

# Chapter 05 Lecture **Outline**

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5-1

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## **Chapter 5**

**Gases and the Kinetic-Molecular Theory** 

#### **Gases and the Kinetic Molecular Theory**

- 5.1 An Overview of the Physical States of Matter
- **5.2 Gas Pressure and Its Measurement**
- 5.3 The Gas Laws and Their Experimental Foundations
- 5.4 Rearrangements of the Ideal Gas Law
- 5.5 The Kinetic-Molecular Theory: A Model for Gas Behavior
- 5.6 Real Gases: Deviations from Ideal Behavior



## An Overview of the Physical States of Matter

Distinguishing gases from liquids and solids.

- Gas volume changes significantly with pressure.
  - Solid and liquid volumes are not greatly affected by pressure.
- Gas volume changes significantly with temperature.
  - Gases expand when heated and shrink when cooled.
  - The volume change is 50 to 100 times greater for gases than for liquids and solids.
- Gases flow very freely.
- Gases have relatively low densities.
- Gases form a solution in any proportions.
  - Gases are freely miscible with each other.



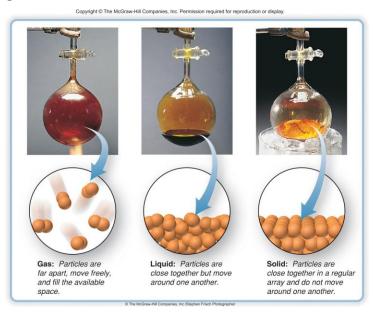


Figure 5.1 The three states of matter.

## **Gas Pressure and its Measurement**

Pressure = 
$$\frac{\text{force}}{\text{area}}$$

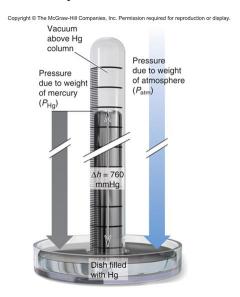
Atmospheric pressure arises from the force exerted by atmospheric gases on the earth's surface.

Atmospheric pressure decreases with altitude.

Figure 5.2 Effect of atmospheric pressure on a familiar object.



Figure 5.3 A mercury barometer.



#### **Table 5.1 Common Units of Pressure**

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Unit	Normal Atmospheric Pressure at Sea Level and 0°C
pascal (Pa); kilopascal (kPa)	1.01325×10 <sup>5</sup> Pa; 101.325 kPa
atmosphere (atm)	1 atm*
millimeters of mercury (mmHg)	760 mmHg*
torr	760 torr*
pounds per square inch (lb/in² or psi)	14.7 lb/in²
bar	1.01325 bar

<sup>\*</sup>This is an exact quantity; in calculations, we use as many significant figures as necessary.

## 5-9

#### Sample Problem 5.1

#### **Converting Units of Pressure**

**PROBLEM:** A geochemist heats a limestone (CaCO<sub>3</sub>) sample and collects the CO<sub>2</sub> released in an evacuated flask attached to a closed-end manometer. After the system comes to room temperature,  $\Delta h = 291.4$  mm Hg. Calculate the CO<sub>2</sub> pressure in torrs, atmospheres, and kilopascals.

**PLAN:** Construct conversion factors to find the other units of pressure.

SOLUTION: 291.4 mmHg x 
$$\frac{1 \text{torr}}{1 \text{ mmHg}}$$
 = 291.4 torr

291.4 torr x  $\frac{1 \text{ atm}}{760 \text{ torr}}$  = 0.3834 atm

0.3834 atm x  $\frac{101.325 \text{ kPa}}{1 \text{ atm}}$  = 38.85 kPa



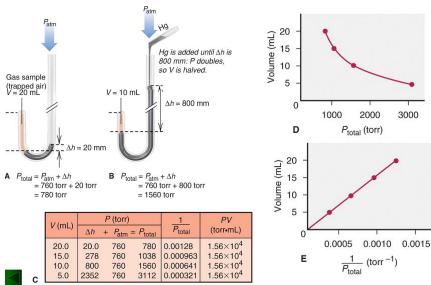
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## The Gas Laws

- The gas laws describe the physical behavior of gases in terms of 4 variables:
  - pressure (P)
  - temperature (T)
  - volume (V)
  - amount (number of moles, *n*)
- An ideal gas is a gas that exhibits linear relationships among these variables.
- No ideal gas actually exists, but most simple gases behave nearly ideally at ordinary temperatures and pressures.



