

## CHAPTER 4

### THE PROPERTIES OF GASES

- 4.1** (a)  $8 \times 10^9$  Pa; (b) 80 kilobars; (c)  $6 \times 10^7$  Torr;  
(d)  $1 \times 10^6$  lb · in<sup>-2</sup>
- 4.3** (a) The difference in column height will be equal to the difference in pressure between atmospheric pressure and pressure in the gas bulb. If the pressures were equal, the height of the mercury column on the air side and on the apparatus side would be the same. The pressure in the gas bulb is 0.890 atm or  $0.890 \times 760 \text{ Torr} \cdot \text{atm}^{-1} = 676 \text{ Torr}$ . The difference would be  $762 \text{ Torr} - 676 \text{ Torr} = 86 \text{ Torr} = 86 \text{ mm Hg}$ . (b) The side attached to the bulb will be higher because the neon pressure is less than the pressure of the atmosphere. (c) If the student had recorded the level in the atmosphere arm to be higher than the level in the bulb arm by 86 mm Hg then the pressure in the bulb would have been reported as  $762 \text{ Torr} + 86 \text{ Torr} = 848 \text{ Torr}$ .
- 4.5**  $d_1 h_1 = d_2 h_2$   
 $73.5 \text{ cm} \times \frac{13.6 \text{ g} \cdot \text{cm}^{-3}}{1.10 \text{ g} \cdot \text{cm}^{-3}} = 909 \text{ cm or } 9.09 \text{ m}$
- 4.7**  $(20. \text{ in})(10. \text{ in})(14.7 \text{ lb} \cdot \text{in}^2) = 2.9 \times 10^3 \text{ lb}$

**4.9** (a) Volume, L       $\frac{nR}{V}$ , atm · K<sup>-1</sup>

0.01                      8.21

0.02                      4.10

0.03                      2.74

0.04                      2.05

0.05                      1.64

(b) The slope is equal to  $\frac{nR}{V}$

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

**4.11** (a) from  $P_1V_1 = P_2V_2$ , we have

$(2.0 \times 10^5 \text{ kPa})(7.50 \text{ mL}) = (P_2)(1000 \text{ mL})$ ; solving for  $P_2$  we get

$1.5 \times 10^3 \text{ kPa}$ ; (b) similar to (a),

$P_1V_1 = P_2V_2$  or  $(643 \text{ Torr})(54.2 \text{ cm}^3) = (P_2)(7.8 \text{ cm}^3)$ ,  $P_2 = 4.5 \times 10^3 \text{ Torr}$

**4.13** Using

$\frac{P_1}{T_1} = \frac{P_2}{T_2}$  and expressing  $T$  in Kelvins,  $\frac{1.10 \text{ atm}}{298 \text{ K}} = \frac{P_2}{898 \text{ K}}$ ;  $P_2 = 3.31 \text{ atm}$

**4.15** Using

$\frac{P_1}{T_1} = \frac{P_2}{T_2}$  and expressing  $T$  in Kelvins,  $\frac{1.5 \text{ atm}}{283 \text{ K}} = \frac{P_2}{303 \text{ K}}$ ;  $P_2 = 1.6 \text{ atm}$

**4.17** If  $P$  and  $T$  are constant, then  $\frac{V_1}{n_1} = \frac{V_2}{n_2}$ , or  $\frac{V_1}{0.100 \text{ mol}} = \frac{V_2}{0.110 \text{ mol}}$ .

Solving for  $V_2$  in terms of  $V_1$ , we obtain  $V_2 = \frac{n_2V_1}{n_1} = \frac{0.110V_1}{0.10} = 1.10V_1$ .

So the volume must be increased by 10.% to keep  $P$  and  $T$  constant.

- 4.19** (a) Because  $P$ ,  $V$ , and  $T$  all change, we use the relation  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ .

Substituting for the appropriate values we get

$$\frac{(0.255 \text{ atm})(35.5 \text{ mL})}{228 \text{ K}} = \frac{(1.00 \text{ atm})(V_2)}{298 \text{ K}}; V_2 = 11.8 \text{ mL}$$

- (b) The same relation holds as in (a) but here the final temperature and volume are known:

$$\frac{(0.255 \text{ atm})(35.5 \text{ mL})}{228 \text{ K}} = \frac{(P_2)(12.0 \text{ mL})}{293 \text{ K}} \cdot P_2 = 0.969 \text{ atm} \quad \text{(c) Similarly,}$$

we can use the same expression, with  $P$  and  $V$  known and  $T$  wanted.

$$\frac{(0.255 \text{ atm})(35.5 \text{ mL})}{228 \text{ K}} = \frac{\left(\frac{(500 \text{ Torr})}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)(12.0 \text{ mL})}{T_2}; T_2 = 199 \text{ K}$$

- 4.21** (a) Using the ideal gas law with the gas constant  $R$  expressed in kPa:

$$P(0.3500 \text{ L}) = (0.1500 \text{ mol})(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(297 \text{ K});$$

$$P = 1.06 \times 10^3 \text{ kPa}$$

- (b)  $\text{BrF}_3$  has a molar mass of  $136.91 \text{ g} \cdot \text{mol}^{-1}$ . We then substitute into the ideal gas equation:

$$\left(\frac{10.0 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)V = \left(\frac{23.9 \times 10^{-3} \text{ g}}{136.91 \text{ g} \cdot \text{mol}^{-1}}\right)(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(373 \text{ K})$$

$$V = 4.06 \times 10^2 \text{ mL}$$

$$(0.77 \text{ atm})(0.1000 \text{ L})$$

$$\text{(c)} = \left(\frac{\mu}{64.06 \text{ g} \cdot \text{mol}^{-1}}\right)(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(303 \text{ K})$$

$$m = 0.20 \text{ g}$$

$$\begin{aligned} \text{(d)} \quad & (129 \text{ kPa})(6.00 \times 10^3 \text{ m}^3) \left(\frac{1 \times 10^6 \text{ cm}^3}{\text{m}^3}\right) \left(\frac{1 \text{ L}}{1000 \text{ cm}^3}\right) \\ & = n(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(287 \text{ K}) \end{aligned}$$

$$n = 3.24 \times 10^5 \text{ mol CH}_4$$

(e) The number of He atoms is the Avogadro constant  $N_A$  multiplied by the number of moles. The number of moles is obtained from the ideal gas equation:

$$PV = nRT$$

$$n = \frac{PV}{RT}; n = \frac{N}{N_A}$$

so the number of atoms  $N$  will be given by

$$\begin{aligned} N &= N_A \left( \frac{PV}{RT} \right) \\ &= (6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}) \left( \frac{(2.00 \text{ kPa}) (1.0 \times 10^{-6} \text{ L})}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) (158 \text{ K})} \right) \\ &= 9.2 \times 10^{14} \text{ atoms} \end{aligned}$$

$$4.23 \quad (a) \quad V = \frac{nRT}{P} = \frac{(1 \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(773 \text{ K})}{1 \text{ atm}} = 63.4 \text{ L}$$

$$(b) \quad V = \frac{nRT}{P} = \frac{(1 \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(77 \text{ K})}{1 \text{ atm}} = 6.32 \text{ L}$$

