William L Masterton
Cecile N. Hurley
Edward J. Neth

cengage.com/chemistry/masterton

Chapter 5
Gases

Edward J. Neth • University of Connecticut

Outline

- Measurements on Gases
- The Ideal Gas Law
- Gas Law Calculations
- Stoichiometry of Gaseous Reactions
- Gas Mixtures: Partial Pressures and Mole Fractions
- Kinetic Theory of Gases
- Real Gases

Introduction to Gases

- Gases have been known to exist since ancient times
  - The Greeks considered gases one of the four fundamental elements of nature
- 18th Century
  - Lavoisier, Cavendish and Priestley: Air is primarily nitrogen and oxygen, with trace components of argon, carbon dioxide and water vapor

Current Interest

- Gases in the news
  - Ozone depletion in the stratosphere
  - Carbon dioxide and global warming

State Variables

- State variables describe the state of a system under study
- To specify the state of a gas, four quantities must be known
  - Volume
  - Amount
  - Temperature
  - Pressure

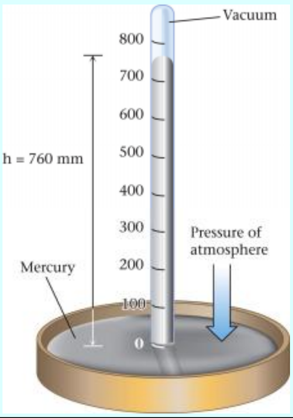
Volume, Amount and Temperature

- A gas expands uniformly to fill the container in which it is placed
  - The volume of the container is the volume of the gas
  - Volume may be in liters, mL, or cm^3
- The temperature of a gas must be indicated on the Kelvin scale
  - Recall that $K = {}^{\circ}C + 273.15$
- Amount of a gas is the number of moles

Pressure

- Pressure is force per unit area
  - In the English system, pounds per square inch or psi
  - Atmospheric pressure is about 14.7 psi

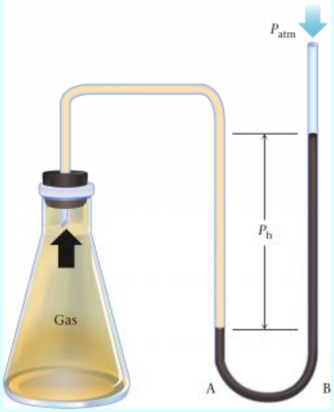
Measuring Pressure – The Barometer



The Barometer

- The barometer measures pressure in terms of the height of a column of liquid mercury
  - The atmosphere exerts a force on a pool of mercury, causing it to rise
  - One standard atmosphere of pressure is a column of mercury 760 mm high
  - Mercury is used to keep the column a manageable height

The Manometer



Gas Pressure Measurement

- The manometer measures gas pressure by differential
  - The height of the column of liquid is proportional to the pressure
  - Gas pressure can be more or less than atmospheric pressure

Other Units of Pressure

- 1 atm = 14.7 psi
- 1 atm = 760 mmHg
  - The mmHg is also called the torr after Torricelli, inventor of the barometer
- SI unit of measurement, the pascal (Pa)
  - 1 Pa is the pressure exerted by a 0.1 mm high film of water on the surface beneath it
  - The bar = 10^5 Pa
  - 1.013 bar = 1 atm = 760 mmHg = 14.7 psi = 101.3 kPa

Example 5.1

EXAMPLE 5.1

At room temperature, dry ice (solid CO_2) becomes a gas. At 77°F, 13.6 oz of dry ice are put into a steel tank with a volume of 10.00 ft³. The tank's pressure gauge registers 11.2 psi. Express the volume (*V*) of the tank in liters, the amount of CO_2 in grams and moles (*n*), the temperature (*T*) in °C and K and the pressure (*P*) in bars, mm Hg, and atmospheres.

ANALYSIS

Information given:	volume (10.00 ft³); pressure (11.2 psi); temperature (77°F); mass of CO_2 (13.6 oz)
Information implied:	molar mass of CO_2 Table 1.3: conversion factors for volume and mass formulas for temperature conversion from °F to °C and from °C to K
Asked for:	volume in L pressure in atm, mm Hg, and bar temperature in °C and K moles of CO_2

continued

Example 5.1, (Cont'd)

STRATEGY

1. Find the necessary conversion factors.
2. Use the temperature conversion formula.
3. Convert oz to grams and use the molar mass of CO_2 as a conversion factor.

   oz → g → mol

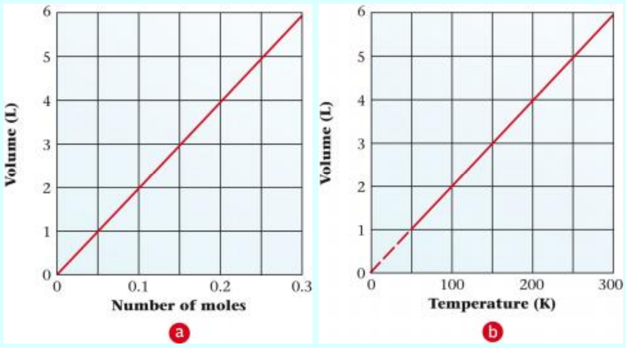
SOLUTION

volume in L	$10.00\ \text{ft}^3 \times \frac{28.32\ \text{L}}{1\ \text{ft}^3} = 283.2\ \text{L}$
pressure in atm	$11.2\ \text{psi} \times \frac{1\ \text{atm}}{14.7\ \text{psi}} = 0.762\ \text{atm}$
pressure in mm Hg	$11.2\ \text{psi} \times \frac{1\ \text{atm}}{14.7\ \text{psi}} \times \frac{760\ \text{mm Hg}}{1\ \text{atm}} = 579\ \text{mm Hg}$
pressure in bar	$11.2\ \text{psi} \times \frac{1.013\ \text{bar}}{14.7\ \text{psi}} = 0.772\ \text{bar}$
temperature in °C	°F = 1.8(°C) + 32; 77° = 1.8(°C) + 32°C; °C = 25°C
temperature in K	K = (°C) + 273.15; K = 25°C + 273.15 = 298 K
mol CO_2	$13.6\ \text{oz} \times \frac{1\ \text{g}}{0.03527\ \text{oz}} \times \frac{1\ \text{mol}}{44.01\ \text{g}} = 8.77\ \text{mol}$

