CHAPTER 6 THERMOCHEMISTRY

6.15 Recall that the work in gas expansion is equal to the product of the external, opposing pressure and the change in volume.

(a)
$$w = -P\Delta V$$

 $w = -(0)(5.4 - 1.6)L = 0$

(b)
$$w = -P\Delta V$$

 $w = -(0.80 \text{ atm})(5.4 - 1.6)L = -3.0 \text{ L} \cdot \text{atm}$

To convert the answer to joules, we write

$$w = -3.0 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -3.0 \times 10^2 \text{ J}$$

(c)
$$w = -P\Delta V$$

 $w = -(3.7 \text{ atm})(5.4 - 1.6)L = -14 \text{ L} \cdot \text{atm}$

To convert the answer to joules, we write

$$w = -14 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -1.4 \times 10^3 \text{ J}$$

6.16 (a) Because the external pressure is zero, no work is done in the expansion.

$$w = -P\Delta V = -(0)(89.3 - 26.7)$$
mL

$$w = -P\Delta V = -(1.5 \text{ atm})(89.3 - 26.7)\text{mL}$$

$$w = -94 \text{ mL} \cdot \text{atm} \times \frac{0.001 \text{ L}}{1 \text{ mL}} = -0.094 \text{ L} \cdot \text{atm}$$

To convert the answer to joules, we write:

$$w = -0.094 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -9.5 \text{ J}$$

(c) The external, opposing pressure is 2.8 atm, so

$$w = -P\Delta V = -(2.8 \text{ atm})(89.3 - 26.7)\text{mL}$$

$$w = (-1.8 \times 10^2 \text{ mL} \cdot \text{atm}) \times \frac{0.001 \text{ L}}{1 \text{ mL}} = -0.18 \text{ L} \cdot \text{atm}$$

To convert the answer to joules, we write:

$$w = -0.18 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -18 \text{ J}$$

An expansion implies an increase in volume, therefore w must be -325 J (see the defining equation for pressure-volume work.) If the system absorbs heat, q must be +127 J. The change in energy (internal energy) is:

$$\Delta E = q + w = 127 \text{ J} - 325 \text{ J} = -198 \text{ J}$$

Strategy: Compression is work done on the gas, so what is the sign for w? Heat is released by the gas to the surroundings. Is this an endothermic or exothermic process? What is the sign for q?

Solution: To calculate the energy change of the gas (ΔE), we need Equation (6.1) of the text. Work of compression is positive and because heat is given off by the gas, q is negative. Therefore, we have:

$$\Delta E = q + w = -26 \text{ kJ} + 74 \text{ kJ} = 48 \text{ kJ}$$

As a result, the energy of the gas increases by 48 kJ.

6.19 We first find the number of moles of hydrogen gas formed in the reaction:

$$50.0 \text{ g Sn} \times \frac{1 \text{ mol Sn}}{118.7 \text{ g Sn}} \times \frac{1 \text{ mol H}_2}{1 \text{ mol Sn}} = 0.421 \text{ mol H}_2$$

The next step is to find the volume occupied by the hydrogen gas under the given conditions. This is the change in volume.

$$V = \frac{nRT}{P} = \frac{(0.421 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{1.00 \text{ atm}} = 10.3 \text{ L H}_2$$

The pressure-volume work done is then:

$$\mathbf{w} = -P\Delta V = -(1.00 \text{ atm})(10.3 \text{ L}) = -10.3 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -1.04 \times 10^3 \text{ J}$$

6.20 Strategy: The work done in gas expansion is equal to the product of the external, opposing pressure and the change in volume.

$$w = -P\Delta V$$

We assume that the volume of liquid water is zero compared to that of steam. How do we calculate the volume of the steam? What is the conversion factor between L-atm and J?

Solution: First, we need to calculate the volume that the water vapor will occupy (V_f) .

Using the ideal gas equation:

$$V_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}RT}{P} = \frac{(1 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (373 \text{ K})}{(1 \text{ 0 atm})} = 31 \text{ L}$$

It is given that the volume occupied by liquid water is negligible. Therefore,

$$\Delta V = V_f - V_i = 31 L - 0 L = 31 L$$

Now, we substitute P and ΔV into Equation (6.3) of the text to solve for w.

$$w = -P\Delta V = -(1.0 \text{ atm})(31 \text{ L}) = -31 \text{ L} \cdot \text{atm}$$

The problems asks for the work done in units of joules. The following conversion factor can be obtained from Appendix 2 of the text.

$$1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$$

Thus, we can write:

$$w = -31 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -3.1 \times 10^3 \text{ J}$$

Check: Because this is gas expansion (work is done by the system on the surroundings), the work done has a negative sign.

6.25 The equation as written shows that 879 kJ of heat is released when two moles of ZnS react. We want to calculate the amount of heat released when 1 g of ZnS reacts.

Let ΔH° be the heat change per gram of ZnS roasted. We write:

$$\Delta H^{\circ} = \frac{-879 \text{ kJ}}{2 \text{ mol ZnS}} \times \frac{1 \text{ mol ZnS}}{97.46 \text{ g ZnS}} = -4.51 \text{ kJ/g ZnS}$$

Strategy: The thermochemical equation shows that for every 2 moles of NO₂ produced, 114.6 kJ of heat are given off (note the negative sign). We can write a conversion factor from this information.

$$\frac{-114.6 \text{ kJ}}{2 \text{ mol NO}_2}$$

How many moles of NO_2 are in 1.26×10^4 g of NO_2 ? What conversion factor is needed to convert between grams and moles?

Solution: We need to first calculate the number of moles of NO_2 in 1.26×10^4 g of the compound. Then, we can convert to the number of kilojoules produced from the exothermic reaction. The sequence of conversions is:

grams of
$$NO_2 \rightarrow moles$$
 of $NO_2 \rightarrow kilojoules$ of heat generated

Therefore, the heat given off is:

$$(1.26 \times 10^4 \text{ g NO}_2) \times \frac{1 \text{ mol NO}_2}{46.01 \text{ g NO}_2} \times \frac{-114.6 \text{ kJ}}{2 \text{ mol NO}_2} = -1.57 \times 10^4 \text{ kJ}$$

6.27 We can calculate ΔE using Equation (6.10) of the text.

$$\Delta E = \Delta H - RT\Delta n$$

We initially have 2.0 moles of gas. Since our products are 2.0 moles of H₂ and 1.0 mole of O₂, there is a net gain of 1 mole of gas (2 reactant \rightarrow 3 product). Thus, $\Delta n = +1$. Looking at the equation given in the problem, it requires 483.6 kJ to decompose 2.0 moles of water ($\Delta H = 483.6$ kJ).

Substituting into the above equation:

$$\Delta E = 483.6 \times 10^3 \text{ J} - (8.314 \text{ J/mol} \cdot \text{K})(398 \text{ K})(+1 \text{ mol})$$

 $\Delta E = 4.80 \times 10^5 \text{ J} = 4.80 \times 10^2 \text{ kJ}$

6.28 We initially have 6 moles of gas (3 moles of chlorine and 3 moles of hydrogen). Since our product is 6 moles of hydrogen chloride, there is no change in the number of moles of gas. Therefore there is no volume change; $\Delta V = 0$.

$$w = -P\Delta V = -(1 \text{ atm})(0 \text{ L}) = 0$$

$$\Delta E^{\circ} = \Delta H^{\circ} - P\Delta V$$

$$-P\Delta V = 0, \text{ so}$$

$$\Delta E = \Delta H$$

$$\Delta H = 3\Delta H_{\text{rxn}}^{\circ} = 3(-184.6 \text{ kJ/mol}) = -553.8 \text{ kJ/mol}$$

We need to multiply $\Delta H_{\rm rxn}^{\circ}$ by three, because the question involves the formation of 6 moles of HCl; whereas, the equation as written only produces 2 moles of HCl.

$$\Delta E^{\circ} = \Delta H^{\circ} = -553.8 \text{ kJ/mol}$$

6.33 Specific heat =
$$\frac{C}{m} = \frac{85.7 \text{ J/°C}}{362 \text{ g}} = 0.237 \text{ J/g ·°C}$$

6.34
$$q = m_{\text{Cu}} s_{\text{Cu}} \Delta t = (6.22 \times 10^3 \text{ g})(0.385 \text{ J/g} \cdot ^{\circ}\text{C})(324.3 ^{\circ}\text{C} - 20.5 ^{\circ}\text{C}) = 7.28 \times 10^5 \text{ J} = 728 \text{ kJ}$$

6.35 See Table 6.2 of the text for the specific heat of Hg.

$$q = ms\Delta t = (366 \text{ g})(0.139 \text{ J/g} \cdot ^{\circ}\text{C})(12.0^{\circ}\text{C} - 77.0^{\circ}\text{C}) = -3.31 \times 10^{3} \text{ J} = -3.31 \text{ kJ}$$

6.36 Strategy: We know the masses of gold and iron as well as the initial temperatures of each. We can look up the specific heats of gold and iron in Table 6.2 of the text. Assuming no heat is lost to the surroundings, we can equate the heat lost by the iron sheet to the heat gained by the gold sheet. With this information, we can solve for the final temperature of the combined metals.

Solution: Treating the calorimeter as an isolated system (no heat lost to the surroundings), we can write:

$$q_{\mathrm{Au}} + q_{\mathrm{Fe}} = 0$$
 or $q_{\mathrm{Au}} = -q_{\mathrm{Fe}}$

The heat gained by the gold sheet is given by:

$$q_{AII} = m_{AII} s_{AII} \Delta t = (10.0 \text{ g})(0.129 \text{ J/g} \cdot ^{\circ}\text{C})(t_f - 18.0)^{\circ}\text{C}$$

where m and s are the mass and specific heat, and $\Delta t = t_{\text{final}} - t_{\text{initial}}$.

The heat lost by the iron sheet is given by:

$$q_{\text{Fe}} = m_{\text{Fe}} s_{\text{Fe}} \Delta t = (20.0 \text{ g})(0.444 \text{ J/g} \cdot ^{\circ}\text{C})(t_{\text{f}} - 55.6)^{\circ}\text{C}$$

Substituting into the equation derived above, we can solve for $t_{\rm f}$.

$$q_{\text{Au}} = -q_{\text{Fe}}$$

 $(10.0 \text{ g})(0.129 \text{ J/g} \cdot ^{\circ}\text{C})(t_{\text{f}} - 18.0)^{\circ}\text{C} = -(20.0 \text{ g})(0.444 \text{ J/g} \cdot ^{\circ}\text{C})(t_{\text{f}} - 55.6)^{\circ}\text{C}$
 $1.29 t_{\text{f}} - 23.2 = -8.88 t_{\text{f}} + 494$
 $10.2 t_{\text{f}} = 517$
 $t_{\text{f}} = 50.7^{\circ}\text{C}$

Check: Must the final temperature be between the two starting values?

6.37 The heat gained by the calorimeter is:

$$q = C_p \Delta t$$

 $q = (3024 \text{ J/°C})(1.126 \text{°C}) = 3.405 \times 10^3 \text{ J}$

The amount of heat given off by burning Mg in kJ/g is:

$$(3.405 \times 10^3 \text{ J}) \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{1}{0.1375 \text{ g Mg}} = 24.76 \text{ kJ/g Mg}$$

The amount of heat given off by burning Mg in kJ/mol is:

$$\frac{24.76 \text{ kJ}}{1 \text{ g Mg}} \times \frac{24.31 \text{ g Mg}}{1 \text{ mol Mg}} = 601.9 \text{ kJ/mol Mg}$$

If the reaction were endothermic, what would happen to the temperature of the calorimeter and the water?

6.38 Strategy: The neutralization reaction is exothermic. 56.2 kJ of heat are released when 1 mole of H⁺ reacts with 1 mole of OH⁻. Assuming no heat is lost to the surroundings, we can equate the heat lost by the reaction to the heat gained by the combined solution. How do we calculate the heat released during the reaction? Are we reacting 1 mole of H⁺ with 1 mole of OH⁻? How do we calculate the heat absorbed by the combined solution?

Solution: Assuming no heat is lost to the surroundings, we can write:

$$q_{
m Soln} + q_{
m rxn} = 0$$
 or
$$q_{
m Soln} = -q_{
m rxn}$$

First, let's set up how we would calculate the heat gained by the solution,

$$q_{\text{soln}} = m_{\text{soln}} s_{\text{soln}} \Delta t$$

where m and s are the mass and specific heat of the solution and $\Delta t = t_f - t_i$.

We assume that the specific heat of the solution is the same as the specific heat of water, and we assume that the density of the solution is the same as the density of water (1.00 g/mL). Since the density is 1.00 g/mL, the mass of 400 mL of solution (200 mL + 200 mL) is 400 g.