4.25 Because  $P$ ,  $V$ , and  $T$  are state functions, the intermediate conditions are irrelevant to the final states. We can simply use the ideal gas law in the form

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

$$\frac{\left( \frac{759 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}} \right) (1.00 \text{ L})}{253 \text{ K}} = \frac{\left( \frac{252 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}} \right) (V_2)}{1523 \text{ K}}$$

$$V_2 = 18.1 \text{ L}$$

4.27 Because  $T$  is constant, we can use

$$\begin{aligned}
 P_1 V_1 &= P_2 V_2 \\
 (1.00 \text{ atm})(1.00 \text{ L}) &= P_2 (0.239 \text{ L}) \\
 P_2 &= 4.18 \text{ atm}
 \end{aligned}$$

**4.29**  $PV = nRT$

$$\begin{aligned}
 &\left( \frac{24.5 \text{ kPa}}{101.325 \text{ kPa} \cdot \text{atm}^{-1}} \right) (0.2500 \text{ L}) \\
 &= n(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(292.7 \text{ K}) \\
 n &= 2.52 \times 10^{-3} \text{ mol}
 \end{aligned}$$

**4.31** (a)  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\begin{aligned}
 \frac{(104 \text{ kPa})(2.0 \text{ m}^3)}{294.3 \text{ K}} &= \frac{(52 \text{ kPa}) V_2}{268.2 \text{ K}} \\
 V_2 &= 3.6 \text{ m}^3
 \end{aligned}$$

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

$$\begin{aligned}
 \frac{(104 \text{ kPa})(2.0 \text{ m}^3)}{294.3 \text{ K}} &= \frac{(0.880 \text{ kPa}) V_2}{221.2 \text{ K}} \\
 V_2 &= 1.8 \times 10^2 \text{ m}^3
 \end{aligned}$$

**4.33** The pressure of the Ar sample will be given by

$$\begin{aligned}
 P_{\text{Ar}} &= \frac{nRT}{V} = \frac{\left( \frac{2.00 \times 10^{-3} \text{ g}}{39.95 \text{ g} \cdot \text{mol}^{-1}} \right) (0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(293 \text{ K})}{0.0500 \text{ L}} \\
 P_{\text{Kr}} &= \frac{\left( \frac{2.00 \times 10^{-3} \text{ g}}{83.80 \text{ g} \cdot \text{mol}^{-1}} \right) (0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(T_2)}{0.0500 \text{ L}}
 \end{aligned}$$

Because we want the pressure to be the same, we can set these two equal to each other. Because volume, mass of the gases, and the gas constant  $R$  are the same on both sides of the equation, they will cancel.

$$\left(\frac{1}{83.80 \text{ g} \cdot \text{mol}^{-1}}\right)(T_2) = \left(\frac{1}{39.95 \text{ g} \cdot \text{mol}^{-1}}\right)(293 \text{ K})$$

Solving for  $T_2$ , we obtain temperature = 615 K or 342°C.

- 4.35** 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 g · mol<sup>-1</sup> for CO(g), 44.01 g · mol<sup>-1</sup> for CO<sub>2</sub>(g),

and 34.01 g · mol<sup>-1</sup> for H<sub>2</sub>S(g). The most dense will be the one with the highest molar mass, which in this case is CO<sub>2</sub>. The order of increasing density will be CO < H<sub>2</sub>S < CO<sub>2</sub>.

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

$$d = \frac{(119.37 \text{ g} \cdot \text{mol}^{-1})\left(\frac{200. \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = 1.28 \text{ g} \cdot \text{L}^{-1}$$

$$(b) \quad d = \frac{(119.37 \text{ g} \cdot \text{mol}^{-1})(1.00 \text{ atm})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(373 \text{ K})} = 3.90 \text{ g} \cdot \text{L}^{-1}$$

**4.39** (a) 
$$M = \frac{dRT}{P} = \frac{(8.0 \text{ g} \cdot \text{L}^{-1})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(300. \text{ K})}{2.81 \text{ atm}}$$

$$= 70. \text{ g} \cdot \text{mol}^{-1}$$

(b) The compound is most likely CHF<sub>3</sub>, for which  $M = 70 \text{ g} \cdot \text{mol}^{-1}$ . It might also be C<sub>2</sub>H<sub>4</sub>F<sub>2</sub>, for which  $M = 66 \text{ g} \cdot \text{mol}^{-1}$ .

(c) You can use the relationship in (a) to calculate the new density, or you can apply the proportionality changes expected from the change in pressure and temperature to the original density:

$$d_2 = (8.0 \text{ g} \cdot \text{L}^{-1}) \left( \frac{1.00 \text{ atm}}{2.81 \text{ atm}} \right) \left( \frac{300. \text{ K}}{298 \text{ K}} \right) = 2.9 \text{ g} \cdot \text{L}^{-1}$$

- 4.41** From the analytical data, an empirical formula of  $\text{CHCl}$  is calculated. The empirical formula mass is  $48.47 \text{ g} \cdot \text{mol}^{-1}$ . The problem may be solved using the ideal gas law:

$$PV = nRT$$

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

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

$$M = \frac{(3.557 \text{ g})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(273 \text{ K})}{(1.10 \text{ atm})(0.755 \text{ L})} = 95.9 \text{ g} \cdot \text{mol}^{-1}$$

$n$  in the formula  $(\text{CHCl})_n$  is equal to

$$95.9 \text{ g} \cdot \text{mol}^{-1} \div 48.47 \text{ g} \cdot \text{mol}^{-1} = 1.98. \text{ The formula}$$

is  $\text{C}_2\text{H}_2\text{Cl}_2$ .

