# CHEMISTRY

#### **Chapter 9 GASES**

Kevin Kolack, Ph.D. The Cooper Union HW problems: 5, 13, 15, 29, 35, 37, 53, 61, 75, 89, 101, 103





# CH. 9 OUTLINE



- 9.1 Gas Pressure
- 9.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law
- 9.3 Stoichiometry of Gaseous Substances, Mixtures, and Reactions
- 9.4 Effusion and Diffusion of Gases
- 9.5 The Kinetic-Molecular Theory
- 9.6 Non-Ideal Gas Behavior

#### CONCEPT MAP



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#### REVIEW: PHYSICAL CHARACTERISTICS OF GASES



- Gases assume the volume and shape of their containers.
- Gases are the most compressible state of matter.
- Gases will mix evenly and completely when confined to the same container.
- Gases have much lower densities than liquids and solids.



 $\mathsf{U}_2$  gas  $\mathsf{NO}_2$  gas



#### PRESSURE

#### Pressure =  $\frac{Force}{Area}$ Area

(force = mass x acceleration)

# Units of pressure

- 1 pascal (Pa) = 1  $N/m^2$  (SI unit)
- 1 atm =  $760 \text{ mmHg} = 760 \text{ torr}$
- 1 atm = 101,325 Pa
- 1 atm =  $101.325$  kPa
- 1 atm =  $1.01325$  bar
- 1 atm = 29.921" Hg
- 1 atm =  $14.7$  psi



#### PRESSURE VS. ALTITUDE (FIG 9.2)



(If you actually put a bowling ball on your thumb, the pressure experienced would be *twice* the usual pressure, and the sensation would be… unpleasant.) Stratosphere 12-50 km 31mi



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#### AMUSING COMPARISONS



pressure per elephant foot = 14,000 
$$
\frac{\text{lb}}{\text{elephant}} \times \frac{1 \text{ elephant}}{4 \text{ feet}} \times \frac{1 \text{ foot}}{250 \text{ in}^2} = 14 \text{ lb/in}^2
$$
  
\npressure per skate blade = 120  $\frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ blades}} \times \frac{1 \text{ blade}}{2 \text{ in}^2} = 30 \text{ lb/in}^2$   
\npressure per human foot = 120  $\frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ feet}} \times \frac{1 \text{ foot}}{30 \text{ in}^2} = 2 \text{ lb/in}^2$ 





#### **QUESTION**



The pressure outside an airplane flying at high altitude falls considerably below standard atmospheric pressure. Therefore, the air inside the cabin must be pressurized to protect the passengers…

What is the pressure in atmospheres in the cabin if the barometer reading is 688 mmHg?pressure = 688 mmHg $\times \frac{1 \text{ atm}}{760 \text{ mmH}}$ 

 $= 0.905$  atm

#### QUESTION



The atmospheric pressure in San Francisco on a certain day is 732 mmHg...

# What is the pressure in kPa?<br>pressure = 732 mmHg  $\times \frac{1.01325\times10^5 \text{ Pa}}{760 \text{ mmHg}}$

$$
= 9.76 \times 10^4
$$
 Pa

#### $= 97.6$  kPa

#### INSTRUMENTS TO MEASURE GAS PRESSURE

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# Barometers measure atmospheric pressure. Manometers measure (other) gas pressures.



A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (*h*) is a measure of the pressure. Mercury is usually used because of its large density.

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#### PUNCH LINE: 2 TYPES OF GAS PROBLEMS

# Fill in the blank

- PV=nRT
	- MUST use the correct units for R to work

# Initial conditions – final conditions

• Since  $PV = nRT$ , then  $PV/nT = constant$ 

• Therefore 
$$
\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}
$$

- Note that at constant n and T, we have Boyle's law
- At constant n and P, we have Charles' law
- At constant P and T, we have Avogadro's law
- Other than T, you can often get away with not converting units



## AMONTON'S LAW (~1700)



# P increases with T at constant V and n  $(Gay-Lussac -1800)$



 $P \alpha T$  *and thus*  $P/T \alpha 1$ 

 $P/T = constant$  $P_1/T_1 = P_2/T_2$ 

# Temperature **must** be in Kelvin (The origin of absolute 0.)

#### CHARLES' LAW

 $V_1/T_1 = V_2/T_2$ 





## CHARLES' LAW (CONT'D)

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display. Heating or cooling a gas at constant pressure





#### BOYLE'S LAW



20.0.9.80

20 25

When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since *P* and *V* are inversely proportional, a graph of  $\frac{1}{R}$  $\boldsymbol{P}$ vs. *V* is linear.