Substituting into the equation above, the heat gained by the solution can be represented as:

$$q_{\text{soln}} = (4.00 \times 10^2 \text{ g})(4.184 \text{ J/g} \cdot ^{\circ}\text{C})(t_f - 20.48 ^{\circ}\text{C})$$

Next, let's calculate q_{rxn} , the heat released when 200 mL of 0.862 M HCl are mixed with 200 mL of 0.431 M Ba(OH)₂. The equation for the neutralization is:

$$2HCl(aq) + Ba(OH)_2(aq) \longrightarrow 2H_2O(l) + BaCl_2(aq)$$

There is exactly enough $Ba(OH)_2$ to neutralize all the HCl. Note that 2 mole HCl = 1 mole $Ba(OH)_2$, and that the concentration of HCl is double the concentration of $Ba(OH)_2$. The number of moles of HCl is:

$$(2.00 \times 10^2 \text{ mL}) \times \frac{0.862 \text{ mol HCl}}{1000 \text{ mL}} = 0.172 \text{ mol HCl}$$

The amount of heat released when 1 mole of H⁺ is reacted is given in the problem (-56.2 kJ/mol). The amount of heat liberated when 0.172 mole of H⁺ is reacted is:

$$q_{\text{rxn}} = 0.172 \text{ mol} \times \frac{-56.2 \times 10^3 \text{ J}}{1 \text{ mol}} = -9.67 \times 10^3 \text{ J}$$

Finally, knowing that the heat lost by the reaction equals the heat gained by the solution, we can solve for the final temperature of the mixed solution.

$$q_{\text{soln}} = -q_{\text{rxn}}$$

 $(4.00 \times 10^2 \text{ g})(4.184 \text{ J/g} \cdot ^{\circ}\text{C})(t_f - 20.48 ^{\circ}\text{C}) = -(-9.67 \times 10^3 \text{ J})$
 $(1.67 \times 10^3)t_f - (3.43 \times 10^4) = 9.67 \times 10^3 \text{ J}$
 $t_f = 26.3 ^{\circ}\text{C}$

- **6.45** CH₄(g) and H(g). All the other choices are elements in their most stable form ($\Delta H_{\rm f}^{\circ} = 0$). The most stable form of hydrogen is H₂(g).
- 6.46 The standard enthalpy of formation of any element in its most stable form is zero. Therefore, since $\Delta H_{\rm f}^{\circ}({\rm O}_2) = 0$, ${\rm O}_2$ is the more stable form of the element oxygen at this temperature.
- **6.47** $H_2O(l) \rightarrow H_2O(g)$ Endothermic

$$\Delta H_{\rm rxn}^{\circ} = \Delta H_{\rm f}^{\circ}[\mathrm{H_2O}(g)] - \Delta H_{\rm f}^{\circ}[\mathrm{H_2O}(l)] > 0$$

 $\Delta H_{\rm f}^{\circ}[{\rm H_2O}(l)]$ is more negative since $\Delta H_{\rm rxn}^{\circ} > 0$.

You could also solve the problem by realizing that $H_2O(l)$ is the stable form of water at 25°C, and therefore will have the more negative ΔH_f° value.

- **6.48** (a) Br₂(l) is the most stable form of bromine at 25°C; therefore, $\Delta H_{\rm f}^{\circ}[{\rm Br}_2(l)] = 0$. Since Br₂(g) is less stable than Br₂(l), $\Delta H_{\rm f}^{\circ}[{\rm Br}_2(g)] > 0$.
 - (b) $I_2(s)$ is the most stable form of iodine at 25°C; therefore, $\Delta H_f^{\circ}[I_2(s)] = 0$. Since $I_2(g)$ is less stable than $I_2(s)$, $\Delta H_f^{\circ}[I_2(g)] > 0$.

6.49 $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$

Because $H_2O(l)$ has a more negative ΔH_f° than $H_2O_2(l)$.

Strategy: What is the reaction for the formation of Ag₂O from its elements? What is the $\Delta H_{\rm f}^{\circ}$ value for an element in its standard state?

Solution: The balanced equation showing the formation of $Ag_2O(s)$ from its elements is:

$$2Ag(s) + \frac{1}{2}O_2(g) \longrightarrow Ag_2O(s)$$

Knowing that the standard enthalpy of formation of any element in its most stable form is zero, and using Equation (6.18) of the text, we write:

$$\Delta H_{\text{rxn}}^{\circ} = \sum n\Delta H_{\text{f}}^{\circ}(\text{products}) - \sum m\Delta H_{\text{f}}^{\circ}(\text{reactants})$$

$$\Delta H_{\text{rxn}}^{\circ} = [\Delta H_{\text{f}}^{\circ}(Ag_{2}O)] - [2\Delta H_{\text{f}}^{\circ}(Ag) + \frac{1}{2}\Delta H_{\text{f}}^{\circ}(O_{2})]$$

$$\Delta H_{\text{rxn}}^{\circ} = [\Delta H_{\text{f}}^{\circ}(Ag_{2}O)] - [0 + 0]$$

$$\Delta H_{\text{f}}^{\circ}(Ag_{2}O) = \Delta H_{\text{rxn}}^{\circ}$$

In a similar manner, you should be able to show that $\Delta H_f^{\circ}(CaCl_2) = \Delta H_{rxn}^{\circ}$ for the reaction

$$Ca(s) + Cl_2(g) \longrightarrow CaCl_2(s)$$

6.51
$$\Delta H^{\circ} = [\Delta H_{\rm f}^{\circ}(\text{CaO}) + \Delta H_{\rm f}^{\circ}(\text{CO}_{2})] - \Delta H_{\rm f}^{\circ}(\text{CaCO}_{3})$$

 $\Delta H^{\circ} = [(1)(-635.6 \text{ kJ/mol}) + (1)(-393.5 \text{ kJ/mol})] - (1)(-1206.9 \text{ kJ/mol}) = 177.8 \text{ kJ/mol}$

Strategy: The enthalpy of a reaction is the difference between the sum of the enthalpies of the products and the sum of the enthalpies of the reactants. The enthalpy of each species (reactant or product) is given by the product of the stoichiometric coefficient and the standard enthalpy of formation, ΔH_f° , of the species.

Solution: We use the $\Delta H_{\rm f}^{\circ}$ values in Appendix 3 and Equation (6.18) of the text.

$$\Delta H_{\rm rxn}^{\circ} = \sum n \Delta H_{\rm f}^{\circ} ({\rm products}) - \sum m \Delta H_{\rm f}^{\circ} ({\rm reactants})$$

(a)
$$HCl(g) \rightarrow H^{+}(aq) + Cl^{-}(aq)$$

$$\Delta H^{\circ}_{rxn} = \Delta H^{\circ}_{f}(H^{+}) + \Delta H^{\circ}_{f}(Cl^{-}) - \Delta H^{\circ}_{f}(HCl)$$

$$-74.9 \text{ kJ/mol} = 0 + \Delta H^{\circ}_{f}(Cl^{-}) - (1)(-92.3 \text{ kJ/mol})$$

$$\Delta H^{\circ}_{f}(Cl^{-}) = -167.2 \text{ kJ/mol}$$

(b) The neutralization reaction is:

$$H^{+}(aq) + OH^{-}(aq) \rightarrow H_{2}O(l)$$
 and,
$$\Delta H^{\circ}_{rxn} = \Delta H^{\circ}_{f}[H_{2}O(l)] - [\Delta H^{\circ}_{f}(H^{+}) + \Delta H^{\circ}_{f}(OH^{-})]$$

$$\Delta H_{\rm f}^{\circ}[{\rm H_2O}(l)] = -285.8 \text{ kJ/mol} \text{ (See Appendix 3 of the text.)}$$

$$\Delta H_{\rm rxn}^{\circ} = (1)(-285.8 \text{ kJ/mol}) - [(1)(0 \text{ kJ/mol}) + (1)(-229.6 \text{ kJ/mol})] = -56.2 \text{ kJ/mol}$$

6.53 (a)
$$\Delta H^{\circ} = 2\Delta H_{\rm f}^{\circ}({\rm H_2O}) - 2\Delta H_{\rm f}^{\circ}({\rm H_2}) - \Delta H_{\rm f}^{\circ}({\rm O_2})$$

 $\Delta H^{\circ} = (2)(-285.8 \text{ kJ/mol}) - (2)(0) - (1)(0) = -571.6 \text{ kJ/mol}$

(b)
$$\Delta H^{\circ} = 4\Delta H_{\rm f}^{\circ}({\rm CO_2}) + 2\Delta H_{\rm f}^{\circ}({\rm H_2O}) - 2\Delta H_{\rm f}^{\circ}({\rm C_2H_2}) - 5\Delta H_{\rm f}^{\circ}({\rm O_2})$$

 $\Delta H^{\circ} = (4)(-393.5 \text{ kJ/mol}) + (2)(-285.8 \text{ kJ/mol}) - (2)(226.6 \text{ kJ/mol}) - (5)(0) = -2599 \text{ kJ/mol}$

6.54 (a)
$$\Delta H^{\circ} = [2\Delta H_{f}^{\circ}(CO_{2}) + 2\Delta H_{f}^{\circ}(H_{2}O)] - [\Delta H_{f}^{\circ}(C_{2}H_{4}) + 3\Delta H_{f}^{\circ}(O_{2})]]$$

 $\Delta H^{\circ} = [(2)(-393.5 \text{ kJ/mol}) + (2)(-285.8 \text{ kJ/mol})] - [(1)(52.3 \text{ kJ/mol}) + (3)(0)]$
 $\Delta H^{\circ} = -1411 \text{ kJ/mol}$

(b)
$$\Delta H^{\circ} = [2\Delta H_{\rm f}^{\circ}({\rm H_2O}) + 2\Delta H_{\rm f}^{\circ}({\rm SO_2})] - [2\Delta H_{\rm f}^{\circ}({\rm H_2S}) + 3\Delta H_{\rm f}^{\circ}({\rm O_2})]$$

 $\Delta H^{\circ} = [(2)(-285.8 \text{ kJ/mol}) + (2)(-296.1 \text{ kJ/mol})] - [(2)(-20.15 \text{ kJ/mol}) + (3)(0)]$
 $\Delta H^{\circ} = -1124 \text{ kJ/mol}$

6.55 The given enthalpies are in units of kJ/g. We must convert them to units of kJ/mol.

(a)
$$\frac{-22.6 \text{ kJ}}{1 \text{ g}} \times \frac{32.04 \text{ g}}{1 \text{ mol}} = -724 \text{ kJ/mol}$$

(b)
$$\frac{-29.7 \text{ kJ}}{1 \text{ g}} \times \frac{46.07 \text{ g}}{1 \text{ mol}} = -1.37 \times 10^3 \text{ kJ/mol}$$

(c)
$$\frac{-33.4 \text{ kJ}}{1 \text{ g}} \times \frac{60.09 \text{ g}}{1 \text{ mol}} = -2.01 \times 10^3 \text{ kJ/mol}$$

6.56
$$\Delta H_{\text{rxn}}^{\circ} = \sum n \Delta H_{\text{f}}^{\circ} (\text{products}) - \sum m \Delta H_{\text{f}}^{\circ} (\text{reactants})$$

The reaction is:

$$H_2(g) \rightarrow H(g) + H(g)$$

and,

$$\Delta H_{\rm rxn}^{\circ} = [\Delta H_{\rm f}^{\circ}({\rm H}) + \Delta H_{\rm f}^{\circ}({\rm H})] - \Delta H_{\rm f}^{\circ}({\rm H}_2)$$

 $\Delta H_{\rm f}^{\circ}({\rm H_2}) = 0$

$$\Delta H_{\rm rxn}^{\circ} = 436.4 \text{ kJ/mol} = 2\Delta H_{\rm f}^{\circ}({\rm H}) - (1)(0)$$

$$\Delta H_{\rm f}^{\circ}({\rm H}) = \frac{436.4 \text{ kJ/mol}}{2} = 218.2 \text{ kJ/mol}$$

6.57
$$\Delta H^{\circ} = 6\Delta H_{\rm f}^{\circ}({\rm CO}_2) + 6\Delta H_{\rm f}^{\circ}({\rm H}_2{\rm O}) - [\Delta H_{\rm f}^{\circ}({\rm C}_6{\rm H}_{12}) + 9\Delta H_{\rm f}^{\circ}({\rm O}_2)]$$

$$\Delta H^{\circ} = (6)(-393.5 \text{ kJ/mol}) + (6)(-285.8 \text{ kJ/mol}) - (1)(-151.9 \text{ kJ/mol}) - (1)(0) = -3924 \text{ kJ/mol}$$
Why is the standard heat of formation of oxygen zero?

