings will do work on the system.

6.10 If the heater operates as rated, then the total amount of heat transferred to the cylinder will be

$$(100 \text{ J} \cdot \text{s}^{-1})(10 \text{ min})(60 \text{ s} \cdot \text{min}^{-1}) = 6.0 \times 10^4 \text{ J or } 60 \text{ kJ}$$

Work will be given by $w = -P_{\text{ext}} \Delta V$ in this case because it is an expansion against a constant opposing pressure:

$$w = -(0.975 \text{ atm})(10.00 \text{ L} - 2.00 \text{ L}) = -7.80 \text{ L} \cdot \text{atm}$$

In order to combine the two terms to get the internal energy change, we must first convert the units on the energy terms to the same values. A handy trick to get the conversion factor for $\text{L} \cdot \text{atm}$ to J or *vice versa* is to make use of the equivalence of the ideal gas constant R in terms of $\text{L} \cdot \text{atm}$ and J:

$$w = -7.80 \text{ L} \cdot \text{atm} \left(\frac{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}{0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \right) = -790 \text{ J or } -0.790 \text{ kJ}$$

The internal energy change is then the sum of these two numbers:

$$\Delta U = q + w = 60 \text{ kJ} + (-0.790 \text{ kJ}) \cong 59 \text{ kJ}$$

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

- 6.12** This is calculated from $\Delta U = q + w$ where we know $\Delta U = -892.4 \text{ kJ}$ and $w = -492 \text{ kJ}$:

$$-892.4 \text{ kJ} = q - 492 \text{ kJ}$$

$$q = -400 \text{ kJ}$$

$4.00 \times 10^2 \text{ kJ}$ of heat are lost from the system.

- 6.14** (a) true only if $q = 0$; (b) always true, volume is fixed and no work can be done; (c) never true; (d) always true; (e) true if $q = 0$

- 6.16** (a) The heat change will be made up of two terms: one term to raise the temperature of the stainless steel and the other to raise the temperature of the water:

$$q = (450.0 \text{ g})(4.18 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(100.0\text{°C} - 25.0\text{°C})$$

$$+ (500.0 \text{ g})(0.51 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(100\text{°C} - 25\text{°C})$$

$$q = 141 \text{ kJ} + 19 \text{ kJ} = 1.60 \times 10^2 \text{ kJ}$$

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

$$\left(\frac{141 \text{ kJ}}{160 \text{ kJ}} \right) (100) = 88.1\%$$

- (c) The use of the copper kettle is more efficient, as a larger percentage of the heat goes into heating the water and not the container holding it.

- 6.18** heat lost by metal = – heat gained by water

$$(20.0 \text{ g})(25.7\text{°C} - 100.0\text{°C})(C_s)$$

$$= -(50.7 \text{ g})(4.18 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(25.7\text{°C} - 22.0\text{°C})$$

$$C_s = 0.53 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1}$$

$$\begin{aligned}
 \mathbf{6.20} \quad C_{\text{cal}} &= \frac{-\left(\frac{1.236 \text{ g benzoic acid}}{122.12 \text{ g} \cdot \text{mol}^{-1} \text{ benzoic acid}}\right)(-3227 \text{ kJ} \cdot \text{mol}^{-1} \text{ benzoic acid})}{2.345^{\circ}\text{C}} \\
 &= 13.93 \text{ kJ} \cdot (^{\circ}\text{C})
 \end{aligned}$$

- 6.22** (a) Because the process is isothermal, $\Delta U = 0$ and $q = -w$. For a reversible process,

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

n is obtained from the ideal gas law:

$$n = \frac{PV}{RT} = \frac{(2.57 \text{ atm})(3.42 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = 0.359 \text{ mol}$$

$$w = -(0.359 \text{ mol})(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K}) \ln \frac{7.39}{3.42} = -685 \text{ J}$$

$$q = +685 \text{ J}$$

- (b) For step 1, because the volume is constant, $w = 0$ and $\Delta U = q$.

In step 2, there is an irreversible expansion against a constant opposing pressure, which is calculated from $w = -P_{\text{ex}}\Delta V$

The constant opposing pressure is given, and ΔV can be obtained from

$$V_{\text{final}} - V_{\text{initial}} = 7.39 \text{ L} - 3.42 \text{ L}$$

$$w = -(1.19 \text{ atm})(7.39 \text{ L} - 3.42 \text{ L})$$

$$= -4.72 \text{ L} \cdot \text{atm} = (-4.72 \text{ L} \cdot \text{atm}) \left(\frac{101.325 \text{ J}}{1 \text{ L} \cdot \text{atm}} \right) = -479 \text{ J}$$

The total work for part B is $0 \text{ J} + (-479 \text{ J}) = -479 \text{ J}$

- 6.24** Molecules have a higher heat capacity than monatomic gases because they are able to store energy in the form of rotations and vibrations, in addition to simple translational kinetic energy, which is the only energy storage mode available to monatomic gases. The heat capacity of C_2H_6 is larger than that of CH_4 because it is a more complicated molecule that has more

possibilities for the molecule to rotate and for more bonds to vibrate than does CH₄.

- 6.26** (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

$$q = \left(\frac{10.35 \text{ g}}{20.18 \text{ g} \cdot \text{mol}^{-1}} \right) (50^\circ\text{C} - 25^\circ\text{C}) (20.8 \text{ J} \cdot \text{mol}^{-1} \cdot (^\circ\text{C})^{-1}) = 2.7 \times 10^2 \text{ J}$$

- (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

$$q = \left(\frac{10.35 \text{ g}}{20.18 \text{ g} \cdot \text{mol}^{-1}} \right) (50^\circ\text{C} - 25^\circ\text{C}) (12.5 \text{ J} \cdot \text{mol}^{-1} \cdot (^\circ\text{C})^{-1}) = 1.6 \times 10^2 \text{ J}$$

- 6.28** (a) BF₃ is a polyatomic, nonlinear molecule. The contribution from molecular motions will be 3R.
(b) N₂O is a polyatomic, linear molecule. The contribution from molecular motions will be 5/2 R.
(c) HCl is a linear molecule. The contribution from molecular motions will be 5/2 R.
(d) SO₂ is a polyatomic, nonlinear molecule. The contribution from molecular motions will be 3R.

- 6.30** No, the gasses do not have the same final temperature. The CH₄ molecules have more internal vibrations in which to store energy than do N₂ molecules. As a result, it will require more energy to increase the temperature of CH₄(g), and if the same amount of energy is supplied to both gasses, the temperature of N₂ will be higher than that of CH₄.

