CHAPTER 7
THERMOCHEMISTRY

PRACTICE EXAMPLES

1A The heat absorbed is the product of the mass of water, its specific heat $\left(4.18 \text{ J g}^{-1}\,{}^\circ\text{C}^{-1}\right)$, and the temperature change that occurs.

$$\text{heat energy} = 237 \text{ g} \times \frac{4.18 \text{ J}}{\text{g}\,{}^\circ\text{C}} \times \left(37.0{}^\circ\text{C} - 4.0{}^\circ\text{C}\right) \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 32.7 \text{ kJ of heat energy}$$

1B The heat absorbed is the product of the amount of mercury, its molar heat capacity, and the temperature change that occurs.

$$\text{heat energy} = \left(2.50 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol Hg}}{200.59 \text{ g Hg}}\right) \times \frac{28.0 \text{ J}}{\text{mol}\,{}^\circ\text{C}} \times \left[-6.0 - (-20.0)\right]{}^\circ\text{C} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$
$$= 4.89 \text{ kJ of heat energy}$$

2A First calculate the quantity of heat lost by the lead. This heat energy must be absorbed by the surroundings (water). We assume 100% efficiency in the energy transfer.

$$q_{\text{lead}} = 1.00 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{0.13 \text{ J}}{\text{g}\,{}^\circ\text{C}} \times \left(35.2{}^\circ\text{C} - 100.0{}^\circ\text{C}\right) = -8.4 \times 10^3 \text{ J} = -q_{\text{water}}$$

$$8.4 \times 10^3 \text{ J} = m_{\text{water}} \times \frac{4.18 \text{ J}}{\text{g}\,{}^\circ\text{C}} \times \left(35.2{}^\circ\text{C} - 28.5{}^\circ\text{C}\right) = 28 m_{\text{water}} \qquad m_{\text{water}} = \frac{8.4 \times 10^3 \text{ J}}{28 \text{ J g}^{-1}} = 3.0 \times 10^2 \text{ g}$$

2B We use the same equation, equating the heat lost by the copper to the heat absorbed by the water, except now we solve for final temperature.

$$q_{\text{Cu}} = 100.0 \text{ g} \times \frac{0.385 \text{ J}}{\text{g}\,{}^\circ\text{C}} \times \left(x{}^\circ\text{C} - 100.0{}^\circ\text{C}\right) = -50.0 \text{ g} \times \frac{4.18 \text{ J}}{\text{g}\,{}^\circ\text{C}} \times \left(x{}^\circ\text{C} - 26.5{}^\circ\text{C}\right) = -q_{\text{water}}$$

$$38.5x - 3850 = -209x + 5539 \text{ J} \qquad 38.5x + 209x = 5539 + 3850 \rightarrow 247.5x = 9389$$

$$x = \frac{9389 \text{ J}}{247.5 \text{ J }{}^\circ\text{C}^{-1}} = 37.9{}^\circ\text{C}$$

3A The molar mass of $C_8H_8O_3$ is 152.15 g/mol. The calorimeter has a heat capacity of $4.90 \text{ kJ}/{}^\circ\text{C}$.

$$q_{\text{calor}} = \frac{4.90 \text{ kJ}\,{}^\circ\text{C}^{-1} \times \left(30.09{}^\circ\text{C} - 24.89{}^\circ\text{C}\right)}{1.013 \text{ g}} \times \frac{152.15 \text{ g}}{1 \text{ mol}} = 3.83 \times 10^3 \text{ kJ/mol}$$

$$\Delta H_{\text{comb}} = -q_{\text{calor}} = -3.83 \times 10^3 \text{ kJ/mol}$$

3B The heat that is liberated by the benzoic acid's combustion serves to raise the temperature of the assembly. We designate the calorimeter's heat capacity by C.

$$q_{\text{rxn}} = 1.176 \text{ g} \times \frac{-26.42 \text{ kJ}}{1 \text{ g}} = -31.07 \text{ kJ} = -q_{\text{calorim}}$$

$$q_{\text{calorim}} = C\Delta t = 31.07 \text{ kJ} = C \times 4.96^{\circ}\text{C} \qquad C = \frac{31.07 \text{ kJ}}{4.96^{\circ}\text{C}} = 6.26 \text{ kJ}/^{\circ}\text{ C}$$

4A The heat that is liberated by the reaction raises the temperature of the reaction mixture. We assume that this reaction mixture has the same density and specific heat as pure water.

$$q_{\text{calorim}} = \left(200.0 \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}}\right) \times \frac{4.18 \text{ J}}{\text{g}^{\circ}\text{C}} \times (30.2 - 22.4)^{\circ}\text{C} = 6.5 \times 10^{3} \text{ J} = -q_{rxn}$$

Owing to the 1:1 stoichiometry of the reaction, the number of moles of AgCl(s) formed is equal to the number of moles of $AgNO_3$(aq) in the original sample.

$$\text{moles AgCl} = 100.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.00 \text{ M AgNO}_3}{1 \text{ L}} \times \frac{1 \text{ mol AgCl}}{1 \text{ mol AgNO}_3} = 0.100 \text{ mol AgCl}$$

$$q_{\text{rxn}} = \frac{-6.5 \times 10^{3} \text{ J}}{0.100 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -65. \text{ kJ/mol}$$

Because q_{rxn} is a negative quantity, the precipitation reaction is exothermic.

4B The assumptions include no heat loss to the surroundings or to the calorimeter, a solution density of 1.00 g/mL, a specific heat of $4.18 \text{ J g}^{-1}\,^{\circ}\text{C}^{-1}$, and that the initial and final solution volumes are the same. The equation for the reaction that occurs is $\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$. Since the two reactants combine in a one to one mole ratio, the limiting reactant is the one present in smaller amount (i.e. the one with a smaller molar quantity).

$$\text{amount HCl} = 100.0 \text{ mL} \times \frac{1.020 \text{ mmol HCl}}{1 \text{ mL soln}} = 102.0 \text{ mmol HCl}$$

$$\text{amount NaOH} = 50.0 \text{ mL} \times \frac{1.988 \text{ mmol NaOH}}{1 \text{ mL soln}} = 99.4 \text{ mmol NaOH}$$

Thus, NaOH is the limiting reactant.

$$q_{\text{neutr}} = 99.4 \text{ mmol NaOH} \times \frac{1 \text{ mmol H}_2\text{O}}{1 \text{ mmol NaOH}} \times \frac{1 \text{ mol H}_2\text{O}}{1000 \text{ mmol H}_2\text{O}} \times \frac{-56 \text{ kJ}}{1 \text{ mol H}_2\text{O}} = -5.57 \text{ kJ}$$

$$q_{\text{calorim}} = -q_{\text{neutr}} = 5.57 \text{ kJ} = (100.0 + 50.0) \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{4.18 \text{ J}}{\text{g}^{\circ}\text{C}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times (t - 24.52^{\circ}\text{C})$$

$$= 0.627t - 15.37 \qquad t = \frac{5.57 + 15.37}{0.627} = 33.4^{\circ}\text{C}$$

5A $w = -P\Delta V = -0.750 \text{ atm}(+1.50 \text{ L}) = -1.12\underline{5} \text{ L atm} \times \dfrac{101.33 \text{ J}}{1 \text{ L atm}} = -114 \text{ J}$

114 J of work is done by system

5B Determine the initial number of moles:

$$n = 50.0\text{ g N}_2 \times \frac{1\text{ mol N}_2}{28.014\text{ g N}_2} = 1.78\underline{5}\text{ moles of N}_2$$

$$V = \frac{nRT}{P} = \frac{(1.785\text{ mol N}_2)(0.08206\text{ Latm K}^{-1}\text{mol}^{-1})(293.15\text{ K})}{2.50\text{ atm}} = 17.2\text{ L}$$

$$\mathit{\Delta} V = 17.2 - 75.0\text{ L} = -57.8\text{ L}$$

$$w = -P\mathit{\Delta} V = -2.50\text{ atm}(-57.8\text{ L}) \times \frac{101.33\text{ J}}{1\text{ L atm}} \times \frac{1\text{ kJ}}{1000\text{ J}} = +14.6\text{ kJ work done on system.}$$

6A The work is $w = +355$ J. The heat flow is $q = -185$ J. These two are related to the energy change of the system by the first law equation: $\Delta U = q + w,$ which becomes

$$\Delta U = +355\text{ J} - 185\text{ J} = +1.70 \times 10^2\text{ J}$$

6B The internal energy change is $\Delta U = -125$ J. The heat flow is $q = +54$ J. These two are related to the work done on the system by the first law equation: $\Delta U = q + w$, which becomes $-125\text{ J} = +54\text{ J} + w.$ The solution to this equation is $w = -125\text{ J} - 54\text{ J} = -179\text{ J}$, which means that 179 J of work is done by the system to the surroundings.

7A Heat that is given off has a negative sign. In addition, we use the molar mass of sucrose, 342.30 g/mol.

$$\text{sucrose mass} = -1.00 \times 10^3\text{ kJ} \times \frac{1\text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{-5.65 \times 10^3\text{ kJ}} \times \frac{342.30\text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{1\text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} = 60.6\text{ g C}_{12}\text{H}_{22}\text{O}_{11}$$

7B Although the equation does not say so explicitly, the reaction of $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ gives off 56 kJ of heat per mole of water formed. The equation then is the source of a conversion factor.

$$\text{heat flow} = 25.0\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} \times \frac{0.1045\text{ mol HCl}}{1\text{ L soln}} \times \frac{1\text{ mol H}_2\text{O}}{1\text{ mol HCl}} \times \frac{56\text{ kJ evolved}}{1\text{ mol H}_2\text{O}}$$

heat flow = 0.15 kJ heat evolved

8A $V_{ice} = (2.00\text{ cm})^3 = 8.00\text{ cm}^3$

$$m_{ice} = m_{water} = 8.00\text{ cm}^3 \times 0.917\text{ g cm}^{-3} = 7.34\text{ g ice} = 7.34\text{ g H}_2\text{O}$$

$$\text{moles of ice} = 7.34\text{ g ice} \times \frac{1\text{ mol H}_2\text{O}}{18.015\text{ g H}_2\text{O}} = 0.407\text{ moles of ice}$$

$$q_{overall} = q_{ice}(-10\text{ to }0\ ^\circ\text{C}) + q_{fus} + q_{water}(0\text{ to }23.2\ ^\circ\text{C})$$

$$q_{overall} = m_{ice}(\text{sp. ht.})_{\text{ice}}\mathit{\Delta} T + n_{ice}\Delta H_{\text{fus}} + m_{water}(\text{sp. ht.})_{\text{water}}\mathit{\Delta} T$$

$$q_{overall} = 7.34\text{ g}(10.0\ ^\circ\text{C})(2.01\frac{\text{J}}{\text{g }^\circ\text{C}}) + 0.407\text{ mol ice}(6.01\frac{\text{kJ}}{\text{mol}}) + 7.34\text{ g}(23.2\ ^\circ\text{C})(4.184\frac{\text{J}}{\text{g }^\circ\text{C}})$$