- 4.43** Density is proportional to the molar mass of the gas as seen from the ideal gas law:

$$PV = nRT$$

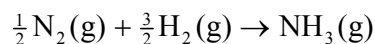
$$PV = \frac{m}{M}RT$$

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

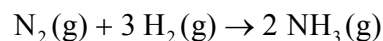
$$0.943 \text{ g} \cdot \text{L}^{-1} = \frac{M \left( \frac{53.1 \text{ kPa}}{101.325 \text{ kPa} \cdot \text{atm}^{-1}} \right)}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}$$

$$M = 44.0 \text{ g} \cdot \text{mol}^{-1}$$

- 4.45** (a) The number of moles of  $\text{H}_2$  needed will be 1.5 times the amount of  $\text{NH}_3$  produced, as seen from the balanced equation:



or



Once the number of moles is known, the volume can be obtained from the ideal gas law.

$$\begin{aligned} V &= \frac{n_{\text{H}_2} RT}{P} = \frac{\left(\frac{3}{2} n_{\text{NH}_3}\right) RT}{P} = \frac{\left(\left(\frac{3 \text{ mol H}_2}{2 \text{ mol NH}_3}\right) \frac{(1.0 \times 10^3 \text{ kg})(10^3 \text{ g} \cdot \text{kg}^{-1})}{17.03 \text{ g} \cdot \text{mol}^{-1}}\right) RT}{P} \\ &= \frac{\left(\frac{3}{2}\right) \left(\frac{10^6 \text{ g}}{17.03 \text{ g} \cdot \text{mol}^{-1}}\right) (0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(623 \text{ K})}{15.00 \text{ atm}} \\ &= 3.0 \times 10^5 \text{ L} \end{aligned}$$

- (b) The ideal gas equation

$$\frac{P_1 V_1}{n_1 R T_1} = \frac{P_2 V_2}{n_2 R T_2} \text{ simplifies to } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

because  $R$  and  $n$  are constant for this problem.

$$\begin{aligned} \frac{(15.00 \text{ atm})(3.0 \times 10^5 \text{ L})}{623 \text{ K}} &= \frac{(376 \text{ atm})V_2}{(523 \text{ K})} \\ V_2 &= 1.0 \times 10^4 \text{ L} \end{aligned}$$

- 4.47** We need to find the number of moles of  $\text{CH}_4(\text{g})$  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  $\text{CH}_4(\text{g})$  should produce the larger volume of  $\text{CO}_2(\text{g})$ . We will use the ideal gas equation to solve for  $n$  in the first case:



$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(2.00 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(348 \text{ K})} = 0.0700 \text{ mol CH}_4$$

$$2.00 \text{ g of CH}_4 \text{ will be } \frac{2.00 \text{ g}}{16.04 \text{ g} \cdot \text{mol}^{-1}} = 0.124 \text{ mol}$$

The latter case will have the greater number of moles of  $\text{CH}_4$  and should produce the larger amount of  $\text{CO}_2(\text{g})$ .

- 4.49** The molar mass of glucose is  $180.15 \text{ g} \cdot \text{mol}^{-1}$ . From this, we can calculate the number of moles of glucose formed and, using the reaction stoichiometry, determine the number of moles of  $\text{CO}_2$  needed. With that information and the other information provided in the problem, we can use the ideal gas law to calculate the volume of air that is needed:

$$PV = nRT$$

$$V = \frac{\left[ \left( \frac{10.0 \text{ g glucose}}{180.15 \text{ g glucose} \cdot \text{mol}^{-1} \text{ glucose}} \right) \left( \frac{6 \text{ mol CO}_2}{1 \text{ mol glucose}} \right) \right]}{\left( \frac{0.26 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}} \right)} \times (0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})$$

$$= 2.4 \times 10^4 \text{ L}$$

- 4.51** (a) This is a limiting reactant problem. Our first task is to determine the number of moles of  $\text{NH}_3$  and  $\text{HCl}$  that are present to start with. This can be done from the ideal gas equation:

$$PV = nRT$$

$$n_{\text{NH}_3} = \frac{PV}{RT} = \frac{\left( \frac{100 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}} \right) (0.0150 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(303 \text{ K})} = 7.94 \times 10^{-5} \text{ mol}$$

$$n_{\text{HCl}} = \frac{PV}{RT} = \frac{\left( \frac{150 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}} \right) (0.0250 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = 2.02 \times 10^{-4} \text{ mol}$$

The ammonia is the limiting reactant. The number of moles of  $\text{NH}_4\text{Cl(s)}$  that form will be equal to the number of moles of  $\text{NH}_3$  that react. From the molar mass of  $\text{NH}_4\text{Cl}$  ( $53.49 \text{ g} \cdot \text{mol}^{-1}$ ) and the number of moles, we can calculate the mass of  $\text{NH}_4\text{Cl}$  that forms:

$$(7.94 \times 10^{-5} \text{ mol } \text{NH}_4\text{Cl(s)})(53.49 \text{ g} \cdot \text{mol}^{-1}) = 4.25 \times 10^{-3} \text{ g}$$

(b) There will be  $(2.02 \times 10^{-4} \text{ mol} - 7.94 \times 10^{-5} \text{ mol}) = 1.23 \times 10^{-4} \text{ mol HCl}$  left after the reaction. This quantity will exist in a total volume after mixing of 40.0 mL or 0.0400 L. Again, we use the ideal gas law to determine the final pressure:

$$PV = nRT$$

$$P = \frac{(1.23 \times 10^{-4} \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(300 \text{ K})}{0.0400 \text{ L}} = 0.0757 \text{ atm}$$

- 4.53** (a) The molar volume of an ideal gas is 22.4 L at 273.15 K. 1.0 mol of ideal gas will exert a pressure of 1.0 atm under those conditions. The partial pressure of  $\text{N}_2(\text{g})$  will be 1.0 atm. Because there are 2.0 mol of  $\text{H}_2(\text{g})$ , the partial pressure of  $\text{H}_2(\text{g})$  will be 2.0 atm. (b) The total pressure will be  $1.0 \text{ atm} + 2.0 \text{ atm} = 3.0 \text{ atm}$ .

- 4.55** (a) We find the pressure of  $\text{SO}_2(\text{g})$  originally present by difference. The initial data gives us the total number of moles present, whereas the data for the gas sample after being passed over  $\text{CaSO}_3(\text{s})$  represents the number of moles of  $\text{N}_2(\text{g})$ .

$$PV = nRT$$

$$n_{\text{total}} = \frac{PV}{RT} = \frac{(1.09 \text{ atm})(0.500 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = 0.0223 \text{ mol}$$

$$n_{\text{N}_2} = \frac{PV}{RT} = \frac{(1.09 \text{ atm})(0.150 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(323 \text{ K})} = 0.00617 \text{ mol}$$

The number of moles of  $\text{SO}_2$  gas is  $0.0223 - 0.00617 \text{ mol} = 0.0161 \text{ mol}$ .

The partial pressure will be given by the mole fraction multiplied by the

total pressure. The mole fraction of  $\text{SO}_2(\text{g})$  will be

$0.0161 \text{ mol} \div 0.0223 \text{ mol} = 0.722$ . The pressure due to  $\text{SO}_2$  in the original mixture is  $(0.722)(1.09 \text{ atm}) = 0.787 \text{ atm}$ .

