

## 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 but the gas loses energy through expansion. Therefore the change in internal energy is:
- $$\Delta U = 524 \text{ kJ} - 340 \text{ kJ} = +184 \text{ kJ}$$

**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

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

**6.27** (a) HCN is a linear molecule. The contribution from molecular motions will be  $5/2 R$ .

(b)  $\text{C}_2\text{H}_6$  is a polyatomic, nonlinear molecule. The contribution from molecular motions will be  $3R$ .

(c) Ar is a monoatomic ideal gas. The contribution from molecular motions to the heat capacity will be  $3/2 R$ .

(d) HBr is a diatomic, linear molecule. The contribution from molecular motions will be  $5/2 R$ .

- 6.29** The strategy here is to determine the amount of energy per photon and the amount of energy needed to heat the water. Dividing the latter by the former will give the number of photons needed. Energy per photon is given by:

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s} (2.9979 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{4.50 \times 10^{-3} \text{ m}} = 4.41 \times 10^{-34} \text{ J} \cdot \text{photon}^{-1}$$

The energy needed to heat the water is:

$$350 \text{ g} (4.184 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}) (100.0^\circ\text{C} - 25.0^\circ\text{C}) = 1.10 \times 10^5 \text{ J}$$

The number of photons needed is therefore:

$$\frac{1.10 \times 10^5 \text{ J}}{4.41 \times 10^{-34} \text{ J} \cdot \text{photon}^{-1}} = 2.49 \times 10^{27} \text{ photons}$$

- 6.31** (a) Using the estimation that  $3R = C$ :

$$3R = C = (0.392 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1})(M)$$

$$M = \frac{3R}{0.392 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}} = 63.6 \text{ g mol}^{-1}$$

This molar mass indicates that the atomic solid is Cu(s)

- (b) From Example 5.3 we find that the density of a substance which form

a face-centered cubic unit cell is given by:  $d = \frac{4M}{8^{3/2} N_A r^3}$ . Therefore, we

expect the density of copper to be:

$$d = \frac{4 (63.55 \text{ g} \cdot \text{mol}^{-1})}{8^{3/2} (6.022 \times 10^{23} \text{ mol}^{-1})(1.28 \times 10^{-8} \text{ cm})^3} = 8.90 \text{ g} \cdot \text{cm}^{-3}$$

- 6.33** (a)  $\Delta H_{\text{vap}} = \frac{1.93 \text{ kJ}}{0.235 \text{ mol}} = 8.21 \text{ kJ} \cdot \text{mol}^{-1}$

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

- 6.35** This process is composed of two steps: melting the ice at 0°C and then raising the temperature of the liquid water from 0°C to 25°C :

$$\text{Step 1: } \Delta H = \left( \frac{80.0 \text{ g}}{18.02 \text{ g} \cdot \text{mol}^{-1}} \right) (6.01 \text{ kJ} \cdot \text{mol}^{-1}) = 26.7 \text{ kJ}$$

$$\text{Step 2: } \Delta H = (80.0 \text{ g})(4.18 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(20.0\text{°C} - 0.0\text{°C}) = 6.69 \text{ kJ}$$

$$\text{Total heat required} = 26.7 \text{ kJ} + 6.69 \text{ kJ} = 33.4 \text{ kJ}$$

- 6.37** The heat gained by the water in the ice cube will be equal to the heat lost by the initial sample of hot water. The enthalpy change for the water in the ice cube will be composed of two terms: the heat to melt the ice at 0°C and the heat required to raise the ice from 0°C to the final temperature.

$$\begin{aligned} \text{heat (ice cube)} &= \left( \frac{50.0 \text{ g}}{18.02 \text{ g} \cdot \text{mol}^{-1}} \right) (6.01 \times 10^3 \text{ J} \cdot \text{mol}^{-1}) \\ &\quad + (50.0 \text{ g})(4.184 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(T_f - 0^\circ) \\ &= 1.67 \times 10^4 \text{ J} + (209 \text{ J} \cdot (\text{°C})^{-1})(T_f - 0^\circ) \end{aligned}$$

$$\begin{aligned} \text{heat (water)} &= (400 \text{ g})(4.184 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{g}^{-1})(T_f - 45^\circ) \\ &= (1.67 \times 10^3 \text{ J} \cdot (\text{°C})^{-1})(T_f - 45^\circ) \end{aligned}$$

Setting these equal:

$$-(1.67 \times 10^3 \text{ J} \cdot (\text{°C})^{-1})T_f + 7.5 \times 10^4 \text{ J} = 1.67 \times 10^4 \text{ J} + (209 \text{ J} \cdot (\text{°C})^{-1})T_f$$

Solving for  $T_f$  :

$$T_f = \frac{5.8 \times 10^4 \text{ J}}{1.88 \times 10^3 \text{ J} \cdot (\text{°C})^{-1}} = 31 \text{ °C}$$

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

$$(b) \Delta H = \left( \frac{197 \text{ g C}}{12.01 \text{ g} \cdot \text{mol}^{-1} \text{ C}} \right) \left( \frac{358.8 \text{ kJ}}{4 \text{ mol C}} \right) = 1.47 \times 10^2 \text{ kJ}$$

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

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

$$6.41 \quad (a) \quad (12 \text{ ft} \times 12 \text{ ft} \times 8 \text{ ft}) \left( \frac{30.48 \text{ cm}}{1 \text{ ft}} \right)^3 = 3.26 \times 10^7 \text{ cm}^3$$

The heat capacity of air is  $1.01 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{mol}^{-1}$  and the average molar mass of air is  $28.97 \text{ g} \cdot \text{mol}^{-1}$  (see Table 4.1). The density of air can be calculated from the ideal gas law:

$$d = \frac{P}{MRT} = \frac{1.00 \text{ atm}}{(28.97 \text{ g} \cdot \text{mol}^{-1})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(277.6 \text{ K})}$$

$$d = 0.00152 \text{ g} \cdot \text{cm}^{-3}$$

$$40^\circ\text{F} = 4.4^\circ\text{C}, 78^\circ\text{F} = 26^\circ\text{C}$$

$$\Delta T = 26^\circ\text{C} - 4.4^\circ\text{C} = 22^\circ$$

The heat required is

$$(3.26 \times 10^7 \text{ cm}^3)(0.00152 \text{ g} \cdot \text{cm}^{-3})(1.01 \text{ J} \cdot (\text{°C})^{-1} \cdot \text{mol}^{-1})(22^\circ\text{C})$$

$$= 1.1 \times 10^3 \text{ kJ}$$

The mass of octane required to produce this much heat will be given by

$$\left( \frac{-1.1 \times 10^3 \text{ kJ}}{-5471 \text{ kJ} \cdot \text{mol}^{-1}} \right) (114.22 \text{ g} \cdot \text{mol}^{-1}) = 23.0 \text{ g}$$

$$(b) \quad \Delta H = \left( \frac{(1.0 \text{ gal})(3.785 \times 10^3 \text{ mL} \cdot \text{gal}^{-1})(0.70 \text{ g} \cdot \text{mL}^{-1})}{114.22 \text{ g} \cdot \text{mol}^{-1}} \right)$$

$$\times \left( \frac{-10942 \text{ kJ}}{2 \text{ mol octane}} \right)$$

$$= -1.3 \times 10^5 \text{ kJ}$$

$$6.43 \quad (a) \quad \left( 1250 \frac{\text{kJ}}{\text{hr}} \right) \left( 1 \frac{\text{hr}}{\text{day}} \right) \left( 150 \frac{\text{days}}{\text{year}} \right) = 1.88 \times 10^5 \frac{\text{kJ}}{\text{year}}$$