- 6.32** Not counting internal vibrations, a nonlinear molecule will have a heat capacity of $C_{V,m} = 3R$. The temperatures at which the three vibrations of SO₂ become available are 1968 K, 1680 K, and 768 K. If a vibration is

accessible, it will contribute a factor of R to the heat capacity. Therefore,

(a) $C_{V,m} = 6R$; (b) $C_{V,m} = 4R$; (c) $C_{V,m} = 3R$

6.34 (a) $\Delta H_{\text{freezing}} = -\Delta H_{\text{fus}}$

$$\Delta H_{\text{fus}} = -\frac{(-4.01 \text{ kJ})}{\left(\frac{25.23 \text{ g}}{32.04 \text{ g} \cdot \text{mol}^{-1}}\right)} = 5.09 \text{ kJ} \cdot \text{mol}^{-1}$$

$$(b) \Delta H_{\text{vap}} = \frac{37.5 \text{ kJ}}{\left(\frac{95 \text{ g}}{78.11 \text{ g} \cdot \text{mol}^{-1}}\right)} = 31 \text{ kJ} \cdot \text{mol}^{-1}$$

6.36 This process is composed of two steps: raising the temperature of the liquid water from 30°C to 100°C and then converting the liquid water to steam at 100°C.

$$\text{Step 1: } \Delta H = (155 \text{ g})(4.18 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(100\text{°C} - 30\text{°C}) = 45.4 \text{ kJ}$$

$$\text{Step 2: } \Delta H = \left(\frac{155 \text{ g}}{18.02 \text{ g} \cdot \text{mol}^{-1}}\right)(40.7 \text{ kJ} \cdot \text{mol}^{-1}) = 350 \text{ kJ}$$

$$\text{Total heat required} = 45.4 \text{ kJ} + 350 \text{ kJ} = 395 \text{ kJ}$$

6.38 The heat lost by the metal must equal the heat gained by the water. Also, the final temperature of the metal must be the same as that of the water. We can set up the following relationship and solve for the specific heat capacity of the metal:

$$\Delta H_{\text{metal}} = -\Delta H_{\text{water}}$$

$$(25.0 \text{ g})(\text{Specific heat})_{\text{metal}}(29.8\text{°C} - 90.0\text{°C})$$

$$= -(50.0 \text{ g})(4.184 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(29.8\text{°C} - 25.0\text{°C})$$

$$(\text{Specific heat})_{\text{metal}} = 0.667 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1}$$

6.40 (a) heat absorbed = $(1.55 \text{ mol NO}) \left(\frac{180.6 \text{ kJ}}{2 \text{ mol NO}} \right) = 140 \text{ kJ}$

$$(b) \quad n_{N_2} = \frac{PV}{RT} = \frac{1.00 \text{ atm} \times 5.45 \text{ L}}{0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 273 \text{ K}} = 0.243 \text{ mol}$$

$$(0.243 \text{ mol } N_2) \left(\frac{180.6 \text{ kJ}}{\text{mol } N_2} \right) = 43.9 \text{ kJ}$$

$$(c) \quad n_{N_2} = \frac{0.492 \text{ kJ}}{180.6 \text{ kJ} \cdot \text{mol}^{-1}} = 0.00272 \text{ mol}$$

$$n_{N_2} = (0.00272 \text{ mol})(28.02 \text{ g} \cdot \text{mol}^{-1}) = 0.0762 \text{ g}$$

$$\begin{aligned} 6.42 \quad (a) \quad \text{heat} &= \frac{(7.0 \text{ cm} \times 6.0 \text{ cm} \times 5.0 \text{ cm})(1.5 \text{ g} \cdot \text{cm}^{-3} \text{ C})}{12.01 \text{ g} \cdot \text{mol}^{-1} \text{ C}} (-394 \text{ kJ} \cdot \text{mol}^{-1} \text{ C}) \\ &= -1.0 \times 10^4 \text{ kJ} \end{aligned}$$

$$(b) \quad \text{mass of water} = \frac{(1.0 \times 10^7 \text{ J})}{(4.18 \text{ J} \cdot (\text{C})^{-1} \cdot \text{g}^{-1})(100^\circ\text{C} - 25^\circ\text{C})} = 3.2 \times 10^4 \text{ g}$$

$$6.44 \quad n_{\text{SO}_2} = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(13.4 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(273 \text{ K})} = 0.598 \text{ mol}$$

$$n_{\text{O}_2} = \frac{15.0 \text{ g } \text{O}_2}{32.0 \text{ g} \cdot \text{mol}^{-1} \text{ O}_2} = 0.469 \text{ mol}$$

The SO_2 is the limiting reactant and can react with 0.299 mol of O_2 :

$$\text{heat evolved} = (0.598 \text{ mol } \text{SO}_2) \left(\frac{-198 \text{ kJ}}{2 \text{ mol } \text{SO}_2} \right) = -59.2 \text{ kJ}$$

$$6.46 \quad \Delta U = -65 \text{ kJ} \quad \text{and} \quad w = -48 \text{ kJ}. \quad \text{At constant pressure, } \Delta U = \Delta H + w.$$

$$\text{Therefore, } \Delta H = \Delta U - w = -65 \text{ kJ} - (-48 \text{ kJ}) = -17 \text{ kJ}$$

6.48 Given the composition of “synthesis gas” it is easiest to first calculate the enthalpy of combustion of 1.000 L of the gas. In 1.000 L of synthesis gas there are 0.40 L of CO. The moles of CO present is given by:

$$n_{\text{CO}} = \frac{P \cdot V}{R \cdot T} = \frac{(1 \text{ atm}) \cdot (0.40 \text{ L})}{\left(0.0820574 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right) \cdot (298 \text{ K})} = 0.0164 \text{ mol of CO}$$

The enthalpy of combustion of CO is calculated, using enthalpies of formation and the balanced reaction $2\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$, to be -566.0 kJ/mol . Therefore, if 1.000L of synthesis gas were to burn, $(0.0164 \text{ mol}) \cdot (-566.0 \text{ kJ/mol}) = -9.26 \text{ kJ}$ of energy would be released due to the combustion of CO. The energies released due to the combustion of $\text{H}_2\text{(g)}$ and $\text{CH}_4\text{(g)}$ when 1.000 L of synthesis gas burns is calculated in a similar way:

$$n_{\text{H}_2} = \frac{P \cdot V}{R \cdot T} = \frac{(1 \text{ atm}) \cdot (0.25 \text{ L})}{(0.0820574 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}) \cdot (298 \text{ K})} = 0.0102 \text{ mol of H}_2$$

$$(0.0102 \text{ mol of H}_2) \cdot (-571.66 \text{ kJ} \cdot \text{mol}^{-1}) = -5.84 \text{ kJ}$$

$$n_{\text{CH}_4} = \frac{P \cdot V}{R \cdot T} = \frac{(1 \text{ atm}) \cdot (0.25 \text{ L})}{(0.0820574 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}) \cdot (298 \text{ K})} = 0.0102 \text{ mol of CH}_4$$

$$(0.0102 \text{ mol of H}_2) \cdot (-890 \text{ kJ} \cdot \text{mol}^{-1}) = -9.10 \text{ kJ}$$

All together, when 1 L of synthesis gas burns, -24.2 kJ of energy is released.