The Ideal Gas Law

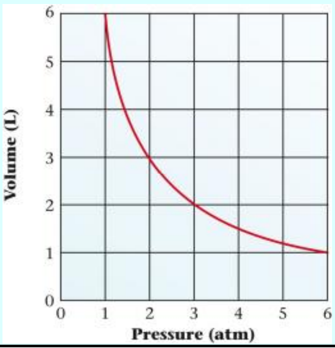
1. Volume is directly proportional to amount
   - $V = k_1 n$ (constant T, P)
2. Volume is directly proportional to absolute temperature
   - $V = k_2 T$ (constant n, P)

Figure 5.3



The Ideal Gas Law

3. Volume is inversely proportional to pressure
   - $V = k_3/P$ (constant n, T)



Temperature Effects – Charles's Law

The Ideal Gas Law

- Collect k_1, k_2 and k_3 into a new constant
- PV = nRT
- R is the gas constant
- Units of R:

$$R = 0.0821 \frac{L \cdot atm}{mol \cdot K}$$

Table 5.1 – Units of R

TABLE 5.1 Values of *R* in Different Units

Value	Where Used	How Obtained
$0.0821 \frac{L \cdot atm}{mol \cdot K}$	Gas law problems with *V* in liters, *P* in atm	From known values of *P*, *V*, *T*, *n*
$8.31 \frac{J}{mol \cdot K}$	Equations involving energy in joules	1 L · atm = 101.3 J
$8.31 \times 10^3 \frac{g \cdot m^2}{s^2 \cdot mol \cdot K}$	Calculation of molecular speed (page 142)	$1\ J = 10^3 \frac{g \cdot m^2}{s^2}$

Standard Temperature and Pressure

- STP
  - 1 atm P
  - 273 K
- At STP, the molar volume of a gas can be calculated as follows:

$$V = \frac{nRT}{P} = \frac{1.00\ mol \times 0.0821 \frac{L \cdot atm}{mol \cdot K} \times 273\ K}{1.00\ atm} = 22.4\ L$$

Gas Law Calculations

- Final and initial state problems
- Single-state problems
- Density or molar mass problem

Final and Initial State Problems

- In this type of problem, a gas undergoes a change from its initial to its final state
- The ideal gas equation is written twice, once for the initial state (1) and once for the final state (2)

Example 5.2

EXAMPLE 5.2

A sealed 15.0-L steel tank is used to deliver propane (C_3H_8) gas. It is filled with 24.6 g of propane at 27°C. The pressure gauge registers 0.915 atm. (Assume that the expansion of steel from an increase in temperature is negligible.)

a. If the tank is heated to 58°C, what is the pressure of propane in the tank?

b. The tank is fitted with a valve to open and release propane to maintain the pressure at 1.200 atm. Will heating the tank to 58°C release propane?

c. At 200°C, the pressure exceeds 1.200 atm. How much propane is released to maintain 1.200 atm pressure?

(a)

ANALYSIS

Information given:	*V* (15.0 L); *P* (0.915 atm); *T* (27°C); mass of propane (24.6 g); *T* (27°C); *T* (58°C)
Information implied:	2 sets of conditions for temperature
Asked for:	pressure after the temperature is increased

STRATEGY

1. Given two sets of conditions, you need to use the formula for initial state-final state conditions.
2. A sealed steel tank implies that the number of moles and the volume are kept constant.
3. Make sure all temperatures are in K.

SOLUTION

P_2

$$\frac{V_1P_1}{n_1T_1} = \frac{V_2P_2}{n_2T_2} \rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2} \rightarrow \frac{0.915}{27 + 273} = \frac{P_2}{58 + 273} \rightarrow P_2 = 1.01\ atm$$

Example 5.2, (Cont'd)

(b)

ANALYSIS	
Information given:	from part (a): P (1.01 atm); T (58°C); condition for valve to open (1.200 atm pressure)
Asked for:	Will the valve open?

SOLUTION		
Will the valve open?	Valve opens at 1.200 atm. 1.01 (from part (a)) < 1.200	The valve will not open.

continued

Example 5.2, (Cont'd)

(c)

ANALYSIS	
Information given:	V (15.0 L); P (0.915 atm); T (27°C); mass of propane (24.6 g) P (1.200 atm); T (200°C)
Information implied:	2 sets of conditions for temperature and pressure
Asked for:	mass of propane released

STRATEGY

1. Convert grams of propane to moles and temperatures in °C to K.
2. Given two sets of conditions, you need to use the formula for initial state-final state conditions to find the number of moles of propane related to the second set of conditions.
3. The steel tank implies that the volume is kept constant.

SOLUTION	
c) mol C_3H_8 initially (n_1)	$24.6\text{ g} \times \frac{1\text{ mol}}{44.1\text{ g}} = 0.558\text{ mol}$
Initial conditions	$P_1 = 0.915$ atm; $T_1 = 27°C + 273 = 300$ K; $n_1 = 0.558$ mol; $V_1 = 15.0$ L
Final conditions	$P_2 = 1.200$ atm; $T_2 = 200°C + 273 = 473$ K; $n_2 = ?$; $V_2 = 15.0$ L
n_2	$\frac{V_1P_1}{n_1T_1} = \frac{V_2P_2}{n_2T_2} \rightarrow \frac{0.915}{0.558 \times 300} = \frac{1.200}{n_2 \times 473}$; $n_2 = 0.464$ mol
Mass C_3H_8 in the tank	(0.464 mol)(44.1 g/mol) = 20.5 g
Mass to be released	24.6 − 20.5 = 4.1 g

END POINT

Note that the volume of the tank is never used in the calculations. It is important not only to read the problem carefully but also to visualize the description of the gas container. If the gas were in a balloon, instead of in a steel tank, the calculations would be different.

Single state problems – Calculating P, V, n or T

- In this type of problem, one of the state variables is not known
- The ideal gas equation can be solved for the unknown
- Take care to follow the units through the calculation!