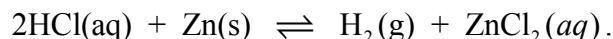
$$(b) \quad \left( 150 \frac{\text{trips}}{\text{year}} \right) \left( 0.40 \frac{\text{gal.}}{\text{trip}} \right) \left( 3.785 \frac{\text{L}}{\text{gal.}} \right) \left( 1000 \frac{\text{mL}}{\text{L}} \right) \left( 0.702 \frac{\text{g}}{\text{mL}} \right)$$

$$\left( \frac{1 \text{ mol}}{114.23 \text{ g}} \right) \left( 5471 \frac{\text{kJ}}{\text{mol}} \right) = 7.6 \times 10^6 \frac{\text{kJ}}{\text{year}}$$

**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  $-15 \text{ kJ} + 22 \text{ kJ} = \Delta U = +7 \text{ kJ}$ .

**6.47** To determine the enthalpy of the reaction we must start with a balanced chemical reaction and determine the limiting reagent:



$$0.800 \text{ L} \cdot 0.500 \text{ M HCl} = 0.400 \text{ mol HCl}$$

$$\frac{8.5 \text{ g}}{65.37 \text{ g} \cdot \text{mol}^{-1}} = 0.130 \text{ mol Zn}$$

Examining the reaction stoichiometry and the initial quantities of HCl and Zn, we note that Zn is the limiting reagent (0.260 mol of HCl is needed to completely react with 0.130 moles of Zn). The enthalpy of reaction may be obtained using tabulated enthalpies of formation:

$$\begin{aligned}\Delta H_r &= -153.89 \frac{\text{kJ}}{\text{mol}} + 2 \left( -167.16 \frac{\text{kJ}}{\text{mol}} \right) - 2 \left( -167.16 \frac{\text{kJ}}{\text{mol}} \right) - 0 \\ &= -153.89 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

This is the enthalpy per mole of Zinc consumed, Therefore, the energy released by the reaction of 8.5 g of Zinc is:

$$\left( -153.89 \frac{\text{kJ}}{\text{mol}} \right) (0.130 \text{ mol}) = -20.0 \text{ kJ}$$

The change in the temperature of the water is then:

$$-20000 \text{ J} = \left( -4.184 \frac{\text{J}}{^\circ\text{C g}} \right) (800 \text{ g}) \Delta T$$

$$\Delta T = 5.98^\circ\text{C} \text{ and } T_f = 25^\circ\text{C} + 5.98^\circ\text{C} = 31^\circ\text{C}$$

**6.49** The enthalpy of reaction for the reaction



may be found using enthalpies of formation:

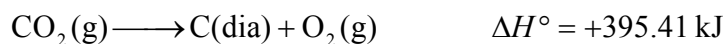
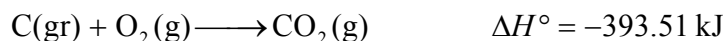
$$28 \left( -393.51 \frac{\text{kJ}}{\text{mol}} \right) + 10 \left( -241.82 \frac{\text{kJ}}{\text{mol}} \right) - 4 \left( -67 \frac{\text{kJ}}{\text{mol}} \right) = -1316.5 \frac{\text{kJ}}{\text{mol}}$$



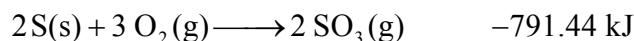
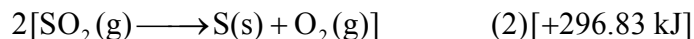
This is the energy released per mole of reaction as written. One fourth of this amount of energy or  $-329.1 \frac{\text{kJ}}{\text{mol}}$  will be released per mole of TNT consumed. The energy density in kJ per gram may be found by dividing this amount of energy by the mass of one mole of TNT:

$$\frac{-329.1 \frac{\text{kJ}}{\text{mol}}}{227.11 \frac{\text{g}}{\text{mol}}} = -14.5 \frac{\text{kJ}}{\text{g}}$$

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

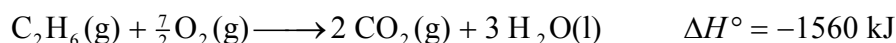
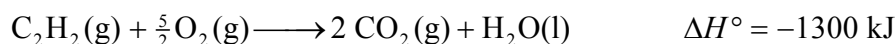


- 6.53** The first reaction is doubled, reversed, and added to the second to give the desired total reaction:

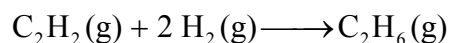
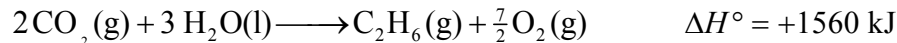
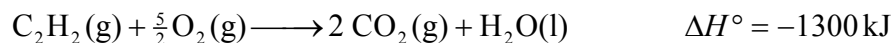


$$\Delta H^\circ = (2)(+296.83 \text{ kJ} \cdot \text{mol}^{-1}) - (791.44 \text{ kJ} \cdot \text{mol}^{-1}) = -197.78 \text{ kJ}$$

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



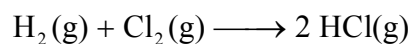
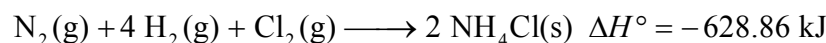
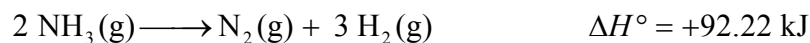
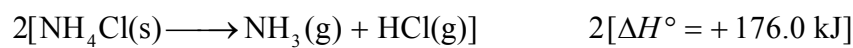
The second equation is reversed and added to the first, plus two times the third:



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

**6.57**  $\Delta H^\circ = 12 \Delta H^\circ_f(\text{H}_2\text{O}, \text{l}) - [4(\Delta H^\circ_f[\text{HNO}_3, \text{l}]) + 5(\Delta H^\circ_f[\text{N}_2\text{H}_4, \text{l}])]$   
 $= 12(-285.83 \text{ kJ} \cdot \text{mol}^{-1}) - [4(-174.10 \text{ kJ} \cdot \text{mol}^{-1})$   
 $+ 5(+50.63 \text{ kJ} \cdot \text{mol}^{-1})]$   
 $= -2480.41 \text{ kJ} \cdot \text{mol}^{-1}$