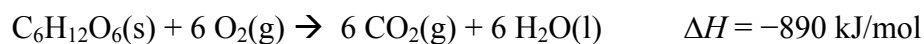
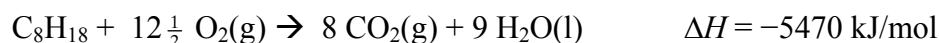
The amount of energy needed to heat 5.5 L of $\text{H}_2\text{O(l)}$ by 5°C is given by:

$$5.5 \text{ L} \cdot \left(\frac{1000 \text{ g}}{\text{L}} \right) \cdot (4.184 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}) \cdot (5^\circ\text{C}) = 115 \text{ kJ}$$

Therefore, the volume of synthesis gas that must be burned to provide this much energy is:

$$\frac{115 \text{ kJ}}{24.2 \text{ kJ} \cdot \text{L}^{-1}} = 4.75 \text{ L}$$

6.50 (a) and (b) The balanced chemical equations and enthalpies of combustion for methane, octane, and glucose are:



Dividing these combustion enthalpies by the moles of $\text{CO}_2\text{(g)}$ produced we find:

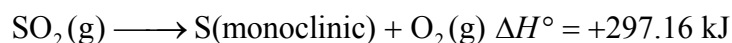
For combustion of $\text{CH}_4(\text{g})$: $\Delta H = -890 \text{ kJ/mol CO}_2(\text{g})$

For combustion of C_8H_{18} : $\Delta H = -684 \text{ kJ/mol CO}_2(\text{g})$

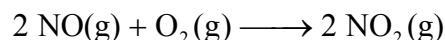
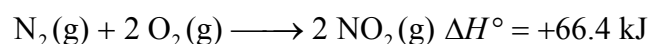
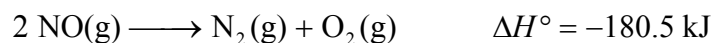
For combustion of $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$: $\Delta H = -468 \text{ kJ/mol CO}_2(\text{g})$

(c) combustion of glucose produces more CO_2 than does generating the same amount of energy using octane.

- 6.52** The combustion of the monoclinic sulfur is reversed and added to the combustion reaction of rhombohedral sulfur:

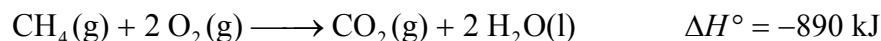


- 6.54** The first reaction is reversed and added to the second:

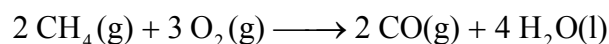
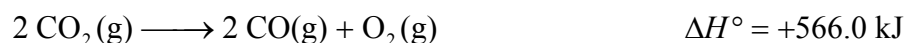
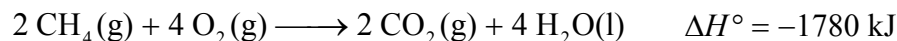


$$\Delta H^\circ = -180.5 \text{ kJ} + 66.4 \text{ kJ} = -114.1 \text{ kJ}$$

- 6.56** First, write the balanced equations for the known reactions:



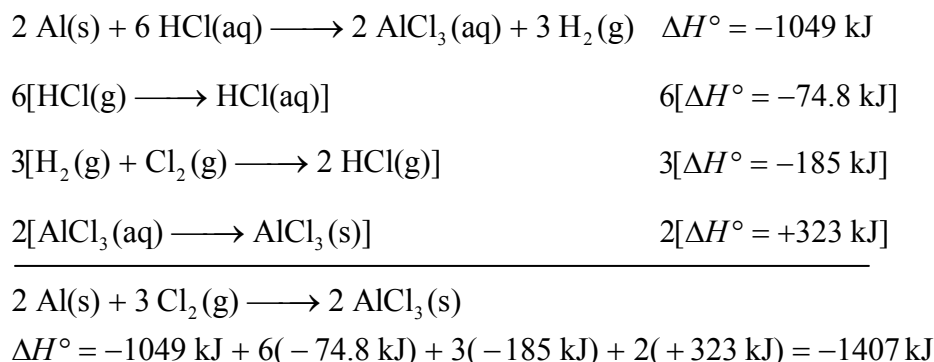
The desired reaction can be obtained by multiplying the first reaction by 2 and adding it to the reverse of the second reaction, also multiplied by 2.



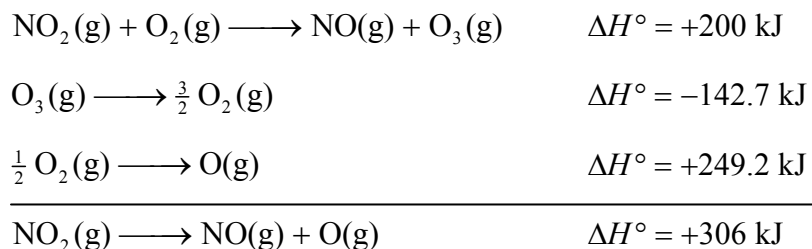
$$\Delta H^\circ = -1780 \text{ kJ} + 566.0 \text{ kJ} = -1214 \text{ kJ}$$

$$\begin{aligned}
 \mathbf{6.58} \quad \Delta H^\circ &= \Delta H^\circ_f(\text{CaCl}_2, \text{aq}) + \Delta H^\circ_f(\text{H}_2\text{O}, \text{l}) + \Delta H^\circ_f(\text{CO}_2, \text{g}) \\
 &\quad - [\Delta H^\circ_f(\text{CaCO}_3, \text{s}) + 2(\Delta H^\circ_f(\text{HCl}, \text{aq}))] \\
 &= -877.1 \text{ kJ} \cdot \text{mol}^{-1} + (-285.83 \text{ kJ} \cdot \text{mol}^{-1}) + (-393.51 \text{ kJ} \cdot \text{mol}^{-1}) \\
 &\quad - [(-1206.9 \text{ kJ} \cdot \text{mol}^{-1}) + 2(-167.16 \text{ kJ} \cdot \text{mol}^{-1})] \\
 &= -15.2 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

6.60 The desired reaction is obtained adding reaction 1 to 6 times reaction 2, 3 times reaction 3, and 2 times the reverse of reaction 4:



6.62 From Appendix 2A, $\Delta H^\circ_f(\text{O}_3) = +142.7 \text{ kJ} \cdot \text{mol}^{-1}$

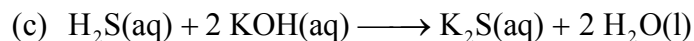


6.64 (a) $3 \text{ NO}_2(\text{g}) + \text{H}_2\text{O(l)} \longrightarrow 2 \text{ HNO}_3(\text{aq}) + \text{NO(g)}$

$$\begin{aligned}
 \Delta H^\circ_r &= 2 \Delta H^\circ_f(\text{HNO}_3, \text{aq}) \\
 &\quad + \Delta H^\circ_f(\text{NO}, \text{g}) - [3 \Delta H^\circ_f(\text{NO}_2, \text{g}) + \Delta H^\circ_f(\text{H}_2\text{O}, \text{l})] \\
 &= 2(-207.36 \text{ kJ} \cdot \text{mol}^{-1}) + 90.25 \text{ kJ} \cdot \text{mol}^{-1} - [3(+33.18 \text{ kJ} \cdot \text{mol}^{-1}) \\
 &\quad + (-285.83 \text{ kJ} \cdot \text{mol}^{-1})] \\
 &= -138.18 \text{ kJ}
 \end{aligned}$$