6.58 Using the $\Delta H_{\rm f}^{\circ}$ values in Appendix 3 and Equation (6.18) of the text, we write

$$\Delta H_{\text{rxn}}^{\circ} = [5\Delta H_{\text{f}}^{\circ}(B_{2}O_{3}) + 9\Delta H_{\text{f}}^{\circ}(H_{2}O)] - [2\Delta H_{\text{f}}^{\circ}(B_{5}H_{9}) + 12\Delta H_{\text{f}}^{\circ}(O_{2})]$$

$$\Delta H^{\circ} = [(5)(-1263.6 \text{ kJ/mol}) + (9)(-285.8 \text{ kJ/mol})] - [(2)(73.2 \text{ kJ/mol}) + (12)(0 \text{ kJ/mol})]$$

$$\Delta H^{\circ} = -9036.6 \text{ kJ/mol}$$

Looking at the balanced equation, this is the amount of heat released for every 2 moles of B_5H_9 reacted. We can use the following ratio

$$\frac{-9036.6 \text{ kJ}}{2 \text{ mol } B_5 H_9}$$

to convert to kJ/g B₅H₉. The molar mass of B₅H₉ is 63.12 g, so

heat released per gram
$$B_5H_9 = \frac{-9036.6 \text{ kJ}}{2 \text{ mol } B_5H_9} \times \frac{1 \text{ mol } B_5H_9}{63.12 \text{ g } B_5H_9} = -71.58 \text{ kJ/g } B_5H_9$$

6.59 The amount of heat given off is:

$$(1.26 \times 10^4 \text{ g NH}_3) \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{-92.6 \text{ kJ}}{2 \text{ mol NH}_3} = -3.43 \times 10^4 \text{ kJ}$$

6.60
$$\Delta H_{\rm rxn}^{\circ} = \sum n \Delta H_{\rm f}^{\circ} ({\rm products}) - \sum m \Delta H_{\rm f}^{\circ} ({\rm reactants})$$

The balanced equation for the reaction is:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$\Delta H_{rxn}^{\circ} = [\Delta H_f^{\circ}(CaO) + \Delta H_f^{\circ}(CO_2)] - \Delta H_f^{\circ}(CaCO_3)$$

$$\Delta H_{rxn}^{\circ} = [(1)(-635.6 \text{ kJ/mol}) + (1)(-393.5 \text{ kJ/mol})] - (1)(-1206.9 \text{ kJ/mol}) = 177.8 \text{ kJ/mol}$$

The enthalpy change calculated above is the enthalpy change if 1 mole of CO₂ is produced. The problem asks for the enthalpy change if 66.8 g of CO₂ are produced. We need to use the molar mass of CO₂ as a conversion factor.

$$\Delta H^{\circ} = 66.8 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{177.8 \text{ kJ}}{1 \text{ mol CO}_2} = 2.70 \times 10^2 \text{ kJ}$$

6.61 Reaction
$$\Delta H^{\circ}$$
 (kJ/mol)
$$S(\text{rhombic}) + O_{2}(g) \rightarrow SO_{2}(g) -296.06$$

$$SO_{2}(g) \rightarrow S(\text{monoclinic}) + O_{2}(g) 296.36$$

$$S(\text{rhombic}) \rightarrow S(\text{monoclinic}) \Delta H^{\circ}_{\text{rxn}} = \textbf{0.30 kJ/mol}$$

Which is the more stable allotropic form of sulfur?

Strategy: Our goal is to calculate the enthalpy change for the formation of C₂H₆ from is elements C and H₂. This reaction does not occur directly, however, so we must use an indirect route using the information given in the three equations, which we will call equations (a), (b), and (c).

Solution: Here is the equation for the formation of C_2H_6 from its elements.

$$2C(graphite) + 3H_2(g) \longrightarrow C_2H_6(g)$$
 $\Delta H_{rxn}^{\circ} = ?$

Looking at this reaction, we need two moles of graphite as a reactant. So, we multiply Equation (a) by two to obtain:

(d)
$$2C(graphite) + 2O_2(g) \longrightarrow 2CO_2(g)$$
 $\Delta H_{rxn}^{\circ} = 2(-393.5 \text{ kJ/mol}) = -787.0 \text{ kJ/mol}$

Next, we need three moles of H₂ as a reactant. So, we multiply Equation (b) by three to obtain:

(e)
$$3H_2(g) + \frac{3}{2}O_2(g) \longrightarrow 3H_2O(l)$$
 $\Delta H_{rxn}^{\circ} = 3(-285.8 \text{ kJ/mol}) = -857.4 \text{ kJ/mol}$

Last, we need one mole of C_2H_6 as a product. Equation (c) has two moles of C_2H_6 as a reactant, so we need to reverse the equation and divide it by 2.

(f)
$$2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) \longrightarrow \text{C}_2\text{H}_6(g) + \frac{7}{2}\text{O}_2(g)$$
 $\Delta H_{\text{rxn}}^{\circ} = \frac{1}{2}(3119.6 \text{ kJ/mol}) = 1559.8 \text{ kJ/mol}$

Adding Equations (d), (e), and (f) together, we have:

	$2C(graphite) + 3H_2(g) \longrightarrow C_2H_6(g)$	$\Delta H^{\circ} = -84.6 \text{ kJ/mol}$
(f)	$2\operatorname{CO}_2(g) + 3\operatorname{H}_2\operatorname{O}(l) \longrightarrow \operatorname{C}_2\operatorname{H}_6(g) + \frac{7}{2}\operatorname{O}_2(g)$	1559.8
(e)	$3H_2(g) + \frac{3}{2}O_2(g) \longrightarrow 3H_2O(l)$	-857.4
(d)	$2C(graphite) + 2O_2(g) \longrightarrow 2CO_2(g)$	-787.0
Reaction		ΔH° (kJ/mol)

6.63 Reaction
$$\Delta H^{\circ}$$
 (kJ/mol)

 $CO_2(g) + 2H_2O(l) \rightarrow CH_3OH(l) + \frac{3}{2}O_2(g)$ 726.4

 $C(graphite) + O_2(g) \rightarrow CO_2(g)$ -393.5

 $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ 2(-285.8)

 $C(graphite) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$ $\Delta H^{\circ}_{rxn} = -238.7 \text{ kJ/mol}$

We have just calculated an enthalpy at standard conditions, which we abbreviate ΔH_{rxn}° . In this case, the reaction in question was for the formation of *one* mole of CH₃OH *from its elements* in their standard state.

Therefore, the $\Delta H_{\rm rxn}^{\circ}$ that we calculated is also, by definition, the standard heat of formation $\Delta H_{\rm f}^{\circ}$ of CH₃OH (**–238.7 kJ/mol**).

6.64 The second and third equations can be combined to give the first equation.

$$2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s)$$

$$\Delta H^{\circ} = -1669.8 \text{ kJ/mol}$$

$$Fe_2O_3(s) \longrightarrow 2Fe(s) + \frac{3}{2}O_2(g)$$

$$\Delta H^{\circ} = 822.2 \text{ kJ/mol}$$

$$2Al(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + Al_2O_3(s)$$

$$\Delta H^{\circ} = -847.6 \text{ kJ/mol}$$

- 6.71 In a chemical reaction the same elements and the same numbers of atoms are always on both sides of the equation. This provides a consistent reference which allows the energy change in the reaction to be interpreted in terms of the chemical or physical changes that have occurred. In a nuclear reaction the same elements are not always on both sides of the equation and no common reference point exists.
- **6.72** Rearrange the equations as necessary so they can be added to yield the desired equation.

$$\begin{array}{cccc}
2B & \longrightarrow & A & -\Delta H_1 \\
A & \longrightarrow & C & \Delta H_2 \\
\hline
2B & \longrightarrow & C & \Delta H^{\circ} = \Delta H_2 - \Delta H_1
\end{array}$$

6.73 The reaction corresponding to standard enthalpy of formation, $\Delta H_{\rm f}^{\circ}$, of AgNO₂(s) is:

$$Ag(s) + \frac{1}{2}N_2(g) + O_2(g) \rightarrow AgNO_2(s)$$

Rather than measuring the enthalpy directly, we can use the enthalpy of formation of AgNO₃(s) and the $\Delta H_{\text{rxn}}^{\circ}$ provided.

$$AgNO_{3}(s) \rightarrow AgNO_{2}(s) + \frac{1}{2}O_{2}(g)$$

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{f}}^{\circ}(AgNO_{2}) + \frac{1}{2}\Delta H_{\text{f}}^{\circ}(O_{2}) - \Delta H_{\text{f}}^{\circ}(AgNO_{3})$$

$$78.67 \text{ kJ/mol} = \Delta H_{\text{f}}^{\circ}(AgNO_{2}) + 0 - (-123.02 \text{ kJ/mol})$$

$$\Delta H_{\text{f}}^{\circ}(AgNO_{2}) = -44.35 \text{ kJ/mol}$$

6.74 (a)
$$\Delta H_{\text{rxn}}^{\circ} = \sum n\Delta H_{\text{f}}^{\circ} (\text{products}) - \sum m\Delta H_{\text{f}}^{\circ} (\text{reactants})$$

$$\Delta H_{\text{rxn}}^{\circ} = [4\Delta H_{\text{f}}^{\circ} (\text{NH}_{3}) + \Delta H_{\text{f}}^{\circ} (\text{N}_{2})] - 3\Delta H_{\text{f}}^{\circ} (\text{N}_{2}\text{H}_{4})$$

$$\Delta H_{\text{rxn}}^{\circ} = [(4)(-46.3 \text{ kJ/mol}) + (0)] - (3)(50.42 \text{ kJ/mol}) = -336.5 \text{ kJ/mol}$$

- **(b)** The balanced equations are:
 - (1) $N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(l)$
 - (2) $4NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(l)$

The standard enthalpy change for equation (1) is:

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{f}}^{\circ}(N_2) + 2\Delta H_{\text{f}}^{\circ}[H_2O(l)] - \{\Delta H_{\text{f}}^{\circ}[N_2H_4(l)] + \Delta H_{\text{f}}^{\circ}(O_2)\}$$

$$\Delta H_{\text{rxn}}^{\circ} = [(1)(0) + (2)(-285.8 \text{ kJ/mol})] - [(1)(50.42 \text{ kJ/mol}) + (1)(0)] = -622.0 \text{ kJ/mol}$$

The standard enthalpy change for equation (2) is:

$$\Delta H_{\text{rxn}}^{\circ} = [2\Delta H_{\text{f}}^{\circ}(N_2) + 6\Delta H_{\text{f}}^{\circ}(H_2O)] - [4\Delta H_{\text{f}}^{\circ}(NH_3) + 3\Delta H_{\text{f}}^{\circ}(O_2)]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(2)(0) + (6)(-285.8 \text{ kJ/mol})] - [(4)(-46.3 \text{ kJ/mol}) + (3)(0)] = -1529.6 \text{ kJ/mol}$$

We can now calculate the enthalpy change per kilogram of each substance. $\Delta H_{\rm rxn}^{\circ}$ above is in units of kJ/mol. We need to convert to kJ/kg.

$$N_2H_4(l)$$
: $\Delta H_{rxn}^{\circ} = \frac{-622.0 \text{ kJ}}{1 \text{ mol } N_2H_4} \times \frac{1 \text{ mol } N_2H_4}{32.05 \text{ g } N_2H_4} \times \frac{1000 \text{ g}}{1 \text{ kg}} = -1.941 \times 10^4 \text{ kJ/kg } N_2H_4$

NH₃(g):
$$\Delta H_{\text{rxn}}^{\circ} = \frac{-1529.6 \text{ kJ}}{4 \text{ mol NH}_3} \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{1000 \text{ g}}{1 \text{ kg}} = -2.245 \times 10^4 \text{ kJ/kg NH}_3$$

Since ammonia, NH₃, releases more energy per kilogram of substance, it would be a better fuel.

6.75 We initially have 8 moles of gas (2 of nitrogen and 6 of hydrogen). Since our product is 4 moles of ammonia, there is a net loss of 4 moles of gas (8 reactant \rightarrow 4 product). The corresponding volume loss is

$$V = \frac{nRT}{P} = \frac{(4.0 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{1 \text{ atm}} = 98 \text{ L}$$

$$w = -P\Delta V = -(1 \text{ atm})(-98 \text{ L}) = 98 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = 9.9 \times 10^3 \text{ J} = 9.9 \text{ kJ}$$

$$\Delta H = \Delta E + P\Delta V$$
 or $\Delta E = \Delta H - P\Delta V$

Using ΔH as -185.2 kJ = $(2 \times -92.6$ kJ), (because the question involves the formation of 4 moles of ammonia, not 2 moles of ammonia for which the standard enthalpy is given in the question), and $-P\Delta V$ as 9.9 kJ (for which we just solved):

$$\Delta E = -185.2 \text{ kJ} + 9.9 \text{ kJ} = -175.3 \text{ kJ}$$

6.76 The reaction is, $2\text{Na}(s) + \text{Cl}_2(g) \rightarrow 2\text{NaCl}(s)$. First, let's calculate ΔH° for this reaction using $\Delta H_{\text{f}}^{\circ}$ values in Appendix 3.

$$\Delta H_{\text{rxn}}^{\circ} = 2\Delta H_{\text{f}}^{\circ}(\text{NaCl}) - [2\Delta H_{\text{f}}^{\circ}(\text{Na}) + \Delta H_{\text{f}}^{\circ}(\text{Cl}_{2})]$$

$$\Delta H_{\text{rxn}}^{\circ} = 2(-411.0 \text{ kJ/mol}) - [2(0) + 0] = -822.0 \text{ kJ/mol}$$

This is the amount of heat released when 1 mole of Cl_2 reacts (see balanced equation). We are not reacting 1 mole of Cl_2 , however. From the volume and density of Cl_2 , we can calculate grams of Cl_2 . Then, using the molar mass of Cl_2 as a conversion factor, we can calculate moles of Cl_2 . Combining these two calculations into one step, we find moles of Cl_2 to be:

$$2.00 \text{ L Cl}_2 \times \frac{1.88 \text{ g Cl}_2}{1 \text{ L Cl}_2} \times \frac{1 \text{ mol Cl}_2}{70.90 \text{ g Cl}_2} = 0.0530 \text{ mol Cl}_2$$

Finally, we can use the $\Delta H_{\rm rxn}^{\circ}$ calculated above to find the amount of heat released when 0.0530 mole of Cl₂ reacts.

$$0.0530 \text{ mol } \text{Cl}_2 \times \frac{-822.0 \text{ kJ}}{1 \text{ mol } \text{Cl}_2} = -43.6 \text{ kJ}$$

6.77 (a) Although we cannot measure $\Delta H_{\text{rxn}}^{\circ}$ for this reaction, the reverse process, is the combustion of glucose. We could easily measure $\Delta H_{\text{rxn}}^{\circ}$ for this combustion in a bomb calorimeter.