(b) The mass of  $\text{SO}_2$  will be obtained by multiplying the number of moles of  $\text{SO}_2$  by the molar mass of  $\text{SO}_2$  :

$$m_{\text{SO}_2} = (0.0161 \text{ mol})(64.06 \text{ g} \cdot \text{mol}^{-1}) = 1.03 \text{ g}$$

- 4.57** (a) Of the 756.7 Torr measured, 17.54 Torr will be due to water vapor. The pressure due to  $\text{H}_2(\text{g})$  will, therefore, be

$$756.7 \text{ Torr} - 17.54 \text{ Torr} = 739.2 \text{ Torr. (b) } \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g});$$

(c) To answer this question, we must determine the number of moles of  $\text{H}_2$  produced in the reaction. Using the partial pressure of  $\text{H}_2$  calculated in part (a) and the ideal gas equation, we can set up the following:

$$\left( \frac{739.2 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}} \right) (0.220 \text{ L}) = n(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(293 \text{ K})$$

Solving for  $n$ , we obtain  $n = 0.00890 \text{ mol}$ . According to the stoichiometry of the reaction, half as much oxygen as hydrogen should be produced, so the number of moles of  $\text{O}_2 = 0.00445 \text{ mol}$ . The mass of  $\text{O}_2$  will be given by  $(0.00445 \text{ mol})(32.00 \text{ g} \cdot \text{mol}^{-1}) = 0.142 \text{ g}$ .

- 4.59** 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:

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

Diffusion also follows this relationship. If we have two different gases whose rates of diffusion are measured under identical conditions, we can take the ratio

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

If a compound takes 1.24 times as long to diffuse as Kr gas, the rate of diffusion of Kr is 1.24 times that of the unknown. We can now use the expression to calculate the molar mass of the unknown, given the mass of Kr:

$$\frac{1.24}{1} = \sqrt{\frac{M_2}{83.80 \text{ g} \cdot \text{mol}^{-1}}}$$

$$M_2 = 129 \text{ g} \cdot \text{mol}^{-1}$$

A mass of  $129 \text{ g} \cdot \text{mol}^{-1}$  corresponds to a molecular formula of  $\text{C}_{10}\text{H}_{10}$ .

- 4.61** The rate of effusion is inversely proportional to the square root of the molar mass. Using a ratio as follows allows us to calculate the time of effusion without knowing the exact conditions of pressure and temperature:

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

The rate will be equal to the number of molecules  $N$  that effuse in a given time interval. For the conditions given,  $N$  will be the same for argon and for the second gas chosen.

$$\frac{\frac{N}{\text{time}}}{\frac{N}{147 \text{ s}}} = \frac{\frac{1}{\text{time}}}{\frac{1}{147 \text{ s}}} = \sqrt{\frac{39.95 \text{ g} \cdot \text{mol}^{-1}}{M_1}}$$

In order to calculate the time of effusion, we need to know only the molar mass of the gases.

(a) For  $\text{CO}_2$  with a molar mass of

$$44.01 \text{ g} \cdot \text{mol}^{-1} : \frac{\frac{1}{\text{time}_{\text{CO}_2}}}{\frac{1}{147 \text{ s}}} = \sqrt{\frac{39.95 \text{ g} \cdot \text{mol}^{-1}}{44.01 \text{ g} \cdot \text{mol}^{-1}}}$$

$$\text{time} = 154 \text{ s}$$

(b) For  $\text{C}_2\text{H}_4$  with a molar mass of

$$28.05 \text{ g} \cdot \text{mol}^{-1} : \frac{\frac{1}{\text{time}_{\text{C}_2\text{H}_4}}}{\frac{1}{147 \text{ s}}} = \sqrt{\frac{39.95 \text{ g} \cdot \text{mol}^{-1}}{28.05 \text{ g} \cdot \text{mol}^{-1}}}$$

$$\text{time} = 123 \text{ s}$$

(c) For  $\text{H}_2$  with a molar mass of

$$2.01 \text{ g} \cdot \text{mol}^{-1} : \frac{\frac{1}{\text{time}_{\text{CO}_2}}}{\frac{1}{147 \text{ s}}} = \sqrt{\frac{39.95 \text{ g} \cdot \text{mol}^{-1}}{2.01 \text{ g} \cdot \text{mol}^{-1}}}$$

$$\text{time} = 33.0 \text{ s}$$

(d) For  $\text{SO}_2$  with a molar mass of

$$64.06 \text{ g} \cdot \text{mol}^{-1} : \frac{\frac{1}{\text{time}_{\text{CO}_2}}}{\frac{1}{147 \text{ s}}} = \sqrt{\frac{39.95 \text{ g} \cdot \text{mol}^{-1}}{64.06 \text{ g} \cdot \text{mol}^{-1}}}$$

$$\text{time} = 186 \text{ s}$$

**4.63** The formula mass of  $\text{C}_2\text{H}_3$  is  $27.04 \text{ g} \cdot \text{mol}^{-1}$ . From the effusion data, we can calculate the molar mass of the sample.

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

Because time is inversely proportional to rate, we can write alternatively

$$\frac{1}{\frac{349 \text{ s}}{210 \text{ s}}} = \sqrt{\frac{39.95 \text{ g} \cdot \text{mol}^{-1}}{M_1}}$$

$$\frac{210}{349} = \sqrt{\frac{39.95 \text{ g} \cdot \text{mol}^{-1}}{M_1}}$$

$$M_1 = 110 \text{ g} \cdot \text{mol}^{-1}$$

The molar mass is 4.1 times that of the empirical formula mass, so the molecular formula is  $\text{C}_8\text{H}_{12}$ .