Example 5.3

EXAMPLE 5.3

Sulfur hexafluoride is a gas used as a long-term tamponade (plug) for a retinal hole to repair detached retinas in the eye. If 2.50 g of this compound is introduced into an evacuated 500.0-mL container at 83°C, what pressure in atmospheres is developed?

continued

Example 5.3 (Cont'd)

(c)

ANALYSIS	
Information given:	V (15.0 L); P (0.915 atm); T (27°C); mass of propane (24.6 g) P (1.200 atm); T (200°C)
Information implied:	2 sets of conditions for temperature and pressure
Asked for:	mass of propane released

STRATEGY

1. Convert grams of propane to moles and temperatures in °C to K.
2. Given two sets of conditions, you need to use the formula for initial state-final state conditions to find the number of moles of propane related to the second set of conditions.
3. The steel tank implies that the volume is kept constant.

SOLUTION	
c) mol C_3H_8 initially (n_1)	$24.6\text{ g} \times \frac{1\text{ mol}}{44.1\text{ g}} = 0.558\text{ mol}$
Initial conditions	$P_1 = 0.915$ atm; $T_1 = 27°C + 273 = 300$ K; $n_1 = 0.558$ mol; $V_1 = 15.0$ L
Final conditions	$P_2 = 1.200$ atm; $T_2 = 200°C + 273 = 473$ K; $n_2 = ?$; $V_2 = 15.0$ L
n_2	$\frac{V_1P_1}{n_1T_1} = \frac{V_2P_2}{n_2T_2} \rightarrow \frac{0.915}{0.558 \times 300} = \frac{1.200}{n_2 \times 473}$; $n_2 = 0.464$ mol
Mass C_3H_8 in the tank	(0.464 mol)(44.1 g/mol) = 20.5 g
Mass to be released	24.6 − 20.5 = 4.1 g

END POINT

Note that the volume of the tank is never used in the calculations. It is important not only to read the problem carefully but also to visualize the description of the gas container. If the gas were in a balloon, instead of in a steel tank, the calculations would be different.

Molar Mass and Density

- Density = mass/volume
- Recall that the molar mass has units of grams (mass) per mole
- Now, look at the ideal gas law:
  - The number of moles appears
  - Moles, n, can be expressed as mass/MM
  - There is also a volume term in the ideal gas law

Rewriting the Ideal Gas Law in Density Terms

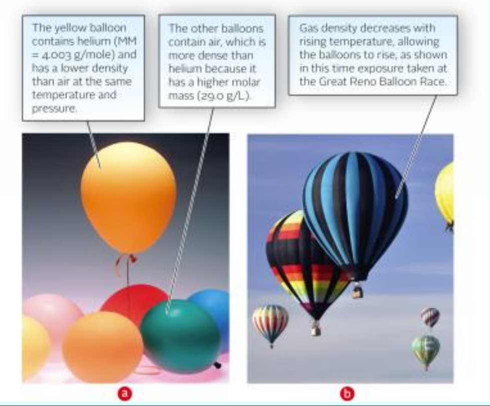
$$PV = \frac{m}{MM}RT$$

$$d = \frac{m}{V} = \frac{P \times MM}{R \times T}$$

Density of Gases

- Density is an intensive property
  - Does not depend on the amount of substance
- Density of a gas does depend on
  - Pressure
  - Temperature
  - Molar mass

Balloons



Example 5.4

EXAMPLE 5.4 GRADED

Acetone is widely used as a nail polish remover. A sample of liquid acetone is placed in a 3.00-L flask and vaporized by heating to 95°C at 1.02 atm. The vapor filling the flask at this temperature and pressure weighs 5.87 g.

(a) What is the density of acetone vapor under these conditions?

(b) Calculate the molar mass of acetone.

(c) Acetone contains the three elements, C, H, and O. When 1.000 g of acetone is burned, 2.27 g of CO_2 and 0.932 g of H_2O are formed. What is the molecular formula of acetone?

(a)

ANALYSIS

Information given:	volume of the flask (3.00 L); mass of acetone vapor (5.87 g)
Information implied:	volume of the vapor
Asked for:	density of acetone vapor

continued

Example 5.4, (Cont'd)

STRATEGY

1. Recall the formula for density (density = mass/volume).
2. A gas occupies the volume of the flask. Volume of vapor = volume of flask

SOLUTION

density	$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.87\text{ g}}{3.00\text{ L}} = 1.96\text{ g/L}$

(b)

ANALYSIS

Information given:	volume of the flask (3.00 L); mass of acetone vapor (5.87 g); pressure (P) (1.02 atm); temperature (T) (95°C)
Asked for:	molar mass of acetone

STRATEGY

1. To find molar mass you need to know mass and n (molar mass = mass/n). Mass is given.
2. Use the ideal gas law to find n ($n = PV/RT$).

SOLUTION

moles (n)	$n = \frac{PV}{RT} = \frac{(1.02\text{ atm} \times 3.00\text{ L})}{(95 + 273)\text{K} \times 0.0821(\text{L}\cdot\text{atm/mol}\cdot\text{K})} = 0.101\text{ mol}$
molar mass	$\text{molar mass} = \frac{\text{mass}}{n} = \frac{5.87\text{ g}}{0.101\text{ mol}} = 58.1\text{ g/mol}$

Example 5.4, (Cont'd)

(c)

ANALYSIS

Information given:	from part (b), molar mass of acetone (58.1 g/mol) The combustion of 1.00 g of sample yields 2.27 g CO_2 and 0.932 g H_2O.
Information implied:	mass of C, H, and O in 1.00-g sample
Asked for:	molecular formula of acetone

STRATEGY

1. Recall from Section 3.2 how to convert the mass of the product of combustion to the mass of the element.
2. Follow Figure 3.5 to obtain the simplest formula for the compound.
3. Compare the simplest formula's molar mass to the molar mass obtained in part (b).

continued

Example 5.4, (Cont'd)