(b) $\text{B}_2\text{O}_3(\text{s}) + 3 \text{ CaF}_2(\text{s}) \longrightarrow 2 \text{ BF}_3(\text{g}) + 3 \text{ CaO(s)}$

$$\begin{aligned}
\Delta H^\circ_r &= 2 \Delta H^\circ_f(\text{BF}_3, \text{g}) + 3 \Delta H^\circ_f(\text{CaO}, \text{s}) \\
&\quad - [\Delta H^\circ_f(\text{B}_2\text{O}_3, \text{s}) + \Delta H^\circ_f(\text{CaF}_2, \text{s})] \\
&= 2(-1137.0 \text{ kJ} \cdot \text{mol}^{-1}) + 3(-635.09 \text{ kJ} \cdot \text{mol}^{-1}) \\
&\quad - [-1272.8 \text{ kJ} \cdot \text{mol}^{-1} + 3(-1219.6 \text{ kJ} \cdot \text{mol}^{-1})] \\
&= +752.3 \text{ kJ}
\end{aligned}$$



$$\begin{aligned}
\Delta H^\circ_r &= \Delta H^\circ_f(\text{K}_2\text{S}, \text{aq}) + 2 \Delta H^\circ_f(\text{H}_2\text{O}, \text{l}) \\
&\quad - [\Delta H^\circ_f(\text{H}_2\text{S}, \text{aq}) + 2 \Delta H^\circ_f(\text{KOH}, \text{aq})] \\
&= -417.5 \text{ kJ} \cdot \text{mol}^{-1} + 2(-285.83 \text{ kJ} \cdot \text{mol}^{-1}) \\
&\quad - [-39.7 \text{ kJ} \cdot \text{mol}^{-1} + 2(-482.37 \text{ kJ} \cdot \text{mol}^{-1})] \\
&= -38.7 \text{ kJ}
\end{aligned}$$

- 6.66** (a) The reaction of interest is: $\frac{1}{2} \text{N}_2(\text{g}) + 1 \frac{1}{2} \text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{l})$. The reaction enthalpy may be calculated using individual bond enthalpies and the enthalpy of vaporization of NH_3 . During the reaction, $\frac{1}{2}$ of a mole of N_2 bonds are broken as are $1 \frac{1}{2}$ moles of $\text{H}-\text{H}$ bonds while three $\text{N}-\text{H}$ bonds are formed. In addition, -23.4 kJ will be released due to condensation of the product. Using the suggested data tables, the enthalpy of formation is estimated to be:

$$\begin{aligned}
&\frac{1}{2} (+944 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \frac{1}{2} (436 \text{ kJ} \cdot \text{mol}^{-1}) \\
&\quad + 3 (-388 \text{ kJ} \cdot \text{mol}^{-1}) + (-23.4 \text{ kJ} \cdot \text{mol}^{-1}) \\
&= -61.4 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

- (b) The reaction of interest is $2 \text{C}(\text{gr}) + 3 \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6\text{O}(\text{l})$. As in part (a) above, the reaction enthalpy may be estimated using the bond enthalpies, the enthalpy of sublimation of $\text{C}(\text{gr})$ and the enthalpy of vaporization of the product. In this reaction, 3 moles of $\text{H}-\text{H}$ bonds and 0.5 moles of $\text{O}=\text{O}$ bonds, are broken while 1 mole of $\text{C}-\text{C}$ bonds, 5 moles of $\text{C}-\text{H}$ bonds, 1 mole of $\text{O}-\text{H}$ bonds, and 1 mole of $\text{C}-\text{O}$ bonds are formed. Furthermore, $717 \text{ kJ} \cdot \text{mol}^{-1}$ are needed to vaporize the graphite and -43.5

kJ mol^{-1} are released when the product condenses into a liquid. Using the suggested data tables, the enthalpy of formation is estimated to be:

$$\begin{aligned} & 3(+436 \text{ kJ} \cdot \text{mol}^{-1}) + \frac{1}{2}(496 \text{ kJ} \cdot \text{mol}^{-1}) + 2(717 \text{ kJ} \cdot \text{mol}^{-1}) \\ & + (-348 \text{ kJ} \cdot \text{mol}^{-1}) + 5(-412 \text{ kJ} \cdot \text{mol}^{-1}) + (-463 \text{ kJ} \cdot \text{mol}^{-1}) \\ & + 2(-743 \text{ kJ} \cdot \text{mol}^{-1}) + (-43.5 \text{ kJ} \cdot \text{mol}^{-1}) \\ & = -668 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

(c) The reaction of interest is $3\text{C}(\text{gr}) + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_3\text{H}_6\text{O}(\text{l})$. As in parts (a) and (b) above, 3 moles of H-H bonds and 0.5 moles of O-O bonds are broken and three moles of C(gr) is vaporized while 2 moles of C-C bonds, 1 mole of C=O bonds and 6 moles of C-H bonds are formed and $-21.9 \text{ kJ mol}^{-1}$ are released when one mole of acetone condenses from a gas to a liquid. Using the suggested data tables, the enthalpy of formation is estimated to be:

$$\begin{aligned} & 3(+436 \text{ kJ} \cdot \text{mol}^{-1}) + \frac{1}{2}(496 \text{ kJ} \cdot \text{mol}^{-1}) + 3(717 \text{ kJ} \cdot \text{mol}^{-1}) \\ & + 2(-348 \text{ kJ} \cdot \text{mol}^{-1}) + 6(-412 \text{ kJ} \cdot \text{mol}^{-1}) + (-743 \text{ kJ} \cdot \text{mol}^{-1}) \\ & + (-29.1 \text{ kJ} \cdot \text{mol}^{-1}) \\ & = -233 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

6.68 For the reaction $\text{AlCl}_3(\text{s}) \longrightarrow \text{Al}^{3+}(\text{g}) + 3 \text{Cl}^{-}(\text{g})$

$$\begin{aligned} \Delta H_{\text{L}} = \Delta H_{\text{f}}^{\circ}(\text{Al}, \text{g}) + 3 \Delta H_{\text{f}}^{\circ}(\text{Cl}, \text{g}) + I_1(\text{Al}) + I_2(\text{Al}) + I_3(\text{Al}) \\ - E_{\text{ea}}(\text{Cl}) - \Delta H_{\text{f}}(\text{AlCl}_3, \text{s}) \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{L}} &= 326 \text{ kJ} \cdot \text{mol}^{-1} + 3(121 \text{ kJ} \cdot \text{mol}^{-1}) + 577 \text{ kJ} \cdot \text{mol}^{-1} \\ &+ 1817 \text{ kJ} \cdot \text{mol}^{-1} + 2744 \text{ kJ} \cdot \text{mol}^{-1} - 349 \text{ kJ} \cdot \text{mol}^{-1} \\ &+ 704.2 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\Delta H_{\text{L}} = 6182 \text{ kJ} \cdot \text{mol}^{-1}$$

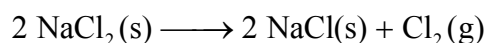
6.70 The process can be broken down into the following steps:

	$\Delta H^\circ, \text{kJ} \cdot \text{mol}^{-1}$
$\text{Na}^+(\text{g}) + 2 \text{Cl}^-(\text{g}) \longrightarrow \text{NaCl}_2(\text{s})$	-2524^*
$\text{Na}(\text{s}) \longrightarrow \text{Na}(\text{g})$	$2(+107.32)$
$\text{Na}(\text{g}) \longrightarrow \text{Na}^+(\text{g}) + \text{e}^-$	$+494$
$\text{Na}^+(\text{g}) \longrightarrow \text{Na}^{2+}(\text{g}) + \text{e}^-$	$+4560$
$\text{Cl}_2(\text{g}) \longrightarrow 2 \text{Cl}(\text{g})$	$+242$
$2 (\text{Cl}(\text{g}) + \text{e}^- \longrightarrow \text{Cl}^-(\text{g}))$	$2(-349)$
<hr/>	
$\text{Na}(\text{s}) + 2 \text{Cl}_2(\text{g}) \longrightarrow \text{NaCl}_2(\text{s})$	$\Delta H^\circ_f = +2289$

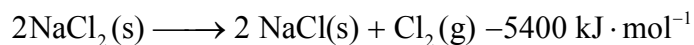
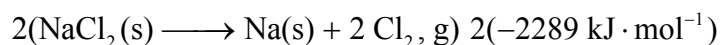
For comparison, the enthalpy of formation of

$\text{NaCl}(\text{s}) = -411.15 \text{ kJ} \cdot \text{mol}^{-1}$. Because the enthalpy of formation of NaCl_2 is a large positive number, NaCl_2 would be considerably unstable.

