

CHAPTER 12. Chemical Calculations for Solutions

12-1. The number of moles of ammonium selenate required is given by

$$n = MV = (0.155 \text{ M})(500 \text{ mL}) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.0775 \text{ mol}$$

The number of grams required is given by

$$\text{mass of } (\text{NH}_4)_2\text{SeO}_4 = (0.0775 \text{ mol } (\text{NH}_4)_2\text{SeO}_4) \left(\frac{179.03 \text{ g } (\text{NH}_4)_2\text{SeO}_4}{1 \text{ mol } (\text{NH}_4)_2\text{SeO}_4} \right) = 13.9 \text{ g}$$

To prepare the solution, we dissolve 13.9 grams of ammonium selenate in less than 500 mL of water and then dilute to 500 mL using a volumetric flask.

12-2. Assume a 100.0 gram sample. The mass of NaOH(aq) is 50.0 grams. The mass of NaOH(aq) in one liter of solution is

$$\begin{aligned} \left(\frac{\text{mass of NaOH}}{\text{per liter of solution}} \right) &= \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) \left(\frac{1.525 \text{ g solution}}{1 \text{ mL solution}} \right) \left(\frac{50.0 \text{ g NaOH}}{100 \text{ g solution}} \right) \\ &= 762.5 \text{ g NaOH per liter of solution} \end{aligned}$$

The molarity is given by

$$M = \left(\frac{762.5 \text{ g NaOH}}{1 \text{ L}} \right) \left(\frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \right) = 19.1 \text{ M}$$

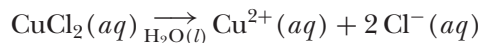
12-3. Using Equation 12.4, we have

$$V = \frac{(1.00 \text{ L})(6.00 \text{ M})}{15.9 \text{ M}} = 0.377 \text{ L} = 377 \text{ mL}$$

Dilute 377 milliliters of 15.9 HNO₃(aq) to one liter using a volumetric flask.

- 12-4. (a) KClO₃(aq) is a strong electrolyte by Rule 3 and the solubility rules on page 329.
(b) (CH₃)₂CO(aq) is a nonelectrolyte by Rule 5.
(c) H₂SO₃(aq) is a weak electrolyte by Rule 1.
(d) Hg(CN)₂(aq) is a weak electrolyte by Rule 4.

12-5. First write



Thus,

$$[\text{Cu}^{2+}] = (0.250 \text{ M CuCl}_2) \left(\frac{1 \text{ mol Cu}^{2+}}{1 \text{ mol CuCl}_2} \right) = 0.250 \text{ M}$$

$$[\text{Cl}^-] = (0.250 \text{ M CuCl}_2) \left(\frac{2 \text{ mol Cl}^-}{1 \text{ mol CuCl}_2} \right) = 0.500 \text{ M}$$

The number of moles of each ion is

$$\text{moles of Cu}^{2+} = (0.250 \text{ M})(0.0350 \text{ L}) = 0.00875 \text{ mol}$$

$$\text{moles of Cl}^- = (0.500 \text{ M})(0.0350 \text{ L}) = 0.0175 \text{ mol}$$

Thus, the total number of moles is $0.00875 \text{ moles} + 0.0175 \text{ moles} = 0.0263 \text{ moles}$.

12-6. The number of moles of $\text{NaOH}(aq)$ is

$$\text{moles of NaOH} = (0.0300 \text{ L}) \left(\frac{6.00 \text{ mol NaOH}}{1 \text{ L}} \right) = 0.180 \text{ mol}$$

The number of grams of aluminum that react is given by

$$\text{mass of Al} = (0.180 \text{ mol NaOH}) \left(\frac{2 \text{ mol Al}}{2 \text{ mol NaOH}} \right) \left(\frac{26.982 \text{ g Al}}{1 \text{ mol Al}} \right) = 4.86 \text{ g Al}$$

12-7. The number of moles of $\text{Ba}(\text{NO}_3)_2(aq)$, or $\text{Ba}^{2+}(aq)$, is given by

$$\text{moles of Ba}^{2+} = n = (0.0250 \text{ L})(0.350 \text{ M}) = 0.00875 \text{ mol}$$

It requires one mole of $\text{K}_2\text{SO}_4(aq)$ to precipitate each mole of $\text{BaSO}_4(s)$, so the volume of $\text{K}_2\text{SO}_4(aq)$ required is

$$V = \frac{0.00875 \text{ mol}}{0.500 \text{ mol} \cdot \text{L}^{-1}} = 0.0175 \text{ L} = 17.5 \text{ mL}$$

12-8. (a) $\text{Cd}(\text{NO}_3)_2(aq) + \text{Na}_2\text{S}(aq) \longrightarrow 2 \text{NaNO}_3(aq) + \text{CdS}(s)$

(b) According to Rule 5 of the solubility rules, $\text{CdS}(s)$ is the precipitate.

