CHAPTER 4

THE PROPERTIES OF GASES

4.2 (a) 161 kPa; (b) 1.52×10^3 Torr; (c) 2.03 bar; (d) 2.00 atm

4.4 The difference in height will be 2×35.96 cmHg which will equal 71.92 cmHg. This is the same as 719.2 mmHg. (a) Because 1 mmHg is approximately equal to 1 Torr, there will be 719.2 Torr; (b) 719.2 Torr $\div$ 760 Torr $\cdot$ atm^{-1} = 0.9463 atm; (c) 719.2 Torr $\times 133.3$ Pa $\cdot$ Torr^{-1} = 9.587×10^4 Pa; (d) 0.9587 bar

4.6 $d_1 h_1 = d_2 h_2$

$$d_1(6.14 \text{ m})(100 \text{ cm} \cdot \text{m}^{-1}) = (13.6 \text{ g} \cdot \text{cm}^{-3}) \frac{(758.7 \text{ mm})}{(10 \text{ mm} \cdot \text{cm}^{-1})}$$

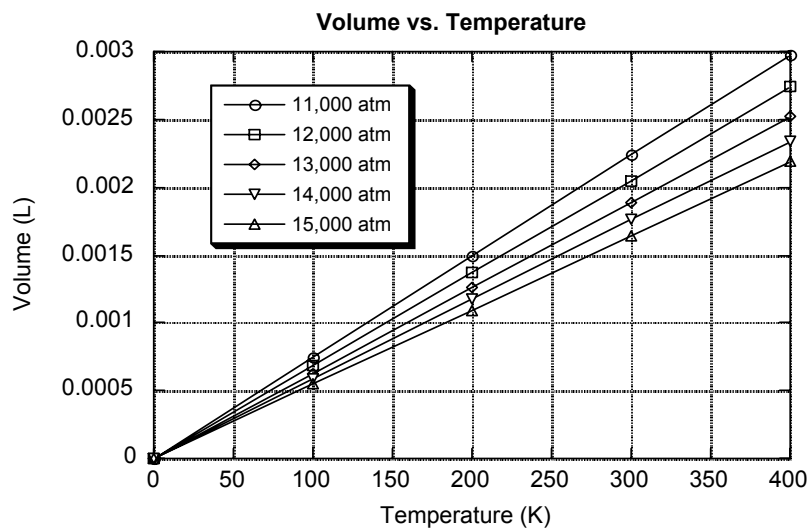$$d_1 = 1.68 \text{ g} \cdot \text{cm}^{-3}$$

4.8 The pressure is inversely proportional to the density:

$$1.5 \text{ in H}_2\text{O} \times \left(\frac{1.0 \text{ g} \cdot \text{cm}^3}{13.5 \text{ g} \cdot \text{cm}^3} \right) = 0.11 \text{ inHg}$$

$$0.11 \text{ in Hg} \times \left(\frac{1.0 \text{ cm}}{0.3937 \text{ in}} \right) \left(\frac{10 \text{ mm}}{1 \text{ cm}} \right) = 2.8 \text{ mmHg}$$

2.8 mmHg or 2.8 Torr

4.10 (a)

Volume vs. Temperature

(b) The slope is equal to $\dfrac{nR}{P}$

Pressure, atm	$\dfrac{nR}{P}$, $L \cdot K^{-1}$
11 000	7.46×10^{-6}
12 000	6.83×10^{-6}
13 000	6.31×10^{-6}
14 000	5.86×10^{-6}
15 000	5.47×10^{-6}

(c) The intercept is equal to 0.00 for all the plots.

4.12 (a) From $P_1 V_1 = P_2 V_2$, we write

$(800.\ \text{Torr})(4.00\ \text{L}) = (P_2)(3.20\ \text{L}); \ P_2 = 1.00 \times 10^3 \ \text{Torr};$

(b) Similarly, from $P_1 V_1 = P_2 V_2$, the expression is

$(158\ \text{Pa})(936\ \text{mL}) = (P_2)(468\ \text{mL}); \ P_2 = 316\ \text{Pa}.$

4.14 Because P is a constant, we can use $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$, which gives

$$\frac{22.5\ \text{L}}{291\ \text{K}} = \frac{V_2}{258\ \text{K}}; V_2 = 19.9\ \text{L}.$$

4.16 Because P is constant, we can use: $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$. Substituting, we obtain

$$\frac{250\ \text{mL}}{338\ \text{K}} = \frac{V_2}{273\ \text{K}};\ V_2 = 202\ \text{mL}.$$ Note: It is not necessary to convert

volume to liters, but the final answer will be found in the same units as the initial volume. It is, however, necessary to convert T to kelvins.

4.18 Because we want P and V to be constant, we can use the relationship $n_1 T_1 = n_2 T_2$. If the number of molecules is halved, the number of moles is also halved, so we can write $n_1 T_1 = (2 n_1) T_2$. Solving, we find $T_2 = 2T_1$. For V and P to remain constant, the temperature must double.

4.20 Because P, V, and T change, we use the relation $\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2}$. Substituting

for the appropriate values, we get

$$\frac{(1.08\ \text{atm})(355\ \text{cm}^3)}{310\ \text{K}} = \frac{(0.958\ \text{atm})(V_2)}{298\ \text{K}}; V_2 = 385\ \text{cm}^3.$$

4.22 (a) From $PV = nRT$, $(1.30\ \text{atm})(0.125\ \text{L}) =$

$n(0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(350\ \text{K})$, $n = 0.005\ 66\ \text{mol}$.

(b) Substituting into the ideal gas law

$$P\,(0.120\ \text{L}) = \left(\frac{2.7 \times 10^{-6}\ \text{g}}{32.00\ \text{g} \cdot \text{mol}^{-1}}\right)(0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(290\ \text{K}).$$

$$= 1.7 \times 10^{-5}\ \text{atm} \times \left(\frac{760\ \text{Torr}}{1\ \text{atm}}\right) = 1.3 \times 10^{-2}\ \text{Torr}$$

(c) The number of mol N_2 present is given by $n = \dfrac{PV}{RT}$. The mass m will

be given by $n \cdot M$ where M is the molar mass of N_2.