The disproportionation reaction



would have an energy of



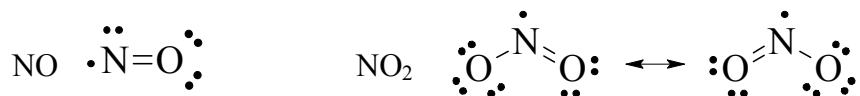
This would be very likely to take place, so NaCl_2 would not be isolated.

6.72 (a)	break:	1 mol H—Cl bonds	$431 \text{ kJ} \cdot \text{mol}^{-1}$
		1 mol F—F bonds	$158 \text{ kJ} \cdot \text{mol}^{-1}$
	form:	1 mol H—F bonds	$-565 \text{ kJ} \cdot \text{mol}^{-1}$
		1 mol Cl—F bonds	$-256 \text{ kJ} \cdot \text{mol}^{-1}$
			<hr/>
Total			$-232 \text{ kJ} \cdot \text{mol}^{-1}$

*From the assumption that ΔH_L is the same as that of MgCl_2 ...

(b) break:	1 mol H—Cl bonds	431 kJ · mol ⁻¹
	1 mol C=C bonds	612 kJ · mol ⁻¹
form:	1 mol C—C bonds	-348 kJ · mol ⁻¹
	1 mol C—H bonds	-412 kJ · mol ⁻¹
	1 mol C—Cl bonds	-338 kJ · mol ⁻¹
	Total	-55 kJ · mol ⁻¹
(c) break:	1 mol H—H bonds	436 kJ · mol ⁻¹
	1 mol C=C bonds	612 kJ · mol ⁻¹
form:	1 mol C—C bonds	-348 kJ · mol ⁻¹
	2 mol C—H bonds	2(-412) kJ · mol ⁻¹
	Total	-124 kJ · mol ⁻¹

- 6.74** (a) The Lewis structures for NO and NO₂ show that the bond order in NO is a double bond and that in NO₂ is 1.5 on average.

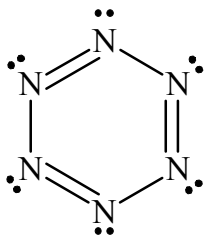


The bond enthalpy of NO at 632 kJ · mol⁻¹ is close to the N=O value listed in the table, whereas the N—O bond enthalpy in NO₂ of 469 kJ · mol⁻¹ is slightly greater than the average of a N—O single and N=O double bond: $\frac{1}{2}(630 \text{ kJ} + 210 \text{ kJ}) = 420 \text{ kJ}$

The extra stability is due to resonance stabilization.

- (b) The bond energies are the same for the two bonds, because the bonds are equivalent due to resonance.

6.76



The reaction in question is $\text{N}_6 \longrightarrow 3 \text{N}_2(\text{g})$

For this to occur, we will need to break 3 N—N and 3 NRN bonds and form 3 N—N triple bonds:

$$3(163 \text{ kJ} \cdot \text{mol}^{-1})$$

$$3(409 \text{ kJ} \cdot \text{mol}^{-1})$$

$$-3(944 \text{ kJ} \cdot \text{mol}^{-1})$$

$$-1116 \text{ kJ} \cdot \text{mol}^{-1}$$

The reaction to form $\text{N}_2(\text{g})$ is very exothermic and so the reaction is likely to occur. Although N_6 might be resonance-stabilized like benzene, it is unlikely that resonance stabilization would overcome the tendency to form the very strong $\text{N} \equiv \text{N}$ triple bond; thus we do not expect N_6 to be a stable molecule.

- 6.78** (a) The enthalpy of vaporization is the heat required for the conversion $\text{CH}_3\text{OH}(\text{l}) \longrightarrow \text{CH}_3\text{OH}(\text{g})$ at constant pressure. The value at 298.2 K will be given by

$$\begin{aligned} \Delta H^\circ_{\text{vap at 298 K}} &= \Delta H^\circ_{\text{f}}(\text{CH}_3\text{OH}, \text{g}) - \Delta H^\circ_{\text{f}}(\text{CH}_3\text{OH}, \text{l}) \\ &= -200.66 \text{ kJ} \cdot \text{mol}^{-1} - (-238.86 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= 38.20 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

- (b) In order to take into account the difference in temperature, we need to use the heat capacities of the reactants and products in order to raise the temperature of the system to 64.5°C. We can rewrite the reactions as follows, to emphasize temperature:



$$\begin{aligned}
 \text{CH}_3\text{OH(l)}_{\text{at } 298 \text{ K}} &\longrightarrow \text{CH}_3\text{OH(l)}_{\text{at } 337.6 \text{ K}} & \Delta H^\circ &= (1 \text{ mol}) \\
 & & &\times (337.8 \text{ K} - 298.2 \text{ K}) \\
 & & &\times (81.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \\
 & & &= 3.23 \text{ kJ}
 \end{aligned}$$

$$\begin{aligned}
 \text{CH}_3\text{OH(g)}_{\text{at } 298 \text{ K}} &\longrightarrow \text{CH}_3\text{OH(g)}_{\text{at } 337.6 \text{ K}} & \Delta H^\circ &= (1 \text{ mol}) \\
 & & &\times (337.8 \text{ K} - 298.2 \text{ K}) \\
 & & &\times (43.89 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \\
 & & &= 1.74 \text{ kJ}
 \end{aligned}$$

To add these together to get the overall equation at 337.6 K, we must reverse the second equation:

$$\begin{array}{ll}
 \text{CH}_3\text{OH(l)}_{\text{at } 298 \text{ K}} \longrightarrow \text{CH}_3\text{OH(g)}_{\text{at } 298 \text{ K}} & \Delta H^\circ = 38.20 \text{ kJ} \\
 \text{CH}_3\text{OH(l)}_{\text{at } 337.8 \text{ K}} \longrightarrow \text{CH}_3\text{OH(l)}_{\text{at } 298 \text{ K}} & \Delta H^\circ = -3.23 \text{ kJ} \\
 \text{CH}_3\text{OH(g)}_{\text{at } 298 \text{ K}} \longrightarrow \text{CH}_3\text{OH(g)}_{\text{at } 337.8 \text{ K}} & \Delta H^\circ = 1.74 \text{ kJ} \\
 \hline
 \text{CH}_3\text{OH(l)}_{\text{at } 337.8 \text{ K}} \longrightarrow \text{CH}_3\text{OH(g)}_{\text{at } 337.8 \text{ K}} & \Delta H^\circ = 34.71 \text{ kJ}
 \end{array}$$

(c) The value in the table is $35.3 \text{ kJ} \cdot \text{mol}^{-1}$ for the enthalpy of vaporization of methanol. The value is close to that calculated as corrected by heat capacities. At least part of the error can be attributed to the fact that heat capacities are not strictly independent of temperature.