(c) To determine the amount of $\text{CdS}(s)$ precipitated, we must first check to see if either reactant is a limiting reactant.

$$\text{moles of Cd}(\text{NO}_3)_2 = (0.0250 \text{ L})(0.100 \text{ M}) = 2.50 \times 10^{-3} \text{ mol}$$

$$\text{moles of Na}_2\text{S} = (0.0200 \text{ L})(0.150 \text{ M}) = 3.00 \times 10^{-3} \text{ mol}$$

According to the chemical equation, one mole of $\text{Cd}(\text{NO}_3)_2(aq)$ reacts with one mole of $\text{Na}_2\text{S}(aq)$, and so $\text{Na}_2\text{S}(aq)$ is in excess. Therefore,

$$\begin{aligned} \text{mass of CdS} &= (2.50 \times 10^{-3} \text{ mol Cd}(\text{NO}_3)_2) \left(\frac{1 \text{ mol CdS}}{1 \text{ mol Cd}(\text{NO}_3)_2} \right) \left(\frac{144.48 \text{ g CdS}}{1 \text{ mol CdS}} \right) \\ &= 0.361 \text{ g} \end{aligned}$$

12-9. The number of millimoles of KOH is given by

$$\text{millimoles KOH} = (40.05 \text{ mL})(0.1065 \text{ M}) = 4.2653 \text{ mmol}$$

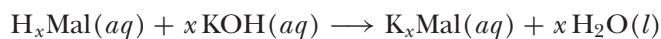
The number of millimoles of oxalic acid is given by

$$\text{millimoles H}_2\text{C}_2\text{O}_4 = (4.2653 \text{ mmol KOH}) \left(\frac{1 \text{ mmol H}_2\text{C}_2\text{O}_4}{2 \text{ mmol KOH}} \right) = 2.1326 \text{ mmol}$$

The molarity of the oxalic acid solution is given by

$$M = \frac{2.1326 \text{ mmol}}{32.10 \text{ mL}} = 0.06644 \text{ M}$$

12-10. Let x be the number of acidic protons in a malonic acid molecule and write



Then,

$$\text{moles of malonic acid} = (2.50 \text{ g malonic acid}) \left(\frac{1 \text{ mol malonic acid}}{104.1 \text{ g malonic acid}} \right) = 0.0240 \text{ mol}$$

The number of moles of KOH(aq) used to neutralize the acid is

$$\text{moles KOH} = (0.0285 \text{ L}) \left(\frac{1.684 \text{ mol KOH}}{1 \text{ L}} \right) = 0.0480 \text{ mol}$$

From the balanced chemical equation, we have

$$\text{moles KOH} = (0.0240 \text{ mol malonic acid}) \left(\frac{x \text{ mol KOH}}{1 \text{ mol malonic acid}} \right) = 0.0480 \text{ mol}$$

Solving for x gives $x = 2$.

12-11. The equation for the reaction is



We must check to see if either reactant is a limiting reactant.

$$\text{millimoles CaCO}_3 = (1.5 \text{ g CaCO}_3) \left(\frac{1 \text{ mol CaCO}_3}{100.09 \text{ g CaCO}_3} \right) = 0.0150 \text{ mol} = 15 \text{ mmol}$$

$$\text{millimoles HCl} = (25 \text{ mL})(3.0 \text{ M}) = 75 \text{ mmol}$$

Thus, from the stoichiometry, we find that $\text{CaCO}_3(s)$ is the limiting reactant. The number of millimoles of $\text{CO}_2(g)$ produced is given by

$$\text{millimoles of CO}_2 = (15 \text{ mmol CaCO}_3) \left(\frac{1 \text{ mmol CO}_2}{1 \text{ mmol CaCO}_3} \right) = 15 \text{ mmol}$$

The number of millimoles of $\text{Ca}^{2+}(aq)$ formed is also 15 millimoles, and so

$$[\text{Ca}^{2+}] = \frac{15 \text{ mmol}}{25 \text{ mL}} = 0.60 \text{ M}$$

All the $\text{Cl}^- (aq)$ from the $\text{HCl}(aq)$ ends up either in unreacted $\text{HCl}(aq)$ or in $\text{CaCl}_2(aq)$ produced, and so

$$[\text{Cl}^-] = \frac{75 \text{ mmol}}{25 \text{ mL}} = 3.0 \text{ M}$$

The number of millimoles of $\text{H}^+(aq)$ remaining is equal to the original number of millimoles of acid minus the number of millimoles that reacted. The number of millimoles of $\text{H}^+(aq)$ that reacted is

$$\text{millimoles of H}^+ = (15 \text{ mol CO}_2) \left(\frac{2 \text{ mmol H}^+}{1 \text{ mmol CO}_2} \right) = 30 \text{ mmol}$$

Thus,

$$[\text{H}^+] = \frac{75 \text{ mmol} - 30 \text{ mmol}}{25 \text{ mL}} = 1.8 \text{ M}$$

CHAPTER 13. Properties of Gases

13-1. The height of the column will be $13.6 / 1.046$ times the height of a corresponding column of mercury. A pressure of 2.00 Torr corresponds to 2.00 millimeters of mercury. Therefore, we have

$$\text{height} = \left(\frac{13.6}{1.046} \right) (2.00 \text{ mm Hg}) = 26.0 \text{ mm}$$