(d)

$$m = \frac{MPV}{RT} = \frac{(28.01 \text{ g} \cdot \text{mol}^{-1})\left(\dfrac{20 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)(20.0 \text{ L})}{(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(215 \text{ K})}; m = 0.84 \text{ g}.$$

$$V = \frac{nRT}{P}; V = \frac{\left(\dfrac{16.7 \text{ g}}{83.80 \text{ g} \cdot \text{mol}^{-1}}\right)(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(317 \text{ K})}{\dfrac{(100 \times 10^{-3} \text{ Torr})}{(760 \text{ Torr} \cdot \text{atm}^{-1})}}$$

$$= 3.94 \times 10^4 \text{ L}$$

(e) To calculate the number of atoms, we multiply the number of moles by the Avogadro constant. To calculate the number of moles, we use the ideal gas law:

$n = \dfrac{PV}{RT}$. The number of atoms of xenon, N_{Xe}, is

$$N_{xe} = \frac{(6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1})(P)(V)}{RT}$$

$$= \frac{(6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1})\left(\dfrac{2.00 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)(2.6 \times 10^{-6} \text{ L})}{(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(288 \text{ K})}$$

$$= 1.7 \times 10^{14} \text{ atoms}$$

4.24 (a) Because n and V are constant, we simply use the relationship $\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$:

$$\frac{1.00 \text{ atm}}{273 \text{ K}} = \frac{P_2}{373 \text{ K}}; P_2 = 1.37 \text{ atm}.$$

(b) $\dfrac{1.00 \text{ atm}}{273 \text{ K}} = \dfrac{P_2}{500 \text{ K}}; P_2 = 1.83 \text{ atm}.$

4.26 The mass of the CO_2 will be 1.04 kg − 0.74 kg = 0.30 kg.

From the ideal gas law

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$P = \frac{\left(\dfrac{0.30 \text{ kg} \times 1000 \text{ g} \cdot \text{kg}^{-1}}{44.01 \text{ g} \cdot \text{mol}^{-1}}\right)(0.083\,145\,1 \text{ L} \cdot \text{bar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(293 \text{ K})}{0.250 \text{ L}}$$

$$= 6.6 \times 10^2 \text{ bar}$$

4.28   Because P is constant, we can use

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{(4.60 \text{ L})}{(400.2 \text{ K})} = \frac{(0.115 \text{ L})}{T_2}$$

$$T_2 = 10.0 \text{ K or} - 263.2°C$$

4.30 $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$ or $\dfrac{V_2}{V_1} = \dfrac{T_2}{T_1}$

We want V_2 to be 1.14 times V_1:

$$1.14 = \frac{T_2}{T_1} = \frac{T_2}{340 \text{ K}}$$

$$T_2 = 388 \text{ K}$$

4.32   Assuming the balloon is spherical, the volume will be determined by

$V = \frac{4}{3}\pi r^3$. Using the ideal gas law, we can calculate P:

$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{P_1V_1}{V_2} = \frac{(1 \text{ atm})\left(\dfrac{4}{3}\pi(1.0 \text{ m})^3\right)}{\dfrac{4}{3}\pi(3.0 \text{ m})^3} = 0.037 \text{ atm}$$

4.34   The key to this problem is to realize that the same number of moles of gas will exert the same pressure, regardless of what the gas is (assuming the

gases are all reasonably ideal). The answer will be given by

$$\left(\frac{12 \text{ mg H}_2\text{S}}{34.08 \text{ g} \cdot \text{mol}^{-1} \text{ H}_2\text{S}}\right)(17.03 \text{ g} \cdot \text{mol}^{-1} \text{ NH}_3) = 6.0 \text{ mg NH}_3$$

4.36 Density is proportional to the molar mass of the gas as seen from the ideal gas law:

$$PV = nRT$$

$$PV = \frac{m}{M}RT$$

$$\text{density} = \text{mass per unit volume} = \frac{m}{V} = \frac{MP}{RT}$$

The molar masses of the gases in question are 28.01 $\text{g} \cdot \text{mol}^{-1}$ for N_2 (g),

17.03 $\text{g} \cdot \text{mol}^{-1}$ for NH_3(g), and 46.01 $\text{g} \cdot \text{mol}^{-1}$ for NO_2(g). The most

dense will be the one with the highest molar mass, which in this case is

NO_2.

The order of increasing density will be $NH_3 < N_2 < NO_2$.

4.38 (a) Density is proportional to the molar mass of the gas as seen from the ideal gas law. See Section 4.9.

$$d = \frac{(34.08 \text{ g} \cdot \text{mol}^{-1})(1.00 \text{ atm})}{(0.082 \text{ 06 L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = 1.39 \text{ g} \cdot \text{L}^{-1}$$

(b) $$d = \frac{(34.08 \text{ g} \cdot \text{mol}^{-1})(0.962 \text{ atm})}{(0.082 \text{ 06 L} \cdot \text{ atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(308.2 \text{ K})} = 1.30 \text{ g} \cdot \text{L}^{-1}$$

4.40 (a) $$0.943 \text{ g} \cdot \text{L}^{-1} = \frac{MP}{RT} = \frac{M\left(\dfrac{727 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)}{(0.082 \text{ 06 L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(420 \text{ K})}$$

$$M = 34.0 \text{ g} \cdot \text{mol}^{-1}$$

(b) $$d = \frac{(34.0 \text{ g} \cdot \text{mol}^{-1})(1.00 \text{ atm})}{(0.082 \text{ 06 L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = 1.39 \text{ g} \cdot \text{L}^{-1}$$

4.42   The empirical formula derived from the elemental analyses is $(CH_2)_n$.

The problem may be solved using the ideal gas law:

$$PV = nRT$$

$$PV = \frac{m}{M}RT$$

$$M = \frac{mRT}{PV}$$

$$M = \frac{(1.77\ g)(0.082\ 06\ L \cdot atm \cdot K^{-1} \cdot mol^{-1})(290\ K)}{\left(\dfrac{508\ Torr}{760\ Torr \cdot atm^{-1}}\right)(1.500\ L)} = 42.0\ g \cdot mol^{-1}$$

The empirical formula mass is $14.01\ g \cdot mol^{-1}$. The value of n in the

formula $(CH_2)_n$ is, therefore, equal to 3.

4.44 $$PV = nRT$$

$$PV = \frac{m}{M}RT$$

$$M = \frac{mRT}{PV} = \frac{(115 \times 10^{-3}\ g)(0.082\ 06\ L \cdot atm \cdot K^{-1} \cdot mol^{-1})(553.2\ K)}{\left(\dfrac{48.3\ Torr}{760\ Torr \cdot atm^{-1}}\right)(0.5000\ L)}$$

$$= 164\ g \cdot mol^{-1}$$

From the combustion analyses, we can calculate the following:

50.0 mg CO_2 = 0.001 14 mol CO_2; contains 0.0136 g C

12.4 mg H_2O = 0.0006 88 mol H_2O; contains 0.001 39 g H

This accounts for 15.0 mg (13.6 + 1.39 mg) of the original 18.8 mg

burned. The remaining 3.8 mg must be due to O. 3.8 mg O corresponds to

0.000 24 mol O. The molar ratio of C:H:O can be calculated and is found

to be 4.8:5.7:1. If these numbers are rounded to the nearest whole

numbers, the ratio will be 5:6:1. The formula C_5H_6O has a mass of 82.10

$g \cdot mol^{-1}$, which is almost exactly half the molecular weight found above.

The molecular formula is $C_{10}H_{12}O_2$.