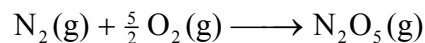
**6.59** The desired reaction may be obtained by reversing the first reaction and multiplying it by 2, reversing the second reaction, and adding these to the third:



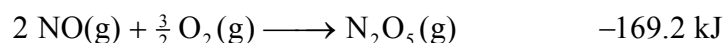
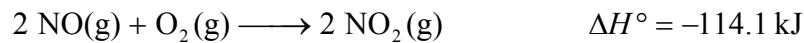
$$\Delta H^\circ = 2(+176.0 \text{ kJ}) + 92.22 \text{ kJ} - 628.86 \text{ kJ} = -184.6 \text{ kJ}$$

**6.61** From Appendix 2A,  $\Delta H^\circ_f(\text{NO}) = +90.25 \text{ kJ}$

The reaction we want is



Adding the first reaction to half of the second gives

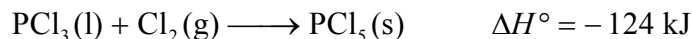


The enthalpy of this reaction equals the enthalpy of formation of  $\text{N}_2\text{O}_5(\text{g})$  minus twice the enthalpy of formation of  $\text{NO}$ , so we can write

$$-169.2 \text{ kJ} = \Delta H^\circ_f (\text{N}_2\text{O}_5) - 2(+90.25 \text{ kJ})$$

$$\Delta H^\circ_f (\text{N}_2\text{O}_5) = +11.3 \text{ kJ}$$

**6.63** The enthalpy of the reaction



is  $\Delta H^\circ_r = \Sigma \Delta H^\circ_f (\text{products}) - \Sigma \Delta H^\circ_f (\text{reactants})$

$$-124 \text{ kJ} = \Delta H^\circ_f (\text{PCl}_5, \text{s}) - \Delta H^\circ_f (\text{PCl}_3, \text{l})$$

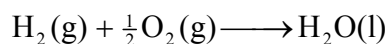
Remember that the standard enthalpy of formation of  $\text{Cl}_2(\text{g})$  will be 0 by definition because this is an element in its reference state. From the Appendix we find that

$$\Delta H^\circ_f (\text{PCl}_3, \text{l}) = -319.7 \text{ kJ} \cdot \text{mol}^{-1}$$

$$-124 \text{ kJ} = \Delta H^\circ_f (\text{PCl}_5, \text{s}) - (-319.7 \text{ kJ})$$

$$\Delta H^\circ_f (\text{PCl}_5, \text{s}) = -444 \text{ kJ} \cdot \text{mol}^{-1}$$

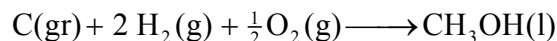
**6.65** (a) For  $\text{H}_2\text{O}(\text{l})$ , we want to find the enthalpy of the reaction



The enthalpy change can be estimated from bond enthalpies. We will need to put in (1 mol)  $(436 \text{ kJ} \cdot \text{mol}^{-1})$  to break the H—H bonds in 1 mol  $\text{H}_2(\text{g})$ ,  $(\frac{1}{2} \text{ mol}) (496 \text{ kJ} \cdot \text{mol}^{-1})$  to break the O—O bonds in  $\frac{1}{2} \text{ mol } \text{O}_2(\text{g})$ ; we will get back (2 mol)  $(463 \text{ kJ} \cdot \text{mol}^{-1})$  for the formation of 2 mol O—H bonds. This will give  $\Delta H = -242 \text{ kJ} \cdot \text{mol}^{-1}$ . This value, however, will be to produce water in the gas phase. In order to get the value for the liquid, we will need to take into account the amount of heat given off when the gaseous water condenses to the liquid phase. This is  $44.0 \text{ kJ} \cdot \text{mol}^{-1}$  at 298 K:

$$\begin{aligned}\Delta H^\circ_{\text{f,water(l)}} &= \Delta H^\circ_{\text{f,water(g)}} - \Delta H^\circ_{\text{vap}} = -242 \text{ kJ} - (1 \text{ mol})(44.0 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -286 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

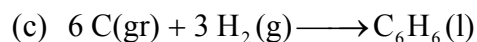
(b) The calculation for methanol is done similarly:



$\Delta H$  for individual bond contributions:

atomize 1 mol C(gr)	(1 mol)(717 kJ · mol <sup>-1</sup> )
break 2 mol H—H bonds	(2 mol)(436 kJ · mol <sup>-1</sup> )
break $\frac{1}{2}$ mol O <sub>2</sub> bonds	( $\frac{1}{2}$ mol)(496 kJ · mol <sup>-1</sup> )
form 3 mol C—H bonds	–(3 mol)(412 kJ · mol <sup>-1</sup> )
form 1 mol C—O bonds	–(1 mol)(360 kJ · mol <sup>-1</sup> )
form 1 mol O—H bonds	–(1 mol)(463 kJ · mol <sup>-1</sup> )
<hr/>	
Total	–222kJ

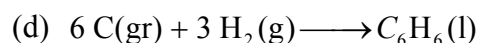
$$\begin{aligned}\Delta H^\circ_{\text{f, methanol(l)}} &= \Delta H^\circ_{\text{f, methanol(g)}} - \Delta H^\circ_{\text{vap}} \\ &= -222 \text{ kJ} - (1 \text{ mol})(35.3 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -257 \text{ kJ}\end{aligned}$$



Without resonance, we do the calculation considering benzene to have three double and three single C—C bonds:

atomize:	6 mol C(gr)	(6 mol)(717 kJ · mol <sup>-1</sup> )
break:	3 mol H—H bonds	(3 mol)(436 kJ · mol <sup>-1</sup> )
form:	3 mol CRC bonds	–(3 mol)(612 kJ · mol <sup>-1</sup> )
form:	3 mol C—C bonds	–(3 mol)(348 kJ · mol <sup>-1</sup> )
form:	6 mol C—H bonds	–(6 mol)(412 kJ · mol <sup>-1</sup> )
<hr/>		
Total		+258 kJ

$$\Delta H_{\text{f,benzene(l)}}^{\circ} = \Delta H_{\text{f,benzene(g)}}^{\circ} = \Delta H_{\text{vap}}^{\circ} = +258 \text{ kJ} - (1 \text{ mol})(30.8 \text{ kJ} \cdot \text{mol}^{-1}) \\ = +227 \text{ kJ}$$