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

(b) We can calculate $\Delta H_{\rm rxn}^{\circ}$ using standard enthalpies of formation.

$$\Delta H_{\rm rxn}^{\circ} = \Delta H_{\rm f}^{\circ} [{\rm C_6 H_{12} O_6}(s)] + 6\Delta H_{\rm f}^{\circ} [{\rm O_2}(g)] - \{6\Delta H_{\rm f}^{\circ} [{\rm CO_2}(g)] + 6\Delta H_{\rm f}^{\circ} [{\rm H_2 O}(l)] \}$$

$$\Delta H_{\rm rxn}^{\circ} = [(1)(-1274.5 \text{ kJ/mol}) + 0] - [(6)(-393.5 \text{ kJ/mol}) + (6)(-285.8 \text{ kJ/mol})] = 2801.3 \text{ kJ/mol}$$

 $\Delta H_{\rm rxn}^{\circ}$ has units of kJ/1 mol glucose. We want the ΔH° change for 7.0×10^{14} kg glucose. We need to calculate how many moles of glucose are in 7.0×10^{14} kg glucose. You should come up with the following strategy to solve the problem.

kg glucose \rightarrow g glucose \rightarrow mol glucose \rightarrow kJ (ΔH°)

$$\Delta H^{\circ} = (7.0 \times 10^{14} \text{ kg}) \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol } C_6 H_{12} O_6}{180.2 \text{ g } C_6 H_{12} O_6} \times \frac{2801.3 \text{ kJ}}{1 \text{ mol } C_6 H_{12} O_6} = 1.1 \times 10^{19} \text{ kJ}$$

- 6.78 The initial and final states of this system are identical. Since enthalpy is a state function, its value depends only upon the state of the system. The enthalpy change is **zero**.
- **6.79** From the balanced equation we see that there is a 1:2 mole ratio between hydrogen and sodium. The number of moles of hydrogen produced is:

$$0.34 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \times \frac{1 \text{ mol H}_2}{2 \text{ mol Na}} = 7.4 \times 10^{-3} \text{ mol H}_2$$

Using the ideal gas equation, we write:

$$V = \frac{nRT}{P} = \frac{(7.4 \times 10^{-3} \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(273 \text{ K})}{(1 \text{ atm})} = 0.17 \text{ L H}_2$$

$$\Delta V = 0.17 L$$

$$\mathbf{w} = -P\Delta V = -(1.0 \text{ atm})(0.17 \text{ L}) = -0.17 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -17 \text{ J}$$

6.80
$$H(g) + Br(g) \longrightarrow HBr(g)$$
 $\Delta H_{rxn}^{\circ} = ?$

Rearrange the equations as necessary so they can be added to yield the desired equation.

$$H(g) \longrightarrow \frac{1}{2} H_2(g) \qquad \Delta H_{\text{rxn}}^{\circ} = \frac{1}{2} (-436.4 \text{ kJ/mol}) = -218.2 \text{ kJ/mol}$$

$$Br(g) \longrightarrow \frac{1}{2} Br_2(g) \qquad \Delta H_{\text{rxn}}^{\circ} = \frac{1}{2} (-192.5 \text{ kJ/mol}) = -96.25 \text{ kJ/mol}$$

$$\frac{1}{2} H_2(g) + \frac{1}{2} Br_2(g) \longrightarrow HBr(g) \qquad \Delta H_{\text{rxn}}^{\circ} = \frac{1}{2} (-72.4 \text{ kJ/mol}) = -36.2 \text{ kJ/mol}$$

$$H(g) + Br(g) \longrightarrow HBr(g) \qquad \Delta H^{\circ} = -350.7 \text{ kJ/mol}$$

6.81 Using the balanced equation, we can write:

$$\Delta H_{\text{rxn}}^{\circ} = [2\Delta H_{\text{f}}^{\circ}(\text{CO}_{2}) + 4\Delta H_{\text{f}}^{\circ}(\text{H}_{2}\text{O})] - [2\Delta H_{\text{f}}^{\circ}(\text{CH}_{3}\text{OH}) + 3\Delta H_{\text{f}}^{\circ}(\text{O}_{2})]$$

$$-1452.8 \text{ kJ/mol} = (2)(-393.5 \text{ kJ/mol}) + (4)(-285.8 \text{ kJ/mol}) - (2)\Delta H_{\text{f}}^{\circ}(\text{CH}_{3}\text{OH}) - (3)(0 \text{ kJ/mol})$$

$$477.4 \text{ kJ/mol} = -(2)\Delta H_{\text{f}}^{\circ}(\text{CH}_{3}\text{OH})$$

$$\Delta H_{\text{f}}^{\circ}(\text{CH}_{3}\text{OH}) = -238.7 \text{ kJ/mol}$$

6.82 $q_{\text{system}} = 0 = q_{\text{metal}} + q_{\text{water}} + q_{\text{calorimeter}}$

$$q_{\text{metal}} + q_{\text{water}} + q_{\text{calorimeter}} = 0$$

$$m_{\text{metal}}s_{\text{metal}}(t_{\text{final}} - t_{\text{initial}}) + m_{\text{water}}s_{\text{water}}(t_{\text{final}} - t_{\text{initial}}) + C_{\text{calorimeter}}(t_{\text{final}} - t_{\text{initial}}) = 0$$

All the needed values are given in the problem. All you need to do is plug in the values and solve for s_{metal} .

$$(44.0 \text{ g})(s_{\text{metal}})(28.4 - 99.0)^{\circ}\text{C} + (80.0 \text{ g})(4.184 \text{ J/g} \cdot ^{\circ}\text{C})(28.4 - 24.0)^{\circ}\text{C} + (12.4 \text{ J/°C})(28.4 - 24.0)^{\circ}\text{C} = 0$$

$$(-3.11 \times 10^{3})s_{\text{metal}} \text{ (g} \cdot ^{\circ}\text{C)} = -1.53 \times 10^{3} \text{ J}$$

$$s_{\text{metal}} = 0.492 \text{ J/g} \cdot ^{\circ}\text{C}$$

6.83 We carry extra significant figures throughout this calculation to limit rounding errors. The original volume of ammonia is:

$$V = \frac{nRT}{P} = \frac{(1.00 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{14.0 \text{ atm}} = 1.7476 \text{ L NH}_3$$

(a)
$$T_2 = \frac{P_2 V_2 T_1}{P_1 V_1} = \frac{(1 \text{ atm})(23.5 \text{ L})(298 \text{ K})}{(14.0 \text{ atm})(1.7476 \text{ L})} = 286.23 \text{ K}$$

(b)
$$\Delta t = (286.23 - 298)^{\circ}\text{C} = -11.77^{\circ}\text{C}$$

 $q = ms\Delta t = (17.03 \text{ g})(0.0258 \text{ J/g} \cdot ^{\circ}\text{C})(-11.77^{\circ}\text{C}) = -5.17 \text{ J}$
 $w = -P\Delta V = -(1 \text{ atm})(23.5 - 1.7476)\text{L} = -21.75 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -2.20 \times 10^3 \text{ J}$
 $\Delta E = q + w = -5.27 \text{ J} - (2.20 \times 10^3 \text{ J}) = -2.21 \times 10^3 \text{ J} = -2.21 \text{ kJ}$

6.84 A good starting point would be to calculate the standard enthalpy for both reactions.

Calculate the standard enthalpy for the reaction: $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

This reaction corresponds to the standard enthalpy of formation of CO, so we use the value of -110.5 kJ/mol (see Appendix 3 of the text).

Calculate the standard enthalpy for the reaction:
$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

$$\Delta H_{\text{rxn}}^{\circ} = [\Delta H_{\text{f}}^{\circ}(\text{CO}) + \Delta H_{\text{f}}^{\circ}(\text{H}_2)] - [\Delta H_{\text{f}}^{\circ}(\text{C}) + \Delta H_{\text{f}}^{\circ}(\text{H}_2O)]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(1)(-110.5 \text{ kJ/mol}) + (1)(0)] - [(1)(0) + (1)(-241.8 \text{ kJ/mol})] = 131.3 \text{ kJ/mol}$$

The first reaction, which is exothermic, can be used to promote the second reaction, which is endothermic. Thus, the two gases are produced alternately.

6.85 Let's start with the combustion of methane: $CH_4(g) + O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$$\Delta H_{\rm rxn}^{\circ} = \Delta H_{\rm f}^{\circ}({\rm CO_2}) + 2\Delta H_{\rm f}^{\circ}({\rm H_2O}) - \Delta H_{\rm f}^{\circ}({\rm CH_4})$$

$$\Delta H_{\rm rxn}^{\circ} = (1)(-393.5 \text{ kJ/mol}) + (2)(-285.8 \text{ kJ/mol}) - (1)(-74.85 \text{ kJ/mol}) = -890.3 \text{ kJ/mol}$$

Now, let's calculate the heat produced by the combustion of water gas. We will consider the combustion of H_2 and CO separately. We can look up the ΔH_f° of $H_2O(l)$ in Appendix 3.

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$$
 $\Delta H_{rxn}^{\circ} = -285.8 \text{ kJ/mol}$

For the combustion of CO(g), we use $\Delta H_{\rm f}^{\circ}$ values from Appendix 3 to calculate the $\Delta H_{\rm rxn}^{\circ}$.

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$
 $\Delta H_{rxn}^{\circ} = ?$
$$\Delta H_{rxn}^{\circ} = \Delta H_{f}^{\circ}(CO_2) - \Delta H_{f}^{\circ}(CO) - \frac{1}{2}\Delta H_{f}^{\circ}(O_2)$$

$$\Delta H_{rxn}^{\circ} = (1)(-393.5 \text{ kJ/mol}) - (1)(-110.5 \text{ kJ/mol}) = -283.0 \text{ kJ/mol}$$

The $\Delta H_{\text{rxn}}^{\circ}$ values calculated above are for the combustion of 1 mole of H₂ and 1 mole of CO, which equals 2 moles of water gas. The total heat produced during the combustion of 1 mole of water gas is:

$$\frac{-(285.8 + 283.0)\text{kJ/mol}}{2} = -284.4 \text{ kJ/mol of water gas}$$

which is less heat than that produced by the combustion of 1 mole of methane.

Additionally, CO is very toxic. Natural gas (methane) is easier to obtain compared to carrying out the high temperature process of producing water gas.

6.86 First, calculate the energy produced by 1 mole of octane, C₈H₁₈.

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$$

$$\Delta H_{rxn}^{\circ} = 8\Delta H_{f}^{\circ}(CO_2) + 9\Delta H_{f}^{\circ}[H_2O(l)] - [\Delta H_{f}^{\circ}(C_8H_{18}) + \frac{25}{2}\Delta H_{f}^{\circ}(O_2)]$$

$$\Delta H_{rxn}^{\circ} = [(8)(-393.5 \text{ kJ/mol}) + (9)(-285.8 \text{ kJ/mol})] - [(1)(-249.9 \text{ kJ/mol}) + (\frac{25}{2})(0)]$$

$$= -5470 \text{ kJ/mol}$$

The problem asks for the energy produced by the combustion of 1 gallon of octane. $\Delta H_{\rm rxn}^{\circ}$ above has units of kJ/mol octane. We need to convert from kJ/mol octane to kJ/gallon octane. The heat of combustion for 1 gallon of octane is:

$$\Delta H^{\circ} = \frac{-5470 \text{ kJ}}{1 \text{ mol octane}} \times \frac{1 \text{ mol octane}}{114.2 \text{ g octane}} \times \frac{2660 \text{ g}}{1 \text{ gal}} = -1.274 \times 10^5 \text{ kJ/gal}$$

The combustion of hydrogen corresponds to the standard heat of formation of water:

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$$

Thus, $\Delta H_{\rm rxn}^{\circ}$ is the same as $\Delta H_{\rm f}^{\circ}$ for H₂O(*l*), which has a value of –285.8 kJ/mol. The number of moles of hydrogen required to produce 1.274×10^5 kJ of heat is:

$$n_{\rm H_2} = (1.274 \times 10^5 \,\text{kJ}) \times \frac{1 \,\text{mol H}_2}{285.8 \,\text{kJ}} = 445.8 \,\text{mol H}_2$$

Finally, use the ideal gas law to calculate the volume of gas corresponding to 445.8 moles of H_2 at 25° C and 1 atm.

$$V_{\text{H}_2} = \frac{n_{\text{H}_2}RT}{P} = \frac{(445.8 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (298 \text{ K})}{(1 \text{ atm})} = 1.09 \times 10^4 \text{ L}$$

That is, the volume of hydrogen that is energy-equivalent to 1 gallon of gasoline is over **10,000 liters** at 1 atm and 25°C!