Figure 5.4 Boyle's law, the relationship between the volume and pressure of a gas.



## Boyle's Law

At constant temperature, the volume occupied by a fixed amount of gas is *inversely* proportional to the external pressure.

$$V \propto \frac{1}{P}$$
 or  $PV = \text{constant}$ 

At fixed *T* and *n*, *P* decreases as *V* increases *P* increases as *V* decreases



Figure 5.5 AB Charles's law, the relationship between the volume and temperature of a gas.

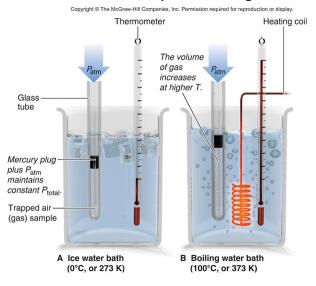
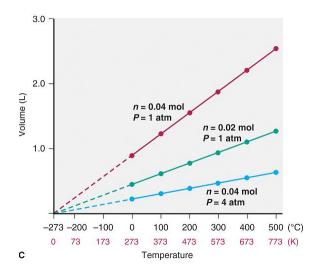


Figure 5.5 C Absolute zero (0 K) is the temperature at which an ideal gas would have a zero volume.





## Charles's Law

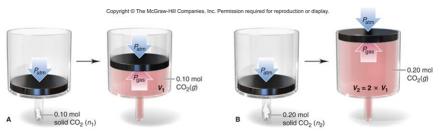
At constant pressure, the volume occupied by a fixed amount of gas is *directly* proportional to its absolute (Kelvin) temperature.

$$V \propto T$$
  $\frac{V}{T} = \text{constant}$ 

At fixed *P* and *n*, *V* inccreases as *T* increases *V* decreases as *V* decreases

Figure 5.6 The relationship between the volume and amount of a gas.

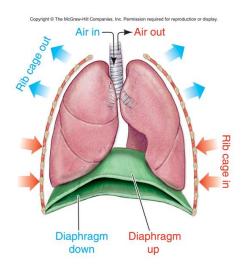
At fixed temperature and pressure, the volume occupied by a gas is directly proportional to the amount of gas.



**Avogadro's Law**: at fixed temperature and pressure, equal volumes of *any* ideal gas contain equal numbers of particles (or moles).



Figure 5.7 The process of breathing applies the gas laws.





9

### **Gas Behavior at Standard Conditions**

STP or standard temperature and pressure specifies a pressure of 1 atm (760 torr) and a temperature of 0°C (273.15 K).

The **standard molar volume** is the volume of 1 mol of an ideal gas at STP.

Standard molar volume = 22.4141 L or **22.4** L



Figure 5.8 Standard molar volume.

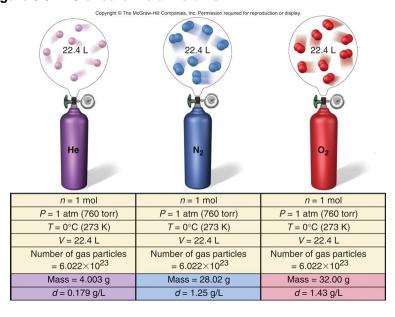


Figure 5.9 The volume of 1 mol (22.4 L) of an ideal gas and of some familiar objects: 1 gal of milk (3.79 L), a basketball (7.50 L) and 2.00 L of a carbonated drink.



## The Ideal Gas Law

$$pV = nRT$$

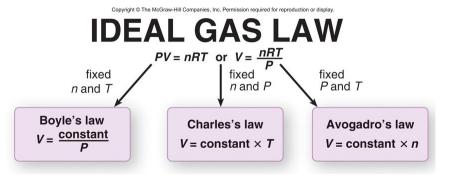
$$R = \frac{PV}{nT} = \frac{1 \text{ atm x } 22.414 \text{ L}}{1 \text{ mol x } 273.15 \text{ K}} = \frac{0.0821 \text{ atm-L}}{\text{mol-K}}$$

*R* is the universal gas constant; the numerical value of *R* depends on the units used.

The ideal gas law can also be expressed by the combined equation:

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

Figure 5.10 The individual gas laws as special cases of the ideal gas law.

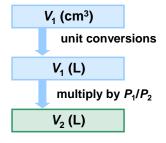




Sample Problem 5.2 **Applying the Volume-Pressure Relationship** 

PROBLEM: Boyle's apprentice finds that the air trapped in a J tube occupies 24.8 cm<sup>3</sup> at 1.12 atm. By adding mercury to the tube, he increases the pressure on the trapped air to 2.64 atm. Assuming constant temperature, what is the new volume of air (in L)?