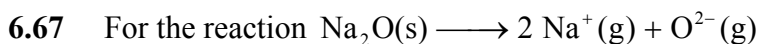
With resonance, we repeat the calculation considering benzene to have six resonance-stabilized C—C bonds:

atomize:	6 mol C(gr)	(6 mol)(717 kJ · mol <sup>-1</sup> )
break:	3 mol H—H bonds	(3 mol)(436 kJ · mol <sup>-1</sup> )
form:	6 mol C—C bonds, resonance	-(6 mol)(518 kJ · mol <sup>-1</sup> )
form:	6 mol C—H bonds	-(6 mol)(412 kJ · mol <sup>-1</sup> )

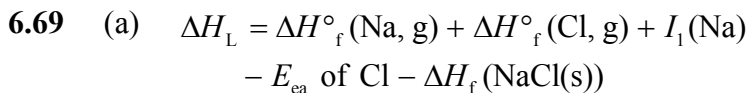
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Total		+30 kJ
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$$\Delta H_{\text{f,benzene(l)}}^{\circ} = \Delta H_{\text{f,benzene(g)}}^{\circ} - \Delta H_{\text{vap}}^{\circ} = +30 \text{ kJ} \cdot \text{mol}^{-1} - (1 \text{ mol})(30.8 \text{ kJ} \cdot \text{mol}^{-1}) \\ = -1 \text{ kJ}$$



$$\Delta H_{\text{L}} = 2 \Delta H_{\text{f}}^{\circ}(\text{Na, g}) + \Delta H_{\text{f}}^{\circ}(\text{O, g}) + 2 I_1(\text{Na}) \\ - E_{\text{ea1}}(\text{O}) - E_{\text{ea2}}(\text{O}) - \Delta H_{\text{f}}(\text{Na}_2\text{O(s)}) \\ \Delta H_{\text{L}} = 2(107.32 \text{ kJ} \cdot \text{mol}^{-1}) + 249 \text{ kJ} \cdot \text{mol}^{-1} + 2(494 \text{ kJ} \cdot \text{mol}^{-1}) \\ -141 \text{ kJ} \cdot \text{mol}^{-1} + 844 \text{ kJ} \cdot \text{mol}^{-1} + 409 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta H_{\text{L}} = 2564 \text{ kJ} \cdot \text{mol}^{-1}$$



$$787 \text{ kJ} \cdot \text{mol}^{-1} = 108 \text{ kJ} \cdot \text{mol}^{-1} + 122 \text{ kJ} \cdot \text{mol}^{-1} + 494 \text{ kJ} \cdot \text{mol}^{-1} \\ - 349 \text{ kJ} \cdot \text{mol}^{-1} - \Delta H_{\text{f}}(\text{NaCl(s)}) \\ \Delta H_{\text{f}}(\text{NaCl(s)}) = -412 \text{ kJ} \cdot \text{mol}^{-1}$$

$$(b) \quad \Delta H_L = \Delta H_f^\circ(\text{K}, g) + \Delta H_f^\circ(\text{Br}, g) + I_1(\text{K}) \\ - E_{\text{ea}}(\text{Br}) - \Delta H_f(\text{KBr}(s))$$

$$\Delta H_L = 89 \text{ kJ} \cdot \text{mol}^{-1} + 97 \text{ kJ} \cdot \text{mol}^{-1} + 418 \text{ kJ} \cdot \text{mol}^{-1} \\ - 325 \text{ kJ} \cdot \text{mol}^{-1} + 394 \text{ kJ} \cdot \text{mol}^{-1} \\ = 673 \text{ kJ} \cdot \text{mol}^{-1}$$

$$(c) \quad \Delta H_L = \Delta H_f^\circ(\text{Rb}, g) + \Delta H_f^\circ(\text{F}, g) + I_1(\text{Rb}) - E_{\text{ea}}(\text{F}) - \Delta H_f(\text{RbF}(s))$$

$$774 \text{ kJ} \cdot \text{mol}^{-1} = \Delta H_f^\circ(\text{Rb}, g) + 79 \text{ kJ} \cdot \text{mol}^{-1} \\ + 402 \text{ kJ} \cdot \text{mol}^{-1} - 328 \text{ kJ} \cdot \text{mol}^{-1} + 558 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta H_f^\circ(\text{Rb}, g) = 63 \text{ kJ} \cdot \text{mol}^{-1}$$

**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> )
<hr/>		
	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> )
<hr/>		
	Total	-115 kJ

**6.75** The value that we want is given simply by the difference between three isolated C=C bonds and three isolated C—C single bonds, versus six resonance-stabilized bonds:

$$3 \text{ C}=\text{C} \text{ bonds} + 3 \text{ C}—\text{C} \text{ bonds} = 3(348 \text{ kJ}) + 3(612 \text{ kJ}) = 2880 \text{ kJ}$$

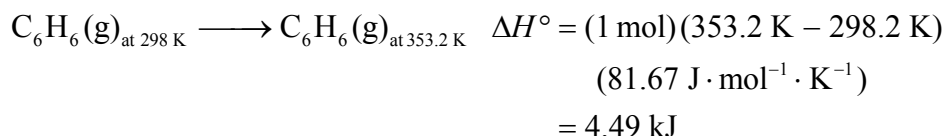
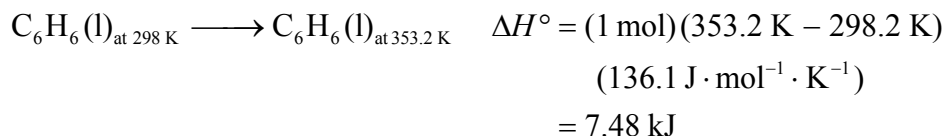
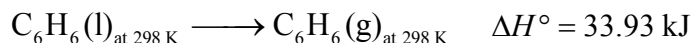
$$6 \text{ resonance-stabilized bonds} = 6(518 \text{ kJ}) = 3108 \text{ kJ}$$

As can be seen, the six resonance-stabilized bonds are more stable by ca. 228 kJ.

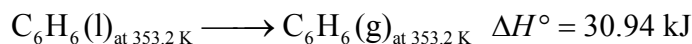
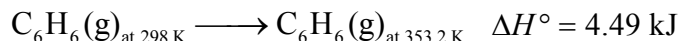
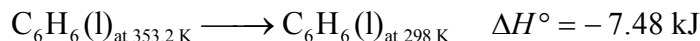
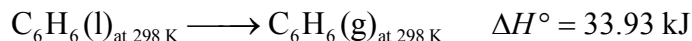
**6.77** (a) The enthalpy of vaporization is the enthalpy change associated with the conversion  $\text{C}_6\text{H}_6(\text{l}) \longrightarrow \text{C}_6\text{H}_6(\text{g})$  at constant pressure. The value at 298.2 K will be given by

$$\begin{aligned} \Delta H^\circ_{\text{vaporization at 298 K}} &= \Delta H^\circ_{\text{f}}(\text{C}_6\text{H}_6, \text{g}) - \Delta H^\circ_{\text{f}}(\text{C}_6\text{H}_6, \text{l}) \\ &= 82.93 \text{ kJ} \cdot \text{mol}^{-1} - (49.0 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= 33.93 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

(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 353.2 K. We can rewrite the reactions as follows, to emphasize temperature, and then combine them according to Hess's law:



To add these together to get the overall equation at 353.2 K, we must reverse the second equation:



(c) The value in the table is  $30.8 \text{ kJ} \cdot \text{mol}^{-1}$  for the enthalpy of vaporization of benzene. 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 constant with temperature.