6.80 The change in the reaction enthalpy is given by:

$$\begin{aligned}
 \Delta H_r(T_2) - \Delta H_r(T_1) &= (T_2 - T_1)\Delta C_p \quad \text{where} \\
 \Delta C_p &= \sum n \cdot C_p(\text{prod.}) - \sum n \cdot C_p(\text{react.})
 \end{aligned}$$

given N_2 and H_2 are linear molecules, their heat capacities are both approximately $\frac{7}{2}R$ while that of NH_3 is $4R$. Therefore, for this reaction the change in the reaction enthalpy is:

$$\begin{aligned}
 \Delta H_r(T_2) - \Delta H_r(T_1) &= (500 \text{ K} - 300 \text{ K}) \left[2(4R) - 3\left(\frac{7}{2}R\right) - \frac{7}{2}R \right] \\
 &= -9.98 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

6.82 (a) The amount of heat lost by the piece of stainless steel must equal the amount of heat absorbed by the water. The specific heat of stainless steel

is found in Table 6.1. This problem is complicated because the water may undergo one or more phase changes during this process. In order to answer this question, we will need to analyze each step of the reaction to determine if the steel can transfer enough heat to the water to cause the given change.

For stainless steel, the enthalpy change will be given by

$$155.7 \text{ g} \times 0.51 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1} \times \Delta T = 79 \text{ J} \cdot (\text{°C})^{-1} \times \Delta T$$

For water, there are five separate processes that may be involved: (1) heating solid water to 0°C, (2) converting the solid water to liquid at 0°C, (3) raising the temperature of the water from 0°C to 100°C, (4) converting the liquid water to vapor at 100°C, (5) heating the vapor above 100°C.

To heat the solid water from -24°C to 0°C:

$$25.34 \text{ g} \times 2.03 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1} \times 24\text{°C} = 1.23 \text{ kJ}$$

For this process the corresponding decrease in temperature of the steel would be

$$1.23 \text{ kJ} \div 0.079 \text{ kJ} \cdot (\text{°C})^{-1} = 16\text{°C}$$

Temperature of the steel after heating the solid water to 0°C will be
 $475\text{°C} - 16\text{°C} = 459\text{°C}$.

Because the temperature of the steel is still above that of the water, there is adequate heat for the next transformation to occur.

To convert all the solid water to liquid water at 0°C, we would require

$$\left(\frac{25.34 \text{ g H}_2\text{O}}{18.01 \text{ g} \cdot \text{mol}^{-1} \text{ H}_2\text{O}} \right) (6.01 \text{ kJ} \cdot \text{mol}^{-1}) = 8.46 \text{ kJ}$$

This change would require the temperature of the steel to decrease further by

$$8.46 \text{ kJ} \div 0.079 \text{ kJ} \cdot (\text{°C})^{-1} = 107\text{°C}$$

The temperature of the steel after melting all of the solid water to 0°C will be $459^{\circ}\text{C} - 107^{\circ}\text{C} = 352^{\circ}\text{C}$. The temperature of the steel is still above that of the water, so more heat can be transferred to heat the liquid water.

To heat the liquid water from 0°C to 100°C:

$$25.34 \text{ g} \times 4.184 \text{ J} \cdot (^{\circ}\text{C})^{-1} \cdot \text{g}^{-1} \times 100^{\circ}\text{C} = 10.6 \text{ kJ}$$

This change would require the temperature of the steel to decrease further by

$$10.6 \text{ kJ} \div 0.079 \text{ kJ} \cdot (^{\circ}\text{C})^{-1} = 134^{\circ}\text{C}$$

The steel is still sufficiently hot enough to cause this transformation, so all of the water will be heated to 100°C. The temperature of the steel after melting all of the solid water to 0°C will be $352^{\circ}\text{C} - 134^{\circ}\text{C} = 218^{\circ}\text{C}$. The steel still has enough heat to convert at least some of the water from liquid to vapor.

$$\left(\frac{25.34 \text{ g H}_2\text{O}}{18.01 \text{ g} \cdot \text{mol}^{-1} \text{ H}_2\text{O}} \right) (40.7 \text{ kJ} \cdot \text{mol}^{-1}) = 57.3 \text{ kJ}$$

$$57.3 \text{ kJ} \div 0.079 \text{ kJ} \cdot (^{\circ}\text{C})^{-1} = 725^{\circ}\text{C}$$

The temperature of the steel is not sufficient to convert all the water to vapor. The final temperature will then be 100°C, with some of the water converted to vapor and some remaining in the liquid phase.

(b) To determine the amount of liquid and gaseous water present, we must determine the amount of heat transferred to the water from the steel at 100°C. The steel should still be at 218°C when all the liquid water has reached 100°C. The final temperature of the steel must also be 100°C, so its change in temperature will be -118°C . To go from 218°C to 100°C, the steel will lose

$$0.079 \text{ kJ} \cdot (^{\circ}\text{C})^{-1} \times 118^{\circ}\text{C} = 9.3 \text{ kJ}$$

We can then calculate the amount of water that can be converted to vapor at 100°C by 9.3 kJ.

$$\left(\frac{9.3 \text{ kJ}}{40.7 \text{ kJ} \cdot \text{mol}^{-1}} \right) (18.02 \text{ g} \cdot \text{mol}^{-1}) = 4.1 \text{ g}$$

4.1 g of water will be converted to vapor, leaving

25.34 g – 4.1 g = 21.2 g of water in the liquid phase.

- 6.84** (a) First, we calculate the amount of heat needed to raise the temperature of the water. Converting the temperatures from °F to °C:

$^{\circ}\text{C} = \frac{5}{9} (^{\circ}\text{F} - 32^{\circ})$, so 65°F corresponds to 18°C and 108°F corresponds to 42°C.

$$\begin{aligned} \Delta H &= (100 \text{ gal})(3.785 \text{ L} \cdot \text{gal}^{-1})(1000 \text{ cm}^3 \cdot \text{L}^{-1})(1.00 \text{ g} \cdot \text{cm}^{-3}) \\ &\quad \times (4.18 \text{ J} \cdot (^{\circ}\text{C})^{-1} \cdot \text{g}^{-1})(42^{\circ}\text{C} - 18^{\circ}\text{C}) \\ &= 38 \text{ MJ} \end{aligned}$$

The enthalpy of combustion of methane is –890 kJ · mol (from Table 6.4).

The mass of methane required will be calculated as follows:

$$\left(\frac{38 \times 10^3 \text{ kJ}}{890 \text{ kJ} \cdot \text{mol}^{-1}} \right) (16.04 \text{ g} \cdot \text{mol}^{-1} \text{ CH}_4) = 6.8 \times 10^2 \text{ g CH}_4$$

- (b) This quantity can be obtained from the ideal gas law. $6.8 \times 10^2 \text{ g}$ of CH₄ is 42 mol of CH₄:

$$V = \frac{nRT}{P} = \frac{(42 \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{1.00 \text{ atm}} = 1030 \text{ L}$$

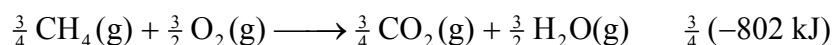
6.86 (a) $w = -(1.00 \text{ mol})(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K}) \ln \frac{15.50 \text{ L}}{7.00 \text{ L}}$
 $= -1.97 \text{ kJ}$

(b) $w = -P_{\text{ext}} \Delta V = -\left(\frac{743 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}} \right) (15.5 \text{ L} - 7.00 \text{ L}) \left(\frac{101.325 \text{ J}}{1 \text{ L} \cdot \text{atm}} \right)$
 $= -0.842 \text{ kJ}$

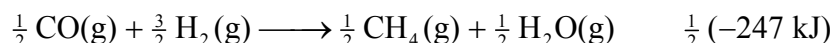
- (c) The fact that the expansion occurs adiabatically—which means that the system is isolated from its surroundings so that no heat is transferred—is important. It tells us that $q = 0$, and therefore $\Delta U = w = -0.842 \text{ kJ}$. But

ΔU will also be equal to $=nC_v\Delta T$ (see equation 19) because U is a state function. The heat capacity of an ideal gas is $12.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ (we will assume it is constant over this temperature range). Therefore, $-0.842 \text{ J} = (1.00 \text{ mol})(12.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(\Delta T)$. $\Delta T = -67.4 \text{ K}$. The final temperature will be $298.2\text{K} - 67.4\text{K} = 230.6\text{K}$.