PLAN: The temperature and amount of gas are fixed, so this problem involves a change in pressure and volume only.





#### **SOLUTION:**

$$P_1 = 1.12 \text{ atm}$$
  $P_2 = 2.64 \text{ atm}$   $V_1 = 24.8 \text{ cm}^3$   $V_2 = \text{unknown}$   $n \text{ and } T \text{ are constant}$ 

$$24.8 \text{ cm}^3 \times \frac{1 \text{ mL}}{1 \text{ cm}^3} \times \frac{L}{10^3 \text{ mL}} = 0.0248 \text{ L}$$

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

$$P_1 V_1 = P_2 V_2$$

$$V_2 = V_1 \times \frac{P_1}{P_2} = 0.0248 \text{ L} \times \frac{1.12 \text{ atm}}{2.46 \text{ atm}} = 0.0105 \text{ L}$$

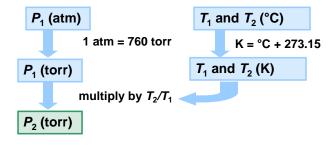
## 5-25

#### Sample Problem 5.3

## Applying the Pressure-Temperature Relationship

**PROBLEM:** A steel tank used for fuel delivery is fitted with a safety valve that opens when the internal pressure exceeds 1.00x10<sup>3</sup> torr. It is filled with methane at 23°C and 0.991 atm and placed in boiling water at exactly 100°C. Will the safety valve open?

**PLAN:** We must determine if the pressure will exceed 1.00x10<sup>3</sup> torr at the new temperature. Since the gas is in a steel tank, the volume remains constant.



#### **SOLUTION:**

$$P_1 = 0.991 \text{ atm}$$
  $P_2 = \text{unknown}$   $T_1 = 23^{\circ}\text{C}$   $T_2 = 100.^{\circ}\text{C}$   $n \text{ and } V \text{ are constant}$ 
 $0.991 \text{ atm } \times \frac{760 \text{ torr}}{1 \text{ atm}} = 753 \text{ torr}$   $T_1 = 23 + 273.15 = 296 \text{ K}$   $T_2 = 100. + 273.15 = 373 \text{ K}$ 

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

 $P_2 = P_1 \times \frac{T_2}{T_1} = 753 \text{ torr } \times \frac{373 \text{ K}}{296 \text{ K}} = 949 \text{ torr}$ 

**5-27** 

The safety valve will not open, since  $P_2$  is less than 1.00 x 10<sup>3</sup> torr.

## Sample Problem 5.4 | Applying the Volume-Amount Relationship

**PROBLEM:** A scale model of a blimp rises when it is filled with helium to a volume of 55.0 dm<sup>3</sup>. When 1.10 mol of He is added to the blimp, the volume is 26.2 dm<sup>3</sup>. How many more grams of He must be added to make it rise? Assume constant *T* and *P*.

**PLAN:** The initial amount of helium  $(n_1)$  is given, as well as the initial volume  $(V_1)$  and the volume needed to make it rise  $(V_2)$ . We need to calculate  $n_2$  and hence the mass of He to be added.

$$n_1$$
 (mol) of He

multiply by  $V_2/V_1$ 
 $n_2$  (mol) of He

subtract  $n_1$ 

mol to be added

multiply by  $\mathcal{M}$ 

g to be added

#### **SOLUTION:**

$$n_1 = 1.10 \text{ mol}$$
  $n_2 = \text{unknown}$   $V_1 = 26.2 \text{ dm}^3$   $V_2 = 55.0 \text{ dm}^3$   $V_3 = 55.0 \text{ dm}^3$   $V_4 = 26.2 \text{ dm}^3$   $V_5 = 55.0 \text{ dm}^3$   $V_6 = 1.10 \text{ mol } \times \frac{V_1}{n_1} = \frac{V_2}{n_2}$   $V_7 = 1.10 \text{ mol } \times \frac{55.0 \text{ dm}^3}{26.2 \text{ dm}^3}$   $V_8 = 2.31 \text{ mol He}$ 

Additional amount of He needed = 2.31 mol - 1.10 mol = 1.21 mol He

1.21 mol He x 
$$\frac{4.003 \text{ g He}}{1 \text{ mol He}}$$
 = 4.84 g He

## 5-29

#### Sample Problem 5.5

## Solving for an Unknown Gas Variable at Fixed Conditions

**PROBLEM:** A steel tank has a volume of 438 L and is filled with 0.885 kg of  $O_2$ . Calculate the pressure of  $O_2$  at 21°C.