**6.79** For the reaction:  $\text{A} + 2\text{B} \rightarrow 3\text{C} + \text{D}$  the molar enthalpy of reaction at temperature 2 is given by:

$$\Delta H_{\text{r},2}^\circ = H_{\text{m},2}^\circ(\text{products}) - H_{\text{m},2}^\circ(\text{reactants})$$



$$\begin{aligned}
&= 3H_{\text{m},2}^{\circ}(\text{C}) + H_{\text{m},2}^{\circ}(\text{D}) - H_{\text{m},2}^{\circ}(\text{A}) - 2H_{\text{m},2}^{\circ}(\text{B}) \\
&= 3[H_{\text{m},1}^{\circ}(\text{C}) + C_{p,m}(\text{C})(T_2 - T_1)] + [H_{\text{m},1}^{\circ}(\text{D}) + C_{p,m}(\text{D})(T_2 - T_1)] \\
&\quad - [H_{\text{m},1}^{\circ}(\text{A}) + C_{p,m}(\text{A})(T_2 - T_1)] - 2[H_{\text{m},1}^{\circ}(\text{B}) + C_{p,m}(\text{B})(T_2 - T_1)] \\
&= 3H_{\text{m},1}^{\circ}(\text{C}) + H_{\text{m},1}^{\circ}(\text{D}) - H_{\text{m},1}^{\circ}(\text{A}) - 2H_{\text{m},1}^{\circ}(\text{B}) \\
&\quad + [3C_{p,m}(\text{C}) + C_{p,m}(\text{D}) - C_{p,m}(\text{A}) - 2C_{p,m}(\text{B})](T_2 - T_1) \\
&= \Delta H_{\text{r},1}^{\circ} + [3C_{p,m}(\text{C}) + C_{p,m}(\text{D}) - C_{p,m}(\text{A}) - 2C_{p,m}(\text{B})](T_2 - T_1)
\end{aligned}$$

**6.81** This process involves five separate steps: (1) raising the temperature of the ice from  $-30.27^{\circ}\text{C}$  to  $0.00^{\circ}\text{C}$ , (2) melting the ice at  $0.00^{\circ}\text{C}$ , (3) raising the temperature of the liquid water from  $0.00^{\circ}\text{C}$  to  $100.00^{\circ}\text{C}$ , (4) vaporizing the water at  $100.00^{\circ}\text{C}$ , and (5) raising the temperature of the water vapor from  $100.00^{\circ}\text{C}$  to  $150.35^{\circ}\text{C}$ .

Step 1:

$$\Delta H = (27.96 \text{ g})(2.03 \text{ J} \cdot (^{\circ}\text{C})^{-1} \cdot \text{g}^{-1})(0.00^{\circ}\text{C} - (-30.27^{\circ}\text{C})) = 1.72 \text{ kJ}$$

Step 2:

$$\Delta H = \left( \frac{27.96 \text{ g}}{18.02 \text{ g} \cdot \text{mol}^{-1}} \right) (6.01 \text{ kJ} \cdot \text{mol}^{-1}) = 9.32 \text{ kJ}$$

Step 3:

$$\Delta H = (27.96 \text{ g})(4.18 \text{ J} \cdot (^{\circ}\text{C})^{-1} \cdot \text{g}^{-1})(100.00^{\circ}\text{C} - 0.00^{\circ}\text{C}) = 11.7 \text{ kJ}$$

Step 4:

$$\Delta H = \left( \frac{27.96 \text{ g}}{18.02 \text{ g} \cdot \text{mol}^{-1}} \right) (40.7 \text{ kJ} \cdot \text{mol}^{-1}) = 63.1 \text{ kJ}$$

Step 5:

$$\Delta H = (27.96 \text{ g})(2.01 \text{ J} \cdot (^{\circ}\text{C})^{-1} \cdot \text{g}^{-1})(150.35^{\circ}\text{C} - 100.00^{\circ}\text{C}) = 2.83 \text{ kJ}$$

$$\begin{aligned}
\text{The total heat required} &= 1.72 \text{ kJ} + 9.32 \text{ kJ} + 11.7 \text{ kJ} + 63.1 \text{ kJ} + 2.83 \text{ kJ} \\
&= 88.7 \text{ kJ}
\end{aligned}$$

**6.83** Appendix 2A provides us with the heat of formation of  $\text{I}_2(\text{g})$  at 298K ( $+62.44 \text{ kJ} \cdot \text{mol}^{-1}$ ) and the heat capacities of

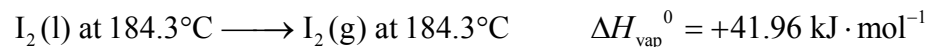
$I_2(g)$  ( $36.90 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) and  $I_2(s)$  ( $54.44 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ). We can calculate the  $\Delta H_{\text{sub}}^0$  at 298K:



We can calculate the enthalpy of fusion from the relationship

$$\Delta H_{\text{sub}}^0 = \Delta H_{\text{fus}}^0 + \Delta H_{\text{vap}}^0$$

but these values need to be at the same temperature. To correct the value for the fact that we want all the numbers for 298K, we need to alter the heat of vaporization, using the heat capacities for liquid and gaseous iodine.



From Section 6.22, we find the following relationship

$$\Delta H_{r,2}^0 = \Delta H_{r,1}^0 + \Delta C_{P,m}^0 (T_2 - T_1)$$

$$\Delta H_{\text{vap},298\text{K}}^0 = \Delta H_{\text{vap},475.5\text{K}}^0 + (C_{P,m}^0(I_2, g) - C_{P,m}^0(I_2, l)) (T_2 - T_1)$$