$$q_{overall} = 0.148\text{ kJ} + 2.45\text{ kJ} + 0.712\text{ kJ}$$

$$q_{overall} = +3.31\text{ kJ (the system absorbs this much heat)}$$

8B $5.00 \times 10^3\ \text{kJ} = q_{\text{ice}}(-15 \text{ to } 0\ ^\circ\text{C}) + q_{\text{fus}} + q_{\text{water}}\ (0 \text{ to } 25\ ^\circ\text{C}) + q_{\text{vap}}$

$$5.00 \times 10^3\ \text{kJ} = m_{\text{ice}}(\text{sp. ht.})_{\text{ice}}\Delta T + n_{\text{ice}}\Delta H_{\text{fus}} + m_{\text{water}}(\text{sp. ht.})_{\text{water}}\Delta T + n_{\text{water}}\Delta H_{\text{vap}}$$

$$5.00 \times 10^6\ \text{J} = \text{m}(15.0\ ^\circ\text{C})(2.01\frac{\text{J}}{\text{g}\ ^\circ\text{C}}) + (\frac{\text{m}}{18.015\ \text{g H}_2\text{O/mol H}_2\text{O}} \times 6.01 \times 10^3 \frac{\text{J}}{\text{mol}})$$

$$+\ \text{m}(25.0\ ^\circ\text{C})(4.184\frac{\text{J}}{\text{g}\ ^\circ\text{C}}) + \frac{\text{m}}{18.015\ \text{g H}_2\text{O/mol}}(44.0 \times 10^3\ \frac{\text{J}}{\text{mol}})$$

$$5.00 \times 10^6\ \text{J} = \text{m}(30.1\underline{5}\ \text{J/g}) + \text{m}(333.\underline{6}\ \text{J/g}) + \text{m}(104.\underline{5}\ \text{J/g}) + \text{m}(2.4\underline{4} \times 10^3\ \text{J/g})$$

$$5.00 \times 10^6\ \text{J} = \text{m}(2.91 \times 10^3\ \text{J/g}) \qquad m = \frac{5.00\times10^6\ \text{J}}{2.91\times10^3\ \text{J/g}} = 1718\ \text{g or } 1.72\ \text{kg H}_2\text{O}$$

9A We combine the three combustion reactions to produce the hydrogenation reaction.

$$\begin{array}{ll}
C_3H_6(g) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l) & \Delta H_{\text{comb}} = \Delta H_1 = -2058\ \text{kJ} \\
H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) & \Delta H_{\text{comb}} = \Delta H_2 = -285.8\ \text{kJ} \\
3CO_2(g) + 4H_2O(l) \rightarrow C_3H_8(g) + 5O_2(g) & -\Delta H_{\text{comb}} = \Delta H_3 = +2219.9\ \text{kJ} \\
\hline
C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g) & \Delta H_{\text{rxn}} = \Delta H_1 + \Delta H_2 + \Delta H_3 = -124\ \text{kJ}
\end{array}$$

9B The combustion reaction has propanol and $O_{2(g)}$ as reactants; the products are $CO_2(g)$ and $H_2O(l)$. Reverse the reaction given and combine it with the combustion reaction of $C_3H_6(g)$.

$$\begin{array}{ll}
C_3H_7OH(l) \rightarrow C_3H_6(g) + H_2O(l) & \Delta H_1 = +52.3\ \text{kJ} \\
C_3H_6(g) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l) & \Delta H_2 = -2058\ \text{kJ} \\
\hline
C_3H_7OH(l) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) & \Delta H_{\text{rxn}} = \Delta H_1 + \Delta H_2 = -2006\ \text{kJ}
\end{array}$$

10A The enthalpy of formation is the enthalpy change for the reaction in which one mole of the product, $C_6H_{13}O_2N(s)$, is produced from appropriate amounts of the reference forms of the elements (in most cases, the most stable form of the elements).

$$6\ C(\text{graphite}) + \tfrac{13}{2}H_2(g) + O_2(g) + \tfrac{1}{2}N_2(g) \rightarrow C_6H_{13}O_2N(s)$$

10B The enthalpy of formation is the enthalpy change for the reaction in which one mole of the product, $NH_3(g)$, is produced from appropriate amounts of the reference forms of the elements, in this case from 0.5 mol $N_2(g)$ and 1.5 mol $H_2(g)$, that is, for the reaction:

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightarrow NH_3(g)$$

The specified reaction is twice the reverse of the formation reaction, and its enthalpy change is minus two times the enthalpy of formation of $NH_3(g)$:

$$-2 \times (-46.11\ \text{kJ}) = +92.22\ \text{kJ}$$

11A $\Delta H^{\circ}_{\text{rxn}} = 2\times\Delta H^{o}_{f}\left[\text{CO}_2(\text{g})\right] + 3\times\Delta H^{o}_{f}\left[\text{H}_2\text{O}(\text{l})\right] - \Delta H^{o}_{f}\left[\text{CH}_3\text{CH}_2\text{OH}(\text{l})\right] - 3\times\Delta H^{o}_{f}\left[\text{O}_2(\text{g})\right]$

$$= \left[2\times(-393.5\text{ kJ})\right] + \left[3\times(-285.8\text{ kJ})\right] - \left[-277.7\text{ kJ}\right] - \left[3\times 0.00\text{ kJ}\right] = -1367\text{ kJ}$$

11B We write the combustion reaction for each compound, and use that reaction to determine the compound's heat of combustion.

$$\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$$

$$\Delta H^{o}_{\text{combustion}} = 3\times\Delta H^{o}_{f}\left[\text{CO}_2(\text{g})\right] + 4\times\Delta H^{o}_{f}\left[\text{H}_2\text{O}(\text{l})\right] - \Delta H^{o}_{f}\left[\text{C}_3\text{H}_8(\text{g})\right] - 5\times\Delta H^{o}_{f}\left[\text{O}_2(\text{g})\right]$$

$$= \left[3\times(-393.5\text{ kJ})\right] + \left[4\times(-285.8\text{ kJ})\right] - \left[-103.8\text{ kJ}\right] - \left[5\times 0.00\text{ kJ}\right]$$

$$= -1181\text{ kJ} - 1143\text{ kJ} + 103.8 - 0.00\text{ kJ} = -2220.\text{ kJ/mol C}_3\text{H}_8$$

$$\text{C}_4\text{H}_{10}(\text{g}) + \tfrac{13}{2}\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l})$$

$$\Delta H^{\circ}_{\text{combustion}} = 4\times\Delta H^{o}_{f}\left[\text{CO}_2(\text{g})\right] + 5\times\Delta H^{o}_{f}\left[\text{H}_2\text{O}(\text{l})\right] - \Delta H^{o}_{f}\left[\text{C}_4\text{H}_{10}(\text{g})\right] - 6.5\times\Delta H^{o}_{f}\left[\text{O}_2(\text{g})\right]$$

$$= \left[4\times(-393.5\text{ kJ})\right] + \left[5\times(-285.8\text{ kJ})\right] - \left[-125.6\right] - \left[6.5\times 0.00\text{ kJ}\right]$$

$$= -1574\text{ kJ} - 1429\text{ kJ} + 125.6\text{ kJ} - 0.00K\text{ kJ} = -2877\text{ kJ/mol C}_4\text{H}_{10}$$

In 1.00 mole of the mixture there are 0.62 mol $\text{C}_3\text{H}_8(\text{g})$ and 0.38 mol $\text{C}_4\text{H}_{10}(\text{g})$.

$$\text{heat of combustion} = \left(0.62\text{ mol C}_3\text{H}_8 \times \frac{-2220.\text{ kJ}}{1\text{ mol C}_3\text{H}_8}\right) + \left(0.38\text{ mol C}_4\text{H}_{10} \times \frac{-2877\text{ kJ}}{1\text{ mol C}_4\text{H}_{10}}\right)$$

$$= -1.4\times 10^{3}\text{ kJ} - 1.1\times 10^{3}\text{ kJ} = -2.5\times 10^{3}\text{ kJ/mole of mixture}$$

12A $6\text{ CO}_2(\text{g}) + 6\text{ H}_2\text{O}(\text{l}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{ O}_2(\text{g})$

$\Delta H^{o}_{\text{rxn}} = 2803\text{ kJ} = \Sigma\,\Delta H^{o}_{f\ \text{products}} - \Sigma\,\Delta H^{o}_{f\ \text{reactants}}$

$$2803\text{ kJ} = [1\text{ mol}(\Delta H^{o}_{f}[\text{C}_6\text{H}_{12}\text{O}_6(\text{s})]) + 6\text{ mol}(0\tfrac{\text{kJ}}{\text{mol}})] - [6\text{ mol}(-393.5\tfrac{\text{kJ}}{\text{mol}}) + 6\text{ mol}(-285.8\tfrac{\text{kJ}}{\text{mol}})]$$

$2803\text{ kJ} = \Delta H^{o}_{f}[\text{C}_6\text{H}_{12}\text{O}_6(\text{s})] - [-4075.8\text{ kJ}]$. Thus, $\Delta H^{o}_{f}[\text{C}_6\text{H}_{12}\text{O}_6(\text{s})] = -1273\text{ kJ/mol C}_6\text{H}_{12}\text{O}_6(\text{s})$

12B $\Delta H^{o}_{\text{comb}}[\text{CH}_3\text{OCH}_3(\text{g})] = -31.70\ \frac{\text{kJ}}{\text{g}}$ molar mass of $\text{CH}_3\text{OCH}_3 = 46.069\text{ g mol}^{-1}$

$$\Delta H^{o}_{\text{comb}}[\text{CH}_3\text{OCH}_3(\text{g})] = -31.70\ \frac{\text{kJ}}{\text{g}} \times 46.069\ \frac{\text{g}}{\text{mol}} = -1460\ \frac{\text{kJ}}{\text{mol}}\text{kJ} = \Delta H^{o}_{rxn}$$

$\Delta H^{o}_{\text{rxn}} = \Sigma\,\Delta H^{o}_{f\ \text{products}} - \Sigma\,\Delta H^{o}_{f\ \text{reactants}}$ Reaction: $\text{CH}_3\text{OCH}_3(\text{g}) + 3\text{ O}_2(\text{g}) \rightarrow 2\text{ CO}_2(\text{g}) + 3\text{ H}_2\text{O}(\text{l})$

$$-1460\text{ kJ} = [2\text{ mol}(-393.5\tfrac{\text{kJ}}{\text{mol}}) + 3\text{ mol}(-285.8\tfrac{\text{kJ}}{\text{mol}})] - [1\text{ mol}(\Delta H^{o}_{f}[\text{CH}_3\text{OCH}_3(\text{g})]) + 3\text{ mol}(0\tfrac{\text{kJ}}{\text{mol}})]$$

$-1460\text{ kJ} = -1644.4\text{ kJ} - \Delta H^{o}_{f}[\text{CH}_3\text{OCH}_3(\text{g})]$

Hence, $\Delta H^{o}_{f}[\text{CH}_3\text{OCH}_3(\text{g})] = -184\text{ kJ/mol CH}_3\text{OCH}_3(\text{g})$

13A The net ionic equation is: $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$ and we have the following:

$$\Delta H^\circ_{rxn} = \Delta H^\circ_f\left[AgI(s)\right] - \left[\Delta H^\circ_f\left[Ag^+(aq)\right] + \Delta H^\circ_f\left[I^-(aq)\right]\right]$$

$$= -61.84 \text{ kJ/mol} - \left[(+105.6 \text{ kJ/mol}) + (-55.19 \text{ kJ/mol})\right] = -112.3 \text{ kJ/mol AgI(s) formed}$$

13B $2\,Ag^+(aq) + CO_3^{2-}(aq) \rightarrow Ag_2CO_3(s)$

$\Delta H^\circ_{rxn} = -39.9 \text{ kJ} = \Sigma\,\Delta H^o_{f\ \text{products}} - \Sigma\,\Delta H^o_{f\ \text{reactants}} =$

$$-39.9 \text{ kJ} = \Delta H^o_f[Ag_2CO_3(s)] - [2 \text{ mol}(105.6\ \frac{\text{kJ}}{\text{mol}}) + 1 \text{ mol}(-677.1\ \frac{\text{kJ}}{\text{mol}})]$$

$$-39.9 \text{ kJ} = \Delta H^o_f[Ag_2CO_3(s)] + 465.9 \text{ kJ}$$

Hence, $\Delta H^o_f[Ag_2CO_3(s)] = -505.8$ kJ/mol $Ag_2CO_3(s)$ formed.