- 4.65** (a) The average kinetic energy is obtained from the expression: average kinetic energy  $= \frac{3}{2} RT$ . The value is independent of the nature of the monatomic ideal gas. The numerical values are:

(a)  $4103.2 \text{ J} \cdot \text{mol}^{-1}$ ; (b)  $4090.7 \text{ J} \cdot \text{mol}^{-1}$ ;

(c)  $4103.2 \text{ J} \cdot \text{mol}^{-1} - 4090.7 \text{ J} \cdot \text{mol}^{-1} = 12.5 \text{ J} \cdot \text{mol}^{-1}$

- 4.67** The root mean square speed is calculated from the following equation:

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

(a) methane,  $\text{CH}_4$ ,  $M = 16.04 \text{ g} \cdot \text{mol}^{-1}$

$$c = \sqrt{\frac{3(8.314 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(253 \text{ K})}{1.604 \times 10^{-2} \text{ kg} \cdot \text{mol}^{-1}}}$$

$$= 627 \text{ m} \cdot \text{s}^{-1}$$

(b) ethane,  $\text{C}_2\text{H}_6$ ,  $M = 30.07 \text{ g} \cdot \text{mol}^{-1}$

$$c = \sqrt{\frac{3(8.314 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(253 \text{ K})}{3.007 \times 10^{-2} \text{ kg} \cdot \text{mol}^{-1}}}$$

$$= 458 \text{ m} \cdot \text{s}^{-1}$$

(c) propane,  $\text{C}_3\text{H}_8$ ,  $M = 44.09 \text{ g} \cdot \text{mol}^{-1}$

$$c = \sqrt{\frac{3(8.314 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(253 \text{ K})}{4.409 \times 10^{-2} \text{ kg} \cdot \text{mol}^{-1}}}$$

$$= 378 \text{ m} \cdot \text{s}^{-1}$$

**4.69** Use the expression for the root mean square speed to determine the temperature.

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

$$T = \frac{v_{rms}^2 \cdot M}{3R} = \frac{(1477 \text{ m} \cdot \text{s}^{-1})^2 \cdot (4.00 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1})}{3(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})}$$

$$= 349.9 \text{ K}$$

Use the Maxwell Distribution of Speeds (Equation 4.29) appropriately for both gases:

$$\frac{f(v_{He})}{f(v_{Ar})} = \frac{4\pi N \left(\frac{M_{He}}{2RT}\right)^{\frac{1}{2}} (v_{He})^2 e^{-M_{He}(v_{He})^2/2RT}}{4\pi N \left(\frac{M_{Ar}}{2RT}\right)^{\frac{1}{2}} (v_{Ar})^2 e^{-M_{Ar}(v_{Ar})^2/2RT}}$$

$$= \frac{(M_{He})^{\frac{1}{2}} (v_{He})^2 e^{-M_{He}(v_{He})^2/2RT}}{(M_{Ar})^{\frac{1}{2}} (v_{Ar})^2 e^{-M_{Ar}(v_{Ar})^2/2RT}}$$

$$= \frac{(4.00 \text{ g} \cdot \text{mol}^{-1})^{\frac{1}{2}} (1477 \text{ m} \cdot \text{s}^{-1})^2}{(39.95 \text{ g} \cdot \text{mol}^{-1})^{\frac{1}{2}} (467 \text{ m} \cdot \text{s}^{-1})^2}$$

$$\times \frac{e^{-\frac{(4.00 \times 10^{-3} \text{ kg/mol})(1477 \text{ m/s})^2}{2(8.314 \text{ J/(K} \cdot \text{mol)})(349.9 \text{ K})}}}{e^{-\frac{(39.95 \times 10^{-3} \text{ kg/mol})(467 \text{ m/s})^2}{2(8.314 \text{ J/(K} \cdot \text{mol)})(349.9 \text{ K})}}}$$

$$= \left(\frac{4.00}{39.95}\right)^{\frac{1}{2}} \left(\frac{1477}{467}\right)^2 (0.9977)$$

$$= 3.16$$

- 4.71** (a) The most probable speed is the one that corresponds to the maximum on the distribution curve. (b) The percentage of molecules having the most probable speed decreases as the temperature is raised (the distribution spreads out).
- 4.73** Hydrogen bonding is important in HF. At low temperatures, this hydrogen bonding causes the molecules of HF to be attracted to each other more strongly, thus lowering the pressure. As the temperature is increased, the hydrogen bonds are broken and the pressure rises more quickly than for an ideal gas. Dimers (2 HF molecules bonded to each other) and chains of HF molecules are known to form.

- 4.75** The pressures are calculated very simply from the ideal gas law:

$$P = \frac{nRT}{V} = \frac{(1.00 \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{V}$$

Calculating for the volumes requested, we obtain  $P =$  (a) 1.63 atm; (b) 48.9 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  $P$ :

$$\begin{aligned} P &= \left( \frac{nRT}{V - nb} \right) - \left( \frac{an^2}{V^2} \right) \\ &= \left( \frac{(1.00 \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{V - (1.00 \text{ mol})(0.04267 \text{ L} \cdot \text{mol}^{-1})} \right) \\ &\quad - \left( \frac{(3.640 \text{ L}^2 \cdot \text{atm} \cdot \text{mol}^{-2})(1.00^2)}{V^2} \right) \end{aligned}$$

Using the three values for  $V$ , we calculate for  $P =$  (a) 1.62; (b) 38.9; (c)  $1.88 \times 10^3$  atm. Note that at low pressures, the ideal gas law gives essentially the same values as the van der Waals equation, but at high pressures there is a very significant differences.



**4.77** The values for the pressures of gas with varying numbers of moles of CO<sub>2</sub> present are calculated as follows:

The ideal gas law values are calculated from

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

values for the van der Waals equation can be obtained by rearranging the equation:

$$\begin{aligned} \left( P + \frac{an^2}{V^2} \right) (V - nb) &= nRT \\ P &= \left( \frac{nRT}{V - nb} \right) - \left( \frac{an^2}{V^2} \right) \\ &= \left( \frac{(n)(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(300 \text{ K})}{1.00 \text{ L} - (n)(0.04267 \text{ L} \cdot \text{mol}^{-1})} \right) \\ &\quad - \left( \frac{(3.640 \text{ L}^2 \cdot \text{atm} \cdot \text{mol}^{-1})(n^2)}{(1.00 \text{ L})^2} \right) \end{aligned}$$

The resulting values are

$n$	$P_{\text{ideal}}$	$P_{\text{van der Waals}}$	% deviation*
0.100	2.46	2.44	0.8
0.200	4.92	4.82	2.1
0.300	7.38	7.15	3.2
0.400	9.85	9.44	4.3
0.500	12.31	11.67	5.5

$$*\% \text{ deviation} = \frac{P_{\text{ideal}} - P_{\text{van der Waals}}}{P_{\text{van der Waals}}} \times 100$$

(b) Consider one point, for example, the case for  $n = 0.400$  mol. The term

$V - nb$  will increase the ideal value  $\frac{nRT}{V}$  by 1.7% of the ideal value

(10.02 atm versus 9.85 atm) whereas the correction from  $\frac{an^2}{V^2}$  will

decrease the value by 0.58 atm, a change of 5.9% over the ideal gas value.

The second effect, which is due to the intermolecular attractions, dominates in this case.

(c) The gas starts to deviate from ideality by more than 5% at pressures above about 10 atm.