 $P \alpha$  1/V and thus PV  $\alpha$  1  $P$  x  $V = constant$  $P_1$  x  $V_1 = P_2$  x  $V_2$ 

(At constant temperature) (And constant amount of gas) <http://openstaxcollege.org/l/16atmospressur1>



#### FIGURE 9.9





 $(a)$ 





 $(c)$ 

In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.



Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

#### AVOGADRO'S LAW



Dependence of volume on amount of gas at constant temperature and pressure Gas cylinder Add gas molecules Remove gas (Volume decreases) (Volume increases) Valve

Avogadro's Law

#### AVOGADRO'S LAW (CONT'D)

V  $\alpha$  number of moles (n) and thus V/n  $\alpha$  1  $V/n = constant$  $V_1 / n_1 = V_2 / n_2$ 

# (At constant T) (And constant P)

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## (COMBINED) IDEAL GAS LAW



Boyle's law: 
$$
P \alpha \frac{1}{V}
$$
 (at constant n and T)

Charles's law:  $V \alpha T$  (at constant n and P) Guy-Lussac's law:  $P \alpha T$  (at constant n and V)

Avogadro's law:  $V \alpha$  n (at constant P and T)

 $PV \alpha nT$ 

 $PV = constant \times nT = nRT$ where R is the ideal gas constant

$$
PV = nRT
$$

#### **QUESTION**

Sulfur hexafluoride  $(SF_6)$ is a colorless and odorless gas.

Due to its lack of chemical reactivity, it is used as an insulator in electronic equipment.

Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a 5.43 L steel vessel at 69.5°C.



#### SOLUTION



Use the ideal gas law, converting the temperature to Kelvin.

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

 $=$   $\frac{(1.82 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(69.5 + 273) \text{K}}{0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol}}$ 5.43 L

 $= 9.42$  atm

#### QUESTION 5.5



An inflated helium balloon with a volume of 0.55 L (not pictured) at sea level (1.0 atm) is allowed to rise to a height of 6.5 km, where the pressure is about 0.40 atm.

Assuming that the temperature remains constant, what is the final volume of the balloon?



*A research He balloon.*

#### SOLUTION



The amount of gas inside the balloon and its temperature remain constant, but both the pressure and the volume change. What gas law do you need?<br> $\frac{P_1V_1}{p_1V_2} = \frac{P_2V_2}{p_2V_2}$ which is Boyle's law:

 $P_1V_1 = P_2V_2$ 

 $V_2 = V_1 \times \frac{P_1}{P_2}$ = 0.55 L $\times \frac{1.0 \text{ atm}}{0.40 \text{ atm}}$  $= 1.4 \; L$ 

*Check* When pressure applied on the balloon is reduced (at constant temperature), the helium gas expands and the balloon's volume increases. The final volume is greater than the initial volume, so the answer is reasonable.

#### QUESTION 5.6

Argon is an inert gas used in light bulbs to retard the vaporization of the tungsten filament.

A certain light bulb containing argon at 1.20 atm and 18.0°C is heated to 85°C at constant V.

Calculate the final P inside the bulb (in atm).





#### SOLUTION



**Strategy** The temperature and pressure of argon change but the amount and volume of gas remain the same.

What equation would you use to solve for the final pressure?  $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ 

which is Charles's law [see Equation (5.6)].

(What temperature unit should you use?)

 $P_2 = P_1 \times \frac{T_2}{T_1}$ = 1.20  $atm \times \frac{358 \text{ K}}{204 \text{ K}}$  $= 1.48$  atm

*Check* At constant volume, the pressure of a given amount of gas is directly proportional to its absolute temperature (ie- P goes up when T goes up). Therefore, the increase in pressure is reasonable.

#### SCUBA DIVING

760 mm Hg = 33 ft of water (density difference)



Since  $V\uparrow$  when P $\downarrow$ , small bubbles in the bloodstream become a big problem when surfacing.