INTEGRATIVE EXAMPLE

A. The combustion reactions of $C_{16}H_{32}$ and $C_{16}H_{34}$ are shown below

(1) $C_{16}H_{32} + 24\,O_2 \rightarrow 16\,CO_2 + 16\,H_2O$ $\Delta H_f = -10539$ kJ
(2) $2\,C_{16}H_{34} + 49\,O_2 \rightarrow 32\,CO_2 + 34\,H_2O$ $\Delta H_f = -10699$ kJ/mol $= -21398$ kJ

Since we are studying the hydrogenation of $C_{16}H_{32}$ to give $C_{16}H_{34}$, the final equation has to include the former as the reactant and the latter as the product. This is done by doubling equation 1 and reversing equation 2:

(3) $2\,C_{16}H_{32} + 48\,O_2 \rightarrow 32\,CO_2 + 32\,H_2O$ $\Delta H_f = -21078$ kJ
(4) $32\,CO_2 + 34\,H_2O \rightarrow 2\,C_{16}H_{34} + 49\,O_2$ $\Delta H_f = +21398$ kJ
(5) $2\,C_{16}H_{32} + 2\,H_2O \rightarrow 2\,C_{16}H_{34} + O_2$ $\Delta H_f = +320$ kJ

Since a hydrogenation reaction involves hydrogen as a reactant, and looking at equation (5), we add the following reaction to (5):

(6) $H_2 + ½\,O_2 \rightarrow H_2O$ $\Delta H_f = -285.5$ kJ/mol

Double equation (6) and add it to equation 5:

(5) $2\,C_{16}H_{32} + 2\,H_2O \rightarrow 2\,C_{16}H_{34} + O_2$ $\Delta H_f = +320$ kJ
(7) $2H_2 + O_2 \rightarrow 2H_2O$ $\Delta H_f = -571$ kJ
(8) $2\,C_{16}H_{32} + 2\,H_2 \rightarrow 2\,C_{16}H_{34}$ $\Delta H_f = -251$ kJ

Since (8) is for 2 moles, ΔH_f is -125.5 kJ/mol

B. This is a multi-stage problem. First, you must determine the amount of material reacted, then you have to determine the amount of heat generated, and then you have to calculate the effect of that heat on water evaporation:

$CaO + H_2O \rightarrow Ca(OH)_2$

56 g CaO × (1 mol CaO/56.0 g CaO) = 1 mol CaO
100 g H_2O × (1 mol H_2O/18.0 g H_2O) = 5.56 mol H_2O

CaO is the limiting reagent. Therefore, amount of unreacted H_2O is = 5.56 – 1.0 = 4.56 mol
The mass of water unreacted = 82.0 g H_2O

$$56 \text{ g CaO} \times \frac{1 \text{ mol CaO}}{56.0 \text{ g CaO}} \times \frac{1 \text{ mol Ca(OH)}_2}{1 \text{ mol CaO}} \times \frac{74.12 \text{ g Ca(OH)}_2}{1 \text{ mol Ca(OH)}_2} = 74.1 \text{ g Ca(OH)}_2$$

$$\Delta H^{o}_{rxn} = H^{o}_{f}\left(Ca(OH)_2 \times mol\right) - \left(H^{o}_{f}\left(CaO\right) \times mol + H^{o}_{f}\left(H_2O\right) \times mol\right)$$

$$\Delta H^{o}_{rxn} = -987 \text{ kJ/mol} \times 1 \text{ mol} - \left(-635 \text{ kJ/mol} \times 1 \text{ mol} + \left(-286 \text{ kJ/mol} \times 1 \text{ mol}\right)\right) = -66 \text{ kJ}$$

As stated before, we have to determine the effects of the heat on the water in the reaction. The water first needs to be heated to 100 ºC, and then evaporated. The energy needed to heat 82.0 g of the water remaining in the reaction is:

$$J = -m \cdot c \cdot \Delta T = -\left(82.0 \text{ g}\right)\left(4.187 \text{J} \cdot \text{g}^{-1}\,{}^{o}\text{C}^{-1}\right)\left(100\,{}^{o}\text{C} - 20\,{}^{o}\text{C}\right) = -27.47 \text{ kJ}$$

Therefore, 27.47 kJ of energy is used up for the water in the reaction to go from 20 to 100 ºC. The energy remaining is -66 – (-27.47) = 38.53 kJ.

Since ΔH_{vap} of water is 44.06 kJ/mol, we can calculate the amount of water evaporated:

$$38.53 \text{ kJ} \times \frac{1 \text{ mol } H_2O}{44.06 \text{ kJ}} \times \frac{18 \text{ g } H_2O}{1 \text{ mol } H_2O} = 15.74 \text{ g } H_2O \text{ evaporated}$$

Based on the above, the contents of the vessel after completion of the reaction are 74.1 g of $Ca(OH)_2$ and 66.3 g of H_2O.

EXERCISES

Heat Capacity (Specific Heat)

1. **(a)** $$q = 9.25\text{ L} \times \frac{1000\text{ cm}^3}{1\text{ L}} \times \frac{1.00\text{ g}}{1\text{ cm}^3} \times \frac{4.18\text{ J}}{1\text{ g}^\circ\text{C}} \times \frac{1\text{ kJ}}{1000\text{ J}}\left(29.4^\circ\text{C} - 22.0^\circ\text{C}\right) = +2.9 \times 10^2\text{ kJ}$$

(b) $$q = 5.85\text{ kg} \times \frac{1000\text{ g}}{1\text{ kg}} \times \frac{0.903\text{ J}}{\text{g}^\circ\text{C}} \times \left(-33.5^\circ\text{C}\right) \times \frac{1\text{ kJ}}{1000\text{ J}} = -177\text{ kJ}$$

3. heat gained by the water = heat lost by the metal; heat = mass × sp.ht. × ΔT

(a) $$50.0\text{ g} \times 4.18\frac{\text{J}}{\text{g}^\circ\text{C}}(38.9 - 22.0)^\circ\text{C} = 3.53 \times 10^3\text{ J} = -150.0\text{g} \times \text{sp. ht.} \times (38.9 - 100.0)^\circ\text{C}$$

$$\text{sp.ht.} = \frac{3.53 \times 10^3\text{ J}}{150.0\text{ g} \times 61.1^\circ\text{C}} = 0.385\text{ J g}^{-1}\ {}^\circ\text{C}^{-1}\text{ for Zn}$$

(b) $$50.0\text{ g} \times 4.18\frac{\text{J}}{\text{g}^\circ\text{C}}(28.8 - 22.0)^\circ\text{C} = 1.4 \times 10^3\text{J} = -150.0\text{g} \times \text{sp. ht.} \times (28.8 - 100.0)^\circ\text{C}$$

$$\text{sp.ht.} = \frac{1.4 \times 10^3\text{ J}}{150.0\text{ g} \times 71.2^\circ\text{C}} = 0.13\text{ J g}^{-1}\ {}^\circ\text{C}^{-1}\text{ for Pt}$$

(c) $$50.0\text{ g} \times 4.18\frac{\text{J}}{\text{g}^\circ\text{C}}(52.7 - 22.0)^\circ\text{C} = 6.42 \times 10^3\text{J} = -150.0\text{g} \times \text{sp. ht.} \times (52.7 - 100.0)^\circ\text{C}$$

$$\text{sp.ht.} = \frac{6.42 \times 10^3\text{ J}}{150.0\text{ g} \times 47.3^\circ\text{C}} = 0.905\text{ J g}^{-1}\ {}^\circ\text{C}^{-1}\text{ for Al}$$

5. $$q_{\text{water}} = 375\text{ g} \times 4.18\frac{\text{J}}{\text{g}^\circ\text{C}}(87 - 26)^\circ\text{C} = 9.5\underline{6} \times 10^4\text{ J} = -q_{\text{iron}}$$

$$q_{\text{iron}} = -9.5\underline{6} \times 10^4\text{ J} = 465\text{g} \times 0.449\frac{\text{J}}{\text{g}^\circ\text{C}}(87 - T_l) = 1.81\underline{6} \times 10^4\text{J} - 2.08\underline{8} \times 10^2\ T_l$$

$$T_l = \frac{-9.5\underline{6} \times 10^4 - 1.81\underline{6} \times 10^4}{-2.08\underline{8} \times 10^2} = \frac{-11.3\underline{8} \times 10^4}{-2.08\underline{8} \times 10^2} = 5.4\underline{48} \times 10^2\,^\circ\text{C} \text{ or } 545\,^\circ\text{C}$$

The number of significant figures in the final answer is limited by the two significant figures for the given temperatures.

7. heat lost by Mg = heat gained by water

$$-\left(1.00\text{ kg Mg} \times \frac{1000\text{ g}}{1\text{ kg}}\right)1.024\frac{\text{J}}{\text{g}^\circ\text{C}}\left(T_f - 40.0^\circ\text{C}\right) = \left(1.00\text{ L} \times \frac{1000\text{ cm}^3}{1\text{ L}} \times \frac{1.00\text{ g}}{1\text{ cm}^3}\right)4.18\frac{\text{J}}{\text{g}^\circ\text{C}}\left(T_f - 20.0^\circ\text{C}\right)$$

$$-1.024 \times 10^3\ T_f + 4.10 \times 10^4 = 4.18 \times 10^3\ T_f - 8.36 \times 10^4$$

$$4.10 \times 10^4 + 8.36 \times 10^4 = \left(4.18 \times 10^3 + 1.024 \times 10^3\right)T_f \rightarrow 12.46 \times 10^4 = 5.20 \times 10^3\ T_f$$

$$T_f = \frac{12.46\times10^4}{5.20\times10^3} = 24.0^\circ\text{C}$$

9. heat lost by copper = heat gained by glycerol

$$-74.8\ \text{g}\times\frac{0.385\ \text{J}}{\text{g}^\circ\text{C}}\times\left(31.1^\circ\text{C}-143.2^\circ\text{C}\right)=165\ \text{mL}\times\frac{1.26\ \text{g}}{1\ \text{mL}}\times\text{sp.ht.}\times\left(31.1^\circ\text{C}-24.8^\circ\text{C}\right)$$

$$3.23\times10^3 = 1.3\times10^3\times(\text{sp.ht.})\qquad \text{sp.ht.}=\frac{3.23\times10^3}{1.3\times10^3}=2.5\ \text{J g}^{-1}{}^\circ\text{C}^{-1}$$

$$\text{molar heat capacity} = 2.5\ \text{J g}^{-1}{}^\circ\text{C}^{-1}\times\frac{92.1\ \text{g}}{1\ \text{mol C}_3\text{H}_8\text{O}_3} = 2.3\times10^2\ \text{J mol}^{-1}{}^\circ\text{C}^{-1}$$

11.

$$\text{heat capacity} = \frac{\text{energy transferred}}{\Delta\text{T}} = \frac{6.052\ \text{J}}{(25.0-20.0\ ^\circ\text{C})} = 1.21\ \text{J/K}$$

*Note: since 1K = 1°C, it is not necessary to convert the temperatures to Kelvin. The change in temperature in both K and °C is the same.