SOLUTION	
Mass of each element	mass C: $2.27\ g\ CO_2 \times \frac{12.01\ g\ C}{44.01\ g\ CO_2} = 0.619\ g$
	mass H: $0.932\ g\ H_2O \times \frac{2(1.008)\ g\ H}{18.02\ g\ H_2O} = 0.104\ g$
	mass O = mass sample − (mass C + mass H) = 1.000 g − (0.619 + 0.104) g = 0.277 g
moles of each element	C: $\frac{0.619\ g}{12.01\ g/mol} = 0.0515$ mol; H: $\frac{0.104\ g}{1.008\ g/mol} = 0.103$ mol;
	O: $\frac{0.277\ g}{16.00\ g/mol} = 0.0173$ mol
Atomic ratios	C: $\frac{0.0515}{0.0173} = 3$; H: $\frac{0.104}{0.0173} = 6$; O: $\frac{0.0173}{0.0173} = 1$
Simplest formula	C_3H_6O
MM of simplest formula	3(12.01) + 6(1.008) + 16.00 = 58.08 g/mol
MM of vapor (from part (b))	58.1 g/mol
Molecular formula	C_3H_6O (simplest formula = molecular formula)

Stoichiometry in Gaseous Reactions

- Gases can participate as reactants or products in any chemical reaction
- Gases are balanced in the same way as liquids, solids, or aqueous solutions in chemical equations

Example 5.5

EXAMPLE 5.5

Hydrogen peroxide, H_2O_2, is a common bleaching agent. It decomposes quickly to water and oxygen gas at high temperatures.

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

How many liters of oxygen are produced at 78°C and 0.934 atm when 1.27 L of H_2O_2 ($d = 1.00$ g/mL) decompose?

continued

Example 5.5, (Cont'd)

ANALYSIS	
Information given:	temperature (78°C); pressure (0.934 atm) H_2O_2: volume (1.27 L); density (1.00 g/mL)
Information implied:	mass and molar mass of H_2O_2 stoichiometric ratio of O_2 to H_2O_2 (2 H_2O_2/1 O_2)
Asked for:	volume of oxygen

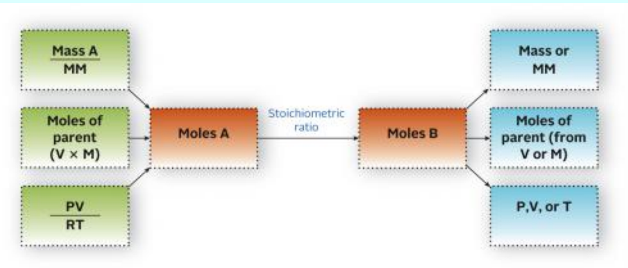
STRATEGY

1. Change °C to K and L of H_2O_2 to mL. (Density is given in g/mL.)
2. Find the mass of H_2O_2. Note that you cannot directly use the volume of H_2O_2 to calculate the volume of O_2 because H_2O_2 is NOT a gas.
3. Follow Figure 5.5.

$$\text{mass } H_2O_2 \xrightarrow{MM} \text{mol } H_2O_2 \xrightarrow[\text{ratio}]{\text{stoichiometric}} \text{moles } O_2 \xrightarrow{nRT/P} \text{volume of oxygen}$$

SOLUTION	
Mass H_2O_2	mass = (density)(volume) = (1.00 g/mL)(1.27 × 10³ mL) = 1.27 × 10³ g
Mol O_2	$1.27 \times 10^3\ g \times \frac{1\ mol\ H_2O_2}{34.02\ g} \times \frac{1\ mol\ O_2}{2\ mol\ H_2O_2} = 18.7\ mol$
Volume O_2	$V = \frac{nRT}{P} = \frac{(18.7\ mol)(0.0821\ L \cdot atm/mol \cdot K)(78 + 273)K}{0.934\ atm} = 576\ L$

Figure 5.5: Flow Chart for Stoichiometric Calculations Involving Gases



Example 5.6

EXAMPLE 5.6 GRADED

Sodium bicarbonate (baking soda) is widely used to absorb odors inside refrigerators. When acid is added to baking soda, the following reaction occurs:

$$NaHCO_3(s) + H^+(aq) \longrightarrow Na^+(aq) + CO_2(g) + H_2O$$

All experiments here are performed with 2.45 *M* HCl and 12.75 g of $NaHCO_3$ at 732 mm Hg and 38°C.

a. If an excess of HCl is used, what volume of CO_2 is obtained?
b. If $NaHCO_3$ is in excess, what volume of HCl is required to produce 2.65 L of CO_2?
c. What volume of CO_2 is produced when all the $NaHCO_3$ is made to react with 50.0 mL of HCl?

a

ANALYSIS	
Information given:	pressure (732 mm Hg); temperature (38°C); mass of $NaHCO_3$ (12.75 g)
Information implied:	molar mass of $NaHCO_3$ stoichiometric ratio: 1 $NaHCO_3$ /1 CO_2
Asked for:	volume of CO_2 produced

continued

Example 5.6, (Cont'd)

STRATEGY

1. Follow the flow chart in Figure 5.5.
2. Convert to appropriate units of pressure and temperature.

$$\text{mass}_{NaHCO_3} \xrightarrow{MM} n_{NaHCO_3} \xrightarrow[\text{ratio}]{\text{stoichiometric}} n_{CO_2} \xrightarrow{PV = nRT} V_{CO_2}$$

SOLUTION

mol CO_2 (n)	$12.75\text{ g } NaHCO_3 \times \frac{1\text{ mol}}{84.01\text{ g}} \times \frac{1\text{ mol } CO_2}{1\text{ mol } NaHCO_3} = 0.1518$
volume CO_2 (V)	$V = \frac{0.1518\text{ mol} \times 0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K} \times (273 + 38)\text{K}}{(732/760)\text{atm}} = 4.02\text{ L}$

(b)

ANALYSIS

Information given:	pressure (732 mm Hg); temperature (38°C); volume of CO_2 produced (2.65 L); molarity of HCl (2.45 M)
Information implied:	H^+ is the reacting species. HCl is the parent compound. stoichiometric ratio: 1 H^+/1 CO_2

Example 5.6, (Cont'd)

STRATEGY

Follow the flowchart in Figure 5.5.

$$V_{CO_2} \xrightarrow{PV = nRT} n_{CO_2} \xrightarrow[\text{ratio}]{\text{stoichiometric}} n_{H^+} \xrightarrow[\text{ratio}]{\text{atom}} n_{HCl} \xrightarrow{M} V_{HCl}$$