#### QUESTION 5.7



A small bubble rises from the bottom of a lake, where the temperature and pressure are 8.0°C and 6.4 atm, to the water's surface, where the temperature is 25.0°C and the pressure is 1.0 atm.

Calculate the final volume (in mL) of the bubble if its initial volume was 2.1 mL. (Divers, beware!)

#### SOLUTION



According to the combined gas law:



We assume that the amount of air in the bubble remains constant, that is,  $n_1 = n_2$ so that:

$$
\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}
$$

 $T_1$  = (8 + 273) K = 281 K  $T_2 = (25 + 273)K = 298 K$ = 2.1 mL  $\times \frac{6.4 \text{ atm}}{1.0 \text{ atm}} \times \frac{298 \text{ K}}{281 \text{ K}}$  $=$  14 mL

#### STANDARD MOLAR VOLUME

The conditions 0 °C and 1 atm are called standard temperature and pressure (STP).

Experiments show that at STP, 1 mole of an ideal gas occupies 22.414 L.

 $PV = nRT$ 

 $R = \frac{PV}{r}$ nT = (1 atm)(22.414L) (1 mol)(273.15 K)

*R* = 0.082057 L • atm / (mol • K)







#### QUESTION

## Calculate the volume (in L) occupied by 7.40 g of NH3 at STP.



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 $NH<sub>3</sub>$ 

Recognizing that 1 mole of an ideal gas occupies 22.41 L at STP and using the molar mass of NH3 (17.03 g), we write the sequence of conversions as:

grams of NH<sub>3</sub>  $\longrightarrow$  moles of NH<sub>3</sub>  $\longrightarrow$  liters of NH<sub>3</sub> at STP

#### SOLUTION



# So the volume of  $NH<sub>3</sub>$  is given by

 $= 9.74 L$ 

Alternately, the problem can also be solved by first converting 7.40 g of NH<sub>3</sub> to number of moles of NH<sub>3</sub>, and then applying the ideal gas equation (*V* = *nRT*/*P*).

**Make sense?** Because  $7.40$  g of  $NH<sub>3</sub>$  is smaller than its molar mass, its volume at STP should be smaller than 22.41 L. Therefore, the answer is reasonable.

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#### GAS DENSITY, MW, & THE GAS LAWS



# Since  $d = m/V$  and  $V=nRT/P$  and  $MW = m/n$

$$
d = \frac{m}{V} = \frac{Pm}{nRT} = \frac{P(MW)}{RT}
$$

#### And thus, the molar mass (MW) of a gas is dRT P MW *=*

#### where d is the density of the gas in g/L

#### QUESTION

Calculate the density of carbon dioxide  $(CO_2)$ in grams per liter (g/L) at 0.990 atm and 55°C.

*T* = 273 + 55 = 328 K  $d = \frac{P\mathcal{M}}{P}$ **RT**  $(0.990 atm)$   $(44.01 g/mol)$  $(0.0821 L \cdot atm/K \cdot mol)(328 K)$  $= 1.62$  g/L

Alternately (preferably),

$$
V = \frac{nRT}{P}
$$
  
=  $\frac{(1 \text{ mol}) (0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol}) (328 \text{ K})}{0.990 \text{ atm}}$   
= 27.2 L

$$
d = \frac{44.01 \,\text{g}}{27.2 \,\text{L}} = 1.62 \,\text{g/L}
$$





#### **QUESTION**



Chemical analysis of a gaseous compound showed that it contained 33.0 percent silicon (Si) and 67.0 percent fluorine (F) by mass.

At 35°C, 0.210 L of the compound exerted a pressure of 1.70 atm.

If the mass of 0.210 L of the compound was 2.38 g, calculate the molecular formula of the compound.

#### SOLUTION



Assume that we have 100 g of the compound, so the percentages are converted to grams.

The number of moles of Si and F are given by

$$
n_{\text{Si}} = 33.0 \text{ g-Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g-Si}} = 1.17 \text{ mol Si}
$$
  

$$
n_{\text{F}} = 67.0 \text{ g-F} \times \frac{1 \text{ mol F}}{19.00 \text{ g-F}} = 3.53 \text{ mol F}
$$

Therefore, the empirical formula is  $Si<sub>1,17</sub>F<sub>3,53</sub>$ , or, dividing by the smaller subscript (1.17), we obtain  $\text{SiF}_3$ .