Heats of Reaction

13.

$$\text{heat} = 283\ \text{kg}\times\frac{1000\ \text{g}}{1\ \text{kg}}\times\frac{1\ \text{mol Ca(OH)}_2}{74.09\ \text{g Ca(OH)}_2}\times\frac{65.2\ \text{kJ}}{1\ \text{mol Ca(OH)}_2} = 2.49\times10^5\ \text{kJ of heat evolved.}$$

15. **(a)**

$$\text{heat evolved} = 1.325\ \text{g C}_4\text{H}_{10}\times\frac{1\ \text{mol C}_4\text{H}_{10}}{58.123\ \text{g C}_4\text{H}_{10}}\times\frac{2877\ \text{kJ}}{1\ \text{mol C}_4\text{H}_{10}} = 65.59\ \text{kJ}$$

(b)

$$\text{heat evolved} = 28.4\ \text{L}_{\text{STP}}\ \text{C}_4\text{H}_{10}\times\frac{1\ \text{mol C}_4\text{H}_{10}}{22.414\ \text{L}_{\text{STP}}\ \text{C}_4\text{H}_{10}}\times\frac{2877\ \text{kJ}}{1\ \text{mol C}_4\text{H}_{10}} = 3.65\times10^3\ \text{kJ}$$

(c) Use the ideal gas equation to determine the amount of propane in moles and multiply this amount by 2877 kJ heat produced per mole.

$$\text{heat evolved} = \frac{\left(738\,\text{mmHg}\times\dfrac{1\,\text{atm}}{760\,\text{mmHg}}\right)\times12.6\,\text{L}}{\dfrac{0.08206\,\text{L atm}}{\text{mol K}}\times(273.2+23.6)\,\text{K}}\times\frac{2877\,\text{kJ}}{1\ \text{mol C}_4\text{H}_{10}} = 1.45\times10^3\,\text{kJ}$$

17.

(a)

$$\text{mass} = 2.80\times10^7\ \text{kJ}\times\frac{1\ \text{mol CH}_4}{890.3\ \text{kJ}}\times\frac{16.04\ \text{g CH}_4}{1\ \text{mol CH}_4}\times\frac{1\ \text{kg}}{1000\ \text{g}} = 504\ \text{kg CH}_4.$$

(b) First determine the moles of CH_4 present, with the ideal gas law.

$$\text{mol CH}_4 = \frac{\left(768\,\text{mmHg}\times\dfrac{1\,\text{atm}}{760\,\text{mmHg}}\right)1.65\times10^4\,\text{L}}{0.08206\dfrac{\text{L atm}}{\text{mol K}}\times(18.6+273.2)\,\text{K}} = 696\ \text{mol CH}_4$$

$$\text{heat energy} = 696\ \text{mol CH}_4 \times \frac{-890.3\ \text{kJ}}{1\ \text{mol CH}_4} = -6.20\times10^5\ \text{kJ of heat energy}$$

(c) $$V_{H_2O} = \frac{6.21\times10^5\ \text{kJ}\times\dfrac{1000\,\text{J}}{1\text{kJ}}}{4.18\dfrac{\text{J}}{\text{g}\,°\text{C}}(60.0-8.8)\,°\text{C}} \times \frac{1\text{mL H}_2\text{O}}{1\text{g}} = 2.90\times10^6\ \text{mL} = 2.90\times10^3\ \text{L H}_2\text{O}$$

19. Since the molar mass of H_2 (2.0 g/mol) is $\frac{1}{16}$ of the molar mass of O_2 (32.0 g/mol) and only twice as many moles of H_2 are needed as O_2, we see that $O_2(g)$ is the limiting reagent in this reaction.

$$\frac{180.}{2}\text{g O}_2 \times \frac{1\ \text{mol O}_2}{32.0\ \text{g O}_2} \times \frac{241.8\ \text{kJ heat}}{0.500\ \text{mol O}_2} = 1.36\times10^3\ \text{kJ heat}$$

21. **(a)** We first compute the heat produced by this reaction, then determine the value of ΔH in kJ/mol KOH.

$$q_{\text{calorimeter}} = (0.205+55.9)\ \text{g}\times4.18\ \frac{\text{J}}{\text{g}^\circ\text{C}}\left(24.4\ ^\circ\text{C}-23.5\ ^\circ\text{C}\right) = 2\times10^2\ \text{J heat} = -q_{\text{rxn}}$$

$$\Delta H = -\frac{2\times10^2\,\text{J}\times\dfrac{1\ \text{kJ}}{1000\,\text{J}}}{0.205\,\text{g}\times\dfrac{1\text{mol KOH}}{56.1\text{g KOH}}} = -5\times10^1\ \text{kJ / mol}$$

(b) The ΔT here is known to just one significant figure (0.9 °C). Doubling the amount of KOH should give a temperature change known to two significant figures (1.6 °C) and using twenty times the mass of KOH should give a temperature change known to three significant figures (16.0 °C). This would require 4.10 g KOH rather than the 0.205 g KOH actually used, and would increase the precision from one part in five to one part in 500, or ~0.2 %. Note that as the mass of KOH is increased and the mass of H_2O stays constant, the assumption of a constant specific heat becomes less valid.

23. Let x be the mass, (in grams), of NH_4Cl added to the water. $\text{heat} = \text{mass}\times\text{sp.ht.}\times\Delta T$

$$x\times\frac{1\ \text{mol NH}_4\text{Cl}}{53.49\ \text{g NH}_4\text{Cl}}\times\frac{14.7\ \text{kJ}}{1\ \text{mol NH}_4\text{Cl}}\times\frac{1000\ \text{J}}{1\ \text{kJ}} = -\left(\left(1400\ \text{mL}\times\frac{1.00\ \text{g}}{1\ \text{mL}}\right)+x\right)4.18\frac{\text{J}}{\text{g}^\circ\text{C}}(10.-25)^\circ\text{C}$$

$$275\,x = 8.8\times10^4 + 63\,x\,; \qquad x = \frac{8.8\times10^4}{275-63} = 4.2\times10^2\ \text{g NH}_4\text{Cl}$$

Our final value is approximate because of the assumed density (1.00 g/mL). The solution's density probably is a bit larger than 1.00 g/mL. Many aqueous solutions are somewhat more dense than water.

25. We assume that the solution volumes are additive; that is, that 200.0 mL of solution is formed. Then we compute the heat needed to warm the solution and the cup, and finally ΔH for the reaction.

$$\text{heat} = \left(200.0\ \text{mL} \times \frac{1.02\ \text{g}}{1\ \text{mL}}\right) 4.02 \frac{\text{J}}{\text{g}\,^\circ\text{C}} \left(27.8\ ^\circ\text{C} - 21.1\ ^\circ\text{C}\right) + 10\ \frac{\text{J}}{^\circ\text{C}} \left(27.8\ ^\circ\text{C} - 21.1\ ^\circ\text{C}\right) = 5.6 \times 10^3\ \text{J}$$

$$\Delta H_{\text{neutr.}} = \frac{-5.6 \times 10^3\,\text{J}}{0.100\ \text{mol}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = -56\ \text{kJ/mol}\ \ \left(-55.6\ \text{kJ/mol to three significant figures}\right)$$

27.

$$5.0\ \text{L C}_2\text{H}_2 \times \frac{1\ \text{m}^3}{1000\ \text{L}} \times \frac{1.0967\ \text{kg}}{\text{m}^3} \times \frac{1000\ \text{g}}{1\ \text{kg}} \times \frac{1\ \text{mol}}{26.04\ \text{g}} = 0.2106\ \text{mol C}_2\text{H}_2$$

$$\frac{1299.5\ \text{kJ heat evolved}}{\text{mol C}_2\text{H}_2} \times 0.2106\ \text{mol C}_2\text{H}_2 = 272.9\ \text{kJ} = 2.7 \times 10^2\ \text{kJ heat evolved}$$

Enthalpy Changes and States of Matter

29. $q_{H_2O(l)} = q_{H_2O(s)}$ $\quad m(\text{sp. ht.})_{H_2O(l)}\Delta T_{H_2O(l)} = \text{mol}_{H_2O(s)}\Delta H_{\text{fus }H_2O(s)}$

$$(3.50\ \text{mol H}_2\text{O} \times \frac{18.015\ \text{g H}_2\text{O}}{1\ \text{mol H}_2\text{O}})(4.184 \frac{\text{J}}{\text{g}\ ^\circ\text{C}})(50.0\ ^\circ\text{C}) = (\frac{m}{\frac{18.015\ \text{g H}_2\text{O}}{1\ \text{mol H}_2\text{O}}} \times 6.01 \times 10^3 \frac{\text{J}}{\text{mol}})$$

$13.2 \times 10^3\ \text{J} = m(333.\underline{6}\ \text{J g}^{-1})$ Hence, $m = 39.6$ g

31. Assume $H_2O(l)$ density = 1.00 g mL^{-1} (at 28.5 °C) $\quad -q_{\text{lost by ball}} = q_{\text{gained by water}} + q_{\text{vap water}}$

$$-[(125\ \text{g})(0.50\ \frac{\text{J}}{\text{g}\ ^\circ\text{C}})(100\ ^\circ\text{C} - 525\ ^\circ\text{C})] = [(75.0\ \text{g})(4.184 \frac{\text{J}}{\text{g}\ ^\circ\text{C}})(100.0\ ^\circ\text{C} - 28.5\ ^\circ\text{C})] + n_{H_2O}\Delta H^\circ_{\text{vap}}$$

$26\underline{562.5}\ \text{J} = 224\underline{36.7}\ \text{J} + n_{H_2O}\Delta H^\circ_{\text{vap}}$ (Note: $n_{H_2O} = \dfrac{\text{mass}_{H_2O}}{\text{molar mass}_{H_2O}}$)

$$4\underline{125.8}\ \text{J} = (m_{H_2O})(\frac{1\ \text{mol H}_2\text{O}}{18.015\ \text{g H}_2\text{O}})\ (40.6 \times 10^3\ \frac{\text{J}}{\text{mol}})$$

$m_{H_2O} = 1.\underline{83}\ \text{g H}_2\text{O} \cong 2\ \text{g H}_2\text{O}$ (1 sig. fig.)