13-2. The conversions are

$$(985 \text{ mbar}) \left(\frac{1 \text{ bar}}{1000 \text{ mbar}} \right) \left(\frac{750.1 \text{ mm Hg}}{1 \text{ bar}} \right) = 739 \text{ mm Hg}$$

$$(985 \text{ mbar}) \left(\frac{1 \text{ bar}}{1000 \text{ mbar}} \right) \left(\frac{0.9869 \text{ atm}}{1 \text{ bar}} \right) = 0.972 \text{ atm}$$

13-3. We use Equation 13.7.

$$V_f = V_i \left(\frac{T_f}{T_i} \right) = (600.0 \text{ mL}) \left[\frac{(250.0 + 273) \text{ K}}{273 \text{ K}} \right] = 1150 \text{ mL}$$

13-4. We use Equation 13.8 with $R = 0.08206 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ to find the number of moles of $\text{N}_2(g)$.

$$n = \frac{PV}{RT} = \frac{(4.15 \text{ atm})(10.0 \text{ L})}{(0.08206 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(293.2 \text{ K})} = 1.725 \text{ mol N}_2$$

The number of grams of $\text{N}_2(g)$ is

$$\text{mass of N}_2 = (1.725 \text{ mol N}_2) \left(\frac{28.01 \text{ g N}_2}{1 \text{ mol N}_2} \right) = 48.3 \text{ g}$$

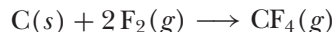
13-5. The number of moles of $\text{O}_2(g)$ generated is

$$\begin{aligned} \text{moles of O}_2 &= (1.34 \text{ g KClO}_3) \left(\frac{1 \text{ mol KClO}_3}{122.55 \text{ g KClO}_3} \right) \left(\frac{3 \text{ mol O}_2}{2 \text{ mol KClO}_3} \right) \\ &= 0.0164 \text{ mol} \end{aligned}$$

Now use Equation 13.8 with $R = 0.083145 \text{ L}\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ to find the pressure.

$$P = \frac{nRT}{V} = \frac{(0.0164 \text{ mol})(0.083145 \text{ L}\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(293.2 \text{ K})}{0.2500 \text{ L}} = 1.60 \text{ bar}$$

13-6. First write the equation for the reaction



We must determine which, if either, reactant is a limiting reactant.

$$\begin{aligned} \text{moles of C} &= (26.2 \times 10^{-3} \text{ g C}) \left(\frac{1 \text{ mol C}}{12.0107 \text{ g C}} \right) = 2.18 \times 10^{-3} \text{ mol} \\ \text{moles of F}_2 &= \frac{PV}{RT} = \frac{(1200.0 \text{ Torr})(0.2500 \text{ L})}{(62.3637 \text{ Torr}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(293.15 \text{ K})} = 0.01641 \text{ mol} \end{aligned}$$

Thus, we see that C(s) is the limiting reactant. Now use Equation 13.8 with $R = 62.3637 \text{ Torr}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

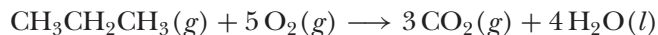
$$\begin{aligned} V &= \frac{nRT}{P} = \frac{(2.18 \times 10^{-3} \text{ mol C}) \left(\frac{1 \text{ mol CF}_4}{1 \text{ mol C}} \right) (62.3637 \text{ Torr}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(293.2 \text{ K})}{760.0 \text{ Torr}} \\ &= 0.0524 \text{ L} = 52.4 \text{ mL} \end{aligned}$$

13-7. We use Equation 13.11 where $V_f = V_i$.

$$P_f = P_i \left(\frac{T_f}{T_i} \right) = (250 \text{ kPa}) \left(\frac{673 \text{ K}}{273 \text{ K}} \right) = 616 \text{ kPa}$$

which exceeds the 500 kPa limit.

13-8. The equation for the reaction is



At constant volume and temperature, the number of moles is directly proportional to the pressure, so we see that the pressure of $\text{CO}_2(g)$ produced is

$$\text{pressure of CO}_2 = (0.20 \text{ bar CH}_3\text{CH}_2\text{CH}_3) \left(\frac{3 \text{ bar CO}_2}{1 \text{ bar CH}_3\text{CH}_2\text{CH}_3} \right) = 0.60 \text{ bar}$$

13-9. The density of the gas is given by

$$\frac{n}{V} = \frac{P}{RT} = \frac{100.0 \times 10^3 \text{ Pa}}{(8.3145 \text{ Pa}\cdot\text{m}^2\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(288.2 \text{ K})} = 41.73 \text{ mol}\cdot\text{m}^{-3}$$

Thus, we have the stoichiometric correspondence

$$4.173 \text{ mol}\cdot\text{m}^{-3} \approx 1.67 \text{ kg}\cdot\text{m}^{-3} = 1670 \text{ g}\cdot\text{m}^{-3}$$

Thus,

$$41.73 \text{ mol} \approx 1670 \text{ g}$$

Dividing both sides by 41.73 gives

$$1 \text{ mol} \approx 40.0 \text{ g}$$

which is consistent with the gas being argon.