4.46 The molar mass of nitroglycerin is 227.1 $g \cdot mol^{-1}$. All products are gases under these conditions, so the total amount of gas produced is the sum of the pressures of the individual gases; the pressure is independent of the type of gas. From the equation we can see that 29 mol of gas is produced for 4 mol of nitroglycerin detonated. We can use this information and the ideal gas equation to calculate the volume of gases produced (nit. = nitroglycerin):

$$V = \frac{n_{gas,\ total} RT}{P}$$

$$= \frac{\left(\dfrac{29 \text{ mol gas}}{4 \text{ mol nit.}}\right)\left(\dfrac{454 \text{ g nit.}}{227.1 \text{ g} \cdot \text{mol}^{-1} \text{ nit.}}\right)}{215 \text{ kPa}} \times$$

$$(8.314\ 51 \text{ L} \cdot \text{kPa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(548 \text{ K})$$

$$= 307 \text{ L}$$

4.48 To answer this, we need to know the number of moles of $C_2H_4(g)$ present in each case. Because the combustion reaction is the same in both cases, as are the temperature and pressure, the larger number of moles of $C_2H_4(g)$ produces the larger volume of CO_2. We use the ideal gas equation to solve for n in the first case:

$$n = \frac{PV}{RT} = \frac{(2.00 \text{ atm})(1.00 \text{ L})}{(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(318 \text{ K})} = 0.0766 \text{ mol CH}_4$$

1.20 g of $C_2H_4(g)$ equals $\dfrac{1.20 \text{ g}}{28.05 \text{ g} \cdot \text{mol}^{-1}} = 0.0428 \text{ mol}$

The first case has the greatest number of moles of CH_4 and produces the largest amount of $CO_2(g)$.

**4.50** The molar mass of urea is 60.06 $g \cdot mol^{-1}$. From the stoichiometry, it is readily seen that the same number of moles of CO_2 is needed as urea produced, and we need twice as many moles of NH_3. From the information given, we can readily calculate the number of moles of urea

and use the ideal gas equation to compute the volume that those gases would occupy.

$$V_{CO_2} = \dfrac{\dfrac{(2.50 \text{ kg urea})(1000 \text{ g} \cdot \text{kg}^{-1})}{(60.06 \text{ g} \cdot \text{mol}^{-1} \text{ urea})}\left(\dfrac{1 \text{ mol CO}}{1 \text{ mol urea}}\right)}{200 \text{ atm}} \times$$

$$(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(723 \text{ K})$$

$$= 12.3 \text{ L}$$

$$V_{NH_3} = \dfrac{\dfrac{(2.50 \text{ kg urea})(1000 \text{ g} \cdot \text{kg}^{-1})}{(60.06 \text{ g} \cdot \text{mol}^{-1} \text{ urea})}\left(\dfrac{2 \text{ mol NH}_3}{1 \text{ mol urea}}\right)}{200 \text{ atm}} \times$$

$$(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(723 \text{ K})$$

$$= 24.7 \text{ L}$$

4.52 First, balance the equation:
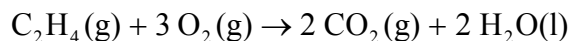
$C_2H_4(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 2\ H_2O(l)$

Because the reaction remains at 1.00 atm pressure and 298 K throughout, we can use the volumes directly to solve the problem. The volume is directly proportional to the number of moles of each species. 1.00 L of ethene requires 3.00 L of O_2 to react in order to go to completion. C_2H_4 is thus the limiting reactant. All the C_2H_4 will react with 3.00 L of O_2. This leaves 1.00 L of unreacted O_2 and produces 2.00 L CO_2.

The total volume is the sum of the volume of O_2 remaining plus the volume of CO_2 produced.

V = 1.00 L + 2.00 L = 3.00 L

4.54 (a) The total volume after opening the stopcock is 14.0 L. Because the temperature is constant, we need only be concerned with the effect that increasing the volume has on the pressure of each gas. The pressure of N_2 and Ar will decrease as shown:

$$P_{N_2} = 803 \text{ kPa}\left(\dfrac{4.0 \text{ L}}{14.0 \text{ L}}\right) = 230 \text{ kPa}; P_{Ar} = 47.2 \text{ kPa}\left(\dfrac{10.0 \text{ L}}{14.0 \text{ L}}\right) = 33.7 \text{ kPa}$$

(b) The total pressure is simply the sum of these two partial pressures:

230 kPa + 33.7 kPa = 260 kPa

4.56 $n_{CH_4} = \dfrac{0.320 \text{ g}}{16.04 \text{ g} \cdot \text{mol}^{-1}} = 0.0200 \text{ mol}$

$n_{Ar} = \dfrac{0.175 \text{ g}}{39.95 \text{ g} \cdot \text{mol}^{-1}} = 0.004\ 38 \text{ mol}$

$n_{N_2} = \dfrac{0.225 \text{ g}}{28.01 \text{ g} \cdot \text{mol}^{-1}} = 0.008\ 03 \text{ mol}$

$n_{total} = 0.0200 \text{ mol} + 0.004\ 38 \text{ mol} + 0.008\ 03 \text{ mol} = 0.0324 \text{ mol}$

(a) $P_{N_2} = 15.2 \text{ kPa}$

$P_{Ar} = \dfrac{n_{Ar}}{n_{N_2}} \times P_{N_2} = \dfrac{0.004\ 38 \text{ mol}}{0.008\ 03 \text{ mol}} \times 15.2 \text{ kPa} = 8.29 \text{ kPa Ar}$

$P_{CH_4} = \dfrac{n_{CH_4}}{n_{N_2}} \times P_{N_2} = \dfrac{0.0200 \text{ mol}}{0.008\ 03 \text{ mol}} \times 15.2 \text{ kPa} = 37.9 \text{ kPa CH}_4$

$P_{total} = 15.2 \text{ kPa} + 8.29 \text{ kPa} + 37.9 \text{ kPa} = 61.4 \text{ kPa}$

(b) $PV = nRT$

$\left(\dfrac{61.4 \text{ kPa}}{101.325 \text{ kPa} \cdot \text{atm}^{-1}} \right) V$

$= (0.0324 \text{ mol})(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(300 \text{ K})$

$V = 1.32 \text{ L}$

4.58   At 21°C the vapor pressure of water is 18.65 Torr, so that of the total
pressure of 755 Torr in the apparatus, only 755 Torr − 18.65 Torr = 736
Torr is due to $N_2O(g)$. We can now use $P_1V_1 = P_2V_2$ to determine the
volume of an equal amount of dry $N_2O(g)$ measured at 755 Torr:
(736 Torr) (126 mL) = (755 Torr) (V_2); V_2 = 123 mL

4.60   Graham's law of effusion states that the rate of effusion of a gas is
inversely proportional to the square root of its molar mass:

$\text{rate of effusion} = \dfrac{1}{\sqrt{M}}$

If we have two different gases whose rates of effusion are measured under identical conditions, we can take the ratio:

$$\frac{rate_1}{rate_2} = \frac{\frac{1}{\sqrt{M_1}}}{\frac{1}{\sqrt{M_2}}} = \sqrt{\frac{M_2}{M_1}}$$