SOLUTION

mol CO_2	$n = \frac{2.65\text{ L} \times (732/760)\text{atm}}{0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K} \times (273 + 38)\text{K}} = 0.100$
mol HCl	$0.100\text{ mol } CO_2 \times \frac{1\text{ mol } H^+}{1\text{ mol } CO_2} \times \frac{1\text{ mol HCl}}{1\text{ mol } H^+} = 0.100$
Volume HCl	$\frac{0.100\text{ mol HCl}}{2.45\text{ mol/L}} = 0.0408\text{ L} = 40.8\text{ mL}$

(c)

ANALYSIS

Information given:	molarity of HCl (2.45 M); volume of HCl (50.0 mL); pressure (732 mm Hg); temperature (38°C)
Information implied:	H^+ is the reacting species. HCl is the parent compound. stoichiometric ratios: 1 H^+/1 CO_2; 1 $NaHCO_3$/1 CO_2 from part (a): mol $NaHCO_3$

continued

Example 5.6, (Cont'd)

STRATEGY

1. The presence of enough given data to calculate the number of moles of each reactant tells you that part (c) is a limiting reactant problem.
2. Follow the flow chart in Figure 5.5 to determine the number of moles of CO_2 obtained if HCl is limiting. You can obtain the moles of CO_2 if $NaHCO_3$ is limiting from part (a).
3. Compare the moles of CO_2 obtained using H^+ as the limiting reactant to the moles of CO_2 obtained using $NaHCO_3$ as the limiting reactant. Choose the smaller number of moles of CO_2.
4. Use the ideal gas law to convert mol CO_2 to the volume of CO_2.

SOLUTION

mol CO_2: $NaHCO_3$ limiting	from part (a): $0.1518\text{ mol } NaHCO_3 \times \frac{1\text{ mol } CO_2}{1\text{ mol } NaHCO_3} = 0.1518$
mol CO_2: HCl limiting	$(0.0500\text{ L} \times 2.45\text{ mol/L})\text{ mol HCl} \times \frac{1\text{ mol } H^+}{1\text{ mol HCl}} \times \frac{1\text{ mol } CO_2}{1\text{ mol } H^+} = 0.122\text{ mol}$
Theoretical yield of CO_2	$0.122 < 0.1518$; 0.122 mol CO_2 obtained
Volume CO_2	$V = \frac{0.122\text{ mol} \times 0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K} \times (273 + 38)\text{K}}{(732/760)\text{atm}} = 3.25\text{ L}$

END POINTS

1. When a problem comes in several parts, you may not need to use all the given information for each part.
2. You should also check to see whether you can use information that you obtained from the preceding parts for subsequent questions.

Figure 5.6: Stoichiometry of the Electrolysis of Water

Example 5.7

EXAMPLE 5.7 GRADED

Consider the reaction

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

a. What volume of $H_2(g)$ at 25°C and 1.00 atm is required to react with 1.00 L of $O_2(g)$ at the same temperature and pressure?
b. What volume of $H_2O(l)$ at 25°C and 1.00 atm ($d = 0.997$ g/mL) is formed from the reaction in (a)?
c. What mass of $H_2O(l)$ is formed from the reaction in (a), assuming a yield of 85.2%?

(a)

ANALYSIS

Information given:	volume O_2 (1.00 L); pressure (1.00 atm); temperature (25°C)
Information implied:	stoichiometric ratio: 1 mol O_2/2 mol H_2 Conditions of temperature and pressure are constant.
Asked for:	Volume of H_2 at constant T and P that reacts with O_2

STRATEGY

Use the law of combining volumes (T and P are constant).

$$V_{O_2} \xrightarrow[\text{ratio}]{\text{stoichiometric}} V_{H_2}$$

SOLUTION

volume of H_2	$1.00\text{ L } O_2 \times \frac{2\text{ L } H_2}{1\text{ L } O_2} = 2.00\text{ L } H_2$

continued

Example 5.7, (Cont'd)

(b)

ANALYSIS

Information given:	volume of $H_2O(l)$ (1.00 L); pressure (1.00 atm); temperature (25°C); density of water (0.997 g/mL)
Asked for:	Volume of water obtained

STRATEGY

1. The law of combining volumes cannot be used here because water is a liquid.
2. Use the ideal gas law to calculate the number of moles of O_2.
3. Follow the flowchart in Figure 5.5 to calculate the volume of water obtained.
4. Use the density of water to calculate its mass.

SOLUTION

Moles of O_2	$n_{O_2} = \frac{PV}{RT} = \frac{(1.00\text{ L})(1.00\text{ atm})}{(0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K})(273 + 25)\text{K}} = 0.0409$
Mass of water	$0.0409\text{ mol } O_2 \times \frac{2\text{ mol } H_2O}{1\text{ mol } O_2} \times \frac{18.02\text{ g } H_2O}{1\text{ mol}} = 1.47\text{ g}$
Volume of water	$V = \frac{\text{mass}}{\text{density}} = \frac{1.47\text{ g}}{0.997\text{ g/mL}} = 1.48\text{ mL}$

Example 5.7, (Cont'd)

c

ANALYSIS

Information given:	% yield (85.2%)
Information implied:	theoretical yield
Asked for:	mass of water obtained (actual yield)

STRATEGY

1. The mass obtained in part (b) is the theoretical yield.
2. Calculate actual yield from percent yield.

$$\%\ \text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

SOLUTION

Actual yield	$\text{actual yield} = \frac{\%\ \text{yield}}{100\%} \times \text{theoretical yield} = \frac{85.2\%}{100\%} \times 1.47\ \text{g} = 1.25\ \text{g}$

Gas Mixtures: Partial Pressures and Mole Fractions

- The ideal gas law applies to all gases, so it applies to mixtures of gases as well
- A new term is needed for a mixture of gases
  - Partial pressure, the part of the total pressure due to each gas in the mixture
  - Sum of the partial pressures is the total pressure

Dalton's Law of Partial Pressures

- The total pressure of a gas mixture is the sum of the partial pressures of the gases in the mixture
- Consider a mixture of hydrogen and helium:
  - P H_2 = 2.46 atm
  - P He = 3.69 atm
  - P total = 6.15 atm

Vapor Pressure

- The vapor pressure of a substance is the pressure of the gaseous form of that substance
  - Vapor pressure is an intensive property
  - Vapor pressure depends on temperature

Collecting a Gas Over Water

- When a gas is collected over water, the total pressure is the pressure of the gas plus the vapor pressure of water

a b

Wet Gases

- P H_2O is the vapor pressure of water
- P H_2O is dependent on temperature
- Consider H_2 gas collected over water:

$$P_{tot} = P_{H_2O} + P_{H_2}$$

Example 5.8

EXAMPLE 5.8

A student prepares a sample of hydrogen gas by electrolyzing water at 25°C. She collects 152 mL of H_2 at a total pressure of 758 mm Hg. Using Appendix 1 to find the vapor pressure of water, calculate

(a) the partial pressure of hydrogen.