**PLAN:** We are given *V*, *T* and mass, which can be converted to moles (*n*). Use the ideal gas law to find *P*.

**SOLUTION:** 
$$V = 438 \text{ L}$$
  $T = 21^{\circ}\text{C} = 294 \text{ K}$   $n = 0.885 \text{ kg O}_2 \text{ (convert to mol)}$   $P \text{ is unknown}$ 

$$0.885 \frac{\text{kg } O_2}{4} \times \frac{10^3 \text{g}}{4} \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 27.7 \text{ mol } O_2$$

$$P = \frac{nRT}{V} = \frac{27.7 \text{ mol } \times 0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 294.15 \frac{\text{K}}{\text{E}}}{438 \text{ L}}$$

Using Gas Laws to Determine a Balanced Equation

**PROBLEM:** The piston-cylinder is depicted before and after a gaseous reaction that is carried out at constant pressure. The temperature is 150 K before the reaction and 300 K after the reaction. (Assume the cylinder is insulated.)



Which of the following balanced equations describes the reaction?

$$(1) A_2(g) + B_2(g) \rightarrow 2AB(g)$$

(2) 
$$2AB(g) + B_2(g) \rightarrow 2AB_2(g)$$

(3) 
$$A(g) + B_2(g) \rightarrow AB_2(g)$$

$$(4) 2AB_2(g) + A_2(g) + 2B_2(g)$$

5-31

Sample Problem 5.6

**PLAN:** We are told that *P* is constant for this system, and the depiction shows that *V* does not change either. Since *T* changes, the volume could not remain the same unless the amount of gas in the system also changes.

**SOLUTION:** 
$$n_1 T_1 = n_2 T_2$$
  $\frac{n_2}{n_1} = \frac{T_1}{T_2} = \frac{150 \text{ K}}{300 \text{ K}} = \frac{1}{2}$ 

Since *T* doubles, the total number of moles of gas must halve – i.e., the moles of product must be half the moles of reactant. This relationship is shown by equation (3).

$$A(g) + B_2(g) \rightarrow AB_2(g)$$

## The Ideal Gas Law and Gas Density

The density of a gas is

- directly proportional to its molar mass and
- inversely proportional to its temperature.

density = 
$$\frac{m}{V}$$
 and moles =  $\frac{m}{\mathcal{M}}$ 

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

$$\frac{m}{V} = d = \frac{\mathcal{M} \times P}{RT}$$



#### Sample Problem 5.7

#### **Calculating Gas Density**

**PROBLEM:** Find the density (in g/L) of CO<sub>2</sub> (g) and the number of molecules per liter

(a) at STP and (b) at room conditions (20.°C and 1.00 atm).

**PLAN:** We can use the molar mass of CO<sub>2</sub> to find its density from the ideal gas equation.

**SOLUTION:** (a) At STP, or 273 K and 1.00 atm:

$$d = \frac{\mathcal{M} \times P}{RT} = \frac{44.01 \text{ g/mol} \times 1.00 \text{ atm}}{0.0821 \frac{\text{atm-L}}{\text{mol-K}} \times 273 \text{ K}} = 1.96 \text{ g/L}$$

= 2.68 x 10<sup>22</sup> molecules CO<sub>2</sub>/L

**SOLUTION:** (b) At 20.°C and 1.00 atm:

$$T = 20.$$
°C + 273.15 = 293 K

$$d = \frac{\mathcal{M} \times P}{RT} = \frac{44.01 \text{ g/mol} \times 1.00 \text{ atm}}{0.0821 \frac{\text{atm} \cdot L}{\text{mol-K}} \times 293 \text{ K}} = 1.83 \text{ g/L}$$

= 2.50 x 10<sup>22</sup> molecules CO<sub>2</sub>/L



### Molar Mass from the Ideal Gas Law

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

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

Finding the Molar Mass of a Volatile Liquid

PROBLEM:

An organic chemist isolates a colorless liquid from a petroleum sample. She places the liquid in a preweighed flask and puts the flask in boiling water, causing the liquid to vaporize and fill the flask with gas. She closes the flask and reweighs it. She obtains the following data:

$$T = 100.0$$
°C  $P = 754$  torr mass of flask = 77.834 g

Calculate the molar mass of the liquid.