13-10. As usual, we take a 100-gram sample and write

$$\begin{aligned} 85.6 \text{ g C} &\approx 14.4 \text{ g H} \\ 7.13 \text{ mol C} &\approx 14.29 \text{ mol H} \\ 1 \text{ mol C} &\approx 2 \text{ mol H} \end{aligned}$$

The empirical formula is CH_2 . To determine the molar mass (see Example 13-10), we solve Equation 13.8 for n/V and write

$$\frac{n}{V} = \frac{P}{RT} = \frac{720.0 \text{ Torr}}{(62.3637 \text{ Torr}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(313.2 \text{ K})} = 0.03686 \text{ mol}\cdot\text{L}^{-1}$$

Taking a one liter sample, we see that

$$\begin{aligned} 1.55 \text{ g} &\approx 0.03686 \text{ mol} \\ 42.1 \text{ g} &\approx 1 \text{ mol} \end{aligned}$$

The empirical formula, CH_2 , has a formula mass of 14.0, so that $42.1/14.0 = 3.00$, or the molecular formula is C_3H_6 .

13-11. We use Equation 13.12 and write

$$\begin{aligned} \rho &= \frac{MP}{RT} = \frac{(46.01 \text{ g}\cdot\text{mol}^{-1})(1.00 \text{ bar})}{(0.083145 \text{ bar}\cdot\text{L}^{-1}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(273 \text{ K})} \\ &= 2.03 \text{ g}\cdot\text{L}^{-1} \end{aligned}$$

13-12. We use Boyle's law ($P_1 V_1 = P_2 V_2$) to write

$$\begin{aligned} P_{\text{O}_2} &= (950.0 \text{ Torr}) \left(\frac{400.0 \text{ mL}}{900.0 \text{ mL}} \right) = 422.2 \text{ Torr} \\ P_{\text{N}_2} &= (700.0 \text{ Torr}) \left(\frac{500.0 \text{ mL}}{900.0 \text{ mL}} \right) = 388.9 \text{ Torr} \end{aligned}$$

The total pressure is $422.2 \text{ Torr} + 388.9 \text{ Torr} = 811.1 \text{ Torr}$.

13-13. The mole fractions of $\text{N}_2(g)$ and $\text{H}_2(g)$ are 0.40 and 0.60, respectively. Because the total pressure of the mixture is one bar, from Equation 13.20, we have

$$\begin{aligned} P_{\text{N}_2} &= x_{\text{N}_2} P_{\text{total}} = (0.40)(1 \text{ bar}) = 0.40 \text{ bar} \\ P_{\text{H}_2} &= x_{\text{H}_2} P_{\text{total}} = (0.60)(1 \text{ bar}) = 0.60 \text{ bar} \end{aligned}$$

The number of moles of each compound in one liter of the mixture is given by

$$\begin{aligned} n_{\text{N}_2} &= \frac{PV}{RT} = \frac{(0.40 \text{ bar})(1.00 \text{ L})}{(0.083145 \text{ bar}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(273.15 \text{ K})} = 0.0176 \text{ mol} \\ n_{\text{H}_2} &= \frac{PV}{RT} = \frac{(0.60 \text{ bar})(1.00 \text{ L})}{(0.083145 \text{ bar}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(273.15 \text{ K})} = 0.0264 \text{ mol} \end{aligned}$$

The mass of each compound in one liter of the mixture is

$$\begin{aligned} \text{mass N}_2 \text{ per liter} &= (0.0176 \text{ mol N}_2) \left(\frac{28.01 \text{ g N}_2}{1 \text{ mol N}_2} \right) = 0.49 \text{ g}\cdot\text{L}^{-1} \\ \text{mass H}_2 \text{ per liter} &= (0.0264 \text{ mol H}_2) \left(\frac{2.016 \text{ g H}_2}{1 \text{ mol H}_2} \right) = 0.053 \text{ g}\cdot\text{L}^{-1} \end{aligned}$$

The total mass per liter is $0.54 \text{ g}\cdot\text{L}^{-1}$.

13-14. The pressure of dry $\text{H}_2(g)$ at 18°C is $742 \text{ Torr} - 15.5 \text{ Torr} = 727 \text{ Torr}$. From Equation 13.11, we have

$$V = (425 \text{ mL}) \left(\frac{727 \text{ Torr}}{760 \text{ Torr}} \right) \left(\frac{273 \text{ K}}{291 \text{ K}} \right) = 381 \text{ mL}$$

13-15. Using Equation 13.30, we have

$$v_{\text{sound}} = \left[\frac{(7)(8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(293 \text{ K})}{(5)(0.02802 \text{ kg}\cdot\text{mol}^{-1})} \right]^{1/2} = 349 \text{ m}\cdot\text{s}^{-1}$$

This is comparable to the speed of sound in air at 20°C and 1 bar, which is about $340 \text{ m}\cdot\text{s}^{-1}$.

13-16. We use Equation 13.32.

$$\begin{aligned} \frac{\text{Rate}_A}{\text{Rate}_B} &= \left(\frac{M_B}{M_A} \right)^{1/2} \\ 5.73 &= \left(\frac{M}{4.003} \right)^{1/2} \\ M &= (5.73)^2(4.003) = 131 \end{aligned}$$

The gas is xenon.