(b) the number of moles of hydrogen collected.

ANALYSIS

Information given:	V_{H_2} (152 mL); pressure (758 mm Hg); temperature (25°C)
Information implied:	vapor pressure of water at 25°C (Appendix 1) Volume and temperature are constant.
Asked for:	(a) P_{H_2} (b) n_{H_2}

STRATEGY

(a) Recall that H_2 and $H_2O(g)$ contribute to the total pressure P_{tot}.

Use Dalton's law: $P_{tot} = P_1 + P_2 + \ldots$

(b) Use the ideal gas law to calculate n_{H_2} at P_{H_2}.

SOLUTION

(a) P_{H_2}

$P_{tot} = P_{H_2} + P_{H_2O}$

$P_{H_2} = 758 \text{ mm Hg} - 23.76 \text{ mm Hg} = 734 \text{ mm Hg}$

(b) n_{H_2}

$$n_{H_2} = \frac{P_{H_2}V}{RT} = \frac{[(734/760)\text{atm}](0.152\text{ L})}{(298\text{ K})(0.0821\text{ L}\cdot\text{atm/mol}\cdot\text{K})} = 0.00600 \text{ mol}$$

Partial Pressure and Mole Fraction

- One can rearrange the Ideal Gas Law for a mixture containing two gases, A and B

$$\frac{P_A}{P_{tot}} = \frac{n_A}{n_{tot}}$$

Mole Fraction

- The mole fraction of gas A is the number of moles of A divided by the total number of moles of gas in the mixture

$$X_A = \frac{n_A}{n_{tot}}$$

Dalton's Law and Mole Fraction

- The partial pressure of gas A is its mole fraction times the total pressure

$$P_A = X_A P_{tot}$$

Example 5.9

EXAMPLE 5.9

When one mole of methane, CH_4, is heated with four moles of oxygen, the following reaction occurs:

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

Assuming all of the methane is converted to CO_2 and H_2O, what are the mole fractions of O_2, CO_2, and H_2O in the resulting mixture? If the total pressure of the mixture is 1.26 atm, what are the partial pressures?

ANALYSIS

Information given:	P_{tot} (1.26 atm) Initial amounts of reactants (1.000 mol CH_4 and 4.000 mol O_2)
Information implied:	stoichiometric ratios: 2 mol O_2/1 mol CH_4/1 mol CO_2/2 mol H_2O limiting reactant (CH_4); reactant in excess (O_2)
Asked for:	mol fraction of each gas after reaction partial pressure of each gas after reaction

STRATEGY

1. Find the moles of reactants left after reaction. (Recall that CH_4 is limiting and thus is completely used up.)

$n_{CH_4} \xrightarrow[\text{ratio}]{\text{stoichiometric}} n_{O_2}$

n_{O_2} after reaction $= n_{O_2}$ initially $- n_{O_2}$ used

2. Find the moles of products.

$n_{CH_4} \xrightarrow[\text{ratio}]{\text{stoichiometric}} n_{CO_2}$ and $n_{CH_4} \xrightarrow[\text{ratio}]{\text{stoichiometric}} n_{H_2O}$

3. Find n_{tot}.

$n_{tot} = n_{CH_4} + n_{O_2} + n_{CO_2} + n_{H_2O}$

4. Find the mol fraction of each gas.

$X_A = \frac{n_A}{n_{tot}}$

5. Find the partial pressure of each gas.

$P_A = (X_A)(P_{tot})$

continued

Example 5.9, (Cont'd)

SOLUTION

1. mol CH_4	mol CH_4 = 0 (Problem states that CH_4 is completely used up.)
mol O_2 reacted	$1.000 \text{ mol } CH_4 \times \frac{2 \text{ mol } O_2}{1 \text{ mol } CH_4} = 2.000$
mol O_2 unreacted	4.000 mol O_2 initially − 2.000 mol reacted = 2.000 mol
2. mol CO_2	$1.000 \text{ mol } CH_4 \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } CH_4} = 1.000$ mol CO_2 are produced
mol H_2O	$1.000 \text{ mol } CH_4 \times \frac{2 \text{ mol } H_2O}{1 \text{ mol } CH_4} = 2.000$ mol H_2O are produced
3. n_{tot}	$n_{tot} = n_{CH_4} + n_{O_2} + n_{CO_2} + n_{H_2O} = 0 + 2.000 + 1.000 + 2.000 = 5.000$
4. X_{CH_4}	$X_{CH_4} = \frac{n_{CH_4}}{n_{tot}} = \frac{0}{5.000} = 0$
X_{O_2}	$X_{O_2} = \frac{n_{O_2}}{n_{tot}} = \frac{2.000}{5.000} = 0.4000$
X_{CO_2}	$X_{CO_2} = \frac{n_{CO_2}}{n_{tot}} = \frac{1.000}{5.000} = 0.2000$
X_{H_2O}	$X_{H_2O} = \frac{n_{H_2O}}{n_{tot}} = \frac{2.000}{5.000} = 0.4000$
5. P_{CH_4}	$(X_{CH_4})(P_{tot}) = (0)(1.26) = 0$
P_{O_2}	$(X_{O_2})(P_{tot}) = (0.4000)(1.26) = 0.504$ atm
P_{CO_2}	$(X_{CO_2})(P_{tot}) = (0.2000)(1.26) = 0.252$ atm
P_{H_2O}	$(X_{H_2O})(P_{tot}) = (0.4000)(1.26) = 0.504$ atm

END POINT

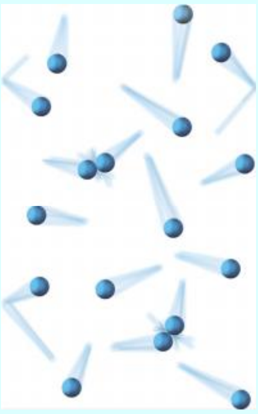
The mole fractions of all the gases should add up to 1. All the partial pressures should add up to 1.26 atm. They do!