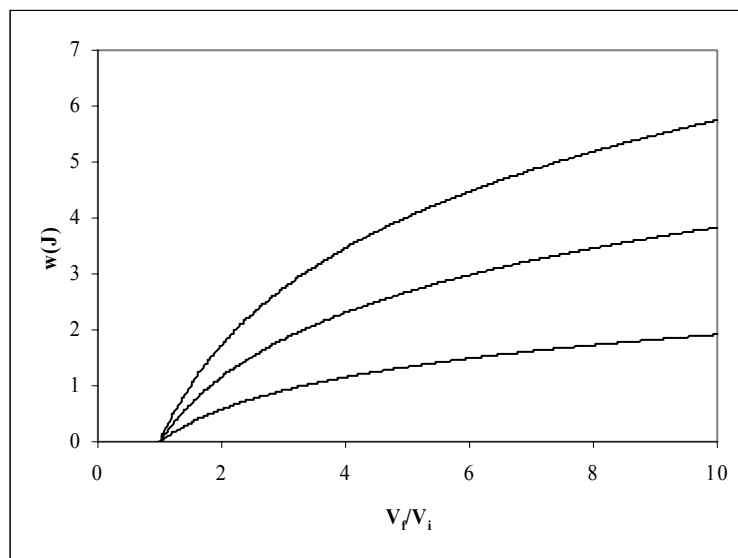
$$\begin{aligned} \Delta H_{\text{vap},298\text{K}}^0 &= +41.96 \text{ kJ} \cdot \text{mol}^{-1} \\ &\quad + (36.90 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - 80.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) (298\text{K} - 475.5\text{K}) \\ &= +49.73 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

So, at 298K:

$$+62.44 \text{ kJ} \cdot \text{mol}^{-1} = \Delta H_{\text{fus}}^0 + 49.73 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_{\text{fus}}^0 = +12.71 \text{ kJ} \cdot \text{mol}^{-1}$$

**6.85** (a)



(b) The amount of work done is greater at the higher temperature. This can be seen from the equation:

$$w = -nRT \ln \frac{V_{\text{final}}}{V_{\text{initial}}}$$

The amount of work done is directly proportional to the temperature at which the expansion takes place.

(c) The comparison requested is the comparison of the terms

$$\ln \frac{V_{\text{final}}}{V_{\text{initial}}}$$

for the two processes. Even though in both cases the gas expands by 4 L, the relative amount of work done is different. We can get a numerical comparison by taking the ratio of this term for the two conditions:

$$\frac{\ln \left( \frac{9.00 \text{ L}}{5.00 \text{ L}} \right)}{\ln \left( \frac{5.00 \text{ L}}{1.00 \text{ L}} \right)} = \frac{0.588}{1.61} = 0.365$$

The second expansion by 4.00 L produces only about one third the amount of work that the first expansion did.

**6.87** First, we need to calculate how much energy from the sunshine will be hitting the surface of the ethanol, so we convert the rate  $\text{kJ} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$  :

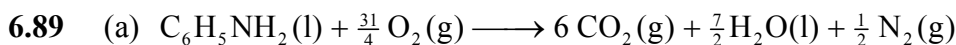
$$1 \text{ kJ} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \left( \frac{1 \text{ m}}{100 \text{ cm}} \right)^2 = 1 \times 10^{-4} \text{ kJ} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$$

$$(1 \times 10^{-4} \text{ kJ} \cdot \text{cm}^{-2} \cdot \text{s}^{-1})(50.0 \text{ cm}^2) \left( 10 \text{ min} \times \frac{60 \text{ s}}{\text{min}} \right) = 3 \text{ kJ}$$

The enthalpy of vaporization of ethanol is  $43.5 \text{ kJ} \cdot \text{mol}^{-1}$  (see Table 6.2).

We will assume that the enthalpy of vaporization is approximately the same at ambient conditions as it would be at the boiling point of ethanol.

$$\left( \frac{3 \text{ kJ}}{43.5 \text{ kJ} \cdot \text{mol}^{-1}} \right) (46.07 \text{ g} \cdot \text{mol}^{-1}) = 3 \text{ g}$$



(b)

$$m_{\text{CO}_2} = \left( \frac{0.1754 \text{ g aniline}}{93.12 \text{ g} \cdot \text{mol}^{-1} \text{ aniline}} \right) \left( \frac{6 \text{ mol CO}_2}{1 \text{ mol aniline}} \right) (28.01 \text{ g} \cdot \text{mol}^{-1} \text{ CO}_2)$$

$$= 0.4873 \text{ g CO}_2(\text{g})$$

$$m_{\text{H}_2\text{O}} = \left( \frac{0.1754 \text{ g aniline}}{93.12 \text{ g} \cdot \text{mol}^{-1} \text{ aniline}} \right) \left( \frac{3.5 \text{ mol H}_2\text{O}}{1 \text{ mol aniline}} \right) (18.02 \text{ g} \cdot \text{mol}^{-1} \text{ H}_2\text{O})$$

$$= 0.1188 \text{ g H}_2\text{O}(\text{l})$$

$$m_{\text{N}_2} = \left( \frac{0.1754 \text{ g aniline}}{93.12 \text{ g} \cdot \text{mol}^{-1} \text{ aniline}} \right) \left( \frac{0.5 \text{ mol N}_2}{1 \text{ mol aniline}} \right) (28.02 \text{ g} \cdot \text{mol}^{-1} \text{ N}_2)$$

$$= 0.02639 \text{ g N}_2(\text{g})$$

(c)  $n_{\text{O}_2} = \left( \frac{0.1754 \text{ g aniline}}{93.12 \text{ g} \cdot \text{mol}^{-1} \text{ aniline}} \right) \left( \frac{\frac{31}{4} \text{ mol O}_2}{1 \text{ mol aniline}} \right)$

$$= 0.01460 \text{ mol O}_2(\text{g})$$

$$P = \frac{nRT}{V} = \frac{(0.01460 \text{ mol O}_2)(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(296 \text{ K})}{0.355 \text{ L}}$$

$$= 0.999 \text{ atm}$$

**6.91** (a) The reaction enthalpy is obtained by Hess's law:

$$\Delta H^\circ_{\text{r}} = \Delta H^\circ_{\text{f}}(\text{CO}, \text{g}) - \Delta H^\circ_{\text{f}}(\text{H}_2\text{O}, \text{g})$$

$$\Delta H^\circ_{\text{r}} = (1)(-110.53 \text{ kJ} \cdot \text{mol}^{-1}) - (1)(-241.82 \text{ kJ} \cdot \text{mol}^{-1})$$

$$\Delta H^\circ_{\text{r}} = +131.29 \text{ kJ} \cdot \text{mol}^{-1}$$

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(b) The number of moles of  $\text{H}_2$  produced is obtained from the ideal gas law:

$$n = \frac{PV}{RT} = \frac{\left( \frac{500 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}} \right) (200 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(338 \text{ K})} = 4.74 \text{ mol}$$

The enthalpy change accompanying the production of this amount of hydrogen will be given by

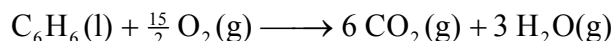
$$\Delta H = (4.74 \text{ mol})(131.29 \text{ kJ} \cdot \text{mol}^{-1}) = 623 \text{ kJ}$$