13-17. The pressure in pascals is

$$P = (1 \times 10^{-5} \text{ Torr}) \left(\frac{1 \times 10^5 \text{ Pa}}{750.1 \text{ Torr}} \right) = 1.33 \times 10^{-3} \text{ Pa}$$

The mean free path is given by Equation 13.34.

$$\begin{aligned} l &= \frac{RT}{(\pi\sqrt{2})d^2 N_A P} \\ &= \frac{(8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(273 \text{ K})}{(\pi\sqrt{2})(2.70 \times 10^{-10} \text{ m})^2(6.022 \times 10^{23} \text{ mol}^{-1})(1.33 \times 10^{-3} \text{ Pa})} \\ &= 9 \text{ m} \end{aligned}$$

CHAPTER 14. Thermochemistry

14-1. We use Equation 14.3.

$$\begin{aligned}w &= -P\Delta V = -(2.00 \text{ atm})(12.00 \text{ L} - 8.50 \text{ L}) \\ &= -7.00 \text{ L}\cdot\text{atm} = -(7.00 \text{ L}\cdot\text{atm}) \left(\frac{101.325 \text{ J}}{1 \text{ L}\cdot\text{atm}} \right) = -709 \text{ J}\end{aligned}$$

14-2. The number of moles of water formed is

$$\text{moles of H}_2\text{O} = (1.00 \text{ mL H}_2\text{O}) \left(\frac{1.00 \text{ g H}_2\text{O}}{1 \text{ mL H}_2\text{O}} \right) \left(\frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right) = 0.0555 \text{ mol}$$

The value of ΔH° given is for the formation of two moles of $\text{H}_2\text{O}(l)$, so we have

$$\Delta H = (0.0555 \text{ mol H}_2\text{O}) \left(\frac{-572 \text{ kJ}}{2 \text{ mol H}_2\text{O}} \right) = -15.9 \text{ kJ}$$

For the combustion of one mole of $\text{H}_2(g)$

$$\Delta H = (1 \text{ mol H}_2) \left(\frac{-572 \text{ kJ}\cdot\text{mol}^{-1}}{2 \text{ mol H}_2} \right) = -286 \text{ kJ}\cdot\text{mol}^{-1}$$

For one gram of $\text{H}_2(g)$

$$\Delta H = (-286 \text{ kJ}\cdot\text{mol}^{-1}) \left(\frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} \right) = -142 \text{ kJ}\cdot\text{g}^{-1}$$

14-3. For the reaction equation as stated, $\Delta v_{\text{gas}} = 0 - 1\frac{1}{2} = -1.5$, and so at 25°C

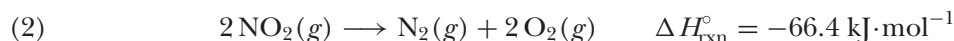
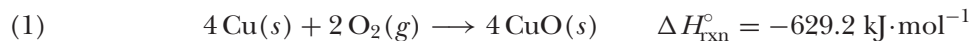
$$\begin{aligned}P\Delta V_{\text{rxn}}^\circ &= \Delta v_{\text{gas}} RT = (-1.5)(8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298 \text{ K}) \\ &= -3.72 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Thus, from Equation 14.16 we have

$$\begin{aligned}\Delta U_{\text{rxn}}^\circ &= \Delta H_{\text{rxn}}^\circ - P\Delta V_{\text{rxn}}^\circ = -285.8 \text{ kJ}\cdot\text{mol}^{-1} + 3.72 \text{ kJ}\cdot\text{mol}^{-1} \\ &= -282.1 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

The answer is one half the value obtained in Example 14-3 because the chemical equation that we used here is one half that used in Example 14-3.

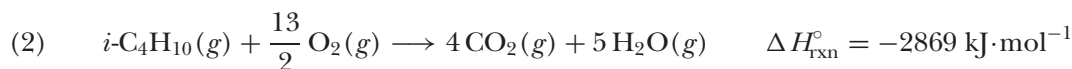
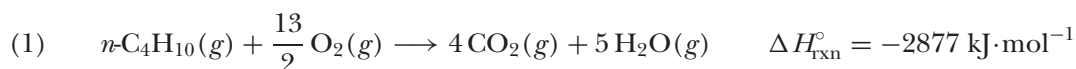
14-4. We multiply equation 1 by 4 and equation 2 by 2 to obtain



If we add equations 1 and 2 above, then we obtain equation 3. The value of $\Delta H_{\text{rxn}}^{\circ}$ (3) is

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} (3) &= \Delta H_{\text{rxn}}^{\circ} (1) + \Delta H_{\text{rxn}}^{\circ} (2) \\ &= -629.2 \text{ kJ}\cdot\text{mol}^{-1} + (-66.4 \text{ kJ}\cdot\text{mol}^{-1}) = -695.6 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

14-5. The reaction equations for the combustion of the two isomers and their corresponding values of $\Delta H_{\text{rxn}}^{\circ}$ at 25°C are



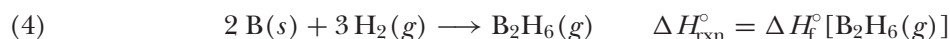
Reversing equation 2 and adding the result to equation 1 yields