33.

$$\frac{571\ \text{kJ}}{\text{kg}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} = 5.71 \times 10^5\ \text{J/kg}$$

$$125.0\ \text{J} \times \frac{1\ \text{kg}}{5.71 \times 10^5\ \text{J}} \times \frac{1000\ \text{g}}{1\ \text{kg}} \times \frac{1\ \text{L}}{1.98\ \text{g}} = 0.111\ \text{L}$$

Calorimetry

35. Heat capacity $= \dfrac{\text{heat absorbed}}{\Delta T} = \dfrac{5228 \text{ cal}}{4.39^\circ\text{C}} \times \dfrac{4.184 \text{ J}}{1 \text{ cal}} \times \dfrac{1 \text{ kJ}}{1000 \text{ J}} = 4.98 \text{ kJ}/^\circ \text{C}$

37. **(a)** $\dfrac{\text{heat}}{\text{mass}} = \dfrac{\text{heat cap.} \times \Delta t}{\text{mass}} = \dfrac{4.728 \text{ kJ}/^\circ \text{C} \times (27.19 - 23.29)^\circ\text{C}}{1.183 \text{ g}} = 15.6 \text{ kJ}/\text{g xylose}$

$\Delta H = \text{heat given off}/\text{g} \times M(\text{g}/\text{mol}) = \dfrac{-15.6 \text{ kJ}}{1 \text{ g } C_5H_{10}O_5} \times \dfrac{150.13 \text{ g } C_5H_{10}O_5}{1 \text{ mol}}$

$\Delta H = -2.34 \times 10^3 \text{ kJ/mol } C_5H_{10}O_5$

(b) $C_5H_{10}O_5(\text{g}) + 5O_2(\text{g}) \rightarrow 5CO_2(\text{g}) + 5H_2O(\text{l}) \qquad \Delta H = -2.34 \times 10^3 \text{ kJ}$

39. **(a)** Because the temperature of the mixture decreases, the reaction molecules (the system) must have absorbed heat from the reaction mixture (the surroundings). Consequently, the reaction must be endothermic.

(b) We assume that the specific heat of the solution is $4.18 \text{ J g}^{-1}\,^\circ\text{C}^{-1}$. The enthalpy change in kJ/mol KCl is obtained by the heat absorbed per gram KCl.

$$\Delta H = -\frac{(0.75 + 35.0)\text{g}\,\dfrac{4.18 \text{ J}}{\text{g}^\circ\text{C}}(23.6 - 24.8)^\circ\text{C}}{0.75 \text{ g KCl}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{74.55 \text{ g KCl}}{1 \text{ mol KCl}} = +18 \text{ kJ}/\text{mol}$$

41. To determine the heat capacity of the calorimeter, recognize that the heat evolved by the reaction is the negative of the heat of combustion.

$$\text{heat capacity} = \frac{\text{heat evolved}}{\Delta T} = \frac{1.620 \text{ g } C_{10}H_8 \times \dfrac{1 \text{ mol } C_{10}H_8}{128.2 \text{ g } C_{10}H_8} \times \dfrac{5156.1 \text{ kJ}}{1 \text{ mol } C_{10}H_8}}{8.44^\circ\text{C}} = 7.72 \text{ kJ}/^\circ\text{C}$$

43. The temperature should increase as the result of an exothermic combustion reaction.

$$\Delta T = 1.227 \text{ g } C_{12}H_{22}O_{11} \times \frac{1 \text{ mol } C_{12}H_{22}O_{11}}{342.3 \text{ g } C_{12}H_{22}O_{11}} \times \frac{5.65 \times 10^3 \text{ kJ}}{1 \text{ mol } C_{12}H_{22}O_{11}} \times \frac{1^\circ\text{C}}{3.87 \text{ kJ}} = 5.23^\circ\text{C}$$

45.

$$5.0\text{ g NaCl}\times\frac{1\text{ mol}}{58.44\text{ g}} = 0.08556\text{ mol NaCl}$$

$$0.08556\text{ mol NaCl}\times\frac{3.76\text{ kJ}}{1\text{ mol}} = 0.322\text{ kJ} = 322\text{ J}$$

$$q = \text{mass}_{H_2O}\times\text{ specific heat }\times\Delta T$$

$$322\text{ J} = \text{mass}_{H_2O}\times 4.18\text{ J/g °C}\times 5.0\text{ °C}$$

$$\text{mass}_{H_2O} = 15\text{ g}$$

Pressure-Volume Work

47. **(a)** $-P\Delta V = 3.5\text{ L}\times(748\text{ mmHg})\left(\frac{1\text{ atm}}{760\text{ mmHg}}\right) = -3.4\underline{4}\text{ L atm}$ or -3.4 L atm

(b) 1 L kPa = 1 J, hence,

$-3.4\underline{4}\text{ L atm}\times\left(\frac{101.325\text{ kPa}}{1\text{ atm}}\right)\times\left(\frac{1\text{ J}}{1\text{ L kPa}}\right) = -3.4\underline{9}\times10^2\text{ J}$ or -3.5×10^2 J

(c) $-3.4\underline{9}\times10^2\text{ J}\times\left(\frac{1\text{ cal}}{4.184\text{ J}}\right) = -83.\underline{4}\text{ cal}$ or -83 cal

49. When the Ne(g) sample expands into an evacuated vessel it does not push aside any matter, hence no work is done.

51. **(a)** No pressure-volume work is done (no gases are formed or consumed).

(b) $2\,NO_2(g)\rightarrow N_2O_4(g)$ $\Delta n_{gas} = -1$ mole. Work is done on the system by the surroundings (compression).

(c) $CaCO_3(s)\rightarrow CaO(s) + CO_2(g)$. Formation of a gas, $\Delta n_{gas} = +1$ mole, results in an expansion. The system does work on the surroundings.

53. We can either convert pressure from atm to Pascals, or convert work from Joules to L·atm.We opt for the latter. Since the conversion between J and L·atm is 101.33 J/(L·atm), the amount of work is 325 J × (1 L·atm/101.33 J) = 3.207 L·atm. Therefore,
$W = -P\Delta V$
3.207 L·atm = (1.0 atm) ΔV. Solving for ΔV, we get a volume of 3.21 L.

First Law of Thermodynamics

55. **(a)** $\Delta U = q + w = +58\text{ J} + (-58\text{ J}) = 0$

(b) $\Delta U = q + w = +125\text{ J} + (-687\text{ J}) = -562\text{ J}$

(c) $280\text{ cal}\times(4.184\frac{\text{J}}{\text{cal}}) = 117\underline{1.52}\text{ J} = 1.17\text{ kJ}$ $\quad\Delta U = q + w = -1.17\text{ kJ} + 1.25\text{ kJ} = 0.08\text{ kJ}$

57. **(a)** Yes, the gas does work (w = negative value).
(b) Yes, the gas exchanges energy with the surroundings, it absorbs energy.
(c) The temperature of the gas stays the same if the process is isothermal.
(d) ΔU for the gas must equal zero by definition (temperature is not changing).

59. This situation is impossible. An ideal gas expanding isothermally means that $\Delta U = 0 = q + w$, or $w = -q$, not $w = -2q$.

61. We note that since the charge of the system is going from 10 to 5, the net flow of the charge is negative. Therefore, w = (5 C – 10 C) = -5 C. Voltage (V) is J/C. The internal energy of the system is:
$\Delta U = q + w = -45\text{ J} + (100\text{ J/C})(-5\text{ C}) = -45\text{ J} + (-500\text{ J}) = -545\text{ J}$

Relating ΔH and ΔU

63. According to the First Law of Thermodynamics, the answer is (c). Both (a) q_v and (b) q_p are heats of chemical reaction carried out under conditions of constant volume and constant pressure, respectively. Both ΔU and ΔH incorporate terms related to work as well as heat.

65. $C_3H_8O(l) + 9/2\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l) \quad \Delta n_{gas} = -1.5\text{ mol}$

(a) $\Delta U = -33.41\dfrac{\text{kJ}}{\text{g}} \times \dfrac{60.096\text{ g }C_3H_8O}{1\text{ mol }C_3H_8O} = -2008\dfrac{\text{kJ}}{\text{mol}}$

(b) $\Delta H = \Delta U - w, = \Delta U - (-P\Delta V) = \Delta U - (-\Delta n_{gas}RT) = \Delta U + \Delta n_{gas}RT$

$$\Delta H = -2008\frac{\text{kJ}}{\text{mol}} + (-1.5\text{ mol})\left(\frac{8.3145 \times 10^{-3}\text{ kJ}}{\text{K mol}}\right)(298.15\text{ K}) = -2012\frac{\text{kJ}}{\text{mol}}$$

Hess's Law

67. The formation reaction for $NH_3(g)$ is $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$. The given reaction is two-thirds the reverse of the formation reaction. The sign of the enthalpy is changed and it is multiplied by two-thirds. Thus, the enthalpy of the given reaction is $-(-46.11\text{ kJ}) \times \frac{2}{3} = +30.74\text{ kJ}$.

69.

$$\begin{array}{lll}
-(3) & 3\ CO_2(g) + 4H_2O(l) \rightarrow C_3H_8(g) + 5\ O_2(g) & \Delta H^\circ = +2219.1\text{ kJ} \\
+(2) & C_3H_4(g) + 4\ O_2(g) \rightarrow 3\ CO_2(g) + 2H_2O(l) & \Delta H^\circ = -1937\text{ kJ} \\
2(1) & 2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) & \Delta H^\circ = -571.6\text{ kJ} \\
\hline
 & C_3H_4(g) + 2H_2(g) \rightarrow C_3H_8(g) & \Delta H^\circ = -290.\text{ kJ}
\end{array}$$

71.

$$\begin{array}{ll}
2\mathrm{HCl(g)}+\mathrm{C_2H_4(g)}+\tfrac{1}{2}\mathrm{O_2(g)}\rightarrow \mathrm{C_2H_4Cl_2(l)}+\mathrm{H_2O(l)} & \Delta H^\circ = -318.7\ \mathrm{kJ} \\
\mathrm{Cl_2(g)}+\mathrm{H_2O(l)}\rightarrow 2\mathrm{HCl(g)}+\tfrac{1}{2}\mathrm{O_2(g)} & \Delta H^\circ = 0.5(+202.4) = +101.2\ \mathrm{kJ} \\
\hline
\mathrm{C_2H_4(g)}+\mathrm{Cl_2(g)}\rightarrow \mathrm{C_2H_4Cl_2(l)} & \Delta H^\circ = -217.5\ \mathrm{kJ}
\end{array}$$

73.

$$\begin{array}{ll}
\mathrm{CO(g)}+\tfrac{1}{2}\mathrm{O_2(g)}\rightarrow \mathrm{CO_2(g)} & \Delta H^\circ = -283.0\ \mathrm{kJ} \\
3\mathrm{C(graphite)}+6\mathrm{H_2(g)}\rightarrow 3\mathrm{CH_4(g)} & \Delta H^\circ = 3(-74.81) = -224.43\ \mathrm{kJ} \\
2\mathrm{H_2(g)}+\mathrm{O_2(g)}\rightarrow 2\mathrm{H_2O(l)} & \Delta H^\circ = 2(-285.8) = -571.6\ \mathrm{kJ} \\
3\mathrm{CO(g)}\rightarrow \tfrac{3}{2}\mathrm{O_2(g)}+3\mathrm{C(graphite)} & \Delta H^\circ = 3(+110.5) = +331.5\ \mathrm{kJ} \\
\hline
4\mathrm{CO(g)}+8\mathrm{H_2(g)}\rightarrow \mathrm{CO_2(g)}+3\mathrm{CH_4(g)}+2\mathrm{H_2O(l)} & \Delta H^\circ = -747.5\ \mathrm{kJ}
\end{array}$$