If a compound takes 2.7 times as long to effuse as XeF_2, the rate of effusion of XeF_2 is 2.7 times that of the compound. We can now plug into the expression to calculate the molar mass:

$$\frac{2.7}{1} = \sqrt{\frac{M_2}{169.3 \text{ g} \cdot \text{mol}^{-1}}}$$

$$M_2 = 1.2 \times 10^3 \text{ g} \cdot \text{mol}^{-1}$$

4.62 The number of collisions a molecule makes is proportional to the average speed of the molecules. Because the kinetic energy of any ideal gas sample is the same at a given temperature and is independent of the mass of the gas, it follows that the gas molecules with more mass travel slower on average than lighter gas molecules (see Figure 4.27). The result is that lighter gases have more collisions per unit time than heavier gases. Because neon is lighter than CO_2 (20.18 g $\cdot$ mol^{-1} versus 44.01 g $\cdot$ mol^{-1}), the sample of neon will have more collisions per second.

4.64 The elemental analyses give an empirical formula of $(C_2H_3Cl)_n$. This formula mass is 62.49 g $\cdot$ mol^{-1}. Because the volume of the gas is proportional to the number of moles and hence molecules of gas that effuse, we can define the rates of effusion as follows:

$$rate_{unknown} \propto \frac{(V_{unknown})}{time} = \frac{(V_{unknown})}{7.73 \text{ min}}$$

$$rate_{Ar} \propto \frac{(V_{Ar})}{time} = \frac{(V_{Ar})}{6.18 \text{ min}}$$

The rate of effusion is inversely proportional to the square root of the molar mass of the substance that is effusing:

$$\text{rate of effusion} \propto \frac{1}{\sqrt{M}}$$

If we have two different gases whose effusion is measured under identical conditions, we can take the ratio of their effusion rates. This is convenient because all of the constants that relate V to number of molecules will be the same for both gases and will cancel from the expression.

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{\dfrac{1}{\sqrt{M_1}}}{\dfrac{1}{\sqrt{M_2}}} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{\dfrac{(V_{unknown})}{7.73 \text{ min}}}{\dfrac{(V_{Ar})}{6.18 \text{ min}}} = \sqrt{\frac{39.95 \text{ g} \cdot \text{mol}^{-1}}{M_{unknown}}}$$

This expression simplifies because the volume of the unknown and the volume of Ar effusing are the same.

$$\frac{\dfrac{1}{7.73 \text{ min}}}{\dfrac{1}{6.18 \text{ min}}} = \sqrt{\frac{39.95 \text{ g} \cdot \text{mol}^{-1}}{M_{unknown}}}$$

$$\left(\frac{6.18}{7.73}\right)^2 = \frac{39.95 \text{ g} \cdot \text{mol}^{-1}}{M_{unknown}}$$

$$M_{unknown} = (39.95 \text{ g} \cdot \text{mol}^{-1})\left(\frac{7.73}{6.18}\right)^2 = 62.5 \text{ g} \cdot \text{mol}^{-1}$$

This mass corresponds to the mass of the empirical formula; the molecular formula is C_2H_3Cl.

4.66 (a) The average kinetic energy is obtained from the expression:

$$\text{average kinetic energy} = \frac{3}{2}RT$$

The value is independent of the nature of the monatomic ideal gas. The numerical values are:

(a) $3718 \text{ J} \cdot \text{mol}^{-1}$;   (b) $3731 \text{ J} \cdot \text{mol}^{-1}$;

(c) $3731 \text{ J} \cdot \text{mol}^{-1} - 3718 \text{ J} \cdot \text{mol}^{-1} = 13 \text{ J} \cdot \text{mol}^{-1}$

4.68 The root mean square speed is calculated from the following equation:

$$c = \sqrt{\frac{3\,RT}{M}}$$

(a) Fluorine gas, F_2, $M = 38.00 \text{ g} \cdot \text{mol}^{-1}$

$$c = \sqrt{\frac{3(8.314 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(623 \text{ K})}{3.800 \times 10^{-2} \text{ kg} \cdot \text{mol}^{-1}}}$$

$= 639 \text{ m} \cdot \text{s}^{-1}$

(b) Chlorine gas, Cl_2, $M = 70.90 \text{ g} \cdot \text{mol}^{-1}$

$$c = \sqrt{\frac{3(8.314 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(623 \text{ K})}{7.090 \times 10^{-2} \text{ kg} \cdot \text{mol}^{-1}}}$$

$= 468 \text{ m} \cdot \text{s}^{-1}$

(c) Bromine gas, Br_2, $M = 159.82 \text{ g} \cdot \text{mol}^{-1}$

$$c = \sqrt{\frac{3(8.314 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(623 \text{ K})}{1.5982 \times 10^{-1} \text{ kg} \cdot \text{mol}^{-1}}}$$

$= 312 \text{ m} \cdot \text{s}^{-1}$

4.70 Note that Equation 29, the Maxwell distribution of speeds, should read

$f(v) = 4\pi \left(\dfrac{M}{2\pi RT} \right)^{3/2} v^2 e^{\frac{-Mv^2}{2RT}}$. (Earlier printings of the textbook might

have a misprint of 1/2 for the 3/2 exponent.)

The first derivative with respect to speed is

$$\frac{d\,f(v)}{dv} = \left(\frac{M}{2\pi RT}\right)^{3/2} e^{\frac{-Mv^2}{2RT}}\left[8\pi v + 4\pi v^2\left(\frac{-Mv}{RT}\right)\right] = 0$$

Solving for v gives the most probable speed in terms of T.

$$v_{mp} = \left(\frac{2RT}{M}\right)^{1/2}$$

Substitution into $f(v)$ gives

$$f(v_{mp}) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\left(\frac{2RT}{M}\right)\cdot e^{-1} = 4\pi\left(\frac{M}{2\pi RT}\right)^{1/2}e^{-1}$$