6.87 The reaction for the combustion of octane is:

$$C_8H_{18}(l) + \frac{25}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$$

 $\Delta H_{\rm rxn}^{\circ}$ for this reaction was calculated in problem 6.86 from standard enthalpies of formation.

$$\Delta H_{\rm rxn}^{\circ} = -5470 \text{ kJ/mol}$$

$$Heat/gal \ of \ octane \ = \ \frac{5470 \ kJ}{1 \ mol \ C_8H_{18}} \times \frac{1 \ mol \ C_8H_{18}}{114.2 \ g} \times \frac{0.7025 \ g}{1 \ mL} \times \frac{3785 \ mL}{1 \ gal}$$

Heat/gal of octane = 1.27×10^5 kJ/gal gasoline

The reaction for the combustion of ethanol is:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

$$\Delta H_{\rm rxn}^{\circ} = 2\Delta H_{\rm f}^{\circ}({\rm CO_2}) + 3\Delta H_{\rm f}^{\circ}({\rm H_2O}) - \Delta H_{\rm f}^{\circ}({\rm C_2H_5OH}) - 3\Delta H_{\rm f}^{\circ}({\rm O_2})$$

$$\Delta H_{\text{TXN}}^{\circ} = (2)(-393.5 \text{ kJ/mol}) + (3)(-285.8 \text{ kJ/mol}) - (1)(-277.0 \text{ kJ/mol}) = -1367 \text{ kJ/mol}$$

$$Heat/gal \ of \ ethanol \ = \ \frac{1367 \ kJ}{1 \ mol \ C_2H_5OH} \times \frac{1 \ mol \ C_2H_5OH}{46.07 \ g} \times \frac{0.7894 \ g}{1 \ mL} \times \frac{3785 \ mL}{1 \ gal}$$

Heat/gal of ethanol = 8.87×10^4 kJ/gal ethanol

For ethanol, what would the cost have to be to supply the same amount of heat per dollar of gasoline? For gasoline, it cost 2.50 to provide 1.27×10^5 kJ of heat.

$$\frac{\$2.50}{1.27 \times 10^5 \text{ kJ}} \times \frac{8.87 \times 10^4 \text{ kJ}}{1 \text{ gal ethanol}} = \$1.75/\text{gal ethanol}$$

6.88 The combustion reaction is: $C_2H_6(l) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

The heat released during the combustion of 1 mole of ethane is:

$$\Delta H_{\text{rxn}}^{\circ} = \left[2\Delta H_{\text{f}}^{\circ}(\text{CO}_{2}) + 3\Delta H_{\text{f}}^{\circ}(\text{H}_{2}\text{O})\right] - \left[\Delta H_{\text{f}}^{\circ}(\text{C}_{2}\text{H}_{6}) + \frac{7}{2}\Delta H_{\text{f}}^{\circ}(\text{O}_{2})\right]$$

$$\Delta H_{\text{rxn}}^{\circ} = \left[(2)(-393.5 \text{ kJ/mol}) + (3)(-285.8 \text{ kJ/mol})\right] - \left[(1)(-84.7 \text{ kJ/mol} + (\frac{7}{2})(0)\right]$$

$$= -1560 \text{ kJ/mol}$$

The heat required to raise the temperature of the water to 98°C is:

$$q = m_{\text{H}_2\text{O}} s_{\text{H}_2\text{O}} \Delta t = (855 \text{ g})(4.184 \text{ J/g} \cdot ^{\circ}\text{C})(98.0 - 25.0)^{\circ}\text{C} = 2.61 \times 10^5 \text{ J} = 261 \text{ kJ}$$

The combustion of 1 mole of ethane produces 1560 kJ; the number of moles required to produce 261 kJ is:

$$261 \text{ kJ} \times \frac{1 \text{ mol ethane}}{1560 \text{ kJ}} = 0.167 \text{ mol ethane}$$

The volume of ethane is:

$$V_{\text{ethane}} = \frac{nRT}{P} = \frac{(0.167 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (296 \text{ K})}{\left(752 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right)} = 4.10 \text{ L}$$

- **6.89** As energy consumers, we are interested in the availability of *usable* energy.
- **6.90** The heat gained by the liquid nitrogen must be equal to the heat lost by the water.

$$q_{\text{N}_2} = -q_{\text{H}_2\text{O}}$$

If we can calculate the heat lost by the water, we can calculate the heat gained by 60.0 g of the nitrogen.

Heat lost by the water =
$$q_{H_2O} = m_{H_2O} s_{H_2O} \Delta t$$

$$q_{\rm H_2O} = (2.00 \times 10^2 \text{ g})(4.184 \text{ J/g} \cdot ^{\circ}\text{C})(41.0 - 55.3)^{\circ}\text{C} = -1.20 \times 10^4 \text{ J}$$

The heat gained by 60.0 g nitrogen is the opposite sign of the heat lost by the water.

$$q_{\text{N}_2} = -q_{\text{H}_2\text{O}}$$

 $q_{\text{N}_2} = 1.20 \times 10^4 \,\text{J}$

The problem asks for the molar heat of vaporization of liquid nitrogen. Above, we calculated the amount of heat necessary to vaporize 60.0 g of liquid nitrogen. We need to convert from J/60.0 g N₂ to J/mol N₂.

$$\Delta H_{\text{vap}} = \frac{1.20 \times 10^4 \text{ J}}{60.0 \text{ g N}_2} \times \frac{28.02 \text{ g N}_2}{1 \text{ mol N}_2} = 5.60 \times 10^3 \text{ J/mol} = 5.60 \text{ kJ/mol}$$

6.91 The evaporation of ethanol is an endothermic process with a fairly high ΔH° value. When the liquid evaporates, it absorbs heat from your body, hence the cooling effect.

- Recall that the standard enthalpy of formation ($\Delta H_{\rm f}^{\circ}$) is defined as the heat change that results when 1 mole of a compound is formed from its elements at a pressure of 1 atm. Only in choice (a) does $\Delta H_{\rm rxn}^{\circ} = \Delta H_{\rm f}^{\circ}$. In choice (b), C(diamond) is *not* the most stable form of elemental carbon under standard conditions; C(graphite) is the most stable form.
- **6.93** $w = -P\Delta V = -(1.0 \text{ atm})(0.0196 0.0180)L = -1.6 \times 10^{-3} \text{ L} \cdot \text{atm}$

Using the conversion factor 1 L·atm = 101.3 J:

$$w = (-1.6 \times 10^{-3} \text{ L} \cdot \text{atm}) \times \frac{101.3 \text{ J}}{\text{L} \cdot \text{atm}} = -0.16 \text{ J}$$

0.16 J of work are done by water as it expands on freezing.

- **6.94** (a) No work is done by a gas expanding in a vacuum, because the pressure exerted on the gas is zero.
 - **(b)** $w = -P\Delta V$ $w = -(0.20 \text{ atm})(0.50 - 0.050)L = -0.090 \text{ L} \cdot \text{atm}$

Converting to units of joules:

$$w = -0.090 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{\text{L} \cdot \text{atm}} = -9.1 \text{ J}$$

(c) The gas will expand until the pressure is the same as the applied pressure of 0.20 atm. We can calculate its final volume using the ideal gas equation.

$$V = \frac{nRT}{P} = \frac{(0.020 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (273 + 20) \text{K}}{0.20 \text{ atm}} = 2.4 \text{ L}$$

The amount of work done is:

$$w = -P\Delta V = (0.20 \text{ atm})(2.4 - 0.050)L = -0.47 \text{ L} \cdot \text{atm}$$

Converting to units of joules:

$$\mathbf{w} = -0.47 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{\text{L} \cdot \text{atm}} = -48 \text{ J}$$

6.95 The equation corresponding to the standard enthalpy of formation of diamond is:

$$C(graphite) \longrightarrow C(diamond)$$

Adding the equations:

C(graphite) +
$$O_2(g)$$
 \longrightarrow $CO_2(g)$ $\Delta H^{\circ} = -393.5 \text{ kJ/mol}$
 $CO_2(g)$ \longrightarrow C(diamond) + $O_2(g)$ $\Delta H^{\circ} = 395.4 \text{ kJ/mol}$

C(graphite) \longrightarrow C(diamond) $\Delta H^{\circ} = 1.9 \text{ kJ/mol}$

Since the reverse reaction of changing diamond to graphite is exothermic, need you worry about any diamonds that you might have changing to graphite?

6.96 (a) The more closely packed, the greater the mass of food. Heat capacity depends on both the mass and specific heat.

$$C = ms$$

The heat capacity of the food is greater than the heat capacity of air; hence, the cold in the freezer will be retained longer.

- **(b)** Tea and coffee are mostly water; whereas, soup might contain vegetables and meat. Water has a higher heat capacity than the other ingredients in soup; therefore, coffee and tea retain heat longer than soup.
- **6.97** The balanced equation is:

$$C_6H_{12}O_6(s) \longrightarrow 2C_2H_5OH(l) + 2CO_2(g)$$

$$\Delta H_{\rm rxn}^{\circ} = \left[2\Delta H_{\rm f}^{\circ}({\rm C_2H_5OH}) + 2\Delta H_{\rm f}^{\circ}({\rm CO_2})\right] - \Delta H_{\rm f}^{\circ}({\rm C_6H_{12}O_6})$$

$$\Delta H_{\text{rxn}}^{\circ} = [(2)(-276.98 \text{ kJ/mol}) + (2)(-393.5 \text{ kJ/mol})] - (1)(-1274.5 \text{ kJ/mol}) = -66.5 \text{ kJ/mol})$$

6.98 $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$. This equation represents twice the standard enthalpy of formation of Fe₂O₃. From Appendix 3, the standard enthalpy of formation of Fe₂O₃ = -822.2 kJ/mol. So, ΔH° for the given reaction is:

$$\Delta H_{\text{ryn}}^{\circ} = (2)(-822.2 \text{ kJ/mol}) = -1644 \text{ kJ/mol}$$

Looking at the balanced equation, this is the amount of heat released when four moles of Fe react. But, we are reacting 250 g of Fe, not 4 moles. We can convert from grams of Fe to moles of Fe, then use ΔH° as a conversion factor to convert to kJ.

250 g Fe ×
$$\frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}}$$
 × $\frac{-1644 \text{ kJ}}{4 \text{ mol Fe}}$ = $-1.84 \times 10^3 \text{ kJ}$

6.99 One conversion factor needed to solve this problem is the molar mass of water. The other conversion factor is given in the problem. It takes 44.0 kJ of energy to vaporize 1 mole of water.

You should come up with the following strategy to solve the problem.

$$4000 \text{ kJ} \rightarrow \text{mol H}_2\text{O} \rightarrow \text{g H}_2\text{O}$$

?
$$\mathbf{g} \ \mathbf{H_2O} = 4000 \ \text{kJ} \times \frac{1 \ \text{mol} \ \mathbf{H_2O}}{44.0 \ \text{kJ}} \times \frac{18.02 \ \text{g} \ \mathbf{H_2O}}{1 \ \text{mol} \ \mathbf{H_2O}} = 1.64 \times 10^3 \ \mathbf{g} \ \mathbf{H_2O}$$

6.100 The heat required to raise the temperature of 1 liter of water by 1°C is:

$$4.184 \frac{J}{g \cdot {}^{\circ}C} \times \frac{1 \text{ g}}{1 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times 1 {}^{\circ}C = 4184 \text{ J/L}$$

Next, convert the volume of the Pacific Ocean to liters.

$$(7.2 \times 10^8 \text{ km}^3) \times \left(\frac{1000 \text{ m}}{1 \text{ km}}\right)^3 \times \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^3 \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 7.2 \times 10^{20} \text{ L}$$

The amount of heat needed to raise the temperature of 7.2×10^{20} L of water is:

$$(7.2 \times 10^{20} \text{ L}) \times \frac{4184 \text{ J}}{1 \text{ L}} = 3.0 \times 10^{24} \text{ J}$$

Finally, we can calculate the number of atomic bombs needed to produce this much heat.

$$(3.0 \times 10^{24} \text{ J}) \times \frac{1 \text{ atomic bomb}}{1.0 \times 10^{15} \text{ J}} = 3.0 \times 10^9 \text{ atomic bombs} = 3.0 \text{ billion atomic bombs}$$

6.101 First calculate the final volume of CO₂ gas:

$$V = \frac{nRT}{P} = \frac{\left(19.2 \text{ g} \times \frac{1 \text{ mol}}{44.01 \text{ g}}\right) (0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol}) (295 \text{ K})}{0.995 \text{ atm}} = 10.6 \text{ L}$$

$$w = -P\Delta V = -(0.995 \text{ atm}) (10.6 \text{ L}) = -10.5 \text{ L} \cdot \text{atm}$$

$$w = -10.5 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -1.06 \times 10^3 \text{ J} = -1.06 \text{ kJ}$$

The expansion work done is 1.06 kJ.