75.

$$\begin{array}{ll}
\mathrm{CH_4(g)}+\mathrm{CO_2(g)}\rightarrow 2\mathrm{CO(g)}+2\mathrm{H_2(g)} & \Delta H^\circ = +247\ \mathrm{kJ} \\
2\mathrm{CH_4(g)}+2\mathrm{H_2O(g)}\rightarrow 2\mathrm{CO(g)}+6\mathrm{H_2(g)} & \Delta H^\circ = 2(+206\ \mathrm{kJ}) = +412\ \mathrm{kJ} \\
\mathrm{CH_4(g)}+2\mathrm{O_2(g)}\rightarrow \mathrm{CO_2(g)}+2\mathrm{H_2O(g)} & \Delta H^\circ = -802\ \mathrm{kJ} \\
\hline
4\mathrm{CH_4(g)}+2\mathrm{O_2(g)}\rightarrow 4\mathrm{CO(g)}+8\mathrm{H_2(g)} & \Delta H^\circ = -143\ \mathrm{kJ} \\
\div 4 \text{ produces } \mathrm{CH_4(g)}+\tfrac{1}{2}\mathrm{O_2(g)}\rightarrow \mathrm{CO(g)}+2\mathrm{H_2(g)} & \Delta H^\circ = -35.8\ \mathrm{kJ}
\end{array}$$

77.

$$\begin{array}{ll}
\mathrm{C_6H_{12}O_6(s)} + 6\ \mathrm{O_2(g)} \rightarrow 6\ \mathrm{CO_2(g)} + 6\ \mathrm{H_2O(l)} & \Delta H^\circ = -2808\ \mathrm{kJ} \\
6\ \mathrm{CO_2(g)} + 6\ \mathrm{H_2O(l)} \rightarrow 2\ \mathrm{CH_3CH(OH)COOH(s)} + 6\ \mathrm{O_2(g)} & \Delta H^\circ = 2(1344)\ \mathrm{kJ} \\
\hline
\mathrm{C_6H_{12}O_6(s)} \rightarrow 2\ \mathrm{CH_3CH(OH)COOH(s)} & \Delta H^\circ = -120.\ \mathrm{kJ}
\end{array}$$

Standard Enthalpies of Formation

79. **(a)**

$$\Delta H^\circ = \Delta H_\mathrm{f}^\circ[\mathrm{C_2H_6(g)}]+\Delta H_\mathrm{f}^\circ[\mathrm{CH_4(g)}]-\Delta H_\mathrm{f}^\circ[\mathrm{C_3H_8(g)}]-\Delta H_\mathrm{f}^\circ[\mathrm{H_2(g)}]$$

$$\Delta H^\circ = (-84.68-74.81-(-103.8)-0.00)\,\mathrm{kJ} = -55.7\ \mathrm{kJ}$$

(b)

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

$$\Delta H^\circ = (2(-296.8)+2(-285.8)-2(-20.63)-3(0.00))\,\mathrm{kJ} = -1124\ \mathrm{kJ}$$

81.

$$\mathrm{ZnO(s)}+\mathrm{SO_2(g)}\rightarrow \mathrm{ZnS(s)}+\tfrac{3}{2}\mathrm{O_2(g)}; \qquad \Delta H^\circ = -(-878.2\ \mathrm{kJ})/2 = +439.1\ \mathrm{kJ}$$

$$439.1\ \mathrm{kJ} = \Delta H_\mathrm{f}^\circ[\mathrm{ZnS(s)}]+\tfrac{3}{2}\Delta H_\mathrm{f}^\circ[\mathrm{O_2(g)}]-\Delta H_\mathrm{f}^\circ[\mathrm{ZnO(s)}]-\Delta H_\mathrm{f}^\circ[\mathrm{SO_2(g)}]$$

$$439.1\ \mathrm{kJ} = \Delta H_\mathrm{f}^\circ[\mathrm{ZnS(s)}]+\tfrac{3}{2}(0.00\ \mathrm{kJ})-(-348.3\ \mathrm{kJ})-(-296.8\ \mathrm{kJ})$$

$$\Delta H_\mathrm{f}^\circ[\mathrm{ZnS(s)}] = (439.1-348.3-296.8)\,\mathrm{kJ} = -206.0\ \mathrm{kJ/mol}$$

83. $\Delta H^\circ = 4\Delta H_f^\circ[\mathrm{HCl(g)}] + \Delta H_f^\circ[\mathrm{O_2(g)}] - 2\Delta H_f^\circ[\mathrm{Cl_2(g)}] - 2\Delta H_f^\circ[\mathrm{H_2O(l)}]$

$$= 4(-92.31) + (0.00) - 2(0.00) - 2(-285.8) = +202.4 \text{ kJ}$$

85. Balanced equation: $\mathrm{C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)}$

$\Delta H^\circ = 2\Delta H_f^\circ[\mathrm{CO_2(g)}] + 3\Delta H_f^\circ[\mathrm{H_2O(l)}] - \Delta H_f^\circ[\mathrm{C_2H_5OH(l)}] - 3\Delta H_f^\circ[\mathrm{O_2(g)}]$

$$= 2(-393.5) + 3(-285.8) - (-277.7) - 3(0.00) = -1366.7 \text{ kJ}$$

87. $\Delta H^\circ = -397.3 \text{ kJ} = \Delta H_f^\circ[\mathrm{CCl_4(g)}] + 4\Delta H_f^\circ[\mathrm{HCl(g)}] - \Delta H_f^\circ[\mathrm{CH_4(g)}] - 4\Delta H_f^\circ[\mathrm{Cl_2(g)}]$

$$= \Delta H_f^\circ[\mathrm{CCl_4(g)}] + (4(-92.31) - (-74.81) - 4(0.00))\text{kJ} = \Delta H_f^\circ[\mathrm{CCl_4(g)}] - 294.4 \text{ kJ}$$

$\Delta H_f^\circ[\mathrm{CCl_4(g)}] = (-397.3 + 294.4) \text{ kJ} = -102.9 \text{ kJ/mol}$

89. $\Delta H^\circ = \Delta H_f^\circ[\mathrm{Al(OH)_3(s)}] - \Delta H_f^\circ[\mathrm{Al^{3+}(aq)}] - 3\Delta H_f^\circ[\mathrm{OH^-(aq)}]$

$$= ((-1276) - (-531) - 3(-230.0))\text{kJ} = -55 \text{ kJ}$$

91. Balanced equation: $\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$

$\Delta H^\circ = \Delta H_f^\circ[\mathrm{CaO(s)}] + \Delta H_f^\circ[\mathrm{CO_2(g)}] - \Delta H_f^\circ[\mathrm{CaCO_3(s)}]$

$$= (-635.1 - 393.5 - (-1207))\text{kJ} = +178 \text{ kJ}$$

$$\text{heat} = 1.35\times10^3 \text{ kg CaCO}_3 \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol CaCO}_3}{100.09 \text{ g CaCO}_3} \times \frac{178 \text{ kJ}}{1 \text{ mol CaCO}_3} = 2.40\times10^6 \text{ kJ}$$

93. The reaction for the combustion of formic acid is:
$\mathrm{HCOOH(s) + \frac{1}{2} O_2(g) \rightarrow CO_2(g) + H_2O(l)}$

$\Delta H^\circ = \Delta H_f^\circ[\mathrm{CO_2(g)}] + \Delta H_f^\circ[\mathrm{H_2O(l)}] - \Delta H_f^\circ[\mathrm{HCOOH(s)}] - \tfrac{1}{2}\Delta H_f^\circ[\mathrm{O_2(g)}]$

$-255 \text{ kJ} = (1(-393.5) + 1(-285.8) - \Delta H_f^\circ[\mathrm{HCOOH(s)}] - 0.5(0.00))\text{kJ}$

$-424 \text{ kJ} = \Delta H_f^\circ[\mathrm{HCOOH(s)}]$

INTEGRATIVE AND ADVANCED EXERCISES

96. Potential energy = mgh = 7.26 kg ×9.81 ms^{-2} × 168 m = 1.20 × 10^4 J. This potential energy is converted entirely into kinetic energy just before the object hits, and this kinetic energy is converted entirely into heat when the object strikes.

$$\Delta t = \frac{\text{heat}}{\text{mass} \times \text{sp. ht.}} = \frac{1.20\times10^4 \text{ J}}{7.26 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{0.47 \text{ J}}{\text{g °C}}} = 3.5 \text{ °C}$$

This large a temperature rise is unlikely, as some of the kinetic energy will be converted into forms other than heat, such as sound and the fracturing of the object along with the surface it strikes. In addition, some heat energy would be transferred to the surface.

97. $\text{heat} = \Delta t\,[\text{heat cap.} + (\text{mass } H_2O \times 4.184\ \frac{\text{J}}{\text{g °C}})] \qquad \text{heat cap.} = \frac{\text{heat}}{\Delta t} - (\text{mass } H_2O \times 4.184\ \frac{\text{J}}{\text{g °C}})$

The heat of combustion of anthracene is -7067 kJ/mol, meaning that burning one mole of anthracene releases $+7067$ kJ of heat to the calorimeter.

$$\text{heat cap.} = \frac{1.354\text{ g } C_{14}H_{10} \times \frac{1\text{ mol } C_{14}H_{10}}{178.23\text{ g } C_{14}H_{10}} \times \frac{7067\text{ kJ}}{1\text{ mol } C_{14}H_{10}}}{(35.63 - 24.87)\text{ °C}} - \left(983.5\text{ g } \times 4.184\ \times 10^{-3}\ \frac{\text{kJ}}{\text{g °C}}\right)$$

$$= (4.990 - 4.115)\text{ kJ/°C} = 0.875\text{ kJ/°C}$$

$$\text{heat} = (27.19 - 25.01)\text{ °C}\,[0.875\text{ kJ/°C} + (968.6\text{ g } H_2O \times 4.184 \times 10^{-3}\text{ kJ g}^{-1}\text{ °C}^{-1})] = 10.7\text{ kJ}$$

$$q_{rxn} = \frac{-10.7\ \text{kJ}}{1.053\ \text{g}\ C_6H_8O_7} \times \frac{192.1\ \text{g}\ C_6H_8O_7}{1\ \text{mol}\ C_6H_8O_7} = -1.95 \times 10^3\ \text{kJ/mol}\ C_6H_8O_7$$

103. We first compute the heats of combustion of the combustible gases.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H°_{\text{rxn}} = \Delta H°_f[CO_2(g)] + 2\Delta H°_f[H_2O(l)] - \Delta H°_f[CH_4(g)] - 2\Delta H°_f[O_2(g)]$$

$$= -393.5\text{ kJ} + 2 \times (-285.8\text{ kJ}) - (-74.81\text{ kJ}) - 2 \times 0.00\text{ kJ} = -890.3\text{ kJ}$$

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$$

$$\Delta H°_{\text{rxn}} = 3\Delta H°_f[CO_2(g)] + 4\Delta H°_f[H_2O(l)] - \Delta H°_f[C_3H_8(g)] - 5\Delta H°_f[O_2(g)]$$

$$= 3 \times (-393.5\text{ kJ}) + 4 \times (-285.8\text{ kJ}) - (-103.8\text{ kJ}) - 5 \times 0.00\text{ kJ} = -2220.\text{ kJ}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H°_{\text{rxn}} = \Delta H°_f[H_2O(l)] = -285.8\text{ kJ}$$

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

$$\Delta H°_{\text{rxn}} = \Delta H°_f[CO_2(g)] - \Delta H°_f[CO(g)] - 0.5\Delta H°_f[O_2(g)] = -393.5 + 110.5 = -283.0\text{ kJ}$$

Then, for each gaseous mixture, we compute the enthalpy of combustion per mole of gas. The enthalpy of combustion per STP liter is 1/22.414 of this value. Recall that volume percents are equal to mole percents.