The problem asks for the temperature that satisfies this relationship:
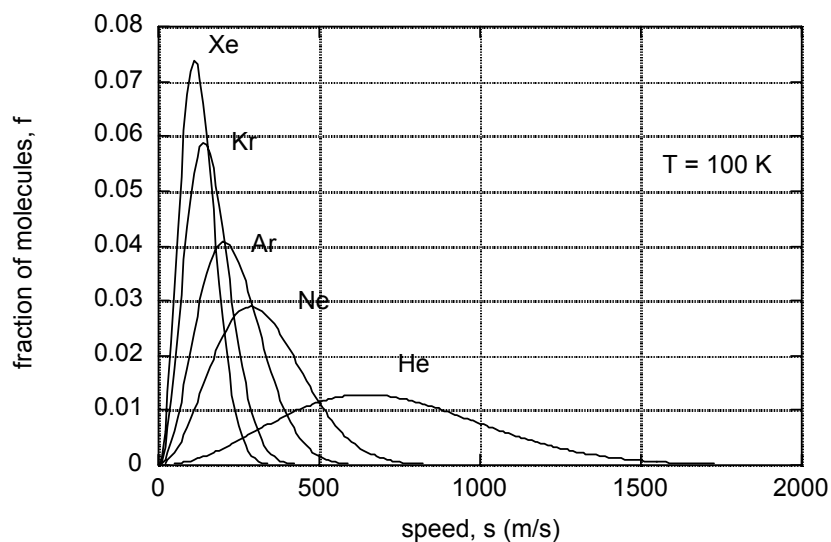
$$f(v_{mp})_T = \frac{1}{2}f(v_{mp})_{300}$$

$$4\pi\left(\frac{M}{2\pi RT}\right)^{1/2}e^{-1} = \left(\frac{1}{2}\right)4\pi\left(\frac{M}{2\pi R(300.\text{ K})}\right)^{1/2}e^{-1}$$

$$\left(\frac{1}{T}\right)^{1/2} = \left(\frac{1}{2}\right)\left(\frac{1}{300.\text{ K}}\right)^{1/2}$$

$$\left(\frac{1}{T}\right) = \left(\frac{1}{4}\right)\left(\frac{1}{300.\text{ K}}\right)$$

$$T = 4 \times 300.\text{ K} = 1.20 \times 10^3 \text{ K}$$

4.72 (a)

$T = 100$ K

(b) As the molar mass increases, the distribution shifts toward lower velocities. The distribution becomes narrower and the fraction of atoms with the most probable speed becomes higher as the molar mass becomes larger. (Note that all distributions are normalized to the total number of atoms. Since total kinetic energy is constant for a given T, there are one-tenth as many Ar atoms as He atoms because its mass is ten times as large.)

(c)
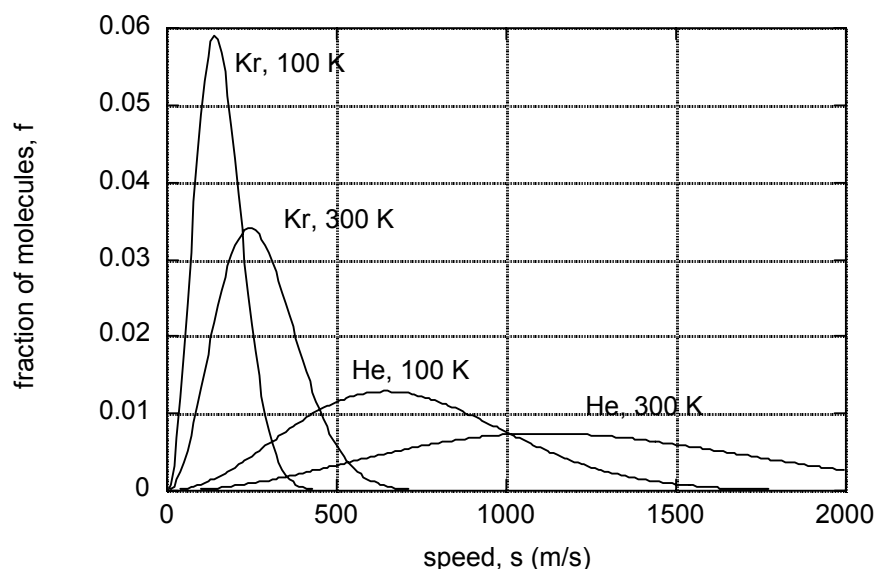
(d) The two distributions for He are clearly much broader and displaced toward higher velocities than that distribution for Kr. As T increases, the curve maximum shifts toward higher speed for each type of atom.

4.74 (a) Real gases are more compressible than ideal gases when the intermolecular forces of attraction dominate.   (b) They are less compressible when the intermolecular repulsions dominate.

4.76 The pressures are calculated from the ideal gas law:

$$P = \frac{nRT}{V} = \frac{(1.00 \text{ mol})(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})\ (298\text{K})}{V}$$

(a) Calculating for the specific volumes requested, we obtain $P = $ (a) 0.815 atm;   (b) 24.5 atm;   (c) 489 atm.

The calculations can now be repeated using the van der Waals equation:

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

We can rearrange this to solve for P:

$$P = \left(\frac{nRT}{V - nb}\right) - \left(\frac{an^2}{V^2}\right)$$

$$= \left(\frac{(1.00 \text{ mol})(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{V - (1.00 \text{ mol})(0.026\ 61 \text{ L} \cdot \text{mol}^{-1})}\right)$$

$$- \left(\frac{(0.2476 \text{ L}^2 \cdot \text{atm} \cdot \text{mol}^{-2})(1.00)^2}{V^2}\right)$$

(a) Using the three values for V, we calculate $P = $ (a) 0.816 atm; (b) 24.9 atm;   (c) 946 atm. Note that at larger volume (lower pressure), the ideal gas law gives essentially the same values as the van der Waals equation but at smaller volume (higher pressure) there is a very significant difference. Since the pressure values calculated from the van der Waals equation are higher than those from the ideal gas law, we would conclude that the repulsive forces represented by b are dominant for hydrogen under these conditions of temperature and volume.

4.78   (a) (1) ideal gas:

$$PV = nRT$$

$$P = \frac{nRT}{V} = \frac{(1.00 \text{ mol})(0.082\ 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(273.15 \text{ K})}{22.414 \text{ L}}$$

$$= 1.00 \text{ atm}$$

(2) van der Waal's gas:

$$\left(P + a\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT$$

$$P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

$$P = \frac{(1.00\ \text{mol})(0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(273.15\ \text{K})}{22.414\ \text{L} - (1.00\ \text{mol})(0.0638\ \text{L} \cdot \text{mol}^{-1})}$$

$$- 4.562\ \text{L}^2 \cdot \text{atm} \cdot \text{mol}^{-2}\left(\frac{1.00\ \text{mol}}{22.414\ \text{L}}\right)^2 = 0.994\ \text{atm}$$
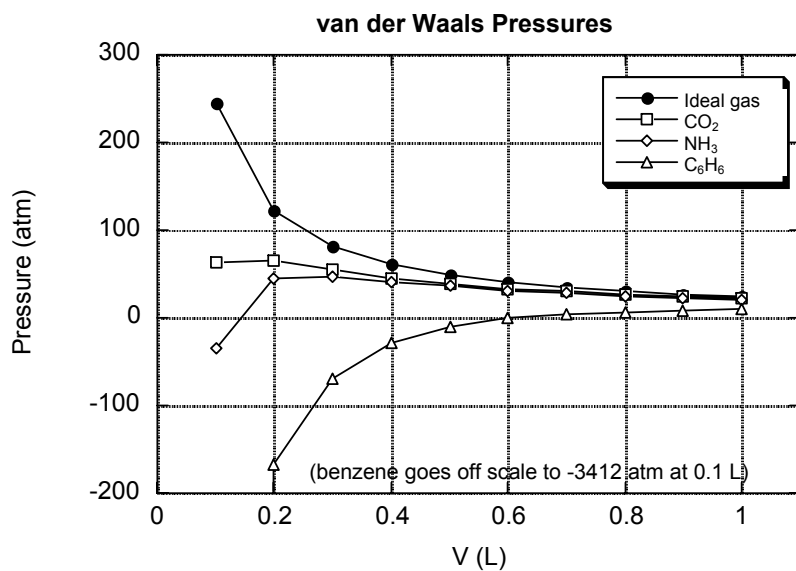
(b) (1) ideal gas:

$$P = \frac{(1.00\ \text{mol})(0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(1000\ \text{K})}{0.100\ \text{L}} = 821\ \text{atm}$$