## SOLUTION (CONT'D)

openst To calculate the molar mass of the compound, we need first to calculate the number of moles contained in 2.38 g of the compound. From the ideal gas equation

$$
n = \frac{PV}{RT}
$$
  
= 
$$
\frac{(1.70 \text{ atm})(0.210 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(308 \text{ K})}
$$
 = 0.0141 mol

Because there are 2.38 g in 0.0141 mole of the compound, the mass in 1 mole, or the molar mass, is given by<br> $M = \frac{2.38 \text{ g}}{0.0141 \text{ mol}} = 169 \text{ g/mol}$ 

## SOLUTION (CONT'D)



- The molar mass of the empirical formula  $\mathsf{SiF}_3$  is 85.09 g.
- Recall that the ratio (molar mass/empirical molar mass) is always an integer  $(169/85.09 \approx 2)$ .
- Therefore, the molecular formula of the compound must be  $(SiF_3)_2$  or  $Si_2F_6$ .



#### DALTON'S LAW OF PARTIAL PRESSURES

At constant V and T, the total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases.

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If equal-volume cylinders containing gas A at a pressure of 300 kPa, gas B at a pressure of 600 kPa, and gas C at a pressure of 450 kPa are all combined in the samesize cylinder, the total pressure of the mixture is 1350 kPa.

#### **MOLE FRACTION AND PART**

Consider a case in which two gases, A and B, are in a container of volume V.

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 $P_{\rm A} =$ *nA*RT *V*  $P_{\rm B} =$  $n_{\textit{B}}$ RT *V*  $n_A$  is the number of moles of A  $n<sub>B</sub>$  is the number of moles of B  $P_{\text{T}} = P_{\text{A}} + P_{\text{B}}$   $X_{\text{A}} =$ *n*A  $n_A + n_B$  $X_{\rm B} =$  $n_{\rm B}$  $n_A + n_B$  $P_A = X_A P_T$   $P_B = X_B P_T$ 

$$
\boxed{P_i = X_i P_{\text{T}}} \quad \text{mole fraction } (X_i) = \frac{n_i}{n_T}
$$

#### QUESTION 5.14

A mixture of gases contains 4.46 moles of neon (Ne), 0.74 mole of argon (Ar), and 2.15 moles of xenon (Xe). need to find

Calculate the partial pressures of the gases if the total pressure is 2.00 atm (at constant T). 4.46 mol  $X_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{Ne}} + n_{\text{Ar}} + n_{\text{Xe}}} = \frac{4.46 \text{ mol}}{4.46 \text{ mol} + 0.74 \text{ mol} + 2.15 \text{ mol}}$ 

 $= 0.607$ 

 $P_{Ar} = X_{Ar}P_T$  $P_{Xe} = X_{Xe}P_T$  (or subtract)  $P_{\text{Na}} = X_{\text{Na}}P_T$  $= 0.607 \times 2.00$  atm  $= 0.10 \times 2.00$  atm  $= 0.293 \times 2.00$  atm  $= 1.21$  atm  $= 0.20$  atm  $= 0.586$  atm







#### COLLECTING A GAS OVER WATER



#### VAPOR PRESSURE OF H<sub>2</sub>O VS. T





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Table 9.2

#### QUESTION



- Oxygen gas generated by the decomposition of potassium chlorate is collected over water.
- 128 mL of gas is collected at 24°C and an atmospheric pressure of 762 mmHg.
- Calculate the mass (in grams) of oxygen gas obtained.
	- The pressure of the water vapor at 24°C is 22.4 mmHg.

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

$$
P_{\text{O}_2} = P_{\text{T}} - P_{\text{H}_2\text{O}}
$$
  
= 762 mmHg - 22.4 mmHg  $m = \frac{PV_{\text{M}}}{RT} = \frac{(740/760)\text{atm}(0.128 \text{ L}) (32.00 \text{ g/mol})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol}) (273 + 24) \text{ K}}$ 

 $= 0.164$  g

#### GAS STOICHIOMETRY

Given a balanced equation and the gas laws, it is possible to determine the amount (mass or volume) of any reactant required or product produced.



