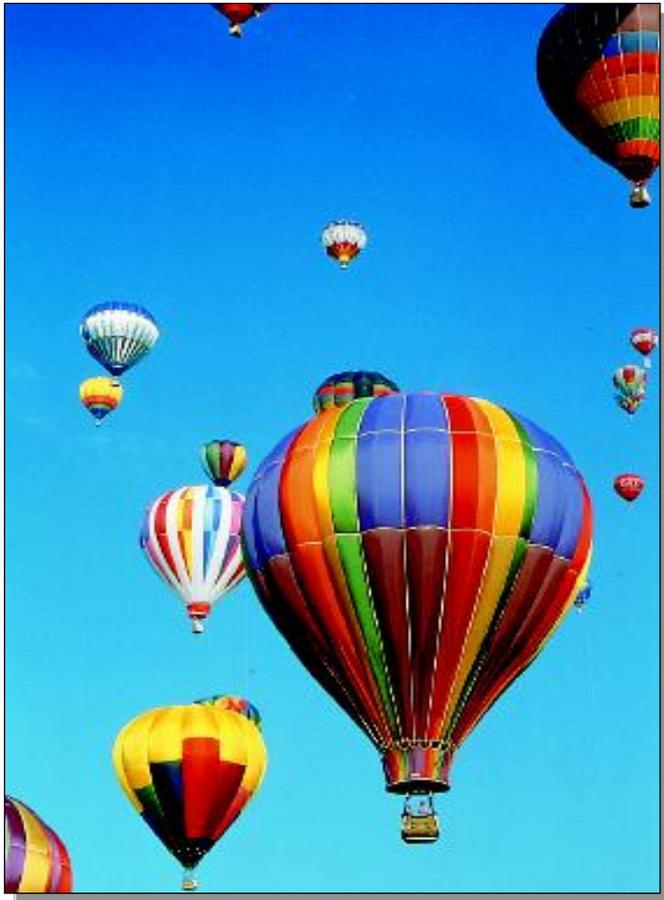


# Chapter 5: GASES & the Kinetic Molecular Theory



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# 5.1 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.

# 5.2 Gas Pressure & its Measurements

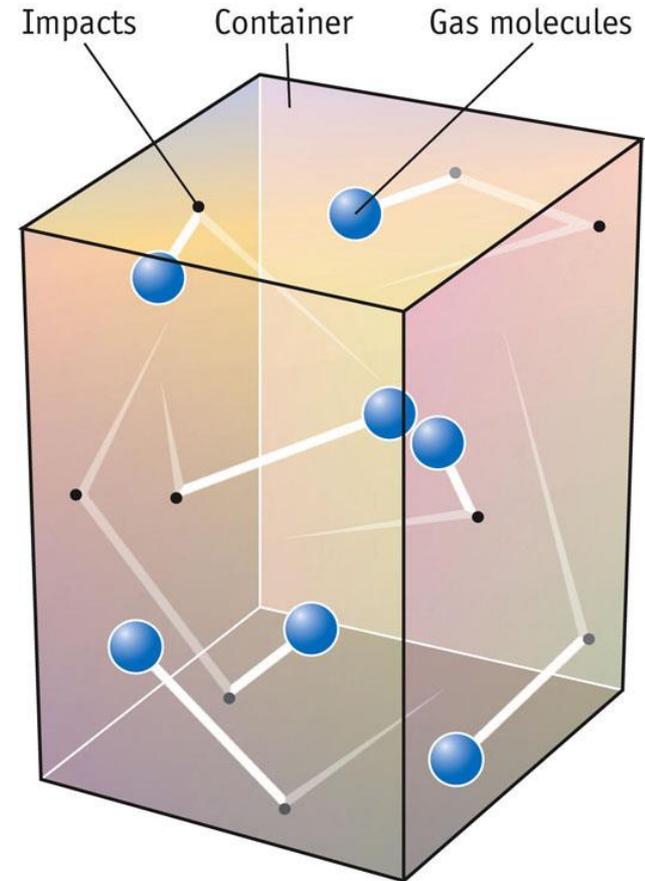
## Gas pressure

- Is the force acting on a specific area.

$$\text{Pressure (} P \text{)} = \frac{\text{force}}{\text{area}}$$

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

Atmospheric pressure decreases with altitude.