(2) van der Waal's gas:

$$P = \frac{(1.00\ \text{mol})(0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(1000\ \text{K})}{0.100\ \text{L} - (1.00\ \text{mol})(0.0638\ \text{L} \cdot \text{mol}^{-1})}$$

$$- 4.562\ \text{L}^2 \cdot \text{atm} \cdot \text{mol}^{-2}\left(\frac{1.00\ \text{mol}}{0.100\ \text{L}}\right)^2 = 1.81 \times 10^3\ \text{atm}$$

4.80

van der Waals Pressures

Legend: Ideal gas, CO_2, NH_3, C_6H_6

(benzene goes off scale to -3412 atm at 0.1 L)

Pressure (atm) vs V (L)

Pressures for the real gases can be calculated from Eq. 33 and the appropriate constants.

$$P = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$$

114

v.d.W. Constants	carbon dioxide	ammonia	benzene
a, $L^2 \cdot atm \cdot mol^{-1}$	3.64	4.225	18.24
b, $L \cdot mol^{-1}$	0.042 67	0.037 07	0.1154

The different shapes of these calculated curves can be attributed to deviations from ideality caused by intermolecular interactions. The constant a corrects for attractions while the constant b corrects for repulsions. As a becomes larger going from carbon dioxide to ammonia to benzene, the effect of the second term in the van der Waals equation is increased proportionally such that it reduces the pressure at any volume. Carbon dioxide deviates least from ideality while benzene deviates most. This effect is more pronounced at small volumes since pressure is reduced by the inverse square of volume multiplied by a. Attractions dominate the non-ideal behavior for all three real gases across the whole volume range where $P_{vdW} < P_{ideal}$. We would expect the real gases to liquefy at their equilibrium vapor pressures, or near the volume that corresponds to zero pressure for each gas (~0.65 L for benzene, ~0.15 L for ammonia).

4.82 $(CH_3)_2 N_2 H_2 (s) + 2 N_2 O_4 (l) \rightarrow 2 CO_2 (g) + 3 N_2 (g) + 4 H_2 O(l)$
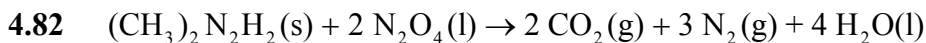
$P_{tot} = P_{CO_2} + P_{N_2} + P_{H_2O} = 2.50$ atm

Since the mole ratio of the gaseous products is 2:3:4 and all three gases are present in the same vessel at the same temperature, the partial pressures will exhibit this ratio as well. Therefore,

$P_{tot} = 2x + 3x + 4x = 9x = 2.50$ atm

$x = 0.278$ atm
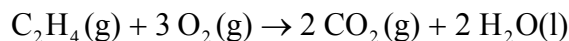
$P_{CO_2} = 2x = 0.556$ atm

$P_{N_2} = 3x = 0.834$ atm

$P_{H_2O} = 4x = 1.11$ atm

4.84 First, balance the equation:

$$C_2H_4(g) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 2\,H_2O(l)$$

Because the reaction remains at 1.00 atm pressure and 298 K throughout, we can use the volumes directly to solve the problem. The volume is directly proportional to the number of moles of each species. 2.00 L of ethene requires 6.00 L of O_2 to react in order to go to completion. O_2 is thus the limiting reactant. All the O_2 will react with 0.667 L of ethene (2.00 L ÷ 3 mol O_2 per mol ethene). This leaves 1.33 L of unreacted ethene and produces 1.33 L CO_2:

$$L \text{ of } CO_2 \text{ produced} = (2.0 \text{ L } O_2 \text{ consumed})\left(\frac{2 \text{ L } CO_2 \text{ produced}}{3 \text{ L } O_2 \text{ consumed}}\right)$$

$$= 1.33 \text{ L } CO_2 \text{ produced}$$

The total volume is the sum of the volume of ethene remaining plus the volume of CO_2 produced.

$$V = 1.33 \text{ L} + 1.33 \text{ L} = 2.66 \text{ L}$$

4.86 (a) Because the gas was collected over water, it contains water vapor. Of the 737.7 Torr of pressure in the vessel, only 737.7 Torr − 9.21 Torr = 728.5 Torr is due to $H_2(g)$. The amount of dry H_2 can be calculated from the ideal gas law:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{\left(\dfrac{728.5 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)(0.127 \text{ L})}{283 \text{ K}} = \frac{(1.00 \text{ atm})(V)}{298 \text{ K}}$$
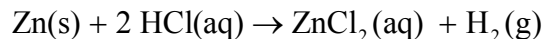
$$V = 0.128 \text{ L}$$

(b)

$$\left(\frac{728.5 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)(0.128 \text{ L}) = n\,(0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(283 \text{ K})$$

$$n = 5.28 \times 10^{-3} \text{ mol}$$

(c) To determine this, we must first write the balanced equation for the reaction of Zn metal with HCl:

$$Zn(s) + 2\ HCl(aq) \rightarrow ZnCl_2\,(aq)\ + H_2\,(g)$$

There should be 1 mol $H_2(g)$ produced per 1 mol Zn(s) consumed. If the zinc metal were 100% pure, the number of moles of zinc would be $0.40\ g \div 65.37\ g \cdot mol^{-1} = 6.12 \times 10^{-3}$ mol and the same number of moles of H_2 should have been produced. Because not enough H_2 was produced for all of the original sample to be Zn, the sample was clearly impure. We can calculate the mass of Zn present in the original sample from the number of moles of H_2 produced, which is also equal to the number of moles of Zn in the initial sample:

5.24×10^{-3} mol $\times\ 65.37\ g \cdot mol^{-1}$ Zn $= 0.34$ g. The percent purity is given by $\dfrac{0.34\ g}{0.40\ g} \times 100 = 85\%$

4.88 The information in the first sentence allows us to calculate the empirical formula of the compound. If 2.36 g of the mass of the phosphorus chloride is phosphorus, then 8.14 g must be Cl. Upon calculation, this gives an empirical formula of PCl_3, which has an empirical formula mass of $137.32\ g \cdot mol^{-1}$. Because the phosphorus chloride took 1.77 times as long to effuse, the rate of effusion of CO_2 must be 1.77 times that of the phosphorus compound. We can then write:

$$\frac{rate_1}{rate_2} = \frac{\dfrac{1}{\sqrt{M_1}}}{\dfrac{1}{\sqrt{M_2}}} = \sqrt{\frac{M_2}{M_1}}$$

$$1.77 = \sqrt{\frac{M_2}{44.01\ g \cdot mol^{-1}}}$$

$$M_2 = 138\ g \cdot mol^{-1}$$

The molar mass determined is close to that of the formula mass, and so the empirical formula must also correspond to the molecular formula.