Chapter 3 mantra: grams to moles to moles to grams Now we are able to use V instead of g to start!

#### QUESTION

Calculate the volume of  $O<sub>2</sub>$  (in liters) required for the complete combustion of 7.64 L of acetylene  $(C_2H_2)$  measured at the same temperature and pressure.

 $2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l)$ 

volume of O<sub>2</sub> = 7.64 
$$
\angle C_2H_2 \times \frac{5 \angle O_2}{2 \angle C_2H_2}
$$
  
= 19.1 L





The reaction of calcium carbide (CaC<sub>2</sub>) with water produces acetylene  $(C_2H_2)$ , a flammable gas.

#### QUESTION

Sodium azide (NaN<sub>3</sub>) is used in some automobile air bags. The impact of a collision triggers the decomposition of NaN $_3$  as follows:

 $2\text{NaN}_3(s) \longrightarrow 2\text{Na}(s) + 3\text{N}_2(g)$ 

The nitrogen gas produced quickly inflates the bag between the driver and the windshield and dashboard.

Calculate the volume of  $N_2$ generated at 80.0°C and 823 mmHg by the decomposition of 60.0  $\breve{\mathsf{g}}$  of NaN $_3$ .





#### QUESTION 5.12 SOLUTION

**First, calculate number of moles of N<sub>2</sub> produced by COLLEGE** 60.0 g NaN<sub>3</sub> using the following sequence of conversions

grams of  $\text{NaN}_3 \longrightarrow$ moles of  $\text{NaN}_3 \longrightarrow$ moles of  $\text{N}_2$ 

moles of N<sub>2</sub> = 60.0 g NaN<sub>3</sub>  $\times \frac{1 \text{ mol-NaN}_3}{65.02 \text{ g NaN}_3} \times \frac{3 \text{ mol N}_2}{2 \text{ mol-NaN}_3}$  $=$  1.38 mol N<sub>2</sub>

The volume of 1.38 moles of  $N<sub>2</sub>$  can be obtained by using the ideal gas equation:

 $V = \frac{nRT}{P} = \frac{(1.38 \text{ mol}) (0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol}) (80 + 273 \text{ K})}{(823/760) \text{ atm}}$  $= 36.9 L$ 

#### QUESTION



Aqueous lithium hydroxide solution is used to purify air in spacecrafts and submarines because it absorbs carbon dioxide, which is an end product of metabolism, according to the equation

 $2LiOH(aq) + CO_2(g) \longrightarrow Li_2CO_3(aq) + H_2O(l)$ 

The pressure of carbon dioxide inside the cabin of a submarine having a volume of 2.4  $\times$  10<sup>5</sup> L is 7.9 × 10−3 atm at 312 K. A solution of lithium hydroxide (LiOH) of negligible volume is introduced into the cabin. Eventually the pressure of  $CO_2$  falls to 1.2 × 10<sup>-4</sup> atm. How many grams of lithium carbonate are formed by this process?

#### SOLUTION



The drop in  $CO<sub>2</sub>$  pressure is

 $(7.9 \times 10^{-3} \text{ atm})$  – (1.2 × 10<sup>-4</sup> atm) or 7.8 × 10<sup>-3</sup> atm

Therefore, the number of moles of CO $_{\rm 2}$  reacted is given by  $= 73$  mol

From the chemical equation, the ratio of carbon dioxide to lithium carbonate is

1 mol  $CO<sub>2</sub>$ : 1 mol  $Li<sub>2</sub>CO<sub>3</sub>$ so the amount of  $\mathsf{Li}_2\mathsf{CO}_3$  formed is also 73 moles. =  $5.4 \times 10^3$  g Li<sub>2</sub>CO<sub>3</sub>

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#### DIFFUSION



**Gas diffusion** is the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties.

#### Lighter is faster.



#### EFFUSION



Gas effusion is the process by which gas under pressure escapes from one compartment of a container to another by passing through a small opening.



Diffusion



Effusion

$$
\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}
$$

**Graham's law of effusion**: *The rate of effusion of a gas is inversely proportional to the square root of the mass of its particles*.