6.102 Strategy: The heat released during the reaction is absorbed by both the water and the calorimeter. How do we calculate the heat absorbed by the water? How do we calculate the heat absorbed by the calorimeter? How much heat is released when 1.9862 g of benzoic acid are reacted? The problem gives the amount of heat that is released when 1 mole of benzoic acid is reacted (-3226.7 kJ/mol).

Solution: The heat of the reaction (combustion) is absorbed by both the water and the calorimeter.

$$q_{\rm rxn} = -(q_{\rm water} + q_{\rm cal})$$

If we can calculate both q_{water} and q_{rxn} , then we can calculate q_{cal} . First, let's calculate the heat absorbed by the water.

$$q_{\text{water}} = m_{\text{water}} s_{\text{water}} \Delta t$$

 $q_{\text{water}} = (2000 \text{ g})(4.184 \text{ J/g} \cdot \text{°C})(25.67 - 21.84) \text{°C} = 3.20 \times 10^4 \text{ J} = 32.0 \text{ kJ}$

Next, let's calculate the heat released (q_{rxn}) when 1.9862 g of benzoic acid are burned. ΔH_{rxn} is given in units of kJ/mol. Let's convert to q_{rxn} in kJ.

$$q_{\text{rxn}} = 1.9862 \text{ g benzoic acid} \times \frac{1 \text{ mol benzoic acid}}{122.1 \text{ g benzoic acid}} \times \frac{-3226.7 \text{ kJ}}{1 \text{ mol benzoic acid}} = -52.49 \text{ kJ}$$

And,

$$q_{\text{cal}} = -q_{\text{rxn}} - q_{\text{water}}$$

 $q_{\text{cal}} = 52.49 \text{ kJ} - 32.0 \text{ kJ} = 20.5 \text{ kJ}$

To calculate the heat capacity of the bomb calorimeter, we can use the following equation:

$$q_{\text{cal}} = C_{\text{cal}}\Delta t$$

$$C_{\text{cal}} = \frac{q_{\text{cal}}}{\Delta t} = \frac{20.5 \text{ kJ}}{(25.67 - 21.84)^{\circ}\text{C}} = 5.35 \text{ kJ/}^{\circ}\text{C}$$

6.103 From thermodynamic data in Appendix 3 of the text, we can calculate the amount of heat released per mole of H₂ and CH₄.

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$
 $\Delta H^\circ = -285.8 \text{ kJ/mol}$ $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H^\circ = -890.3 \text{ kJ/mol}$

We know that 2354 kJ of heat is released from the combustion of 25.0 g of the gaseous mixture of H₂ and CH₄.

$$m_{\rm H_2} + m_{\rm CH_4} = 25.0 \text{ g}$$

and

$$m_{\text{CH}_4} = 25.0 \text{ g} - m_{\text{H}_2}$$

We know the amount of heat released per mole of each substance. We need to convert from grams to moles of each substance, and then we can convert to kJ of heat released.

$$\left(m_{\text{H}_2} \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \times \frac{285.8 \text{ kJ}}{1 \text{ mol H}_2}\right) + \left((25.0 - m_{\text{H}_2}) \times \frac{1 \text{ mol CH}_4}{16.04 \text{ g CH}_4} \times \frac{890.3 \text{ kJ}}{1 \text{ mol CH}_4}\right) = 2354 \text{ kJ}$$

$$141.8 m_{\text{H}_2} + (1.39 \times 10^3) - 55.50 m_{\text{H}_2} = 2354$$

$$86.30 m_{\text{H}_2} = 964$$

$$m_{\text{H}_2} = 11.2 \text{ g}$$

$$m_{\text{CH}_4} = 25.0 \text{ g} - 11.2 \text{ g} = 13.8 \text{ g}$$

6.104 First, let's calculate the standard enthalpy of reaction.

$$\Delta H_{\text{rxn}}^{\circ} = 2\Delta H_{\text{f}}^{\circ}(\text{CaSO}_{4}) - [2\Delta H_{\text{f}}^{\circ}(\text{CaO}) + 2\Delta H_{\text{f}}^{\circ}(\text{SO}_{2}) + \Delta H_{\text{f}}^{\circ}(\text{O}_{2})]$$

$$= (2)(-1432.7 \text{ kJ/mol}) - [(2)(-635.6 \text{ kJ/mol}) + (2)(-296.1 \text{ kJ/mol}) + 0]$$

$$= -1002 \text{ kJ/mol}$$

This is the enthalpy change for every 2 moles of SO_2 that are removed. The problem asks to calculate the enthalpy change for this process if 6.6×10^5 g of SO_2 are removed.

$$(6.6 \times 10^5 \text{ g SO}_2) \times \frac{1 \text{ mol SO}_2}{64.07 \text{ g SO}_2} \times \frac{-1002 \text{ kJ}}{2 \text{ mol SO}_2} = -5.2 \times 10^6 \text{ kJ}$$

6.105 Volume of room =
$$(2.80 \text{ m} \times 10.6 \text{ m} \times 17.2 \text{ m}) \times \frac{1000 \text{ L}}{1 \text{ m}^3} = 5.10 \times 10^5 \text{ L}$$

$$PV = nRT$$

$$n_{\text{air}} = \frac{PV}{RT} = \frac{(1.0 \text{ atm})(5.10 \times 10^5 \text{ L})}{(0.0821 \text{ L atm/K} \cdot \text{mol})(32 + 273 \text{ K})} = 2.04 \times 10^4 \text{ mol air}$$

mass air =
$$(2.04 \times 10^4 \text{ mol air}) \times \frac{29.0 \text{ g air}}{1 \text{ mol air}} = 5.9 \times 10^5 \text{ g air}$$

Heat to be removed from air:

$$q = m_{\text{air}} s_{\text{air}} \Delta t$$

 $q = (5.9 \times 10^5 \text{ g})(1.2 \text{ J/g} \cdot ^{\circ}\text{C})(-8.2 ^{\circ}\text{C})$
 $q = -5.8 \times 10^6 \text{ J} = -5.8 \times 10^3 \text{ kJ}$

Conservation of energy:

$$q_{\text{air}} + q_{\text{salt}} = 0$$

$$q_{\text{air}} + n\Delta H_{\text{fus}} = 0$$

$$q_{\text{air}} + \frac{m_{\text{salt}}}{\mathcal{M}_{\text{salt}}} \Delta H_{\text{fus}} = 0$$

$$m_{\text{salt}} = \frac{-q_{\text{air}} \mathcal{M}_{\text{salt}}}{\Delta H_{\text{fus}}}$$

$$m_{\text{salt}} = \frac{-(-5.8 \times 10^3 \text{ kJ})(322.3 \text{ g/mol})}{74.4 \text{ kJ/mol}} = 2.5 \times 10^4 \text{ g}$$

$$m_{\text{salt}} = 25 \text{ kg}$$

6.106 First, we need to calculate the volume of the balloon.

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi (8 \text{ m})^3 = (2.1 \times 10^3 \text{ m}^3) \times \frac{1000 \text{ L}}{1 \text{ m}^3} = 2.1 \times 10^6 \text{ L}$$

(a) We can calculate the mass of He in the balloon using the ideal gas equation.

$$n_{\text{He}} = \frac{PV}{RT} = \frac{\left(98.7 \text{ kPa} \times \frac{1 \text{ atm}}{1.01325 \times 10^2 \text{ kPa}}\right) (2.1 \times 10^6 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (273 + 18) \text{K}} = 8.6 \times 10^4 \text{ mol He}$$

mass He =
$$(8.6 \times 10^4 \text{ mol He}) \times \frac{4.003 \text{ g He}}{1 \text{ mol He}} = 3.4 \times 10^5 \text{ g He}$$

(b) Work done =
$$-P\Delta V$$

= $-\left(98.7 \text{ kPa} \times \frac{1 \text{ atm}}{1.01325 \times 10^2 \text{ kPa}}\right) (2.1 \times 10^6 \text{ L})$
= $(-2.0 \times 10^6 \text{ L} \cdot \text{atm}) \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}}$

Work done = -2.0×10^8 J

6.107 The heat produced by the reaction heats the solution and the calorimeter: $q_{\text{rxn}} = -(q_{\text{soln}} + q_{\text{cal}})$

$$q_{\text{soln}} = ms\Delta t = (50.0 \text{ g})(4.184 \text{ J/g} \cdot ^{\circ}\text{C})(22.17 \cdot ^{\circ}\text{C} - 19.25 \cdot ^{\circ}\text{C}) = 611 \text{ J}$$

 $q_{\text{cal}} = C\Delta t = (98.6 \text{ J/}^{\circ}\text{C})(22.17 \cdot ^{\circ}\text{C} - 19.25 \cdot ^{\circ}\text{C}) = 288 \text{ J}$
 $-q_{\text{rxn}} = (q_{\text{soln}} + q_{\text{cal}}) = (611 + 288)\text{J} = 899 \text{ J}$

The 899 J produced was for 50.0 mL of a 0.100 M AgNO₃ solution.

$$50.0 \text{ mL} \times \frac{0.100 \text{ mol Ag}^+}{1000 \text{ mL soln}} = 5.00 \times 10^{-3} \text{ mol Ag}^+$$

On a molar basis the heat produced was:

$$\frac{899 \text{ J}}{5.00 \times 10^{-3} \text{ mol Ag}^{+}} = 1.80 \times 10^{5} \text{ J/mol Ag}^{+} = 180 \text{ kJ/mol Ag}^{+}$$

The balanced equation involves 2 moles of Ag^+ , so the heat produced is 2 mol × 180 kJ/mol = 360 kJ

Since the reaction produces heat (or by noting the sign convention above), then:

$$q_{\rm rxn} = -360 \text{ kJ/mol Zn} \text{ (or } -360 \text{ kJ/2 mol Ag}^{+}\text{)}$$

6.108 (a) The heat needed to raise the temperature of the water from 3°C to 37°C can be calculated using the equation:

$$q = ms\Delta t$$

First, we need to calculate the mass of the water.

4 glasses of water
$$\times \frac{2.5 \times 10^2 \text{ mL}}{1 \text{ glass}} \times \frac{1 \text{ g water}}{1 \text{ mL water}} = 1.0 \times 10^3 \text{ g water}$$

The heat needed to raise the temperature of 1.0×10^3 g of water is:

$$q = ms\Delta t = (1.0 \times 10^3 \text{ g})(4.184 \text{ J/g} \cdot ^{\circ}\text{C})(37 - 3)^{\circ}\text{C} = 1.4 \times 10^5 \text{ J} = 1.4 \times 10^2 \text{ kJ}$$

(b) We need to calculate both the heat needed to melt the snow and also the heat needed to heat liquid water form 0°C to 37°C (normal body temperature).

The heat needed to melt the snow is:

$$(8.0 \times 10^2 \text{ g}) \times \frac{1 \text{ mol}}{18.02 \text{ g}} \times \frac{6.01 \text{ kJ}}{1 \text{ mol}} = 2.7 \times 10^2 \text{ kJ}$$

The heat needed to raise the temperature of the water from 0°C to 37°C is:

$$q = ms\Delta t = (8.0 \times 10^2 \text{ g})(4.184 \text{ J/g} \cdot \text{°C})(37 - 0) \text{°C} = 1.2 \times 10^5 \text{ J} = 1.2 \times 10^2 \text{ kJ}$$

The total heat lost by your body is:

$$(2.7 \times 10^2 \text{ kJ}) + (1.2 \times 10^2 \text{ kJ}) = 3.9 \times 10^2 \text{ kJ}$$

6.109 We assume that when the car is stopped, its kinetic energy is completely converted into heat (friction of the brakes and friction between the tires and the road). Thus,

$$q = \frac{1}{2}mu^2$$

Thus the amount of heat generated must be proportional to the braking distance, d:

$$d \propto q$$
$$d \propto u^2$$

Therefore, as u increases to 2u, d increases to $(2u)^2 = 4u^2$ which is proportional to 4d.

6.110 (a)
$$\Delta H^{\circ} = \Delta H_{\rm f}^{\circ}({\rm F}^{-}) + \Delta H_{\rm f}^{\circ}({\rm H_2O}) - [\Delta H_{\rm f}^{\circ}({\rm HF}) + \Delta H_{\rm f}^{\circ}({\rm OH}^{-})]$$

 $\Delta H^{\circ} = [(1)(-329.1 \text{ kJ/mol}) + (1)(-285.8 \text{ kJ/mol})] - [(1)(-320.1 \text{ kJ/mol}) + (1)(-229.6 \text{ kJ/mol})]$
 $\Delta H^{\circ} = -65.2 \text{ kJ/mol}$

(b) We can add the equation given in part (a) to that given in part (b) to end up with the equation we are interested in.

$$HF(aq) + OH^{-}(aq) \longrightarrow F^{-}(aq) + H_2O(l) \qquad \Delta H^{\circ} = -65.2 \text{ kJ/mol}$$

$$H_2O(l) \longrightarrow H^{+}(aq) + OH^{-}(aq) \qquad \Delta H^{\circ} = +56.2 \text{ kJ/mol}$$

$$HF(aq) \longrightarrow H^{+}(aq) + F^{-}(aq) \qquad \Delta H^{\circ} = -9.0 \text{ kJ/mol}$$

- Water has a larger specific heat than air. Thus cold, damp air can extract more heat from the body than cold, dry air. By the same token, hot, humid air can deliver more heat to the body.
- **6.112** The equation we are interested in is the formation of CO from its elements.

$$C(graphite) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$
 $\Delta H^{\circ} = ?$

Try to add the given equations together to end up with the equation above.