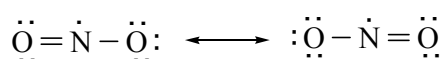
**4.79** Ammonia:  $a = 4.225 \text{ L}^2 \cdot \text{atm} \cdot \text{mol}^{-2}$ ;  $b = 0.03707 \text{ L} \cdot \text{atm}^{-1}$

Oxygen:  $a = 1.378 \text{ L}^2 \cdot \text{atm} \cdot \text{mol}^{-2}$ ;  $b = 0.031883 \text{ L} \cdot \text{atm}^{-1}$

Volume	$P$ , ammonia	$P$ , oxygen	$P$ , ideal
0.05	3581	1897	489
0.1	811	497	245
0.2	256	180	122
0.3	140	106	82
0.4	94	75	61
0.5	70	58	49
0.6	55	47	41
0.7	46	39	35
0.8	39	34	31
0.9	34	30	27
1	30	27	24

Clearly, the greatest deviation from the ideal gas law values occurs at low volumes or higher pressures. Ammonia deviates more strongly and its van der Waals constants are larger than those for oxygen. This may likely arise because ammonia is more polar and will have stronger intermolecular interactions.

**4.81** (a)



(b) Since the wavelength of the absorbed photons is 197 nm, we can find the energy per photon.

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}) \left( \frac{10^9 \text{ nm}}{\text{m}} \right)}{197 \text{ nm}}$$

$$= 1.006 \times 10^{-18} \text{ J}$$

The number of photons in 1.07 mJ must be equal to the number of NO<sub>2</sub> molecules.

$$\begin{aligned} ? \text{ photons} &= 1.07 \text{ mJ} \left( \frac{1 \text{ J}}{1000 \text{ mJ}} \right) \left( \frac{1 \text{ photon}}{1.006 \times 10^{-18} \text{ J}} \right) \\ &= 1.064 \times 10^{15} \text{ photons} = 1.064 \times 10^{15} \text{ NO}_2 \text{ molecules} \end{aligned}$$

The pressure is created by all the molecules in the sample, so the ideal gas law can be used to find the total molecules.

$$\begin{aligned} ? \text{ molecules total} &= N_{AV} \times n_{\text{tot}} = N_{AV} \times \frac{P_{\text{tot}} V}{RT} \\ &= (6.022 \times 10^{23} \text{ molecules} \cdot \text{mol}^{-1}) \\ &\quad \times \left( \frac{(0.85 \text{ atm})(2.5 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(293 \text{ K})} \right) \\ &= 5.32 \times 10^{22} \text{ molecules total} \end{aligned}$$

Therefore, the proportion of NO<sub>2</sub> molecules in the sample is

$$\frac{1.064 \times 10^{15} \text{ NO}_2 \text{ molecules}}{5.32 \times 10^{22} \text{ molecules total}} = 0.020 \text{ ppm}$$

**4.83** Use the ideal gas law to calculate the number of moles of HCl.

$$\begin{aligned} n &= \frac{PV}{RT} = \frac{(690. \text{ Torr})(200. \text{ mL})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mL}^{-1})(293 \text{ K})} \cdot \frac{(1 \text{ atm})}{(760 \text{ Torr})} \cdot \frac{(1 \text{ L})}{(1000 \text{ mL})} \\ &= 7.55 \times 10^{-3} \text{ mol HCl} \end{aligned}$$

Since the reaction between HCl and NaOH occurs in a 1:1 mole ratio, this number of moles of NaOH is also present in the volume of NaOH(aq) required to reach the stoichiometric point of the titration. Therefore, the molarity of the NaOH solution is

$$\frac{\text{moles NaOH}}{1 \text{ L of solution}} = \frac{(7.55 \times 10^{-3} \text{ mol NaOH})}{(15.7 \text{ mL})} \cdot \frac{1000 \text{ mL}}{1 \text{ L}}$$

$$= 0.481 \text{ M}$$

- 4.85** (a)  $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$ ; (b) If all the gas were  $\text{N}_2\text{O}_4(\text{g})$ , then the moles can be calculated from the ideal gas equation:

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

$$= \frac{\left( \frac{43.78 \text{ g}}{92.02 \text{ g} \cdot \text{mol}^{-1}} \right) (0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) (298 \text{ K})}{5.00 \text{ L}}$$

$$= 2.33 \text{ atm}$$

- (c) The only difference in the calculation between part (b) and part (c) is that the molar mass of  $\text{NO}_2$  is half that of  $\text{N}_2\text{O}_4$ .

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

$$= \frac{\left( \frac{43.78 \text{ g}}{46.01 \text{ g} \cdot \text{mol}^{-1}} \right) (0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) (298 \text{ K})}{5.00 \text{ L}}$$

$$= 4.65 \text{ atm}$$

- (d) Because both  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are present, we need to determine some way of calculating the relative amounts of each present. This can be done by taking advantage of the gas law relationships. The total pressure at the end of the reaction will give us the total number of moles present:

$$P_{\text{total}} = 2.96 \text{ atm}$$

$$(2.96 \text{ atm})(5.00 \text{ L}) = n_{\text{total}} (0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) (298 \text{ K})$$

$$n_{\text{total}} = 0.605 \text{ mol}$$

$$\therefore n_{\text{N}_2\text{O}_4} + n_{\text{NO}_2} = 0.605 \text{ mol}$$

This gives us one equation, but we have two unknowns, so another relationship is needed. We can take advantage of knowing the stoichiometry of the reaction. If we assume that all of the gas begins at  $\text{N}_2\text{O}_4$  and we allow some to react, we can write the following:

Initial amount of  $\text{N}_2\text{O}_4$  0.476 mol

Amount of  $\text{N}_2\text{O}_4$  that reacts  $x$  (mol)

Amount of  $\text{NO}_2$  formed  $2x$  (mol)

When the reaction is completed, there will be  $0.476 - x$  mole of  $\text{N}_2\text{O}_4$  and  $2x$  mole  $\text{NO}_2$ . The total number of moles will be given by:

$$(0.476 - x) + 2x = n_{\text{total}}$$

$$0.605 \text{ mol} = 0.476 \text{ mol} + x$$

$$x = 0.129 \text{ mol}$$

$$n_{\text{NO}_2} = 2x$$

$$= 2(0.129 \text{ mol})$$

$$= 0.258 \text{ mol}$$

$$n_{\text{N}_2\text{O}_4} = 0.476 \text{ mol} - x$$

$$= 0.347 \text{ mol}$$

$$X_{\text{NO}_2} = \frac{0.258 \text{ mol}}{0.605 \text{ mol}} = 0.426$$

$$X_{\text{N}_2\text{O}_4} = \frac{0.347 \text{ mol}}{0.605 \text{ mol}} = 0.574$$

- 4.87** (a) The elemental analyses yield an empirical formula of  $\text{NH}_2$ . The formula unit has a mass of  $16.02 \text{ g} \cdot \text{mol}^{-1}$ . The mass, volume, pressure, and temperature data will allow us to calculate the molar mass, using the ideal gas equation:

$$PV = nRT$$

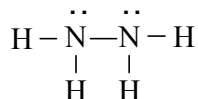
$$PV = \frac{m}{M} RT$$

$$M = \frac{mRT}{PV} = \frac{(0.473 \text{ g})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{(1.81 \text{ atm})(0.200 \text{ L})} = 31.9 \text{ g} \cdot \text{mol}^{-1}$$

The molar mass divided by the mass of the empirical formula mass will give the value of  $n$  in the formula

$(\text{NH}_2)_n \cdot 31.9 \text{ g} \cdot \text{mol}^{-1} \div 16.02 \text{ g} \cdot \text{mol}^{-1} = 1.99$ , so the molecular formula is  $\text{N}_2\text{H}_4$ , which corresponds to the molecule known as hydrazine.