#### EXAMPLE 9.20

#### **Example 9.20**

#### **Applying Graham's Law to Rates of Effusion**

Calculate the ratio of the rate of effusion of hydrogen to the rate of effusion of oxygen.

#### **Solution**

From Graham's law, we have:

$$
\frac{\text{ate of effusion of ydrogen}}{\text{rate of effusion of xygen}} = \frac{\sqrt{1.43 \text{ g L}^{-1}}}{\sqrt{0.0899 \text{ g L}^{-1}}} = \frac{1.20}{0.300} = \frac{4}{1}
$$

Using molar masses:

rate of effusion of ydrogen  
rate of effusion of xygen = 
$$
\frac{\sqrt{32 \text{ g mol}^{-1}}}{\sqrt{2 \text{ g mol}^{-1}}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}
$$

Hydrogen effuses four times as rapidly as oxygen.

#### **Check Your Learning**

At a particular pressure and temperature, nitrogen gas effuses at the rate of 79 mL/s. Using the same apparatus at the same temperature and pressure, at what rate will sulfur dioxide effuse?



#### QUESTION

A flammable gas made up only of carbon and hydrogen is found to effuse through a porous barrier in 1.50 min.

Under the same conditions of temperature and pressure, it takes an equal volume of bromine vapor 4.73 min to effuse through the same barrier.

Calculate the molar mass of the unknown gas, and suggest what this gas might be.



**Effusion** 



#### SOLUTION



From the molar mass of  $Br<sub>2</sub>$ , we write

$$
\frac{1.50 \text{ min}}{4.73 \text{ min}} = \sqrt{\frac{\text{m}}{159.8 \text{ g/mol}}}
$$

Where  $\mathcal M$  is the molar mass of the unknown gas. Solving for  $\mathcal M$  we obtain

$$
\mathcal{M} = \left(\frac{1.50 \text{ min}}{4.73 \text{ min}}\right)^2 \times 159.8 \text{ g/mol}
$$
  
= 16.1 g/mol  
Because the molar mass of carbon is 12.01 g and

that of hydrogen is 1.008 g, the gas is methane  $(CH_4).$ 

#### EXAMPLE

#### Use of Diffusion for Nuclear Energy Applications: Uranium Enrichment

Gaseous diffusion has been used to produce enriched uranium for use in nuclear power plants and weapons. Naturally occurring uranium contains only 0.72% of  $^{235}$ U, the kind of uranium that is "fissile," that is, capable of sustaining a nuclear fission chain reaction. Nuclear reactors require fuel that is 2–5% <sup>235</sup>U, and nuclear bombs need even higher concentrations. One way to enrich uranium to the desired levels is to take advantage of

Graham's law. In a gaseous diffusion enrichment that is volatile enough to work) is slowly pump contain porous barriers with microscopic openi of the barrier is not evacuated. The  $^{235}$ UF<sub>6</sub> mol barrier a little faster than the heavier  $^{238}$ UF<sub>6</sub> mol enriched in  $^{235}$ UF<sub>6</sub> and the residual gas is slightly <sup>235</sup>UF<sub>6</sub> and <sup>238</sup>UF<sub>6</sub> only about 0.4% enrichment many diffusers in a sequence of stages (called a



Figure 9.30 In a diffuser, gaseous UF<sub>6</sub> is pumped through a porous barrier, which partially separates 235UF<sub>6</sub> from <sup>238</sup>UF<sub>6</sub> The UF<sub>6</sub> must pass through many large diffuser units to achieve sufficient enrichment in <sup>235</sup>U.

The large scale separation of gaseous 235UF<sub>6</sub> from 238UF<sub>6</sub> was first done during the World War II, at the atomic energy installation in Oak Ridge, Tennessee, as part of the Manhattan Project (the development of the first atomic bomb). Although the theory is simple, this required surmounting many daunting technical challenges to make it work in practice. The barrier must have tiny, uniform holes (about 10<sup>-6</sup> cm in diameter) and be porous enough to produce high flow rates. All materials (the barrier, tubing, surface coatings, lubricants, and gaskets) need to be able to contain, but not react with, the highly reactive and corrosive UF6.