- 6.93** (a) The number of moles burned may be obtained by taking the difference in the number of moles of gas present in the tank before and after the drive using the ideal gas equation:

$$\begin{aligned} n_1 - n_2 &= \frac{P_1 V}{RT} - \frac{P_2 V}{RT} = (P_1 - P_2) \left( \frac{V}{RT} \right) \\ &= (16.0 \text{ atm} - 4.0 \text{ atm}) \left( \frac{30.0 \text{ L}}{(0.0820578 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})} \right) \\ &= 14.7 \text{ mol} \end{aligned}$$

- (b) From a table of enthalpies of formation, the enthalpy of combustion of  $\text{H}_2$  is found to be  $-241.82 \text{ kJ} \cdot \text{mol}^{-1}$ . The energy released was, therefore,  
 $(14.7 \text{ mol})(-241.82 \text{ kJ} \cdot \text{mol}^{-1}) = -3560 \text{ kJ}$

- 6.95** (a) First we must balance the chemical reaction:



For 1 mol  $\text{C}_6\text{H}_6(\text{l})$  burned, the change in the number of moles of gas is

$$(9.00 - 7.50) \text{ mol} = +2.50 \text{ mol} = \Delta n$$

$$w = -P\Delta V = -P \left( \frac{\Delta n RT}{P} \right) = -\Delta n RT$$

$$w = -(+2.50 \text{ mol})(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K}) = -6.19 \times 10^3 \text{ J} = -6.19 \text{ kJ}$$

$$\begin{aligned} \text{(b)} \quad \Delta H_c &= 6(-393.51 \text{ kJ} \cdot \text{mol}^{-1}) + 3(-241.82 \text{ kJ} \cdot \text{mol}^{-1}) - (+49.0 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -3135.5 \text{ kJ} \end{aligned}$$

$$\text{(c)} \quad \Delta U^\circ = \Delta H^\circ + w = (-3135.5 - 6.19) \text{ kJ} = -3141.7 \text{ kJ}$$

- 6.97** (a) The heat given off by the reaction, which was absorbed by the calorimeter, is given by

$$\Delta H = -(525.0 \text{ J} \cdot (^\circ\text{C})^{-1})(20.0^\circ\text{C} - 18.6^\circ\text{C}) = -0.74 \text{ kJ}$$

This, however, is not all the heat produced, as the 100.0 mL of solution resulting from mixing also absorbed some heat. If we assume that the

volume of NaOH and  $\text{HNO}_3$  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 heat of the solution is given by

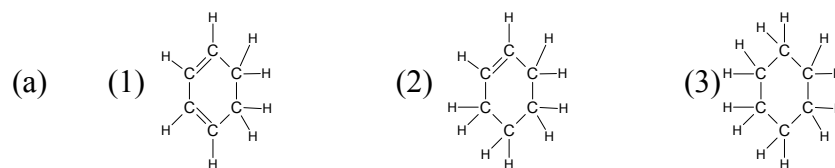
$$\Delta H = -(20.0^\circ\text{C} - 18.6^\circ\text{C})(4.18 \text{ J} \cdot (^\circ\text{C})^{-1} \cdot \text{g}^{-1})(100.0 \text{ g}) = -0.59 \text{ kJ}$$

The total heat given off will be  $-0.74 \text{ kJ} + (-0.59 \text{ kJ}) = -1.33 \text{ kJ}$

(b) This heat is for the reaction of  $(0.500 \text{ M})(0.0500 \text{ L}) = 0.0250 \text{ mol HNO}_3$ , so the amount of heat produced per mole of  $\text{HNO}_3$  will be given by

$$\frac{-1.33 \text{ kJ}}{0.0250 \text{ mol}} = -53.2 \text{ kJ} \cdot \text{mol}^{-1}$$

**6.99**



(b) From bond enthalpies, each step is identical, as the number and types of bonds broken and formed are the same:

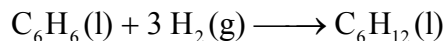
break:	1 mol C=C bonds	612 kJ
	1 mol H—H bonds	436 kJ
form:	1 mol C—C bonds	-348 kJ
	2 mol C—H bonds	2(-412 kJ)

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Total: -124 kJ

The total energy change should be equal to the sum of the three steps or  $3(-124 \text{ kJ}) = -372 \text{ kJ}$ .

(c) The Hess's law calculation using standard enthalpies of formation is easily performed on the composite reaction:

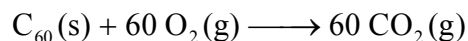


$$\Delta H^\circ_{\text{r}} = \Sigma \Delta H^\circ_{\text{f}}(\text{products}) - \Sigma \Delta H^\circ_{\text{f}}(\text{reactants})$$

$$\begin{aligned}
 &= \Delta H^\circ_f(\text{cyclohexane}) - \Delta H^\circ_f(\text{benzene}) \\
 &= -156.4 \text{ kJ} \cdot \text{mol}^{-1} - (+49.0 \text{ kJ} \cdot \text{mol}^{-1}) \\
 &= -205.4 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

(d) The hydrogenation of benzene is much less exothermic than predicted by bond enthalpy estimations. Part of this difference can be due to the inherent inaccuracy of using average values, but the difference is so large that this cannot be the complete explanation. As may be expected, the resonance energy of benzene makes it more stable than would be expected by treating it as a set of three isolated double and three isolated single bonds. The difference in these two values  $[-205 \text{ kJ} - (-372 \text{ kJ}) = 167 \text{ kJ}]$  is a measure of how much more stable benzene is than the Kekulé structure would predict.

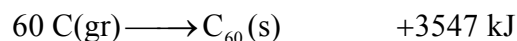
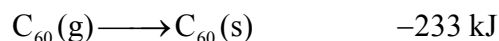
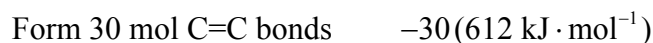
**6.101** (a) The combustion reaction is



The enthalpy of formation of  $\text{C}_{60}(\text{s})$  will be given by

$$\begin{aligned}
 \Delta H^\circ_c &= 60 \Delta H^\circ_f(\text{CO}_2, \text{g}) - \Delta H^\circ_f(\text{C}_{60}, \text{s}) \\
 -25\,937 \text{ kJ} &= 60 \text{ mol} \times (-393.51 \text{ kJ} \cdot \text{mol}^{-1}) - \Delta H^\circ_f(\text{C}_{60}, \text{s}) \\
 \Delta H^\circ_f(\text{C}_{60}, \text{s}) &= +2326 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

(b) The bond enthalpy calculation is



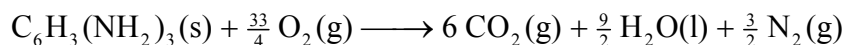
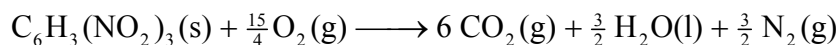
(c) From the experimental data, the enthalpy of formation of  $\text{C}_{60}$  shows that it is *more* stable by  $(3547 \text{ kJ} - 2326 \text{ kJ}) = 1221 \text{ kJ}$  than predicted by the isolated bond model.