**PLAN:** The variables V, T and P are given. We find the mass of the gas by subtracting the mass of the flask from the mass of the flask with the gas in it, and use this information to calculate  $\mathcal{M}$ .



Sample Problem 5.8

**SOLUTION:** m of gas = (78.416 - 77.834) = 0.582 g

$$V = 213 \text{ mL x} \frac{1 \text{ L}}{10^3 \text{ mL}} = 0.213 \text{ L}$$
  $T = 100.0 \text{ °C} + 273.15 = 373.2 \text{ K}$ 

$$P = 754 \text{ torr.} \times \frac{1 \text{ atm}}{760 \text{ torr.}} = 0.992 \text{ atm.}$$

$$\mathcal{M} = \frac{mRT}{PV} = \frac{0.582 \text{ g x } 0.0821 \frac{\text{atm-L}}{\text{mol-K}} \text{ x } 373 \text{ K}}{0.213 \text{ L x } 0.992 \text{ atm}} = 84.4 \text{ g/mol}$$

## **Mixtures of Gases**

- Gases mix homogeneously in any proportions.
  - Each gas in a mixture behaves as if it were the only gas present.
- The pressure exerted by each gas in a mixture is called its partial pressure.
- Dalton's Law of partial pressures states that the total pressure in a mixture is the sum of the partial pressures of the component gases.
- The partial pressure of a gas is proportional to its mole fraction:

$$P_{A} = X_{A} \times P_{\text{total}}$$
  $X_{A} = \frac{n_{A}}{n_{\text{total}}}$ 

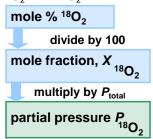


Sample Problem 5.9

**Applying Dalton's Law of Partial Pressures** 

**PROBLEM:** In a study of  $O_2$  uptake by muscle at high altitude, a physiologist prepares an atmosphere consisting of 79 mole %  $N_2$ , 17 mole %  $^{16}O_2$ , and 4.0 mole %  $^{18}O_2$ . (The isotope  $^{18}O$  will be measured to determine the  $O_2$  uptake.) The pressure of the mixture is 0.75 atm to simulate high altitude. Calculate the mole fraction and partial pressure of  $^{18}O_2$  in the mixture.

**PLAN:** Find  $X_{^{18}\text{O}_2}$  and  $P_{^{18}\text{O}_2}$  from  $P_{\text{total}}$  and mol %  $^{18}\text{O}_2$ .





#### **SOLUTION:**

$$X_{18O_2} = \frac{4.0 \text{ mol } \%^{18}O_2}{100} = 0.040$$

$$P_{^{18}\text{O}_2} = X_{^{18}\text{O}_2} \times P_{\text{total}} = 0.040 \times 0.75 \text{ atm}$$
 = **0.030 atm**



Table 5.2 Vapor Pressure of Water ( $P_{H_2O}$ ) + at Different T

T (°C)	P <sub>H₂</sub> O <sup>(torr)</sup>	T (°C)	P <sub>H2</sub> O(torr)
0	4.6	40	55.3
5	6.5	45	71.9
10	9.2	50	92.5
12	10.5	55	118.0
14	12.0	60	149.4
16	13.6	65	187.5
18	15.5	70	233.7
20	17.5	75	289.1
22	19.8	80	355.1
24	22.4	85	433.6
26	25.2	90	525.8
28	28.3	95	633.9
30	31.8	100	760.0
35	42.2		



The vapor pressure  $(P_{H,O})$  adds to  $P_{gas}$  to give  $P_{total}$ . Here, the water level in the vessel is above the level in the beaker, so  $P_{total} < P_{atm}$ .

Molecules of  $H_2O$  enter bubbles of gas.

Water-insoluble gaseous product bubbles through water into collection vessel until the water level in it equals the level in the beaker.

Plant equals  $P_{gas}$  plus  $P_{H,O}$  at the temperature of the experiment. Therefore,  $P_{gas} = P_{total} - P_{H,O}$ .

Figure 5.11 Collecting a water-insoluble gaseous product and determining its pressure.

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Sample Problem 5.10

Calculating the Amount of Gas Collected over Water

**PROBLEM:** Acetylene  $(C_2H_2)$  is produced in the laboratory when calcium carbide  $(CaC_2)$  reacts with water:

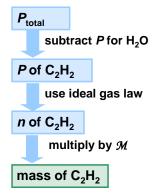
$$\mathsf{CaC}_2(s) \ + \ 2\mathsf{H}_2\mathsf{O}(\mathit{I}) \longrightarrow \ \mathsf{C}_2\mathsf{H}_2(\mathit{g}) \ + \ \mathsf{Ca}(\mathsf{OH})_2(\mathit{aq})$$

A collected sample of acetylene has a total gas pressure of 738 torr and a volume of 523 mL. At the temperature of the gas (23°C), the vapor pressure of water is 21 torr. How many grams of acetylene are collected?