(a) $H_2\text{ combustion} = 0.497\text{ mol } H_2 \times \frac{-285.8\text{ kJ}}{1\text{ mol } H_2} = -142\text{ kJ}$

$$\mathrm{CH_4\ combustion} = 0.299\,\mathrm{mol\,CH_4} \times \frac{-890.3\,\mathrm{kJ}}{1\,\mathrm{mol\,CH_4}} = -266\,\mathrm{kJ}$$

$$\mathrm{CO\ combustion} = 0.069\,\mathrm{mol\,CO} \times \frac{-283.0\,\mathrm{kJ}}{1\,\mathrm{mol\,CO}} = -20\,\mathrm{kJ}$$

$$\mathrm{C_3H_8\ combustion} = 0.031\,\mathrm{mol\,C_3H_8} \times \frac{-2220.\,\mathrm{kJ}}{1\,\mathrm{mol\,C_3H_8}} = -69\,\mathrm{kJ}$$

$$\text{total enthalpy of combustion} = \frac{(-142-266-20-69)\,\mathrm{kJ}}{1\,\mathrm{mol\,gas}} \times \frac{1\,\mathrm{mol\,gas}}{22.414\,\mathrm{L\,STP}} = -22.2\,\mathrm{kJ/L}$$

(b) CH_4 is the only combustible gas present in sewage gas.

$$\text{total enthalpy of combustion} = 0.660\,\mathrm{mol\,CH_4} \times \frac{-890.3\,\mathrm{kJ}}{1\,\mathrm{mol\,CH_4}} \times \frac{1\,\mathrm{mol\,gas}}{22.414\,\mathrm{L\,STP}} = -26.2\,\mathrm{kJ/L}$$

Thus, sewage gas produces more heat per liter at STP than does coal gas.

107. $\text{work} = 4 \times mgh = 4 \times 58.0\,\mathrm{kg} \times 9.807\,\mathrm{m\,s^{-2}} \times 1450\,\mathrm{m} \times \frac{1\,\mathrm{kJ}}{1000\,\mathrm{J}} = 3.30 \times 10^3\,\mathrm{kJ}$

We compute the enthalpy change for the metabolism (combustion) of glucose.

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

$$\begin{aligned}\Delta H^\circ_{\mathrm{rxn}} &= 6\Delta H^\circ_{\mathrm{f}}[\mathrm{CO_2(g)}] + 6\Delta H^\circ_{\mathrm{f}}[\mathrm{H_2O(l)}] - \Delta H^\circ_{\mathrm{f}}[\mathrm{C_6H_{12}O_6(s)}] - 6\Delta H^\circ_{\mathrm{f}}[\mathrm{O_2(g)}] \\ &= 6 \times (-393.5\,\mathrm{kJ}) - 6 \times (-285.8\,\mathrm{kJ}) - (-1273.3\,\mathrm{kJ}) - 6 \times 0.00\,\mathrm{kJ} = -2802.5\,\mathrm{kJ}\end{aligned}$$

Then we compute the mass of glucose needed to perform the necessary work.

$$\begin{aligned}\text{mass } \mathrm{C_6H_{12}O_6} &= 3.30 \times 10^3\,\mathrm{kJ} \times \frac{1\,\mathrm{kJ\ heat}}{0.70\,\mathrm{kJ\ work}} \times \frac{1\,\mathrm{mol\,C_6H_{12}O_6}}{2802.5\,\mathrm{kJ}} \times \frac{180.2\,\mathrm{g\,C_6H_{12}O_6}}{1\,\mathrm{mol\,C_6H_{12}O_6}} \\ &= 303\,\mathrm{g\ C_6H_{12}O_6}\end{aligned}$$

109. First determine the molar heats of combustion for CH_4 and C_2H_6.

$$\mathrm{CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)}$$

$$\begin{aligned}\Delta H^\circ &= \Delta H^\circ_{\mathrm{f}}[\mathrm{CO_2(g)}] + 2\Delta H^\circ_{\mathrm{f}}[\mathrm{H_2O(l)}] - \Delta H^\circ_{\mathrm{f}}[\mathrm{CH_4(g)}] - 2\Delta H^\circ_{\mathrm{f}}[\mathrm{O_2(g)}] \\ &= \big((-393.5) + 2(-285.8) - (-74.81) - 2(0.00)\big)\,\mathrm{kJ} = -890.3\,\mathrm{kJ/mol}\end{aligned}$$

$$\mathrm{C_2H_6(g) + \tfrac{7}{2}\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)}$$

$$\begin{aligned}\Delta H^\circ &= 2\Delta H^\circ_{\mathrm{f}}[\mathrm{CO_2(g)}] + 3\Delta H^\circ_{\mathrm{f}}[\mathrm{H_2O(l)}] - \Delta H^\circ_{\mathrm{f}}[\mathrm{C_2H_6(g)}] - \tfrac{7}{2}\Delta H^\circ_{\mathrm{f}}[\mathrm{O_2(g)}] \\ &= \big(2(-393.5) + 3(-285.8) - (-84.68) - \tfrac{7}{2}(0.00)\big)\,\mathrm{kJ} = -1559.7\,\mathrm{kJ}\end{aligned}$$

Since the STP molar volume of an ideal gas is 22.4 L, there is 1/22.4 of a mole of gas present in the sample. We first compute the heat produced by one mole (that is 22.4 L at STP) of the mixed gas.

$$\text{heat} = \frac{43.6\,\mathrm{kJ}}{1.00\,\mathrm{L}} \times \frac{22.4\,\mathrm{L}}{1\,\mathrm{mol}} = 977\,\mathrm{kJ/mol}$$

Then, if we let the number of moles of CH_4 be represented by *x*, the number of moles of C_2H_6 is represented by $(1.00 - x)$. Now we can construct an equation for the heat evolved per mole of mixture and solve this equation for *x*.

$$977\,\text{kJ} = 890.3\,x + 1559.7\,(1.00 - x) = 1559.7 + (890.3 - 1559.7)x = 1559.7 - 669.4\,x$$

$$x = \frac{1559.7 - 977}{669.4} = 0.870\,\text{mol}\,CH_4/\text{mol}\,\text{mixture}$$

By the ideal gas law, gases at the same temperature and pressure have the same volume ratio as their molar ratio. Hence, this gas mixture contains 87.0% CH_4 and 13.0% C_2H_6, both by volume.

112.

$$n = \frac{(765.5/760)\text{atm}}{(0.08206\text{ L atm K}^{-1}\text{ mol}^{-1})}\frac{0.582\text{L}}{298.15\text{K}} = 2.40\times10^{-2}\text{mol}$$

$$\text{molar mass} = \frac{1.103\text{g}}{2.40\times10^{-2}\text{mol}} = 46.0\text{ g/mol}$$

moles of CO_2 = 2.108/44.01 = 0.04790 (0.0479 mol C in unknown)

moles of H_2O = 1.294/18.02 = 0.0719 (0.144 mol H in unknown)

$$\text{moles of O in unknown} = \frac{1.103\text{ g - }0.04790\text{ g }(12.011\text{g C/mol})\text{-}0.144(1.00794)}{15.9994\text{ g mol}^{-1}} = 0.0239\text{ mol O}$$

So C:H:O ratio is 2:6:1 and the molecular formula is C_2H_6O.

ΔT = 31.94 - 25.00 = 6.94 °C $\qquad q = 6.94\ ^{\circ}\text{C}\times5.015\text{kJ/}^{\circ}\text{C} = -34.8\text{kJ}$

$$\Delta H = \frac{-34.8\text{kJ}}{0.0240\text{mol}} = -1.45\times10^{3}\text{kJ/mol} \qquad 3\ O_2(g) + C_2H_6O(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$$

113. Energy needed = $mc\Delta T = (250\text{ g})((50\text{-}4)\ ^{\circ}\text{C})(4.2\text{J/g }^{\circ}\text{C}) = 4.8\times10^{4}\text{ J}$
A 700-watt oven delivers a joule of energy/sec.

$$\text{time} = \left(\frac{4.8\times10^{4}\text{ J}}{700\text{ J sec}^{-1}}\right) = 69\text{ seconds}$$

114. $w = -P\Delta V$, $V_i = (3.1416)(6.00\text{ cm})^2(8.10\text{ cm}) = 916.1\text{ cm}^3$

$$P = \frac{\text{force}}{\text{area}} = \frac{(3.1416)(5.00)^2(25.00)(7.75\text{g/cm}^3)(1\text{kg/1000g})(9.807\text{m/sec}^2)}{(3.1416)(6.00\text{ cm})^2(1\text{m/100cm})^2}$$

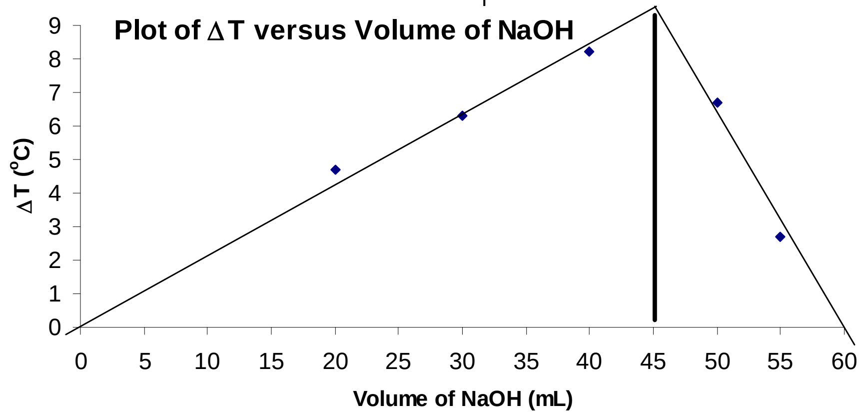
$$= 1.320\times10^{4}\text{ Pa} = \frac{1.320\times10^{4}\text{ Pa}}{101325\text{ Pa atm}^{-1}} = 0.130\text{ atm difference} \qquad \text{Use: } P_1V_1 = P_2V_2$$

$$V_2 = \frac{((745/760) + 0.130\text{atm})\times(0.9161\text{L})}{(745/760)\text{atm}} = 1.04\text{ L}$$

$$-P\Delta V = \frac{745}{760}\times(1.04 - 0.916) = -0.121\text{ L} - \text{atm} = w = (-0.121\text{ L} - \text{atm})\frac{101\text{ J}}{\text{L} - \text{atm}} = -12\text{ J}$$

FEATURE PROBLEMS

122. The plot's maximum is the equivalence point. (Assume ΔT = 0 at 0 mL of added NaOH, (i.e., only 60 mL of citric acid are present), and that ΔT = 0 at 60 mL of NaOH (i.e. no citric acid added).