- 6.88** In order to solve this problem, we must be able to add reactions (a), (b), and (c) to give the reaction desired. The most logical starting point for solving this problem is to find the reactant or product that appears only once in (a), (b), or (c), as this will determine how that equation must be used. Because O_2 only appears in (a), equation (a) must be multiplied by $\frac{3}{4}$ and left in its original direction in order to obtain the correct amount of $\text{O}_2(\text{g})$.



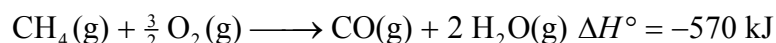
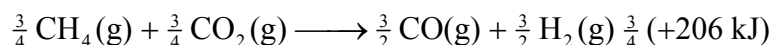
We now consider how to combine this equation with (b) and (c) to give the desired overall reaction. Because $\text{H}_2\text{O}(\text{g})$ appears in (c) and not in (b), we must add equation (c) to the transformed (a) so as to obtain a total of two $\text{H}_2\text{O}(\text{g})$. To do this, we must reverse (c) and multiply it by $\frac{1}{2}$:



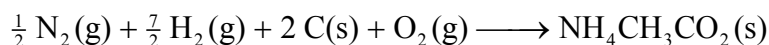
Equation (b) must be multiplied by $\frac{3}{4}$ and left in its original direction in order that the $\text{CO}_2(\text{g})$ will be cancelled from the overall equation:



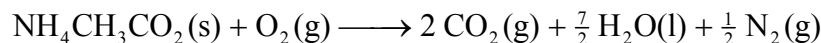
The net result is



6.90 The formation reaction is



The combustion reaction that we want is:



Using Hess' Law

$$\begin{aligned} \Delta H^\circ_{\text{combustion}} &= 2 \Delta H^\circ_{\text{f}}(\text{CO}_2, \text{g}) + \frac{7}{2} \Delta H^\circ_{\text{f}}(\text{H}_2\text{O}, \text{l}) \\ &\quad - \Delta H^\circ_{\text{f}}(\text{NH}_4\text{CH}_3\text{CO}_2, \text{s}) \\ &= 2(-393.15 \text{ kJ} \cdot \text{mol}^{-1}) + \frac{7}{2}(-285.83 \text{ kJ} \cdot \text{mol}^{-1}) \\ &\quad - (-616.14 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -117.28 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

6.92 (a) The heat output of each sample is found using the heat capacity of the calorimeter and the observed change in temperature of the calorimeter. For Brand X, ΔT was 8.8°C and the energy content of 1.00 g is:

$$(8.8^\circ\text{C}) \cdot (600 \text{ J} \cdot \text{K}^{-1}) = 5300 \text{ J} \cdot \text{g}^{-1}. \text{ For the ABC product, } \Delta T \text{ was } 8.5^\circ\text{C} \text{ and the energy content of 1.00 g is: } (8.5^\circ\text{C}) \cdot (600 \text{ J} \cdot \text{K}^{-1}) = 5100 \text{ J} \cdot \text{g}^{-1}.$$

(b) 30 g of Brand X cereal contains

$$(30 \text{ g}) (5.3 \text{ kJ} \cdot \text{g}^{-1}) \left(\frac{1 \text{ Calorie}}{4.184 \text{ kJ}} \right) = 38 \text{ Calories while 30 g of ABC product contains } (30 \text{ g}) (5.1 \text{ kJ} \cdot \text{g}^{-1}) \left(\frac{1 \text{ Calorie}}{4.184 \text{ kJ}} \right) = 36 \text{ Calories}$$

6.94 (a) and (b)

	M	ΔH_c	density			
compound	($\text{g} \cdot \text{mol}^{-1}$)	($\text{kJ} \cdot \text{mol}^{-1}$)	($\text{kJ} \cdot \text{g}^{-1}$)	($\text{g} \cdot \text{cm}^{-3}$)	($\text{L} \cdot \text{mol}^{-1}$)	($\text{MJ} \cdot \text{L}^{-1}$)
benzene	78.11	-3268	-41.84	0.8786	0.088 90	-36.76
ethanol	46.07	-1368	-29.69	0.7893	0.058 37	-23.44
hexane	86.18	-4163	-48.30	0.6603	0.1305	-31.89
octane	114.23	-5471	-47.89	0.7025	0.1626	-33.64

(c) On a per-liter basis, the chemicals increase in cost in the following order: ethanol < benzene ~ hexane < octane; (d) The choice of fuel is not a simple matter. Although it would appear that benzene is the best as far as heat production per liter is concerned, the cost of ethanol is roughly two-thirds that of the cost of benzene, making the heat produced per dollar about the same. Other issues such as cleanliness of burning, ecological impact of the production of the fuel, capacity of fuel tanks (and how far a car can drive on a tank of gas) then become important issues.

- 6.96** In step 1, $\Delta U = q_V = 50 \text{ J}$ and $w = 0$. In step 2, $q = -5 \text{ J}$ and $\Delta U = -50 \text{ J}$; therefore, $-50 \text{ J} = -5 \text{ J} + w$; $w = -45 \text{ J}$. Because $w = -P\Delta V$ and $P = 1.00 \text{ atm}$

$$\Delta V = \left(\frac{+45 \text{ J}}{1.00 \text{ atm}} \right) \left(\frac{0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \right) = +0.44 \text{ L}$$

The gas constants are used to convert the units of J to L · atm. Because the value ΔV is positive, this change will represent an expansion.

- 6.98** The heat given off by the reaction that was absorbed by the calorimeter is given by

$$\Delta H = -(488.1 \text{ J} \cdot (\text{°C})^{-1})(21.34\text{°C} - 20.00\text{°C}) = -654 \text{ J}$$

This, however, is not all the heat produced, as the 50.0 mL of solution resulting from mixing also absorbed some heat. If we assume that the volume of NaOH and HCl are negligible compared to the volume of water present and that the density of the solution is $1.00 \text{ g} \cdot \text{mL}^{-1}$, then the change in enthalpy of the solution is given by

$$\Delta H = -(21.34\text{°C} - 20.00\text{°C})(4.18 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(50.0 \text{ g}) = -280 \text{ J}$$

The total heat given off will be $-654 \text{ J} + (-280 \text{ J}) = -934 \text{ J}$

This heat is for the reaction of $(0.700 \text{ M})(0.0250 \text{ L}) = 0.0175 \text{ mol HCl}$, so the amount of heat produced per mole of HCl will be given by

$$\frac{-934 \text{ J}}{0.0175 \text{ mol}} = -53.4 \text{ kJ} \cdot \text{mol}^{-1} \text{ HCl}$$

6.100 From Appendix 2A we can find the enthalpies of combustion of the gases involved:

Compound	Enthalpy of combustion ($\text{kJ} \cdot \text{mol}^{-1}$)
$\text{CH}_4(\text{g})$, methane	-890
$\text{C}_2\text{H}_6(\text{g})$, ethane	-1560
$\text{C}_3\text{H}_8(\text{g})$, propane	-2220
$\text{C}_4\text{H}_{10}(\text{g})$, butane	-2878

(a) To calculate the mass of CO_2 produced, we simply need to realize that there will be one mole of CO_2 produced per mole of carbon present in the starting compound. So there will be one mole of CO_2 produced per mole of CH_4 , two per mole of C_2H_6 , three per mole of C_3H_8 , and four per mole of C_4H_{10} .