Kinetic Theory of Gases

The kinetic-molecular model

1. Gases are mostly empty space. The total volume of the molecules is small
2. Gas molecules are in constant, random motion
3. Collisions of gas particles are elastic
4. Gas pressure is caused by collisions of molecules with the walls of the container

Figure 5.8 – The Kinetic Molecular Model



New Variables

- N, the number of gas particles
- m, the mass of the gas particle
- u, the average speed of a gas particle

Pressure and the Molecular Model

$$P = \frac{Nmu^2}{3V}$$

- Notes:
  - N/V is the concentration of gas particles
  - mu^2 is a measure of the energy of the collisions

Average Kinetic Energy of Translational Motion

$$E = \frac{3RT}{2N_A}$$

- Notes:
  - R is the gas constant
  - T is the Kelvin temperature
  - N_A is Avogadro's number

Results from Kinetic Energy of Translational Motion

- At a given temperature, all molecules of all gases have the same average kinetic energy of translational motion
- The average kinetic energy of a gas particle is directly proportional to the Kelvin temperature

Average Speed, u

$$u = \left(\frac{3RT}{MM}\right)^{\frac{1}{2}}$$

- The average speed is proportional to the square root of the Kelvin temperature
- The average speed is proportional to the inverse of the square root of the molar mass of the gas

Figure 5.9 – Ammonia and Hydrogen Chloride

Example 5.10

EXAMPLE 5.10

Calculate the average speed, u, of an N_2 molecule at 25°C.

ANALYSIS	
Information given:	temperature (25°C)
Information implied:	$R = 8.31 \times 10^3\ g \cdot m^2/s^2 \cdot mol \cdot K$ MM of N_2
Asked for:	average speed, u, of N_2 at 25°C

continued

Example 5.10 ,(Cont'd)

STRATEGY

1. Change T to the appropriate units.
2. Note the units of the constant R.
3. Substitute into the equation: $u = \left(\frac{3RT}{MM}\right)^{1/2}$

SOLUTION

Average speed	$u = \left(\frac{3 \times 8.31 \times 10^3 \frac{g \cdot m^2}{s^2 \cdot mol \cdot K} \times 298\ K}{28.02 \frac{g}{mol}}\right)^{1/2} = 515\ m/s$

END POINT

Converting the speed of the nitrogen molecule obtained above to miles per hour:

$$515 \frac{m}{s} \times \frac{1\ mi}{1.609 \times 10^3\ m} \times \frac{3600\ s}{1\ h} = 1.15 \times 10^3\ mi/h$$

Note that the average cruising speed of a Boeing 777 is about 580 mi/h and the speed of sound is 768 mi/h.

Effusion of Gases

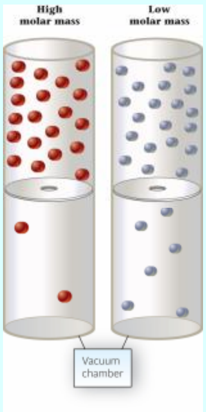
- Diffusion
  - Gases move through space from a region of high concentration to a region of low concentration
    - You can smell an apple pie baking as the particles responsible for the odor diffuse through the room
- Effusion
  - Gas particles will escape through a small hole (orifice) in a container
    - Air will slowly leak out of a tire or balloon through pores in the rubber

Graham's Law of Effusion

$$\frac{\text{rate of effusion of B}}{\text{rate of effusion of A}} = \left(\frac{MM_A}{MM_B}\right)^{\frac{1}{2}}$$

- The rate at which gas B escapes divided by the rate at which gas A escapes is equal to the square root of the ratio of the molar mass of gas A to gas B

Effusion of Gases



Example 5.11

EXAMPLE 5.11

In an effusion experiment, argon gas is allowed to expand through a tiny opening into an evacuated flask of volume 120 mL for 32.0 s, at which point the pressure in the flask is found to be 12.5 mm Hg. This experiment is repeated with a gas X of unknown molar mass at the same *T* and *P*. It is found that the pressure in the flask builds up to 12.5 mm Hg after 48.0 s. Calculate the molar mass of X.

ANALYSIS

Information given:	volume of both flasks (120 mL); pressure in both flasks (12.5 mm Hg); time for Ar effusion (32.0 s); time for gas (X) effusion (48.0 s)
Information implied:	Temperature, pressure, and volume are the same for both flasks. rate of effusion for each gas MM of argon
Asked for:	MM of X

STRATEGY

1. Since *T*, *P*, and *V* are the same for both gases, the number of moles of gas in both flasks is the same.

$$n_{Ar} = n_X = n$$

2. The rate of effusion is in mol/time.

$$\text{rate} = \frac{n_{Ar}}{\text{time}} = \frac{n_X}{\text{time}} = \frac{n}{\text{time}}$$

3. Substitute into Graham's law of effusion, where A = gas X and B = Ar.

$$\frac{\text{rate B}}{\text{rate A}} = \left(\frac{MM_A}{MM_B}\right)^{1/2} \longrightarrow \frac{\text{rate Ar}}{\text{rate X}} = \left(\frac{MM_X}{MM_{Ar}}\right)^{1/2}$$

Example 5.11, (Cont'd)

SOLUTION

rates	$\text{rate X} = \frac{n}{48.0\text{ s}} \qquad \text{rate Ar} = \frac{n}{32.0\text{ s}}$
MM_X	$\frac{\frac{n}{32.0\text{ s}}}{\frac{n}{48.0\text{ s}}} = \left(\frac{MM_X}{39.95\text{ g/mol}}\right)^{1/2} \longrightarrow 1.50 = \left(\frac{MM_X}{39.95\text{ g/mol}}\right)^{1/2}$
	$(1.50)^2 = \left(\left(\frac{MM_X}{39.95\text{ g/mol}}\right)^{1/2}\right)^2 \longrightarrow 2.25 = \frac{MM_X}{39.95\text{ g/mol}} \rightarrow MM_X = 89.9\text{ g/mol}$

END POINT

Since the unknown gas takes longer to effuse, it should have a larger molar mass than argon. It does!