**PLAN:** The difference in pressures will give P for the  $C_2H_2$ . The number of moles (n) is calculated from the ideal gas law and converted to mass using the molar mass.







#### **SOLUTION:**

$$P_{C_2H_2} = (738 - 21) \text{ torr} = 717 \text{ torr}$$

$$P = 717 \frac{1}{100} \times \frac{1}{100} \times \frac{1}{100} = 0.943 \text{ atm}$$

$$V = 523 \frac{1}{100} \times \frac{1}{100} = 0.523 \text{ L}$$

$$T = 23 \text{°C} + 273.15 \text{ K} = 296 \text{ K}$$

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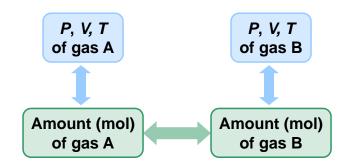
#### Sample Problem 5.10

#### **SOLUTION:**

$${}^{n}C_{2}H_{2} = \frac{PV}{RT} = \frac{0.943 \text{ atm.} \times 0.523 \text{ L}}{0.0821 \text{ atm.} \times 296 \text{ K}} = 0.0203 \text{ mol}$$

$$0.0203 \frac{\text{mol }}{\text{1 mol }} \times \frac{26.04 \text{ g C}_2 \text{H}_2}{1 \text{ mol }} = 0.529 \text{ g C}_2 \text{H}_2$$

## The Ideal Gas Law and Stoichiometry



**Figure 15.12** 

The relationships among the amount (mol, n) of gaseous reactant (or product) and the gas pressure (P), volume (V), and temperature (T).

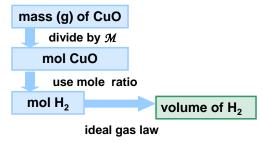


Sample Problem 5.11

Using Gas Variables to Find Amounts of Reactants and Products I

**PROBLEM:** What volume of H<sub>2</sub> gas at 765 torr and 225°C is needed to reduce 35.5 g of copper(II) oxide to form pure copper and water?

**PLAN:** Write a balanced equation. Convert the mass of copper (II) oxide to moles and find the moles of H<sub>2</sub>, using the mole ratio from the balanced equation. Calculate the corresponding volume of H<sub>2</sub> using the ideal gas law.



**SOLUTION:** 
$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$$

$$35.5 \frac{\text{g CuO}}{79.55 \frac{\text{g CuO}}{\text{g CuO}}} \times \frac{1 \text{ mol CuO}}{1 \text{ mol CuO}} = 0.446 \text{ mol H}_2$$

$$P = 765 \frac{\text{torr}}{\text{T}} \times \frac{1 \text{ atm}}{760 \frac{\text{torr}}{\text{T}}} = 1.01 \text{ atm}$$
  $T = 225 \text{°C} + 273.15 \text{ K} = 498 \text{ K}$ 

$$V = \frac{nRT}{P} = \frac{0.446 \text{ mol H}_2 \times 0.0821 \frac{\text{atm-L}}{\text{mol K}} \times 498 \text{ K}}{1.01 \text{ atm-}}$$
= 18.1 L H<sub>2</sub>



#### **Sample Problem 5.12**

## Using Gas Variables to Find Amounts of Reactants and Products II

**PROBLEM:** What mass of potassium chloride forms when 5.25 L of chlorine gas at 0.950 atm and 293 K reacts with 17.0 g of potassium metal?

**PLAN:** First we must write a balanced equation. Since the quantities of both reactants are given, we must next determine which reactant is limiting. We will use the ideal gas law to calculate the moles of Cl<sub>2</sub> present.