(b)



(c)

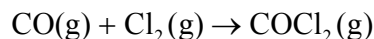
$$\begin{aligned} \frac{\text{rate}_A}{\text{rate}_B} &= \sqrt{\frac{M_B}{M_A}} \\ \frac{\frac{3.5 \times 10^{-4} \text{ mol}}{15.0 \text{ min}}}{\frac{X}{25.0 \text{ min}}} &= \sqrt{\frac{32.05 \text{ g} \cdot \text{mol}^{-1}}{17.03 \text{ g} \cdot \text{mol}^{-1}}} \\ X &= \left( \frac{3.5 \times 10^{-4} \text{ mol}}{15.0 \text{ min}} \right) (25.0 \text{ min}) \sqrt{\frac{17.03 \text{ g} \cdot \text{mol}^{-1}}{32.05 \text{ g} \cdot \text{mol}^{-1}}} \\ &= 4.2 \times 10^{-4} \text{ mol} \end{aligned}$$

**4.89** Using  $v_{rms}$  = root mean square speed and Equation 4.29 (the Maxwell Distribution of Speeds):

$$\begin{aligned} \frac{f(10v_{rms})}{f(v_{rms})} &= \frac{4\pi N \left( \frac{M}{2RT} \right)^{\frac{1}{2}} (10v_{rms})^2 e^{-M(10v_{rms})^2/2RT}}{4\pi N \left( \frac{M}{2RT} \right)^{\frac{1}{2}} (v_{rms})^2 e^{-M(v_{rms})^2/2RT}} \\ &= \frac{100v_{rms}^2 e^{-M100v_{rms}^2/2RT}}{v_{rms}^2 e^{-Mv_{rms}^2/2RT}} = 100e^{(-M100v_{rms}^2/2RT + Mv_{rms}^2/2RT)} \\ &= 100e^{-99Mv_{rms}^2/2RT} \end{aligned}$$

The ratio is not independent of temperature since the variable  $T$  appears in the denominator of a negative exponent on  $e$ . It makes sense that the ratio should become bigger at higher temperatures as the distribution spreads out such that the number of molecules with higher speeds increases while the number with lower speeds decreases.

**4.91** The gases react according to the equation:



(a) We can write the following relationship based upon the stoichiometry of the reaction:

$$P_{\text{final}} = P_{\text{final, CO}} + P_{\text{final, chlorine}} + P_{\text{final, phosgene}}$$

By the stoichiometry, we can write

$$P_{\text{final, phosgene}} = x$$

$$P_{\text{final, CO}} = P_{\text{initial, CO}} - x$$

$$P_{\text{final, chlorine}} = P_{\text{initial, chlorine}} - x$$

$$P_{\text{final}} = P_{\text{initial, CO}} - x + P_{\text{initial, CO}} - x + x = P_{\text{initial, CO}} + P_{\text{initial, CO}} - x$$

The initial pressures, however, must be adjusted to the new temperature:

$$P_{\text{initial, CO, 223}^\circ\text{C}} = (3.59 \text{ atm}) \left( \frac{500 \text{ K}}{298 \text{ K}} \right) = 6.02 \text{ atm}$$

$$P_{\text{initial, Cl}_2, 223^\circ\text{C}} = (2.75 \text{ atm}) \left( \frac{500 \text{ K}}{298 \text{ K}} \right) = 4.61 \text{ atm}$$

$$P_{\text{final}} = 6.02 \text{ atm} + 4.61 \text{ atm} - x = 9.75 \text{ atm}$$

$$x = 0.88 \text{ atm}$$

$$P_{\text{final, CO}} = 6.02 \text{ atm} - 0.88 \text{ atm} = 5.14 \text{ atm}$$

$$P_{\text{final, chlorine}} = 4.61 \text{ atm} - 0.88 \text{ atm} = 3.73 \text{ atm}$$

The mole fractions are proportional to the pressure so we can write

$$X_{\text{COCl}_2} = \frac{0.88}{9.75} = 0.090$$

$$X_{\text{CO}} = \frac{5.14}{9.75} = 0.527$$

$$X_{\text{Cl}_2} = \frac{3.73}{9.75} = 0.383$$

(b) The gas density will not change over the course of the reaction because the steel cylinder is a fixed size. The density can be calculated from the relationship

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

$$= \frac{PM}{RT}$$

We do not know the mass of samples added, nor the volume of the container, but we can calculate the density from the individual densities of the gases put into the cylinder initially. Because no mass is added or subtracted from the cylinder and its volume does not change, the density will be the same at the end of the reaction as at the beginning.

$$d_{\text{COCl}_2} = \frac{PM}{RT}$$

$$= \frac{(3.51 \text{ atm})(28.01 \text{ g} \cdot \text{mol}^{-1})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}$$

$$= 2.45 \text{ g} \cdot \text{L}^{-1}$$

$$d_{\text{Cl}_2} = \frac{(2.75 \text{ atm})(70.90 \text{ g} \cdot \text{mol}^{-1})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}$$

$$= 4.75 \text{ g} \cdot \text{L}^{-1}$$

$$d_{\text{total}} = 2.45 \text{ g} \cdot \text{L}^{-1} + 4.75 \text{ g} \cdot \text{L}^{-1} = 7.20 \text{ g} \cdot \text{L}^{-1}$$

One could do a similar calculation for all three gases at 500 K to obtain the same answer.

**4.93** The two scents will diffuse according to Eqn 4.19.

$$\frac{\text{rate}_{\text{fruity}}}{\text{rate}_{\text{minty}}} = \sqrt{\frac{M_{\text{C}_8\text{H}_{18}\text{O}_2}}{M_{\text{C}_{10}\text{H}_{20}\text{O}_2}}} = \sqrt{\frac{136}{172}} = 0.889$$

Let  $x$  = the distance traveled by ethyl octanoate (fruity) and  $y$  = the distance traveled by  $p$ -anisaldehyde (minty) in the same amount of time.