Applying Hess's law to this equation, we find that the corresponding value of $\Delta H_{\text{rxn}}^{\circ}$ is

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} (1) - \Delta H_{\text{rxn}}^{\circ} (2) = -2877 \text{ kJ}\cdot\text{mol}^{-1} - (-2869 \text{ kJ}\cdot\text{mol}^{-1}) \\ &= -8 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

14-6. We want to determine the value of $\Delta H_{\text{rxn}}^{\circ}$ for the equation



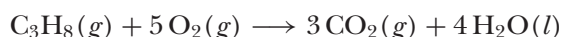
We see that

$$\text{Equation 4} = \frac{1}{2}(\text{Equation 1}) + \frac{3}{2}(\text{Equation 2}) - \text{Equation 3}$$

$$\begin{aligned} \Delta H_{\text{f}}^{\circ} [\text{B}_2\text{H}_6(g)] &= \frac{1}{2}(-2547.0 \text{ kJ}\cdot\text{mol}^{-1}) + \frac{3}{2}(-571.6 \text{ kJ}\cdot\text{mol}^{-1}) - (-2167.3 \text{ kJ}\cdot\text{mol}^{-1}) \\ &= 36.4 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

14-7. See the text. Remember that $\Delta H_{\text{f}}^{\circ} [\text{O}_2(g)] = 0$.

14-8. The chemical equation describing the combustion of propane at 25°C is

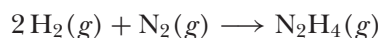


$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= 3\Delta H_f^{\circ}[\text{CO}_2(g)] + 4\Delta H_f^{\circ}[\text{H}_2\text{O}(l)] - \{\Delta H_f^{\circ}[\text{C}_3\text{H}_8(g)] + 5\Delta H_f^{\circ}[\text{O}_2(g)]\} \\ &= (3)(-393.5 \text{ kJ}\cdot\text{mol}^{-1}) + (4)(-285.8 \text{ kJ}\cdot\text{mol}^{-1}) \\ &\quad - \{(-103.8 \text{ kJ}\cdot\text{mol}^{-1}) + (5)(0 \text{ kJ}\cdot\text{mol}^{-1})\} \\ &= -2219.9 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

The value of $\Delta H_{\text{rxn}}^{\circ}$ per gram is

$$\Delta H_{\text{rxn}}^{\circ} = (-2219.9 \text{ kJ}\cdot\text{mol}^{-1}) \left(\frac{1 \text{ mol C}_3\text{H}_8}{44.095 \text{ g C}_3\text{H}_8} \right) = -50.34 \text{ kJ}\cdot\text{g}^{-1}$$

14-9. The relevant chemical equation for the formation of hydrazine from its elements is



Using the Lewis formula of hydrazine shown in the margin of the text,

$$\begin{aligned}\Delta H_f^{\circ}[\text{N}_2\text{H}_4(g)] &= 2 H_{\text{bond}}[\text{H-H}] + H_{\text{bond}}[\text{N}\equiv\text{N}] - 4 H_{\text{bond}}[\text{N-H}] - H_{\text{bond}}[\text{N-N}] \\ &= (2)(435 \text{ kJ}\cdot\text{mol}^{-1}) + 945 \text{ kJ}\cdot\text{mol}^{-1} - (4)(390 \text{ kJ}\cdot\text{mol}^{-1}) - (159 \text{ kJ}\cdot\text{mol}^{-1}) \\ &= 96 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

The value of ΔH_f° for $\text{N}_2\text{H}_4(g)$ given in Table 14.3 is $95.4 \text{ kJ}\cdot\text{mol}^{-1}$. Thus, the molar bond enthalpy estimate has a 0.6% error compared with the experimental value.

14-10. We use Equation 14.27 in the form

$$\Delta T = \frac{q_P}{c_P}$$

Substituting the values given into the equation gives

$$\Delta T = \frac{200 \text{ J}}{37.7 \text{ J}\cdot\text{K}^{-1}} = 5.3 \text{ K} = 5.3^{\circ}\text{C}$$

Thus, the final temperature will be $-20.0^{\circ}\text{C} + 5.3^{\circ}\text{C} = -14.7^{\circ}\text{C}$.

14-11. The number of moles of $\text{H}_2\text{O}(g)$ in the swimming pool is

$$\begin{aligned}\text{moles H}_2\text{O} &= (25 \text{ ft})(12 \text{ ft})(6.0 \text{ ft}) \left(\frac{12 \text{ in}}{1 \text{ ft}} \right)^3 \left(\frac{2.54 \text{ cm}}{1 \text{ in}} \right)^3 (1.0 \text{ g}\cdot\text{cm}^{-3}) \left(\frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \right) \\ &= 2.83 \times 10^6 \text{ mol}\end{aligned}$$

The energy required to raise the temperature by 10°C (10 K) is given by Equation 14.30

$$\begin{aligned}\Delta H &= nC_P\Delta T = (2.83 \times 10^6 \text{ mol})(75.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(10 \text{ K}) \\ &= 2.13 \times 10^9 \text{ J} = 2.1 \times 10^6 \text{ kJ}\end{aligned}$$

$$\text{cost} = (2.1 \times 10^6 \text{ kJ}) \left(\frac{1 \text{ Btu}}{1.055 \text{ kJ}} \right) \left(\frac{1 \text{ therm}}{10^5 \text{ Btu}} \right) \left(\frac{100\%}{75\%} \right) \left(\frac{\$1.55}{1 \text{ therm}} \right) = \$42$$

14-12. (a) The steel will undergo the larger temperature increase because it has a smaller specific heat ($\Delta T = q_P/c_P$).