**SOLUTION:** The balanced equation is:

$$\text{Cl}_2(g) + 2\text{K}(s) \rightarrow 2\text{KCl}(s)$$

For 
$$Cl_2$$
:  
 $P = 0.950$  atm  $V = 5.25$  L  
 $T = 293$  K  $n = unknown$ 

$$n_{\text{Cl}_2} = \frac{PV}{RT} = \frac{0.950 \text{ atm} \times 5.25 \text{ L}}{0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293 \text{ K}} = 0.207 \text{ mol Cl}_2$$

For Cl<sub>2</sub>: 
$$0.207 \frac{\text{mol Cl}_2}{\text{1-mol Cl}_2} \times \frac{2 \text{ mol KCl}}{\text{1-mol Cl}_2} = 0.414 \text{ mol KCl}$$

For K: 
$$17.0 \frac{\text{g K}}{\text{g K}} \times \frac{1 \text{ mol K}}{39.10 \frac{\text{g K}}{\text{g K}}} \times \frac{2 \text{ mol KCl}}{2 \text{ mol K}} = 0.435 \text{ KCl}$$

Cl<sub>2</sub> is the limiting reactant.



# The Kinetic-Molecular Theory: A Model for Gas Behavior

#### Postulate 1:

Gas particles are tiny with large spaces between them. The volume of each particle is so small compared to the total volume of the gas that it is assumed to be zero.

#### Postulate 2:

Gas particles are in constant, random, straight-line motion except when they collide with each other or with the container walls.

#### Postulate 3:

Collisions are elastic, meaning that colliding particles exchange energy but do not lose any energy due to friction. Their *total kinetic energy is constant*. Between collisions the particles do not influence each other by attractive or repulsive forces.

Figure 5.13 Distribution of molecular speeds for  $N_2$  at three temperatures.

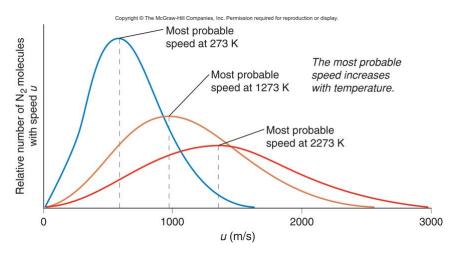




Figure 5.14 Pressure arises from countless collisions between gas particles and walls.

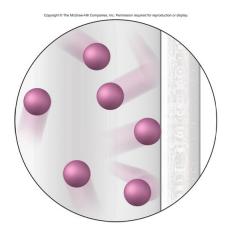


Figure 5.15 A molecular view of Boyle's law.

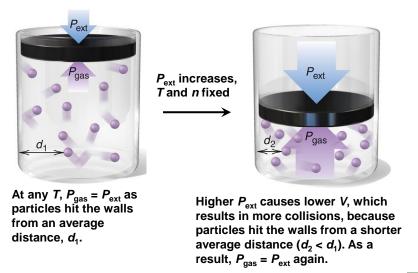
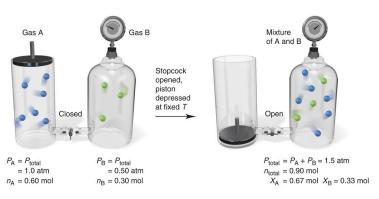


Figure 5.16 A molecular view of Dalton's law

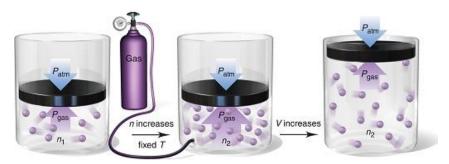


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Figure 5.17 A molecular view of Charles's law



Figure 5.18 A molecular view of Avogadro's law



For a given amount,  $n_1$ , of gas,  $P_{\text{gas}} = P_{\text{atm}}$ .

When gas is added to reach  $n_2$  the collision frequency of the particles increases, so  $P_{\rm gas}$ ,  $P_{\rm atm}$ .

As a result, V increases until  $P_{gas} = P_{atm}$  again.



## **Kinetic Energy and Gas Behavior**

At a given *T*, all gases in a sample have the same average kinetic energy.

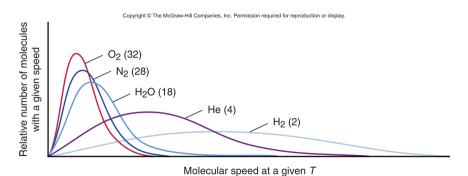
$$E_{\rm k} = \frac{1}{2}$$
 mass x speed<sup>2</sup>

Kinetic energy depends on both the mass and the speed of a particle.

At the same T, a <u>heavier</u> gas particle moves more slowly than a <u>lighter</u> one.



Figure 5.19 The relationship between molar mass and molecular speed.