C(graphite) + O₂(g)
$$\longrightarrow$$
 CO₂(g) $\Delta H^{\circ} = -393.5 \text{ kJ/mol}$
CO₂(g) \longrightarrow CO(g) + $\frac{1}{2}$ O₂(g) $\Delta H^{\circ} = +283.0 \text{ kJ/mol}$
C(graphite) + $\frac{1}{2}$ O₂(g) \longrightarrow CO(g) $\Delta H^{\circ} = -110.5 \text{ kJ/mol}$

We cannot obtain $\Delta H_{\rm f}^{\circ}$ for CO directly, because burning graphite in oxygen will form both CO and CO₂.

6.113 Energy intake for mechanical work:

$$0.17 \times 500 \text{ g} \times \frac{3000 \text{ J}}{1 \text{ g}} = 2.6 \times 10^5 \text{ J}$$

$$2.6 \times 10^5 \, \mathrm{J} = mgh$$

$$1 J = 1 kg \cdot m^2 s^{-2}$$

$$2.6 \times 10^5 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} = (46 \text{ kg})(9.8 \text{ m/s}^2)h$$

$$h = 5.8 \times 10^2 \,\mathrm{m}$$

6.114 (a) mass = 0.0010 kg

Potential energy
$$= mgh$$

$$= (0.0010 \text{ kg})(9.8 \text{ m/s}^2)(51 \text{ m})$$

Potential energy = 0.50 J

(b) Kinetic energy =
$$\frac{1}{2}mu^2 = 0.50 \text{ J}$$

$$\frac{1}{2}(0.0010 \text{ kg})u^2 = 0.50 \text{ J}$$

$$u^2 = 1.0 \times 10^3 \,\mathrm{m}^2/\mathrm{s}^2$$

$$u = 32 \text{ m/s}$$

(c)
$$q = ms\Delta t$$

$$0.50 \text{ J} = (1.0 \text{ g})(4.184 \text{ J/g}^{\circ}\text{C})\Delta t$$

$$\Delta t = 0.12$$
°C

6.115 For Al: $(0.900 \text{ J/g} \cdot ^{\circ}\text{C})(26.98 \text{ g}) = 24.3 \text{ J/}^{\circ}\text{C}$

This law does not hold for Hg because it is a liquid.

The reaction we are interested in is the formation of ethanol from its elements. 6.116

$$2C(graphite) + \frac{1}{2}O_2(g) + 3H_2(g) \longrightarrow C_2H_5OH(l)$$

Along with the reaction for the combustion of ethanol, we can add other reactions together to end up with the above reaction.

Reversing the reaction representing the combustion of ethanol gives:

$$2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) \longrightarrow \text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g)$$
 $\Delta H^{\circ} = +1367.4 \text{ kJ/mol}$

We need to add equations to add C (graphite) and remove H₂O from the reactants side of the equation. We write:

$$2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) \longrightarrow \text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \qquad \Delta H^\circ = +1367.4 \text{ kJ/mol}$$

$$2\text{C}(\text{graphite}) + 2\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) \qquad \Delta H^\circ = 2(-393.5 \text{ kJ/mol})$$

$$3\text{H}_2(g) + \frac{3}{2} \text{O}_2(g) \longrightarrow 3\text{H}_2\text{O}(l) \qquad \Delta H^\circ = 3(-285.8 \text{ kJ/mol})$$

$$2\text{C}(\text{graphite}) + \frac{1}{2} \text{O}_2(g) + 3\text{H}_2(g) \longrightarrow \text{C}_2\text{H}_5\text{OH}(l) \qquad \Delta H^\circ_\mathbf{f} = -277.0 \text{ kJ/mol}$$

$$2C(\text{graphite}) + \frac{1}{2}O_2(g) + 3H_2(g) \longrightarrow C_2H_5OH(l) \qquad \Delta H_f^{\circ} = -277.0 \text{ kJ/mol}$$

6.117 (a)
$$C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$$
 $\Delta H^{\circ} = -3267.4 \text{ kJ/mol}$

(b)
$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$$
 $\Delta H^{\circ} = -1299.4 \text{ kJ/mol}$

(c) C(graphite) +
$$O_2 \rightarrow CO_2(g)$$
 $\Delta H^{\circ} = -393.5 \text{ kJ/mol}$

(d)
$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$$
 $\Delta H^{\circ} = -285.8 \text{ kJ/mol}$

Using Hess's Law, we can add the equations in the following manner to calculate the standard enthalpies of formation of C_2H_2 and C_6H_6 .

$$C_2H_2$$
: $-(b) + 2(c) + (d)$

$$2C(graphite) + H_2(g) \rightarrow C_2H_2(g)$$
 $\Delta H^{\circ} = +226.6 \text{ kJ/mol}$

Therefore, $\Delta H_f^{\circ}(C_2H_2) = 226.6 \text{ kJ/mol}$

$$C_6H_6$$
: $-(a) + 6(c) + 3(d)$

$$6C(graphite) + 3H_2(g) \rightarrow C_6H_6(l)$$
 $\Delta H^{\circ} = 49.0 \text{ kJ/mol}$

Therefore, $\Delta H_f^{\circ}(C_6H_6) = 49.0 \text{ kJ/mol}$

Finally:

$$3C_2H_2(g) \rightarrow C_6H_6(l)$$

$$\Delta H_{\text{rxn}} = (1)(49.0 \text{ kJ/mol}) - (3)(226.6 \text{ kJ/mol}) = -630.8 \text{ kJ/mol}$$

6.118 Heat gained by ice = Heat lost by the soft drink

$$m_{\rm ice} \times 334 \text{ J/g} = -m_{\rm sd} s_{\rm sd} \Delta t$$

$$m_{\rm ice} \times 334 \text{ J/g} = -(361 \text{ g})(4.184 \text{ J/g} \cdot {}^{\circ}\text{C})(0 - 23){}^{\circ}\text{C}$$

$$m_{\rm ice} = 104 \, \rm g$$

6.119 The heat required to heat 200 g of water (assume d = 1 g/mL) from 20°C to 100°C is:

$$q = ms\Delta t$$

$$q = (200 \text{ g})(4.184 \text{ J/g} \cdot ^{\circ}\text{C})(100 - 20)^{\circ}\text{C} = 6.7 \times 10^4 \text{ J}$$

Since 50% of the heat from the combustion of methane is lost to the surroundings, twice the amount of heat needed must be produced during the combustion: $2(6.7 \times 10^4 \text{ J}) = 1.3 \times 10^5 \text{ J} = 1.3 \times 10^2 \text{ kJ}$.

Use standard enthalpies of formation (see Appendix 3) to calculate the heat of combustion of methane.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
 $\Delta H^{\circ} = -890.3 \text{ kJ/mol}$

The number of moles of methane needed to produce 1.3×10^2 kJ of heat is:

$$(1.3 \times 10^2 \text{ kJ}) \times \frac{1 \text{ mol CH}_4}{890.3 \text{ kJ}} = 0.15 \text{ mol CH}_4$$

The volume of 0.15 mole CH₄ at 1 atm and 20°C is:

$$V = \frac{nRT}{P} = \frac{(0.15 \text{ mol})(0.0821 \text{ L atm/K} \cdot \text{mol})(293 \text{ K})}{1.0 \text{ atm}} = 3.6 \text{ L}$$

Since we have the volume of methane needed in units of liters, let's convert the cost of natural gas per 15 ft³ to the cost per liter.

$$\frac{\$1.30}{15 \text{ ft}^3} \times \left(\frac{1 \text{ ft}}{12 \text{ in}}\right)^3 \times \left(\frac{1 \text{ in}}{2.54 \text{ cm}}\right)^3 \times \frac{1000 \text{ cm}^3}{1 \text{ L}} = \frac{\$3.1 \times 10^{-3}}{1 \text{ L CH}_4}$$

The cost for 3.6 L of methane is:

3.6 L CH₄×
$$\frac{\$3.1 \times 10^{-3}}{1 \text{ L CH}_4}$$
 = **\$0.011** or about **1.1¢**

6.120 From Chapter 5, we saw that the kinetic energy (or internal energy) of 1 mole of a gas is $\frac{3}{2}RT$. For 1 mole of an ideal gas, PV = RT. We can write:

internal energy =
$$\frac{3}{2}RT = \frac{3}{2}PV$$

= $\frac{3}{2}(1.2 \times 10^5 \text{ Pa})(5.5 \times 10^3 \text{ m}^3)$
= $9.9 \times 10^8 \text{ Pa·m}^3$
1 Pa·m³ = 1 $\frac{N}{m^2}$ m³ = 1 N·m = 1 J

Therefore, the internal energy is 9.9×10^8 J.

The final temperature of the copper metal can be calculated. (10 tons = 9.07×10^6 g)

$$q = m_{\text{Cu}} s_{\text{Cu}} \Delta t$$

$$9.9 \times 10^8 \text{ J} = (9.07 \times 10^6 \text{ g})(0.385 \text{ J/g}^{\circ}\text{C})(t_f - 21^{\circ}\text{C})$$

$$(3.49 \times 10^6)t_f = 1.06 \times 10^9$$

$$t_f = 304^{\circ}\text{C}$$

- **6.121** Energy must be supplied to break a chemical bond. By the same token, energy is released when a bond is formed.
- **6.122** (a) $CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g)$
 - **(b)** The reaction for the combustion of acetylene is:

$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l)$$

We can calculate the enthalpy change for this reaction from standard enthalpy of formation values given in Appendix 3 of the text.

$$\Delta H_{\text{rxn}}^{\circ} = [4\Delta H_{\text{f}}^{\circ}(\text{CO}_{2}) + 2\Delta H_{\text{f}}^{\circ}(\text{H}_{2}\text{O})] - [2\Delta H_{\text{f}}^{\circ}(\text{C}_{2}\text{H}_{2}) + 5\Delta H_{\text{f}}^{\circ}(\text{O}_{2})]$$

$$\Delta H_{\text{rxn}}^{\circ} = [(4)(-393.5 \text{ kJ/mol}) + (2)(-285.8 \text{ kJ/mol})] - [(2)(226.6 \text{ kJ/mol}) + (5)(0)]$$

$$\Delta H_{\text{rxn}}^{\circ} = -2599 \text{ kJ/mol}$$

Looking at the balanced equation, this is the amount of heat released when two moles of C_2H_2 are reacted. The problem asks for the amount of heat that can be obtained starting with 74.6 g of CaC_2 . From this amount of CaC_2 , we can calculate the moles of C_2H_2 produced.

74.6 g
$$CaC_2 \times \frac{1 \text{ mol } CaC_2}{64.10 \text{ g } CaC_2} \times \frac{1 \text{ mol } C_2H_2}{1 \text{ mol } CaC_2} = 1.16 \text{ mol } C_2H_2$$

Now, we can use the $\Delta H_{\text{rxn}}^{\circ}$ calculated above as a conversion factor to determine the amount of heat obtained when 1.16 moles of C_2H_2 are burned.

1.16 mol
$$C_2H_2 \times \frac{2599 \text{ kJ}}{2 \text{ mol } C_2H_2} = 1.51 \times 10^3 \text{ kJ}$$

- 6.123 Since the humidity is very low in deserts, there is little water vapor in the air to trap and hold the heat radiated back from the ground during the day. Once the sun goes down, the temperature drops dramatically. 40°F temperature drops between day and night are common in desert climates. Coastal regions have much higher humidity levels compared to deserts. The water vapor in the air retains heat, which keeps the temperature at a more constant level during the night. In addition, sand and rocks in the desert have small specific heats compared with water in the ocean. The water absorbs much more heat during the day compared to sand and rocks, which keeps the temperature warmer at night.
- 6.124 When 1.034 g of naphthalene are burned, 41.56 kJ of heat are evolved. Let's convert this to the amount of heat evolved on a molar basis. The molar mass of naphthalene is 128.2 g/mol.

$$q = \frac{-41.56 \text{ kJ}}{1.034 \text{ g C}_{10}\text{H}_8} \times \frac{128.2 \text{ g C}_{10}\text{H}_8}{1 \text{ mol C}_{10}\text{H}_8} = -5153 \text{ kJ/mol}$$

q has a negative sign because this is an exothermic reaction.

This reaction is run at constant volume ($\Delta V = 0$); therefore, no work will result from the change.

$$w = -P\Delta V = 0$$

From Equation (6.4) of the text, it follows that the change in energy is equal to the heat change.

$$\Delta E = q + w = q_{\rm V} = -5153 \text{ kJ/mol}$$

To calculate ΔH , we rearrange Equation (6.10) of the text.

$$\Delta E = \Delta H - RT\Delta n$$

$$\Delta H = \Delta E + RT\Delta n$$

To calculate ΔH , Δn must be determined, which is the difference in moles of *gas* products and moles of *gas* reactants. Looking at the balanced equation for the combustion of naphthalene:

$$C_{10}H_8(s) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(l)$$

$$\Delta n = 10 - 12 = -2$$

$$\Delta H = \Delta E + RT\Delta n$$

$$\Delta H = -5153 \text{ kJ/mol} + (8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})(-2) \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta H = -5158 \text{ kJ/mol}$$

Is ΔH equal to q_p in this case?