(b) The ratio of the temperature increases is

$$\text{ratio} = \frac{1.8 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}}{0.46 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}} = 3.9$$

14-13. Let the final temperature be T_f . The heat capacities of the steel and water are

$$c_P[\text{steel}] = (500.0 \text{ g})(0.46 \text{ J} \cdot \text{C}^{-1} \cdot \text{g}^{-1}) = 230 \text{ J} \cdot \text{C}^{-1}$$

$$c_P[\text{H}_2\text{O}(l)] = (100.0 \times 10^3 \text{ g}) \left(\frac{1 \text{ mol}}{18.02 \text{ g}} \right) (75.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{C}^{-1}) = 418 \times 10^3 \text{ J} \cdot \text{C}^{-1}$$

Applying Equation 14.33, we have

$$(230 \text{ J} \cdot \text{C}^{-1})(T_f - 1200^\circ\text{C}) + (418 \times 10^3 \text{ J} \cdot \text{C}^{-1})(T_f - 15^\circ\text{C}) = 0$$

or

$$2.76 \times 10^5 \text{ J} - (230 \text{ J} \cdot \text{C}^{-1}) T_f = (4.18 \times 10^5 \text{ J} \cdot \text{C}^{-1}) T_f - 6.27 \times 10^6 \text{ J}$$

Solving for T_f gives

$$T_f = \frac{2.76 \times 10^5 \text{ J} + 6.27 \times 10^6 \text{ J}}{4.18 \times 10^5 \text{ J} \cdot \text{C}^{-1} + 230 \text{ J} \cdot \text{C}^{-1}} = 16^\circ\text{C}$$

to two significant figures.

14-14. Using Equation 14.33, we have

$$\Delta H = -c_{P,\text{cal}} \Delta T = -(418 \text{ J} \cdot \text{K}^{-1})(-1.65 \text{ K}) = 690 \text{ J}$$

The number of moles of ammonium chloride dissolved is

$$\text{moles of NH}_4\text{Cl} = (2.50 \text{ g NH}_4\text{Cl}) \left(\frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g NH}_4\text{Cl}} \right) = 0.0467 \text{ mol}$$

The value of $\Delta H_{\text{rxn}}^\circ$ for the dissolution of ammonium chloride in water is

$$\Delta H_{\text{rxn}}^\circ = \frac{690 \text{ J}}{0.0467 \text{ mol}} = +14.8 \times 10^3 \text{ J} \cdot \text{mol}^{-1} = +14.8 \text{ kJ} \cdot \text{mol}^{-1}$$

The dissolution is endothermic.

14-15. We have that

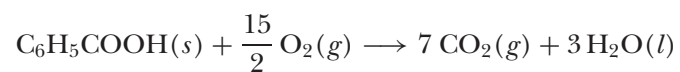
$$\Delta U = -c_{V,\text{cal}} \Delta T = -(18.94 \text{ kJ} \cdot \text{K}^{-1})(3.094 \text{ K}) = -58.60 \text{ kJ per 2.218 g benzoic acid}$$

$$\Delta U \text{ per gram} = -\frac{58.60 \text{ kJ}}{2.218 \text{ g}} = -26.42 \text{ kJ} \cdot \text{g}^{-1}$$

The value of $\Delta U_{\text{rxn}}^\circ$ is

$$\Delta U_{\text{rxn}}^\circ = (-26.42 \text{ kJ} \cdot \text{g}^{-1}) \left(\frac{122.12 \text{ g C}_6\text{H}_5\text{COOH}}{1 \text{ mol C}_6\text{H}_5\text{COOH}} \right) = -3226 \text{ kJ} \cdot \text{mol}^{-1}$$

The relevant equation is



$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= (7)(-393.5 \text{ kJ}\cdot\text{mol}^{-1}) + (3)(-285.8 \text{ kJ}\cdot\text{mol}^{-1}) \\ &\quad - \{(-385.2 \text{ kJ}\cdot\text{mol}^{-1}) + 0 \text{ kJ}\cdot\text{mol}^{-1}\} \\ &= -3226.7 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

which is very close to the value of $\Delta U_{\text{rxn}}^{\circ}$.