Because gaseous diffusion plants require very large amounts of energy (to compress the gas to the high pressures required and drive it through the diffuser cascade, to remove the heat produced during compression, and so on), it is now being replaced by gas centrifuge technology, which requires far less energy. A current hot political issue is how to deny this technology to Iran, to prevent it from producing enough enriched uranium for them to use to make nuclear weapons.



# CH. 9 OUTLINE



- 9.1 Gas Pressure
- 9.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law
- 9.3 Stoichiometry of Gaseous Substances, Mixtures, and Reactions
- 9.4 Effusion and Diffusion of Gases
- **9.5 The Kinetic-Molecular Theory**
- 9.6 Non-Ideal Gas Behavior

## KINETIC-MOLECULAR THEORY (KMT)

- Openstington 1. Gases are composed of particles that are in continuous motion, travelling in straight lines and changing direction only when they collide with other particles or with the walls of a container.
- 2. The particles composing the gas are negligibly small compared to the distances between them. ("Gases are point masses." They possess mass but have negligible volume.)
- 3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
- 4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are perfectly elastic (do not involve a loss of energy).
- 5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas. ("Hotter is faster.")
	- KE is energy of motion, but is NOT the same as speed...

$$
KE = \frac{1}{2} m v^2
$$

#### KMT EXPLAINS THE GAS LAWS





#### MOLECULAR SPEEDS



The distribution of speeds for nitrogen gas molecules at four different temperatures

$$
u_{\rm rms} = \sqrt{\frac{3RT}{\mathcal{M}\mathcal{W}}}
$$

The distribution of speeds of five different gases at the same temperature







#### FIGURE 9.32



The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, *v*<sub>p</sub>, is a little less than 400 m/s, while the root mean square speed,  $u_{\rm rms}$ , is closer to 500 m/s.

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Chapter 5

Section 5.8



# CH. 9 OUTLINE



- 9.1 Gas Pressure
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#### DEVIATIONS FROM IDEAL BEHAVIOR





 $Z =$ *PV RT* measured A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law.

## DEVIATIONS (CONT'D)



What would be the effect of intermolecular (attractive) forces on the pressure exerted by a gas?

When would this happen?



Ideal Real Also, at high P (or small V), the volume of the particles begins to matter.



#### THE REAL GAS EQUATION



#### van der Waals Constants of Some Common Gases  $\mathbf b$  $\overline{a}$  $\text{atm} \cdot \textsf{L}^2$  $L$ Gas  $mol<sup>2</sup>$ mol He 0.034 0.0237 Ne 0.211 0.0171 Ar 1.34 0.0322 0.0398 Kr 2.32 4.19 0.0266 Xe  $H<sub>2</sub>$ 0.244 0.0266  $N_{2}$ 1.39 0.0391 0.0318  $O<sub>2</sub>$ 1.36  $Cl<sub>2</sub>$ 6.49 0.0562  $CO<sub>2</sub>$ 3.59 0.0427  $CH<sub>4</sub>$ 2.25 0.0428  $CCl<sub>4</sub>$ 20.4 0.138  $NH<sub>3</sub>$ 4.17 0.0371 0.0305  $H_2O$ 5.46

# *Van der Waals equation* nonideal gas

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

Correction for molecular attraction

on for volume of molecules

#### **QUESTION**



# Given that 3.50 moles of  $NH<sub>3</sub>$  occupy 5.20 L at 47°C, calculate the pressure of the gas (in atm) using

# (a) the ideal gas equation, and

# (b) the van der Waals equation.

#### SOLUTION



 $= 17.7$  atm

$$
\frac{an^2}{V^2} = \frac{(4.17 \text{ atm} \cdot L^2/\text{mol}^2) (3.50 \text{ mol})^2}{(5.20 \text{ L})^2} = 1.89 \text{ atm}
$$

 $nb = (3.50 \text{ mol}) (0.0371 \text{ L/mol}) = 0.130 \text{ L}$ 

 $(P + 1.89$  atm)  $(5.20 \text{ L} - 0.130 \text{ L}) = (3.50 \text{ mol})$   $(0.0821 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol})$  (320 K)

 $P = 16.2$  atm



#### HW problems: 5, 13, 15, 29, 35, 37, 53, 61, 75, 89, 101, 103

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