- 6.125 Let's write balanced equations for the reactions between Mg and CO₂, and Mg and H₂O. Then, we can calculate ΔH_{rxn}° for each reaction from ΔH_{f}° values.
 - (1) $2Mg(s) + CO_2(g) \rightarrow 2MgO(s) + C(s)$
 - (2) $Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)$

For reaction (1), $\Delta H_{\rm rxn}^{\circ}$ is:

$$\Delta H_{\text{rxn}}^{\circ} = 2\Delta H_{\text{f}}^{\circ}[\text{MgO}(s)] + \Delta H_{\text{f}}^{\circ}[\text{C}(s)] - \{2\Delta H_{\text{f}}^{\circ}[\text{Mg}(s)] + \Delta H_{\text{f}}^{\circ}[\text{CO}_{2}(g)]\}$$

$$\Delta H_{\text{rxn}}^{\circ} = (2)(-601.8 \text{ kJ/mol}) + (1)(0) - [(2)(0) + (1)(-393.5 \text{ kJ/mol})] = -810.1 \text{ kJ/mol}$$

For reaction (2), $\Delta H_{\rm rxn}^{\circ}$ is:

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{f}}^{\circ}[\text{Mg(OH)}_{2}(s)] + \Delta H_{\text{f}}^{\circ}[\text{H}_{2}(g)] - \{\Delta H_{\text{f}}^{\circ}[\text{Mg}(s)] + 2\Delta H_{\text{f}}^{\circ}[\text{H}_{2}\text{O}(l)]\}$$

$$\Delta H_{\text{rxn}}^{\circ} = (1)(-924.66 \text{ kJ/mol}) + (1)(0) - [(1)(0) + (2)(-285.8 \text{ kJ/mol})] = -353.1 \text{ kJ/mol}$$

Both of these reactions are highly exothermic, which will promote the fire rather than extinguishing it.

6.126 We know that $\Delta E = q + w$. $\Delta H = q$, and $w = -P\Delta V = -RT\Delta n$. Using thermodynamic data in Appendix 3 of the text, we can calculate ΔH .

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l), \Delta H = 2(-285.8 \text{ kJ/mol}) = -571.6 \text{ kJ/mol}$$

Next, we calculate w. The change in moles of gas (Δn) equals -3.

$$w = -P\Delta V = -RT\Delta n$$

 $w = -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})(-3) = +7.43 \times 10^3 \text{ J/mol} = 7.43 \text{ kJ/mol}$
 $\Delta E = q + w$
 $\Delta E = -571.6 \text{ kJ/mol} + 7.43 \text{ kJ/mol} = -564.2 \text{ kJ/mol}$

Can you explain why ΔE is smaller (in magnitude) than ΔH ?

6.127 (a) We carry an extra significant figure throughout this calculation to avoid rounding errors. The number of moles of water present in 500 g of water is:

moles of
$$H_2O = 500 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 27.75 \text{ mol } H_2O$$

From the equation for the production of $Ca(OH)_2$, we have 1 mol $H_2O \simeq 1$ mol $CaO \simeq 1$ mol $Ca(OH)_2$. Therefore, the heat generated by the reaction is:

27.75 mol Ca(OH)₂ ×
$$\frac{-65.2 \text{ kJ}}{1 \text{ mol Ca(OH)}_2} = -1.809 \times 10^3 \text{ kJ}$$

Knowing the specific heat and the number of moles of Ca(OH)₂ produced, we can calculate the temperature rise using Equation (6.12) of the text. First, we need to find the mass of Ca(OH)₂ in 27.7 moles.

27.75 mol Ca(OH)₂ ×
$$\frac{74.10 \text{ g Ca(OH)}_2}{1 \text{ mol Ca(OH)}_2}$$
 = 2.056 × 10³ g Ca(OH)₂

From Equation (6.12) of the text, we write:

$$q = ms\Delta t$$

Rearranging, we get

$$\Delta t = \frac{q}{ms}$$

$$\Delta t = \frac{1.809 \times 10^6 \text{ J}}{(2.056 \times 10^3 \text{ g})(1.20 \text{ J/g} \cdot ^{\circ}\text{C})} = 733^{\circ}\text{C}$$

and the final temperature is

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

$$t_{\text{final}} = 733^{\circ}\text{C} + 25^{\circ}\text{C} = 758^{\circ}\text{C}$$

A temperature of 758°C is high enough to ignite wood.

(b) The reaction is:

$$CaO(s) + H2O(l) \rightarrow Ca(OH)2(s)$$

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{f}}^{\circ} [\text{Ca}(\text{OH})_2] - [\Delta H_{\text{f}}^{\circ}(\text{CaO}) + \Delta H_{\text{f}}^{\circ}(\text{H}_2\text{O})]$$

 ΔH_{rxn}° is given in the problem (-65.2 kJ/mol). Also, the ΔH_{f}° values of CaO and H₂O are given. Thus, we can solve for ΔH_{f}° of Ca(OH)₂.

$$-65.2 \text{ kJ/mol} = \Delta H_f^{\circ} [\text{Ca}(\text{OH})_2] - [(1)(-635.6 \text{ kJ/mol} + (1)(-285.8 \text{ kJ/mol})]$$

$$\Delta H_{\rm f}^{\circ}[{\rm Ca}({\rm OH})_2] = -986.6 \text{ kJ/mol}$$

6.128 First, we calculate ΔH for the combustion of 1 mole of glucose using data in Appendix 3 of the text. We can then calculate the heat produced in the calorimeter. Using the heat produced along with ΔH for the combustion of 1 mole of glucose will allow us to calculate the mass of glucose in the sample. Finally, the mass % of glucose in the sample can be calculated.

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

$$\Delta H_{\text{TXN}}^{\circ} = (6)(-393.5 \text{ kJ/mol}) + (6)(-285.8 \text{ kJ/mol}) - (1)(-1274.5 \text{ kJ/mol}) = -2801.3 \text{ kJ/mol}$$

The heat produced in the calorimeter is:

$$(3.134^{\circ}C)(19.65 \text{ kJ/}^{\circ}C) = 61.58 \text{ kJ}$$

Let *x* equal the mass of glucose in the sample:

$$x$$
 g glucose $\times \frac{1 \text{ mol glucose}}{180.2 \text{ g glucose}} \times \frac{2801.3 \text{ kJ}}{1 \text{ mol glucose}} = 61.58 \text{ kJ}$

$$x = 3.961 \,\mathrm{g}$$

% glucose =
$$\frac{3.961 \text{ g}}{4.117 \text{ g}} \times 100\% = 96.21\%$$

In (b), the internal energy of an ideal gas depends only on temperature. Since temperature is held constant, $\Delta E = 0$. Also, $\Delta H = 0$ because $\Delta H = \Delta E + \Delta (PV) = \Delta E + \Delta (nRT) = 0$.

6.130 (a) From the mass of CO_2 produced, we can calculate the moles of carbon in the compound. From the mass of H_2O produced, we can calculate the moles of hydrogen in the compound.

$$1.419 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 0.03224 \text{ mol C}$$

$$0.290 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \ = \ 0.03219 \text{ mol H}$$

The mole ratio between C and H is 1:1, so the empirical formula is CH.

(b) The empirical molar mass of CH is 13.02 g/mol.

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{76 \text{ g}}{13.02 \text{ g}} = 5.8 \approx 6$$

Therefore, the molecular formula is C_6H_6 , and the hydrocarbon is benzene. The combustion reaction is:

$$2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$$

17.55 kJ of heat is released when 0.4196 g of the hydrocarbon undergoes combustion. We can now calculate the enthalpy of combustion ($\Delta H_{\rm rxn}^{\circ}$) for the above reaction in units of kJ/mol. Then, from the enthalpy of combustion, we can calculate the enthalpy of formation of C₆H₆.

$$\begin{split} &\frac{-17.55 \text{ kJ}}{0.4196 \text{ g C}_6 \text{H}_6} \times \frac{78.11 \text{ g C}_6 \text{H}_6}{1 \text{ mol C}_6 \text{H}_6} \times 2 \text{ mol C}_6 \text{H}_6 = -6534 \text{ kJ/mol} \\ &\Delta H_{\text{rxn}}^{\circ} = (12) \Delta H_{\text{f}}^{\circ} (\text{CO}_2) + (6) \Delta H_{\text{f}}^{\circ} (\text{H}_2 \text{O}) - (2) \Delta H_{\text{f}}^{\circ} (\text{C}_6 \text{H}_6) \\ &-6534 \text{ kJ/mol} = (12) (-393.5 \text{ kJ/mol}) + (6) (-285.8 \text{ kJ/mol}) - (2) \Delta H_{\text{f}}^{\circ} (\text{C}_6 \text{H}_6) \\ &\Delta H_{\text{f}}^{\circ} (\text{C}_6 \text{H}_6) = \textbf{49 kJ/mol} \end{split}$$

6.131 If the body absorbs all the heat released and is an isolated system, the temperature rise, Δt , is:

$$q = ms\Delta t$$

$$\Delta t = \frac{q}{ms} = \frac{1.0 \times 10^7 \text{ J}}{(50.000 \text{ g})(4.184 \text{ J/g} \cdot ^{\circ}\text{C})} = 48^{\circ}\text{C}$$

If the body temperature is to remain constant, the heat released by metabolic activity must be used for the evaporation of water as perspiration, that is,

$$\frac{1 \text{ g H}_2\text{O}}{2.41 \text{ kJ}} \times (1.0 \times 10^4 \text{ kJ}) = 4.1 \times 10^3 \text{ g H}_2\text{O}$$

Assuming that the density of perspiration is 1 g/mL, this mass corresponds to a volume of 4.1 L. The actual amount of perspiration is less than this because part of the body heat is lost to the surroundings by convection and radiation.

Begin by using Equation (6.20) of the text, $\Delta H_{\text{soln}} = U + \Delta H_{\text{hydr}}$, where U is the lattice energy. 6.132

(1)
$$\text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$$
 $\Delta H_{\text{hydr}} = (4.0 - 788) \text{ kJ/mol} = -784.0 \text{ kJ/mol}$

(2)
$$Na^{+}(g) + I^{-}(g) \rightarrow Na^{+}(aq) + I^{-}(aq)$$
 $\Delta H_{\text{hydr}} = (-5.1 - 686) \text{ kJ/mol} = -691.1 \text{ kJ/mol}$

(3)
$$K^+(g) + Cl^-(g) \rightarrow K^+(aq) + Cl^-(aq)$$
 $\Delta H_{\text{hydr}} = (17.2 - 699) \text{ kJ/mol} = -681.8 \text{ kJ/mol}$

Adding together equation (2) and (3) and then subtracting equation (1) gives the equation for the hydration of KI.

(2)
$$Na^{+}(g) + \bar{\Gamma}(g) \rightarrow Na^{+}(aq) + \bar{\Gamma}(aq)$$
 $\Delta H = -691.1 \text{ kJ/mol}$

(3)
$$K^{+}(g) + Cl^{-}(g) \rightarrow K^{+}(aq) + Cl^{-}(aq)$$
 $\Delta H = -681.8 \text{ kJ/mol}$

(3)
$$K^{+}(g) + CI^{-}(g) \rightarrow K^{+}(aq) + CI^{-}(aq)$$
 $\Delta H = -681.8 \text{ kJ/mol}$
(1) $Na^{+}(aq) + CI^{-}(aq) \rightarrow Na^{+}(g) + CI^{-}(g)$ $\Delta H = +784.0 \text{ kJ/mol}$
 $K^{+}(g) + I^{-}(g) \rightarrow K^{+}(aq) + I^{-}(aq)$ $\Delta H = -588.9 \text{ kJ/mol}$

We combine this last result with the given value of the lattice energy to arrive at the heat of solution of KI.

$$\Delta H_{\text{soln}} = U + \Delta H_{\text{hydr}} = (632 \text{ kJ/mol} - 588.9 \text{ kJ/mol}) = 43 \text{ kJ/mol}$$

6.133
$$A \rightarrow B$$
 $w = 0$, because $\Delta V = 0$
 $B \rightarrow C$ $w = -P\Delta V = -(2 \text{ atm})(2 - 1)L = -2 \text{ L} \cdot \text{atm}$
 $C \rightarrow D$ $w = 0$, because $\Delta V = 0$
 $D \rightarrow A$ $w = -P\Delta V = -(1 \text{ atm})(1 - 2)L = +1 \text{ L} \cdot \text{atm}$

The total work done = $(-2 \text{ L} \cdot \text{atm}) + (1 \text{ L} \cdot \text{atm}) = -1 \text{ L} \cdot \text{atm}$

Converting to units of joules,

$$-1 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{1 \text{ L} \cdot \text{atm}} = -101.3 \text{ J}$$

In a cyclic process, the change in a state function must be zero. We therefore conclude that work is not a state function. Note that the total work done equals the area of the enclosure.