4.90 (a) The number of moles of nitrogen required to fill the air bag can be found from the ideal gas law.

$$? \text{ mol N}_2 = \frac{pV}{RT} = \frac{(1.37 \text{ atm})(57.0 \text{ L N}_2)}{(0.0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = 3.19 \text{ mol N}_2$$

The mass of sodium azide required to produce this amount of nitrogen depends upon the balanced chemical reaction.

$$2 \text{ NaN}_3(s) \rightarrow 3 \text{ N}_2(g) + 2 \text{ Na}(s)$$
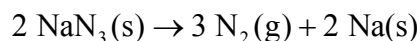
$$? \text{ g NaN}_3 = 3.19 \text{ mol N}_2 \left(\frac{2 \text{ mol NaN}_3}{3 \text{ mol N}_2} \right) \left(\frac{65.02 \text{ g NaN}_3}{1 \text{ mol NaN}_3} \right) = 138 \text{ g NaN}_3$$

(b) $v_{rms} = \sqrt{\dfrac{3RT}{M}}$

$$= \left(\frac{3(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{(28.0 \text{ g} \cdot \text{mol}^{-1})} \left(\frac{\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2}}{\text{J}} \right) \left(\frac{1000 \text{ g}}{\text{kg}} \right) \right)^{\frac{1}{2}}$$

$$= 515 \text{ m} \cdot \text{s}^{-1}$$

4.92 To answer this question, we need to find which gases are lighter than the average density of the atmosphere in which the balloons are supposed to float. The density will depend on the molecular weight of the sample:

$$PV = nRT$$

$$PV = \frac{m}{M} RT$$

$$d = \frac{m}{V} = \frac{PM}{RT}$$

The problem then reduces to finding which of these gases have a molar mass less than the average molar mass of the atmosphere. The average molar mass of the atmosphere will be the weighted average of the molar masses of the components. Because Ar and O_2 make up the greatest part of the atmospheric composition, we can neglect the other minor components that are present. Average molar mass

$= 0.79 \,(39.95 \text{ g} \cdot \text{mol}^{-1}) + 0.20 \,(32.00 \text{ g} \cdot \text{mol}^{-1}) = 38 \text{ g} \cdot \text{mol}^{-1}$. The molar

masses of Kr, CO_2, CH_4, C_3H_8, N_2, CO are 83.80, 44.01, 16.04, 44.09, 28.02, and 28.01 $g \cdot mol^{-1}$, respectively. The gases that would produce balloons that would float include methane, nitrogen and carbon monoxide. Because methane is flammable and carbon monoxide is toxic, the best choice would be nitrogen, which is chemically inert.

4.94 We can use the ideal gas law to determine the number of moles of hydrocarbon equivalent to 2.55 g in order to get the molar mass of the compound.

$$? \text{ mol } = \frac{PV}{RT} = \frac{(0.950 \text{ atm})(3.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(355 \text{ K})} = 0.0978 \text{ mol}$$

$$\text{molar mass} = \frac{2.55 \text{ g}}{0.0978 \text{ mol}} = 26.1 \text{ g} \cdot \text{mol}^{-1}$$

This molar mass fits a molecular formula of C_2H_2 so the hydrocarbon is acetylene.

H–C $\equiv$C–H
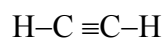
4.96 (a) $4 \text{ FeS}_2 \text{ (s)} + 11 \text{ O}_2 \text{ (g)} \rightarrow 2 \text{ Fe}_2\text{O}_3 \text{ (s)} + 8 \text{ SO}_2 \text{ (g)}$

(b) First we calculate the number of moles of O_2 present at the conditions given, using the ideal gas law:

$PV = nRT$

$(2.33 \text{ atm})(75.0 \text{ L}) = n \, (0.082 \, 06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(423 \text{ K})$

$n = 5.03 \text{ mol}$

Then, using the stoichiometry of the reaction and the molar mass of Fe_2O_3, we can calculate the mass of Fe_2O_3 produced:

$$\text{mass of Fe}_2\text{O}_3 = (159.70 \text{ g Fe}_2\text{O}_3 \cdot \text{mol}^{-1} \text{ Fe}_2\text{O}_3)(5.03 \text{ mol O}_2)$$
$$\times \left(\frac{2 \text{ mol Fe}_2\text{O}_3}{11 \text{ mol O}_2} \right)$$
$$= 146 \text{ g Fe}_2\text{O}_3$$

(c) The number of moles of SO_2 produced can be obtained from the stoichiometry:

$$n_{SO_2} = (5.03\ n_{O_2}) \left(\frac{8\ n_{SO_2}}{11\ n_{O_2}} \right) = 3.66\ \text{mol}$$

3.66 mol of SO_2 will dissolve in 5.00 L of water to form a solution that is

$(3.66\ \text{mol} \div 5.00\ \text{L}) = 0.732\ \text{M in } H_2SO_3$, according to the equation

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$.
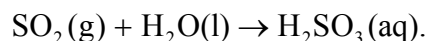
(d) $\text{mass of } SO_2 = 1 \times 10^3\ \text{kg coal} \left(\frac{5 \times 10^3\ \text{g FeS}_2}{100\ \text{kg coal}} \right) \left(\frac{1\ \text{mol FeS}_2}{119.99\ \text{g FeS}_2} \right)$

$$\times \left(\frac{8\ \text{mol SO}_2}{4\ \text{mol FeS}_2} \right) \left(\frac{64.07\ \text{g SO}_2}{1\ \text{mol SO}_2} \right)$$

$$= 5 \times 10^4\ \text{g SO}_2 = 50\ \text{kg SO}_2$$

(e) $n_{SO_2} = 5 \times 10^4\ \text{g SO}_2 \left(\frac{1\ \text{mol SO}_2}{64.07\ \text{g SO}_2} \right) = 800\ \text{mol SO}_2$

$$V = \frac{nRT}{P} = \frac{(800\ \text{mol})\ (0.082\ 06\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298\ \text{K})}{(1.00\ \text{atm})}$$

$$= 2 \times 10^4\ \text{L}$$

4.98 (a), (b) and (c)

The values of the three quantities are:

$$v = \sqrt{\frac{3\ RT}{M}}$$

$$v_{average} = \sqrt{\frac{8\ RT}{\pi M}}$$

$$v_{most\ probable} = \sqrt{\frac{2\ RT}{M}}$$

The quantities can be rewritten to emphasize their relationship because all

contain the same $\sqrt{\dfrac{RT}{M}}$ term:

$$v = \sqrt{3} \times \sqrt{\frac{RT}{M}} = 1.732 \sqrt{\frac{RT}{M}}$$

$$v_{\text{average}} = \sqrt{\frac{8}{\pi}} \times \sqrt{\frac{RT}{M}} = 1.596 \sqrt{\frac{RT}{M}}$$

$$v_{\text{most probable}} = \sqrt{2} \times \sqrt{\frac{RT}{M}} = 1.414 \sqrt{\frac{RT}{M}}$$

It can be easily seen that $v_{\text{most probable}}$ is the smallest followed by v_{average} and then v. The numerical ratio between them will be 1.414 : 1.596 : 1.732 or 1 : 1.13 : 1.22.