Then

$$x + y = 5 \text{ m} \quad \text{and} \quad \frac{x}{y} = \frac{0.889 \text{ m}}{1 \text{ m}}, \text{ or } x = 0.889y$$

Substituting for  $x$  gives



$$0.889y + y = 5$$

$$1.889y = 5$$

$$y = 2.65$$

So the fruity smell will travel  $5 - 2.65 = 2.35$  m in the same time that the minty smell will travel 2.65 m. A person must stand more than 2.35 m away from the north end of the room where the fruity smell originates in order to smell the minty scent first. (Note: the problem only gives 1 SF for the length of the room. If we round off to 1 SF for each distance, the answers are 2 m and 3 m respectively.)

**4.95** The molar mass calculation follows from the ideal gas law:

$$PV = nRT$$

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

$$M = \frac{mRT}{PV} = \frac{(1.509 \text{ g})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(473 \text{ K})}{\left(\frac{745 \text{ Torr}}{760 \text{ Torr} \cdot \text{atm}^{-1}}\right)(0.235 \text{ L})}$$

$$= 254 \text{ g} \cdot \text{mol}^{-1}$$

If the molecular formula is  $\text{OsO}_x$ , then the molar mass will be given by:

$$190.2 \text{ g} \cdot \text{mol}^{-1} + x(16.00 \text{ g} \cdot \text{mol}^{-1}) = 254 \text{ g} \cdot \text{mol}^{-1}$$

$$x = 3.99$$

The formula is  $\text{OsO}_4$ .

**4.97** In this problem, the volume, pressure, and molar mass of the substance stay constant. In order to calculate the new mass with the same conditions, we can resort to using the ideal gas equation rearranged to group the constant terms on one side of the equation:

$$PV = nRT$$

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

but  $M$ ,  $P$ , and  $V$  are constants, so we can write

$$\frac{MPV}{R} = mT$$

Now we have two sets of conditions, 1 and 2, for which  $\frac{MPV}{R}$  is constant

so we can set them equal:

$$m_1 T_1 = m_2 T_2$$

$$(46.2 \text{ g})(300. \text{ K}) = (m_2)(600. \text{ K}); \text{ therefore } m_2 = 23.1 \text{ g}$$

The mass of gas released must therefore be  $46.2 \text{ g} - 23.1 \text{ g} = 23.1 \text{ g}$ .

- 4.99** (a) volume of one atom = molar volume  $\div$  Avogadro's number

$$2.370 \times 10^{-2} \text{ L} \cdot \text{mol}^{-1} \div 6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1} = 3.936 \times 10^{-26} \text{ L} \cdot \text{atom}^{-1}$$

$$3.936 \times 10^{-26} \text{ L} \cdot \text{atom}^{-1} \times 1000 \text{ cm}^3 \cdot \text{L}^{-1} = 3.936 \times 10^{-23} \text{ cm}^3 \cdot \text{atom}^{-1}$$

$$3.936 \times 10^{-23} \text{ cm}^3 \cdot \text{atom}^{-1} \times (10^{10} \text{ pm} \cdot \text{cm}^{-1})^3 = 3.936 \times 10^7 \text{ pm}^3$$

$$3.936 \times 10^7 \text{ pm}^3 = \frac{4}{3} \pi r^3$$

$$r = 211 \text{ pm}$$

- (b) The atomic radius of He is 128 pm (Appendix 2D).

The volume of the He atom, based upon this radius, is

$$V = \frac{4}{3} \pi r^3$$

$$= \frac{4}{3} \pi (128 \text{ pm})^3$$

$$= 8.78 \times 10^6 \text{ pm}^3$$

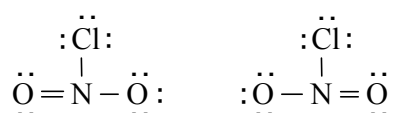
- (c) The difference in these values illustrates that there is no easy definition for the boundaries of an atom. The van der Waals value obtained from the correction for molar volume is considerably larger than the atomic radius, owing perhaps to longer range and weak interactions between atoms. One should also bear in mind that the value for the van der

Waals  $b$  is a parameter used to obtain a good fit to a curve, and its interpretation is more complicated than a simple molar volume.

**4.101** (a)  $\text{ClNO}_2$

(b)  $\text{ClNO}_2$

(c)



(d) trigonal planar

**4.103** (a) Substitute the van der Waals parameters for ammonia as well as the given values of  $n$ ,  $R$ ,  $P$ , and  $T$  into the vdW equation, then solve for  $V$ . Since the equation is cubic, solve graphically for the three roots or use an appropriate program such as Math Cad. Only one of the three roots is physically possible:

$$\begin{aligned} V^3 + n\left(\frac{RT + bP}{P}\right)V^2 + \left(\frac{n^2a}{P}\right)V - \frac{n^3ab}{P} &= 0 \\ V^3 + (0.505 \text{ mol}) & \\ \times \left( \frac{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K}) + (3.707 \text{ L} \cdot \text{mol}^{-1})(95.0 \text{ atm})}{(95.0 \text{ atm})} \right) V^2 & \\ + \left( \frac{(0.505 \text{ mol})^2 (4.225 \text{ L}^2 \cdot \text{atm} \cdot \text{mol}^{-2})}{(95.0 \text{ atm})} \right) V & \\ - \frac{(0.505 \text{ mol})^3 (4.225 \text{ L}^2 \cdot \text{atm} \cdot \text{mol}^{-2})(3.707 \text{ L} \cdot \text{mol}^{-1})}{(95.0 \text{ atm})} &= 0 \\ V^3 + (2.002 \text{ L})V^2 + (0.01134 \text{ L}^2)V - 0.02123 \text{ L}^3 &= 0 \\ V = -1.991, \text{ or } -0.1089, \text{ or } 0.09789 \text{ L} & \\ \text{but only the positive root is physically possible, so} & \\ V = 0.0979 \text{ L} & \end{aligned}$$

(b) Compare the volume calculated in part (a) to that of an ideal gas under the same conditions.

$$PV = nRT$$

$$V = \frac{(0.505 \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{95.0 \text{ atm}} = 0.130 \text{ L}$$

$V_{\text{ideal}} = 0.130 \text{ L} < V_{\text{vdW}} = 0.0979 \text{ L}$ . Attractive forces dominate because the van der Waals, or “real”, gas occupies less volume than the “ideal” gas. If the molecules are attracted to one another they will behave less independently, reducing the effective number of moles of gas.