(a) The equivalence point occurs with 45.0 mL of 1.00 M NaOH(aq) [45.0 mmol NaOH] added and 15.0 mL of 1.00 M citric acid [15.0 mmol citric acid]. Again, we assume that ΔT = zero if no NaOH added (V_{NaOH} = 0 mL) and $\Delta T = 0$ if no citric acid is added (V_{NaOH} = 60).

(b) Heat is a product of the reaction, as are chemical species (products). Products are maximized at the exact stoichiometric proportions. Since each reaction mixture has the same volume, and thus about the same mass to heat, the temperature also is a maximum at this point.

(c) $\text{H}_3\text{C}_6\text{H}_5\text{O}_7(\text{s}) + 3\,\text{OH}^-(\text{aq}) \rightarrow 3\,\text{H}_2\text{O(l)} + \text{C}_6\text{H}_5\text{O}_7^{\,3-}(\text{aq})$

125.

(a) Here we must determine the volume between 2.40 atm and 1.30 atm using $PV = nRT$

$$V = \frac{0.100\,\text{mol} \times 0.08206\,\frac{\text{L atm}}{\text{K mol}} \times 298\ \text{K}}{P} = \frac{2.44\underline{5}\,\text{L atm}}{P}$$

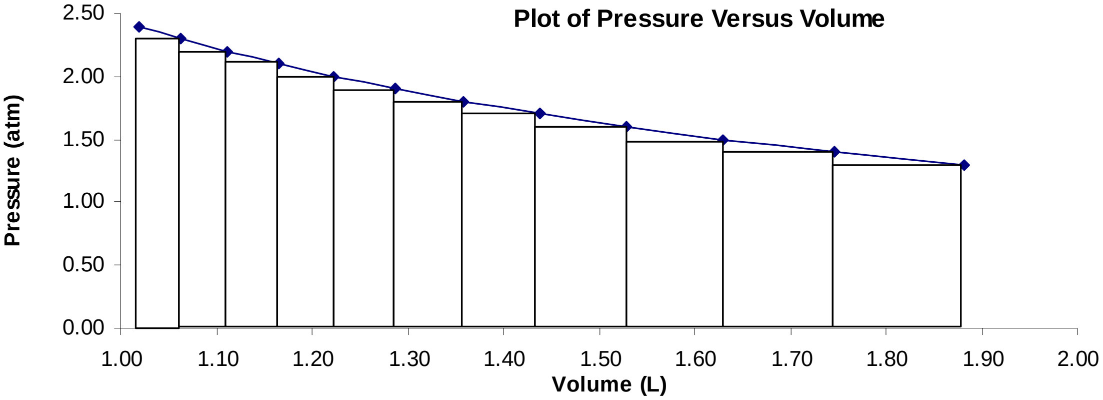
For P = 2.40 atm: V = 1.02 L
For P = 2.30 atm: V = 1.06 L $\quad P\Delta V = 2.30\ \text{atm} \times -0.04\ \text{L} = -0.09\underline{2}\ \text{L atm}$
For P = 2.20 atm: V = 1.11 L $\quad P\Delta V = 2.20\ \text{atm} \times -0.05\ \text{L} = -0.1\underline{1}\ \text{L atm}$
For P = 2.10 atm: V = 1.16 L $\quad P\Delta V = 2.10\ \text{atm} \times -0.05\ \text{L} = -0.1\underline{1}\ \text{L atm}$
For P = 2.00 atm: V = 1.22 L $\quad P\Delta V = 2.00\ \text{atm} \times -0.06\ \text{L} = -0.1\underline{2}\ \text{L atm}$
For P = 1.90 atm: V = 1.29 L $\quad P\Delta V = 1.90\ \text{atm} \times -0.06\ \text{L} = -0.1\underline{2}\ \text{L atm}$
For P = 1.80 atm: V = 1.36 L $\quad P\Delta V = 1.80\ \text{atm} \times -0.07\ \text{L} = -0.1\underline{3}\ \text{L atm}$
For P = 1.70 atm: V = 1.44 L $\quad P\Delta V = 1.70\ \text{atm} \times -0.08\ \text{L} = -0.1\underline{4}\ \text{L atm}$
For P = 1.60 atm: V = 1.53 L $\quad P\Delta V = 1.60\ \text{atm} \times -0.09\ \text{L} = -0.1\underline{4}\ \text{L atm}$

For $P = 1.50$ atm: $V = 1.63$ L $\quad P\Delta V = 1.50 \text{ atm} \times -0.10 \text{ L} = -0.1\underline{5} \text{ L atm}$
For $P = 1.40$ atm: $V = 1.75$ L $\quad P\Delta V = 1.40 \text{ atm} \times -0.12 \text{ L} = -0.1\underline{7} \text{ L atm}$
For $P = 1.30$ atm: $V = 1.88$ L $\quad P\Delta V = 1.30 \text{ atm} \times -0.13 \text{ L} = -0.1\underline{7} \text{ L atm}$

total work = $-\Sigma\, P\Delta V = -1.4\underline{5}$ L atm

Expressed in joules, the work is $-1.4\underline{5}$ L atm × 101.325 J/L atm = $-14\underline{7}$ J.

(b)



(c) The total work done in the two-step expansion is minus one times the total of the area of the two rectangles under the graph, which turns out to be -1.29 L·atm or -131 J. In the 11-step expansion in (b), the total area of the rectangles is 1.45 L atm or -14$\underline{7}$ J. If the expansion were divided into a larger number of stages, the total area of the rectangles would be even greater. The maximum amount of work is for an expansion with an infinite number of stages and is equal to the area under the pressure-volume curve between $V = 1.02$ L and 1.88 L. This area is also obtained as the integral of the expression:

$dw = -PdV = -nRT(dV/V)$. The value obtained is:
$w = -nRT \times \ln V_f/Vi = 0.100 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln(1.88 \text{ L}/1.02 \text{ L})$
$w = -152$ J

(d) The maximum work of compression is for a one-stage compression using an external pressure of 2.40 atm and producing a compression in volume of 1.02 L − 1.88 L = −0.86 L: $\quad w = -P\Delta V = (2.40 \text{ atm} \times 0.86 \text{ L}) \times 101.33 \text{ J/L atm} = 209 \text{ J}$

The minimum work would be that done in an infinite number of steps and would be the same as the work determined in (c) but with a positive sign, namely, +152 J.

(e) Because the internal energy of an ideal gas is a function only of temperature, and the temperature remains constant, $\Delta U = 0$. Because $\Delta U = q + w = 0$, $q = -w$. This means that −209 J corresponds to the maximum work of compression, and −152 J corresponds to the minimum work of compression.

(f) For the expansion described in part in (c),
$q = -w = \text{nRT} \ln V_f/Vi$ and $q/T = nR \ln V_f/V_i$
Because the terms on the right side are all constants or functions of state, so too is the term on the left, *q*/*T*. In Chapter 19, we learn that *q*/*T* is equal to Δ*S*, the change in a state function called *entropy*.

SELF-ASSESSMENT EXERCISES

130. The answer is (b), Al, because it has the highest heat capacity.

131. The answer is (c). We know that $m_1c\Delta T_1$=- $m_2c\Delta T_2$, where m_1 and m_2 are the masses of each quantity of water. Therefore, the equation above can be expanded and simplified as follows:
$75\ (T_f\text{-}80) = \text{-}100\ (T_f\text{-}20)$
Solving for T_f gives a value of 45.7 °C.

132. The answer is (d). U = q + w. Since q = -100 J, w = +200 J, or the system has 200 J of work done on it.

133. The answer is (a). The heat generated by NaOH is absorbed by the system.

134. The answer is (b). As graphite is burned in O_2, it generates CO_2. Enthalpy of formation of CO_2 is therefore the same as enthalpy of combustion of C.

135. The answer is (a), because q_V and q_P are not the same.

136. **(a)** We have to solve for the heat capacity (C_p) of Fe:
$m\cdot C_p\cdot\Delta T\ (H_2O) = -\ m\cdot C_p\cdot\Delta T\ (Fe)$

$$(981\text{g})(4.189)(12.3\ ^\circ\text{C}) = -(1220)(C_{P(Fe)})(-92.1\ ^\circ\text{C})$$

Solving for Cp_{Fe}, the heat capacity of Fe is $0.449\ J\cdot g^{-1}\cdot{}^\circ C^{-1}$

(b) Now knowing the Cp of Fe, we can calculate the T_f of the iron-glycerol system:

$$(409.5)(2.378)(T_f - 26.2) = -(1220)(0.4489)(T_f - 99.8)$$

Solving $T_f = 52.7\ ^\circ C$

137. **(a)** $2\ N_2 + O_2 \rightarrow 2\ N_2O$
(b) $S + O_2 + Cl_2 \rightarrow SO_2Cl_2$
(c) $2\ CH_3CH_2COOH + 7\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$

138. First, determine the ΔH_f° of CO, which is used to make $COCl_2$. This is done by using the equations for the combustion of C and CO gases:

(1) $CO + \frac{1}{2} O_2 \rightarrow CO_2$	-283.0 kJ/mol
(2) $C + O_2 \rightarrow CO_2$	-393.5 kJ/mol

To determine the ΔH_f° of CO, reverse and double equation (1) and double equation (2):

(1) $2 CO_2 \rightarrow 2 CO + O_2$	566.0 kJ
(2) $2C + 2 O_2 \rightarrow 2 CO_2$	-787.0 kJ
(3) $2 C + O_2 \rightarrow 2 CO$	-221.0 kJ or -110.5 kJ/mol of CO

Now, we use the equation for the formation of $COCl_2$ with equation (3) times ½.

(4) $CO + Cl_2 \rightarrow COCl_2$	-108.0 kJ
(3) $C + \frac{1}{2} O_2 \rightarrow CO$	-110.5 kJ
(3) $C + \frac{1}{2} O_2 + Cl_2 \rightarrow COCl_2$	-218.5 kJ

Therefore, ΔH_f° of $COCl_2$ is -218 kJ/mol.

139. Enthalpy of formation for elements (even molecular ones, such as O_2 or Cl_2) is by convention set to 0. While it is possible for the enthalpy of formation of a compound to be near zero, it is unlikely.

140. We note that $\Delta H = \Delta U + \Delta(PV)$. From a theoretical standpoint, one can have a situation where the $\Delta U < 0$, but there is enough work done on the system that makes $\Delta H > 0$. In reality, because the $\Delta(PV)$ is relatively small, ΔH and ΔU often have the same sign.

141. A gas stove works by combustion of a flammable fuel. The amount of heat can be controlled by a valve. Once shut off, the heat source instantly disappears. However, an electric stove works by the principle of heat conduction, where the heat coil on the stove transfers heat to the pot through direct contact. Even after the electricity is shut off to the heating coil, it takes time for the coil to cool because of its heat capacity, and therefore it continues to supply heat to the pot.

142. The answer is (a), 0. This is because there is no loss of energy to or gain of energy from the surroundings.

143. The answer is (b), the temperature decreases (or at least it increases at a slower rate than it would if there was no moisture on the outside). The moisture put outside of the pot evaporates mainly because of removing heat from the pot. Therefore, the moisture on the outside of the pot removes heat from the pot as it evaporates, therefore slightly cooling the pot.