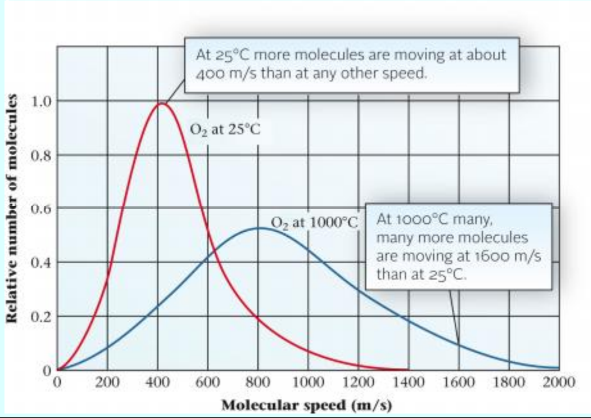
Gaseous Effusion and the Manhattan Project

- Effusion was used to separate U-238 from U-235
  - Recall that isotopes have the same chemical properties, and so cannot be separated by chemical means
- The mass of $^{238}UF_6$ is heavier than the mass of $^{235}UF_6$
  - Very small difference in mass
  - $^{235}UF_6$ effuses more quickly because of its smaller mass

Distribution of Molecular Speeds

- At a given temperature, gas particles will have a set of speeds, not a single fixed value for speeds
- Maxwell-Boltzmann Distribution

Figure 5.10: Distribution of Molecular Speed



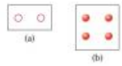
Distribution of Molecular Speeds

- Plot the fraction of molecules having a given speed vs. the molecular speed
- Curve that results has a maximum in the number of molecules with the given speed
  - Most probable speed
- As the temperature increases
  - The maximum shifts toward higher speed
  - The relative number of molecules at that speed decreases

Example 5.12

EXAMPLE 5.12 **CONCEPTUAL**

Consider the two boxes A and B shown below. Box B has a volume exactly twice that of box A. The circles ○ and ● represent one mole of HCl and He, respectively. The two boxes are at the same temperature.



(a) Compare the pressures of the gases in the two containers.
(b) Compare the densities of the two gases.
(c) Compare the number of atoms in the two boxes.
(d) If the HCl in box A were transferred to box B, what would be the mole fraction of HCl in the mixture?
(e) Which of the two gases effuses faster?

SOLUTION

(a) Since n/V and T are the same in both cases, $P = nRT/V$ is the same for the two gases.
(b) The mass of HCl is 2(36.5 g) = 73.0 g; that of He is 4(4.00 g) = 16.0 g. Since $73.0\ g/V > 16.0\ g/2V$, HCl has the higher density.
(c) Two moles of diatomic HCl contain the same number of atoms as four moles of He.
(d) $X_{HCl} = 2/6 = 1/3$
(e) Because HCl and He are at the same pressure, the lighter gas, He, effuses faster.

Real Gases

- Recall that the molar volume of a gas at STP is 22.4 L from the ideal gas law
- There are deviations from this volume that depend on the gas being studied
  - The molar volume of a real gas is less than that calculated by the ideal gas law

Table 5.2

TABLE 5.2 Real Versus Ideal Gases, Percent Deviation* in Molar Volume

	O_2			CO_2		
P(atm)	50°C	0°C	−50°C	50°C	0°C	−50°C
1	−0.0%	−0.1%	−0.2%	−0.4%	−0.7%	−1.4%
10	−0.4%	−1.0%	−2.1%	−4.0%	−7.1%	
40	−1.4%	−3.7%	−8.5%	−17.9%		
70	−2.2%	−6.0%	−14.4%	−34.2%	Condenses to liquid	
100	−2.8%	−7.7%	−19.1%	−59.0%		

*Percent deviation $= \frac{(V_m - V_m^\circ)}{V_m^\circ} \times 100\%$

Liquefaction of Gases

- All gases can be liquefied
  - Lowering the temperature
  - Increasing the pressure
- When a gas is liquefied, the attractive forces between gas particles becomes significant
- The closer a gas is to the liquid state, the more it will deviate from the ideal gas law

Two Factors for Real Gases

- Two factors are important to real gases
  1. The attractive forces between the gas particles
  2. The volume of the gas particles
- Both of these are ignored by the ideal gas law

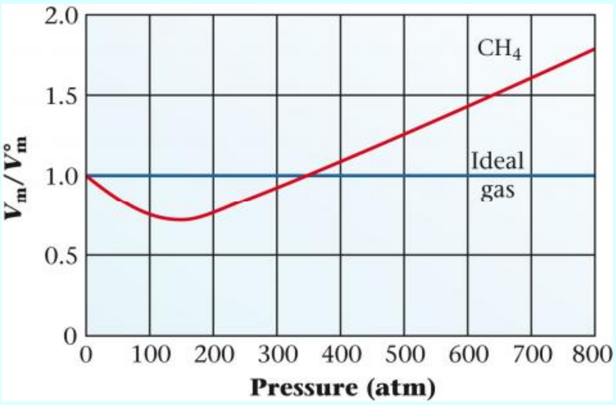
Attractive Forces

- Note that the observed molar volume for gases is lower than that calculated by the ideal gas law
  - The forces between particles pull the particles together
  - The volume occupied by the gas is then decreased
  - This is a negative deviation from the ideal gas law

Particle Volume

- Consider a plot of the observed molar volume/ideal molar volume for methane vs. pressure
  - Up to 150 atm, the deviation from ideality steadily increases
  - The volume of the gas particles becomes a more significant factor in determining the volume of the gas as the pressure increases

Figure 5.11 – Deviation from Ideal Volume



Key Concepts

1. Conversion between P, V, T and n
2. Use of the ideal gas law to:
   - Solve initial and final state problems
   - Solve single-state problems
   - Calculate the density or molar mass of a gas
   - Relate amounts of gases in reactions
3. Use Dalton's Law
4. Calculate the speed of gas molecules
5. Use Graham's Law to relate the rate of effusion to the molar mass of a gas