Total moles of CO_2 produced per minute

$$\begin{aligned}
 &= \frac{1 \text{ mol CO}_2}{1 \text{ mol CH}_4} \times 9.3 \text{ mol CH}_4 \\
 &\quad + \frac{2 \text{ mol CO}_2}{1 \text{ mol C}_2\text{H}_6} \times 3.1 \text{ mol C}_2\text{H}_6 \\
 &\quad + \frac{3 \text{ mol CO}_2}{1 \text{ mol C}_3\text{H}_8} \times 0.40 \text{ mol C}_3\text{H}_8 \\
 &\quad + \frac{4 \text{ mol CO}_2}{1 \text{ mol C}_4\text{H}_{10}} \times 0.20 \text{ mol C}_4\text{H}_{10} \\
 &= 17.5 \text{ mol} \cdot \text{min}^{-1}
 \end{aligned}$$

The mass of CO_2 produced per minute will be

$$17.5 \text{ mol} \cdot \text{min}^{-1} \times 44.01 \text{ g} \cdot \text{mol}^{-1} = 7.70 \times 10^2 \text{ g} \cdot \text{min}^{-1}$$

(b) The heat released per minute will be given by the enthalpies of combustion multiplied by the number of moles of each gas combusted in that time period:

$$\text{heat released} = (9.3 \text{ mol CH}_4)(-890 \text{ kJ} \cdot \text{mol}^{-1} \text{ CH}_4)$$

$$\begin{aligned}
 &+ (3.1 \text{ mol C}_2\text{H}_6)(-1560 \text{ kJ} \cdot \text{mol}^{-1} \text{ C}_2\text{H}_6) \\
 &+ (0.40 \text{ mol C}_3\text{H}_8)(-2220 \text{ kJ} \cdot \text{mol}^{-1}) \\
 &+ (0.20 \text{ mol C}_4\text{H}_{10})(-2878 \text{ kJ} \cdot \text{mol}^{-1} \text{ C}_4\text{H}_{10}) \\
 &= -1.5 \times 10^4 \text{ kJ} \cdot \text{min}^{-1}
 \end{aligned}$$

6.102 The total amount of heat released by the reaction will be given by

$$-5.270 \text{ kJ} \cdot (\text{°C})^{-1} \times 1.140\text{°C} = -6.008 \text{ kJ}$$

In this case, the heats of reaction for the two different outcomes will be given simply by the ΔH°_f values for SO_2 ($-296.83 \text{ kJ} \cdot \text{mol}^{-1}$) and

SO_3 ($-395.72 \text{ kJ} \cdot \text{mol}^{-1}$). The number of moles of sulfur is

$0.6192 \text{ g S(s)} \div 32.06 \text{ kJ} \cdot \text{mol}^{-1} = 0.01931 \text{ mol S(s)}$. We do not know the relative amounts of SO_2 versus SO_3 formed, but these can be determined using the following two relationships, which are required by the stoichiometries of the reactions.

Let x = number of moles of SO_2 formed

Let y = number of moles of SO_3 formed

Then $x + y = 0.01931 \text{ mol}$

$$(-296.83 \text{ kJ} \cdot \text{mol}^{-1})x + (-395.72 \text{ kJ} \cdot \text{mol}^{-1})y = -6.008 \text{ kJ}$$

$$x = 0.01652 \text{ mol}$$

$$y = 0.00279 \text{ mol}$$

The ratio of SO_2 to SO_3 will be $0.01652 \text{ mol} \div 0.00279 \text{ mol} = 5.92 : 1$.

6.104 In order of increasing enthalpy of vaporization: N_2 , CH_4 , C_6H_6 , H_2O ,

NaCl . A large enthalpy of vaporization indicates strong intermolecular interactions in the liquid phase. The stronger these interactions the larger the amount of energy needed to free a molecule into the gas phase.

Nitrogen, being a homonuclear diatomic molecule interacts through other N_2 molecules in the condensed phase through very weak London forces.

CH_4 , being a nonpolar molecule also interacts with other CH_4 molecules through weak London forces. However, the electron distribution along the

C-H bonds is not uniform leading to stronger interactions than in N_2 . C_6H_6 has no net dipole moment but, due to p bonding, above and below the ring of carbons tends to be negative compared to the hydrogen atoms along the edge of the ring giving rise to stronger bonding interactions than in CH_4 and N_2 . H_2O is a highly polar molecule that can bind to other water molecules through relatively strong hydrogen bonding interactions, making its enthalpy of vaporization higher than that of the previous molecules. Finally, $NaCl$ forms an ionic solid with strong ionic bonds extending throughout a three-dimensional crystalline lattice, requiring a large amount of energy to free a $NaCl$ molecule from the condensed phase.

- 6.106** The energy released by a falling body is given by: $E = mgh$ where m is the mass of the object, g is the acceleration due to free fall, and h is the height through which the object falls. The energy deposited into the water was therefore, $E = (15 \text{ kg})(20 \text{ m})(9.8067 \text{ m} \cdot \text{s}^{-2}) = 2940 \text{ J}$. If all of this energy is deposited into the water upon impact, the change in the temperature of the water would be:

$$(2500 \text{ g})(4.184 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1})\Delta T = 2940 \text{ J}$$

$$\Delta T = 0.28 ^\circ\text{C}$$

If the falling body does 900.0 J of work before impacting the water, only 2040 J will be deposited into the water, resulting in a temperature change of:

$$(2500 \text{ g})(4.184 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1})\Delta T = 2040 \text{ J}$$

$$\Delta T = 0.20 ^\circ\text{C}$$

- 6.108** The amount of calcium chloride in the pipes is

$$(45.6 \text{ kJ} \cdot \text{pipe}^{-1})(60 \text{ pipes}) = 2736 \text{ kJ} \text{ or } 1.25 \times 10^4 \text{ moles of}$$

$CaCl_2 \cdot 6H_2O$. Given the enthalpy of fusion of $CaCl_2 \cdot 6H_2O$, the amount of energy released as the Ca recrystallizes is:

$(27 \text{ kJ} \cdot \text{mol}^{-1})(1.25 \times 10^4 \text{ mol}) = 3.37 \times 10^5 \text{ kJ}$. The mass of water that may be heated by 10°C (from 15°C to 25°C) is:

$$m(4.184 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1})(10^\circ\text{C}) = 3.37 \times 10^5 \text{ kJ}$$

$$m = 8100 \text{ g} \quad \text{or} \quad 8.1 \text{ kg}$$