### Graham's Law of Effusion

**Effusion** is the process by which a gas escapes through a small hole in its container into an evacuated space.

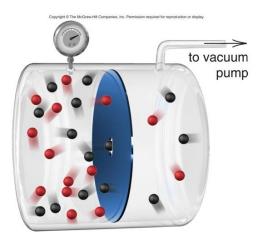
**Graham's law of effusion** states that the rate of effusion of a gas is inversely proportional to the square root of its molar mass.

A lighter gas moves more quickly and therefore has a higher rate of effusion than a heavier gas at the same T.

Rate of effusion 
$$\infty \frac{1}{\sqrt{\mathcal{M}}}$$

5-61

Figure 5.20 Effusion. Lighter (*black*) particles effuse faster than heavier (*red*) particles.



**Applying Graham's Law of Effusion** 

**PROBLEM:** A mixture of helium (He) and methane (CH<sub>4</sub>) is placed in an effusion apparatus. Calculate the ratio of their effusion rates.

**PLAN:** The effusion rate is inversely proportional  $\sqrt{\mathcal{M}}$  for each gas, so we find the molar mass for each substance using its formula and take the square root. The ratio of the effusion rates is the inverse of the ratio of these square roots.

 $\mathcal{M}$  of He = 4.003 g/mol **SOLUTION:**  $\mathcal{M}$  of CH<sub>4</sub> = 16.04 g/mol

$$\frac{\text{rate}}{\text{rate}}_{\text{CH}}^{\text{He}} = \sqrt{\frac{16.04}{4.003}} = 2.002$$



5-63

### Real Gases: Deviations from Ideal Behavior

- The kinetic-molecular model describes the behavior of ideal gases. Real gases deviate from this behavior.
- Real gases have real volume.
  - Gas particles are **not** points of mass, but have volumes determined by the sizes of their atoms and the bonds between them.
- Real gases do experience attractive and repulsive forces between their particles.
- Real gases deviate most from ideal behavior at low temperature and high pressure.



Table 5.3 Molar Volume of Some Common Gases at STP (0°C and 1 atm)

Gas	Molar Volume (L/mol)	Boiling Point (°C)
He	22.435	-268.9
$H_2$	22.432	-252.8
Ne	22.422	-246.1
Ideal gas	22.414	-
Ar	22.397	-185.9
$N_2$	22.396	-195.8
$O_2$	22.390	-183.0
CO	22.388	-191.5
Cl <sub>2</sub>	22.184	-34.0
$NH_3$	22.079	-33.4



Figure 5.21 Deviations from ideal behavior with increasing external pressure

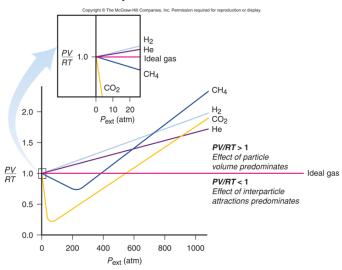
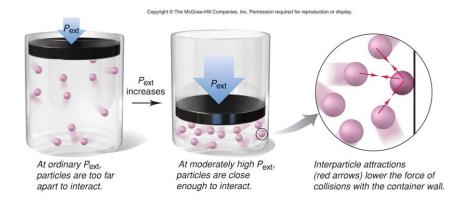
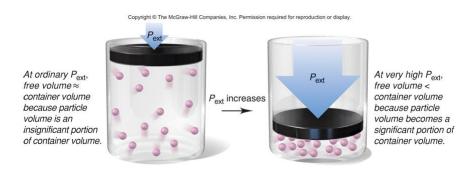


Figure 5.22 The effect of interparticle attractions on measured gas pressure.



## Figure 5.23 The effect of particle volume on measured gas volume.



## The van der Waals equation

- The van der Waals equation adjusts the ideal gas law to take into account
  - the real volume of the gas particles and
  - the effect of interparticle attractions.

Van der Waals equation for 
$$n$$
 moles of a real gas 
$$(P + \frac{n^2 a}{V^2})(V - nb) = nRT$$

The constant a relates to factors that influence the attraction between particles.

The constant *b* relates to particle volume.



#### **Table 5.4 Van der Waals Constants for Some Common Gases**

Gas	$a \left( \frac{\text{atm} \cdot L^2}{\text{mol}^2} \right)$	$b\left(\frac{L}{mol}\right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
$H_2$	0.244	0.0266
$N_2$	1.39	0.0391
$O_2$	1.36	0.0318
Cl <sub>2</sub>	6.49	0.0562
CH₄	2.25	0.0428
CO	1.45	0.0395
$CO_2$	3.59	0.0427
$NH_3$	4.17	0.0371
$H_2O$	5.46	0.0305