(d)  $1221 \text{ kJ} \div 60 = 20 \text{ kJ}$  per carbon atom

(e)  $150 \text{ kJ} \div 6 = 25 \text{ kJ}$  per carbon atom

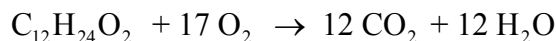
(f) Although the comparison of the stabilization of benzene with that of  $\text{C}_{60}$  should be treated with caution, it does appear that there is slightly less stabilization per carbon atom in  $\text{C}_{60}$  than in benzene. This fits with expectations, as the  $\text{C}_{60}$  molecule is forced by its geometry to be curved. This means that the overlap of the  $p$ -orbitals, which gives rise to the delocalization that results in resonance, will not be as favourable as in the planar benzene molecule. Another perspective on this is obtained by noting that the C atoms in  $\text{C}_{60}$  are forced to be partially  $sp^3$  hybridized because they are rigorously planar as required by  $sp^2$  hybridization.

**6.103** The balanced combustion reactions are



Because the fundamental structures of the two molecules are the same, we need only look at the differences between the two, which in this case are concerned with the groups attached to nitrogen. From the combustion equations we can see that the differences are (1) the consumption of  $\frac{18}{4}$  more moles of  $\text{O}_2(\text{g})$  and (2) the production of six more moles of  $\text{H}_2\text{O}(\text{l})$  for the combustion of aniline. Because the  $\Delta H^\circ_f$  of  $\text{O}_2(\text{g})$  is 0, the net difference will be the production of 6 more moles of  $\text{H}_2\text{O}(\text{l})$  or  $6 \times (-285.83 \text{ kJ} \cdot \text{mol}^{-1}) = -1715.0 \text{ kJ}$ .

**6.105** Start by calculating the amount of energy generated by the decomposition of lauric acid:



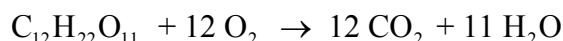
$$\begin{aligned}\Delta H_r &= 12(-393.51 \text{ kJ} \cdot \text{mol}^{-1}) + 12(-285.83 \text{ kJ} \cdot \text{mol}^{-1}) - (-774.6 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -7377.48 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$



if 15.0 g are consumed, then the energy released

$$\text{is: } -7377.48 \text{ kJ} \cdot \text{mol}^{-1} \frac{15.0 \text{ g}}{200.32 \text{ g} \cdot \text{mol}^{-1}} = -552 \text{ kJ}$$

The enthalpy for the decomposition of sucrose may be calculated given standard enthalpies of formation:

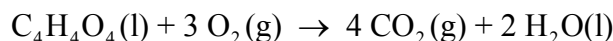


$$\begin{aligned} \Delta H_r &= 12(-393.51 \text{ kJ} \cdot \text{mol}^{-1}) + 11(-285.83 \text{ kJ} \cdot \text{mol}^{-1}) - (-2222 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -5644.3 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

The amount of sucrose needed to produce the same amount of energy as

$$\begin{aligned} 15.0 \text{ g of lauric acid is: } &= \frac{-552 \text{ kJ}}{5644.3 \text{ kJ} \cdot \text{mol}^{-1}} = 0.0979 \text{ mol} \\ &\text{or } (0.0979 \text{ mol})(342.3 \text{ g} \cdot \text{mol}^{-1}) = 33.5 \text{ g} \end{aligned}$$

**6.107** (a) Given the enthalpy of combustion, the enthalpy of formation of each compound may be found using:



$$\Delta H_c(\text{X}) = 4(-393.51 \text{ kJ} \cdot \text{mol}^{-1}) + 2(-285.83 \text{ kJ} \cdot \text{mol}^{-1}) - \Delta H_f(\text{X})$$

$$\Delta H_f(\text{X}) = 4(-393.51 \text{ kJ} \cdot \text{mol}^{-1}) + 2(-285.83 \text{ kJ} \cdot \text{mol}^{-1}) - \Delta H_c(\text{X})$$

where X is either maleic or fumaric acid. Plugging in the appropriate enthalpies of combustion, the enthalpies of formation are found to be:

$$\oplus \Delta H_f(\text{maleic acid}) = -790.5 \text{ kJ} \cdot \text{mol}^{-1} \text{ and } \Delta H_f(\text{fumaric acid}) = -811.0 \text{ kJ} \cdot \text{mol}^{-1}$$

The cis-trans isomerization reaction: maleic acid  $\rightarrow$  fumaric acid has an enthalpy of  $20.5 \text{ kJ} \cdot \text{mol}^{-1}$

(b) Fumaric acid has the lower enthalpy of formation.

(c) Because one mole of gas is produced for each mole of acid consumed, work is done on the surroundings by the system under constant pressure conditions, *i.e.* work for the system will be negative. Therefore,  $U_c$  will be less negative than  $H_c$

$$\begin{aligned} \text{6.109 (a) } V_{\text{init}} &= \frac{nRT}{P} = \frac{(0.060 \text{ mol})(0.0820578 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.15 \text{ K})}{1.00 \text{ atm}} \\ &= 1.47 \text{ L} \end{aligned}$$

(b) The combustion reaction is:  $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$ . If equal molar amounts of  $\text{SO}_2$  and  $\text{O}_2$  are mixed, as in this case,  $\text{SO}_2$  is the limiting reagent.

(c) The total number of moles remaining in the container will be : 0.030 mol  $\text{SO}_3(\text{g}) + 0.015 \text{ mol O}_2(\text{g}) = 0.045 \text{ mol}$  of gas at the end of the reaction. The final volume will, therefore, be:

$$V_f = \frac{nRT}{P} = \frac{(0.045 \text{ mol})(0.0820578 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.15 \text{ K})}{1.00 \text{ atm}} \\ = 1.10 \text{ L}$$

$$(d) \quad w = -P\Delta V = (1.00 \text{ atm})(-0.367 \text{ L})(101.325 \text{ J} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}) \\ = 37.2 \text{ J of work done on the system (work is positive)}$$

$$\Delta H_r = 2(-395.72 \text{ kJ} \cdot \text{mol}^{-1}) - 2(-296.83 \text{ kJ} \cdot \text{mol}^{-1}) = -197.78 \text{ kJ} \cdot \text{mol}^{-1}$$

if 0.015 mol of  $\text{SO}_2$  are consumed, then the enthalpy of reaction is:

$$(-197.78 \text{ kJ} \cdot \text{mol}^{-1})(0.015 \text{ mol}) = -2970 \text{ J}$$

Enthalpy is negative indicating that energy leaves the system.

(e) The enthalpy of reaction may be found using standard enthalpies of formation and the balanced equation given above:

$$(f) \quad \Delta U_r = q + w = -2970 \text{ J} + 37.2 \text{ J} = -2933 \text{ J}$$