4.100 (a) $\dfrac{\text{rate}_1}{\text{rate}_2} = \sqrt{\dfrac{M_2}{M_1}}$

Because the rate is proportional to the number of moles of compound, we can write

$$\frac{\dfrac{0.9560 \text{ g}}{16.01 \text{ g} \cdot \text{mol}^{-1}}}{\dfrac{2.292 \text{ g}}{M_2}} = \sqrt{\frac{M_2}{16.01 \text{ g} \cdot \text{mol}^{-1}}}$$

$$\left[\left(\frac{0.9560 \text{ g}}{16.01 \text{ g} \cdot \text{mol}^{-1}}\right)\left(\frac{M_2}{2.292 \text{ g}}\right)\right]^2 = \frac{M_2}{16.01 \text{ g} \cdot \text{mol}^{-1}}$$

$$\left(\frac{1}{16.01 \text{ g} \cdot \text{mol}^{-1}}\right)\left(\frac{0.9560 \text{ g}}{2.292 \text{ g}}\right)^2 (M_2)^2 - M_2 = 0$$

$$M_2\left[\left(\frac{1}{16.01 \text{ g} \cdot \text{mol}^{-1}}\right)\left(\frac{0.9560 \text{ g}}{2.292 \text{ g}}\right)^2 M_2 - 1\right] = 0$$

$$M_2 = 92.02 \text{ g} \cdot \text{mol}^{-1}$$

(b) C_7H_8. We could consider molecules with other carbon counts; however, these prove to be impossible. Molecules with six carbon atoms or fewer would have too many hydrogen atoms. The formula C_6H_{20} would be required to have a molar mass of 92, but if there are 20 C—H bonds and each C atom can at most make four bonds to other atoms, then there are only $(6 \times 4) - 20 = 4$ bonds remaining, and that is too few to bond

together six carbon atoms. If we had eight carbon atoms, the mass would be 96 from carbon alone and that exceeds the observed mass.

(c) There are many structures possible. The formula C_7H_8, however, can provide clues about the types of molecules that can be drawn. The saturated hydrocarbon based on seven carbon atoms has a formula of C_7H_{16}. There are 6 C—C and 16 C—H bonds in that molecule. For every two H atoms we remove, we create a site of unsaturation. That is, we introduce either a double bond or a ring structure. A triple bond counts as two sites of unsaturation. Thus C_7H_8 has eight fewer hydrogen atoms and should contain four sites of unsaturation. Examples include:
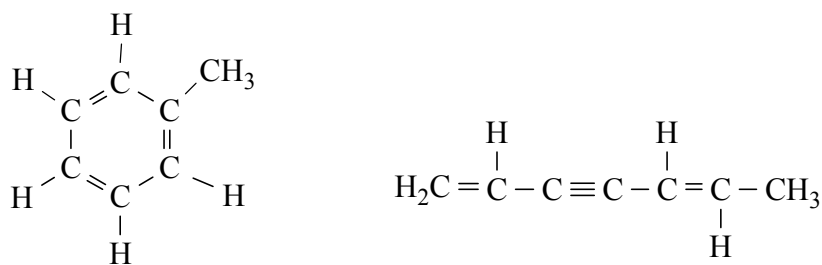
4.102 First we can use the ideal gas law to determine the number of moles of arsine present initially in the flask.

$$? \, \text{mol} \; = \frac{PV}{RT} = \frac{(300. \, \text{Torr})(0.500 \, 0 \, \text{L})}{(0.08206 \, \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(223 \, \text{K})} \left(\frac{1 \, \text{atm}}{760. \, \text{Torr}} \right)$$
$$= 0.0108 \, \text{mol AsH}_3$$

If this amount of arsine were to decompose completely according to this balanced reaction

$$\text{AsH}_3(g) \rightarrow \text{As}(s) + \tfrac{3}{2} \text{H}_2(g)$$

then (1.5)(0.0108 mol) = 0.0162 mol of hydrogen gas would be produced for 100% decomposition. If less than 100% decomposes, the observed pressure in the flask will be due to both unreacted arsine and product hydrogen. The actual number of moles of gas in the flask for the final conditions is

$$? \text{ mol } = \frac{PV}{RT} = \frac{(508. \text{ Torr})(0.500\ 0\ \text{L})}{(0.08206\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(273\ \text{K})} \left(\frac{1\ \text{atm}}{760.\ \text{Torr}} \right)$$

$= 0.0149$ mol gas

Setting x = number of moles of arsine that decomposed also requires that $1.5x$ moles of hydrogen were formed. Then

$n_{total} = 0.0149$ mol $= (0.0108$ mol $- x) + 1.5x$

0.0041 mo l$= 0.5x$

$x = 0.0082$ mol

Then $(1.5)(0.0082$ moles$) = 0.0123$ moles of hydrogen were formed so

$\dfrac{0.0123 \text{ mol}}{0.0162 \text{ mol}} \times 100 = 75.9\%$ of the arsine decomposed.

(Equivalently, $\dfrac{0.0082 \text{ mol}}{0.0108 \text{ mol}} \times 100 = 75.9\%$.)

4.104 Since the van der Waals a parameter represents the role of attractions, it will become larger as the strength of the intermolecular attractions increases. Acetonitrile is polar and would be expected to have the strongest intermolecular forces and the highest value of a. The three non-polar species can be ranked in order of the polarizability of their electron clouds. Carbon dioxide has the largest, most polarizable electron cloud, so it should have the strongest London dispersion forces of these three species and the highest value of a after acetonitrile. Methane would be next, while neon would exhibit the weakest London dispersion forces and the lowest value of a. We can check this reasoning by first noting that acetonitrile is the only one of these four substances that is a liquid at room temperature. In fact, the normal boiling points of these chemical substances, as given in the third column of the table, fall in the same order as their van der Waals a parameters.

a ($L^2 \cdot atm \cdot mol^{-2}$)	substance	normal b. pt. (°C)
17.58	CH_3CN	81.6
3.392	CO_2	−78.5 (subl.)
2.253	CH_4	−164.76
0.2107	Ne	−246.048