CHAPTER 15. Liquids and Solids

15-1. The number of moles of sodium is given by

$$\text{moles Na} = (100.0 \text{ g Na}) \left(\frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \right) = 4.350 \text{ mol}$$

Thus

$$t_{20 \rightarrow 97.8} = \frac{(4.350 \text{ mol})(28.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(371.0 \text{ K} - 293.2 \text{ K})}{8.0 \times 10^3 \text{ J} \cdot \text{min}^{-1}} = 1.2 \text{ min}$$

$$t_{\text{fus}} = \frac{(4.350 \text{ mol})(2.60 \text{ kJ} \cdot \text{mol}^{-1})}{8.0 \text{ kJ} \cdot \text{min}^{-1}} = 1.4 \text{ min}$$

$$t_{97.8 \rightarrow 883} = \frac{(4.350 \text{ mol})(30.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(1156 \text{ K} - 371 \text{ K})}{8.0 \times 10^3 \text{ J} \cdot \text{min}^{-1}} = 13 \text{ min}$$

$$t_{\text{vap}} = \frac{(4.350 \text{ mol})(97.4 \times 10^3 \text{ J} \cdot \text{mol}^{-1})}{8.0 \times 10^3 \text{ J} \cdot \text{min}^{-1}} = 53 \text{ min}$$

$$t_{883 \rightarrow 1000} = \frac{(4.350 \text{ mol})(20.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(117 \text{ K})}{8.0 \times 10^3 \text{ J} \cdot \text{min}^{-1}} = 1.3 \text{ min}$$

The total time is 70 minutes.

15-2. The number of moles of mercury in 25.0 grams is 0.1246 moles. Thus, we have that

$$\begin{aligned} \Delta H_{573.2 \rightarrow 234.32} &= (0.1246 \text{ mol Hg})(28.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(234.32 - 573.2 \text{ K}) \\ &= -1180 \text{ J} = -1.18 \text{ kJ} \end{aligned}$$

$$\Delta H_{\text{fus}} = -(0.1246 \text{ mol Hg})(2.29 \text{ kJ} \cdot \text{mol}^{-1}) = -0.285 \text{ kJ}$$

$$\begin{aligned} \Delta H_{234.32 \rightarrow 213.2} &= (0.1246 \text{ mol Hg})(28.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(213.2 \text{ K} - 234.32 \text{ K}) \\ &= -74.4 \text{ J} = -0.0744 \text{ kJ} \end{aligned}$$

The total is -1.54 kilojoules.

- 15-3. (a) C_2Cl_4 is a planar symmetric molecule like C_2H_4 . It is nonpolar.
(b) PCl_3 is an AX_3E molecule (trigonal pyramidal), and so is polar.
(c) SO_2 is an AX_3E_2 molecule (bent), and so is polar.
(d) CH_3Cl is an AX_4 molecule (tetrahedral with a unique atom), and so is polar.
(e) CCl_4 is a symmetric tetrahedral molecule like CH_4 . It is nonpolar.

15-4. See the text.

15-5. The amount of water vapor in the container at 0.308 atm is given by

$$n = \frac{(0.308 \text{ atm})(0.2500 \text{ L})}{(0.08206 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(343.2 \text{ K})} = 2.73 \times 10^{-3} \text{ mol} = 0.0493 \text{ g}$$

Therefore, $0.0896 \text{ g} - 0.0493 \text{ g} = 0.0403 \text{ grams}$ will condense.

15-6. When the relative humidity is 78% at 20°C, the vapor pressure of water is

$$P_{\text{H}_2\text{O}} = \left(\frac{78}{100}\right) (17.5 \text{ Torr}) = 14 \text{ Torr}$$

Referring to Table 15.7, we see that the equilibrium vapor pressure is 14 Torr at about 17°C.

15-7. See the text.

15-8. At the triple point, $\ln P_s = \ln P_l$, and so we write

$$22.383 - \frac{4699 \text{ K}}{T_t} = 15.400 - \frac{2579 \text{ K}}{T_t}$$

or $T_t = 303.6 \text{ K}$. The pressure is given by either equation

$$\ln P_t = 22.383 - \frac{4699 \text{ K}}{303.6 \text{ K}} = 6.905$$

or $P_t = e^{6.905} = 998 \text{ Torr}$.

15-9. According to Figure 15.29, there are two atoms per unit cell in a body-centered cubic lattice.

15-10. We use Equation 15.8.

$$V_{\text{unit cell}} = \frac{(2 \text{ atom}\cdot\text{unit cell}^{-1})(151.964 \text{ g}\cdot\text{mol}^{-1})}{(5.244 \text{ g}\cdot\text{cm}^{-3})(6.022 \times 10^{23} \text{ atom}\cdot\text{mol}^{-1})} = 9.624 \times 10^{-23} \text{ cm}^3$$

$$l = (V_{\text{unit cell}})^{1/3} = 4.583 \times 10^{-8} \text{ cm}$$

$$r = \frac{\sqrt{3}l}{4} = 1.984 \times 10^{-8} \text{ cm} = 198.4 \text{ pm}$$

15-11. We use Equation 15.8.

$$\begin{aligned} N_A &= \frac{nM}{d V_{\text{unit cell}}} = \frac{(4 \text{ atom}\cdot\text{unit cell}^{-1})(140.116 \text{ g}\cdot\text{mol}^{-1})}{(6.770 \text{ g}\cdot\text{cm}^{-3})(516.10 \times 10^{-10} \text{ cm})^3} \\ &= 6.022 \times 10^{23} \text{ atom}\cdot\text{mol}^{-1} \end{aligned}$$