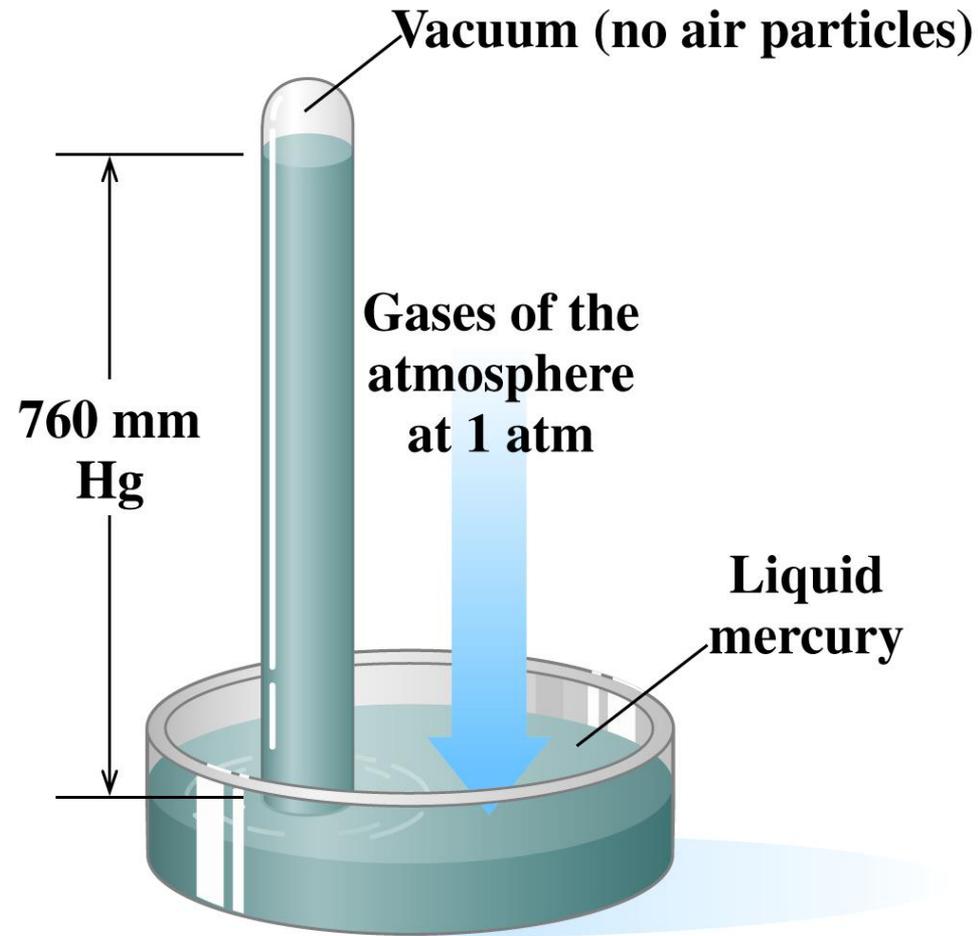
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# Laboratory Devices for Measuring Pressure

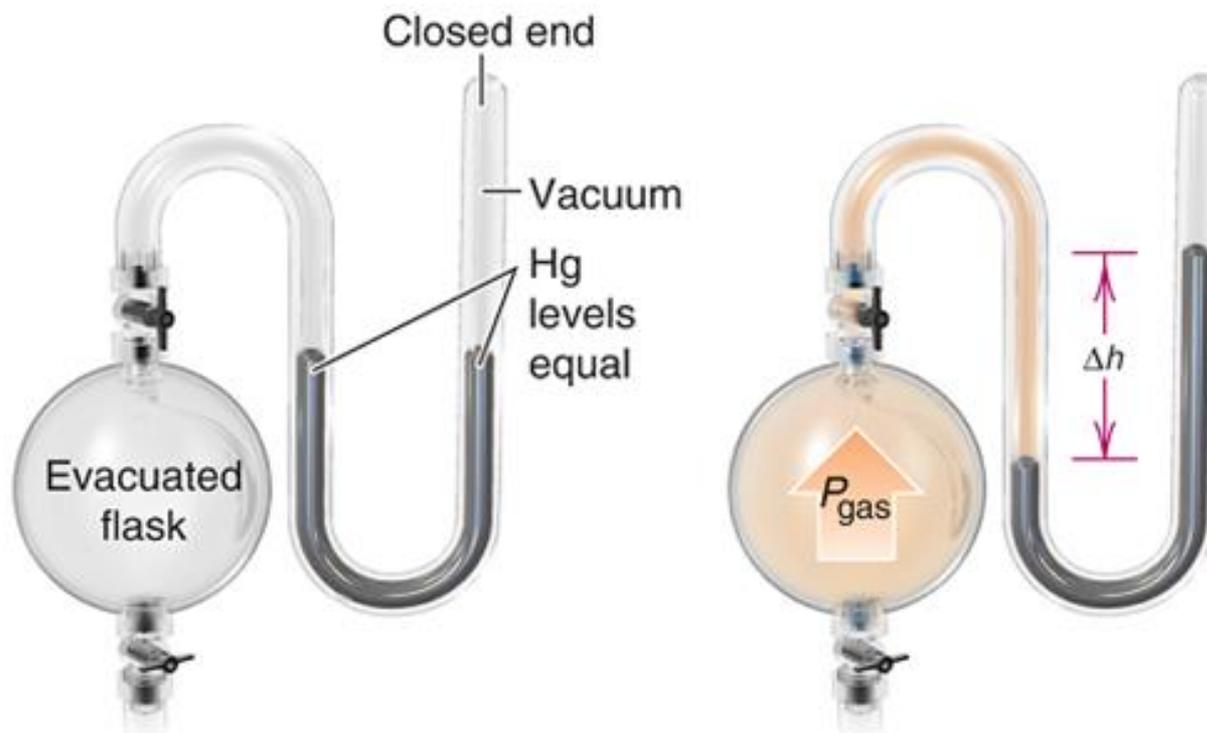
## A barometer

- Measures the pressure exerted by the gases in the atmosphere.
- Indicates atmospheric pressure as the height in millimeters of the mercury column.

$$h_{H_2O} \times d_{H_2O} = h_{Hg} \times d_{Hg}$$



# Closed-end manometer



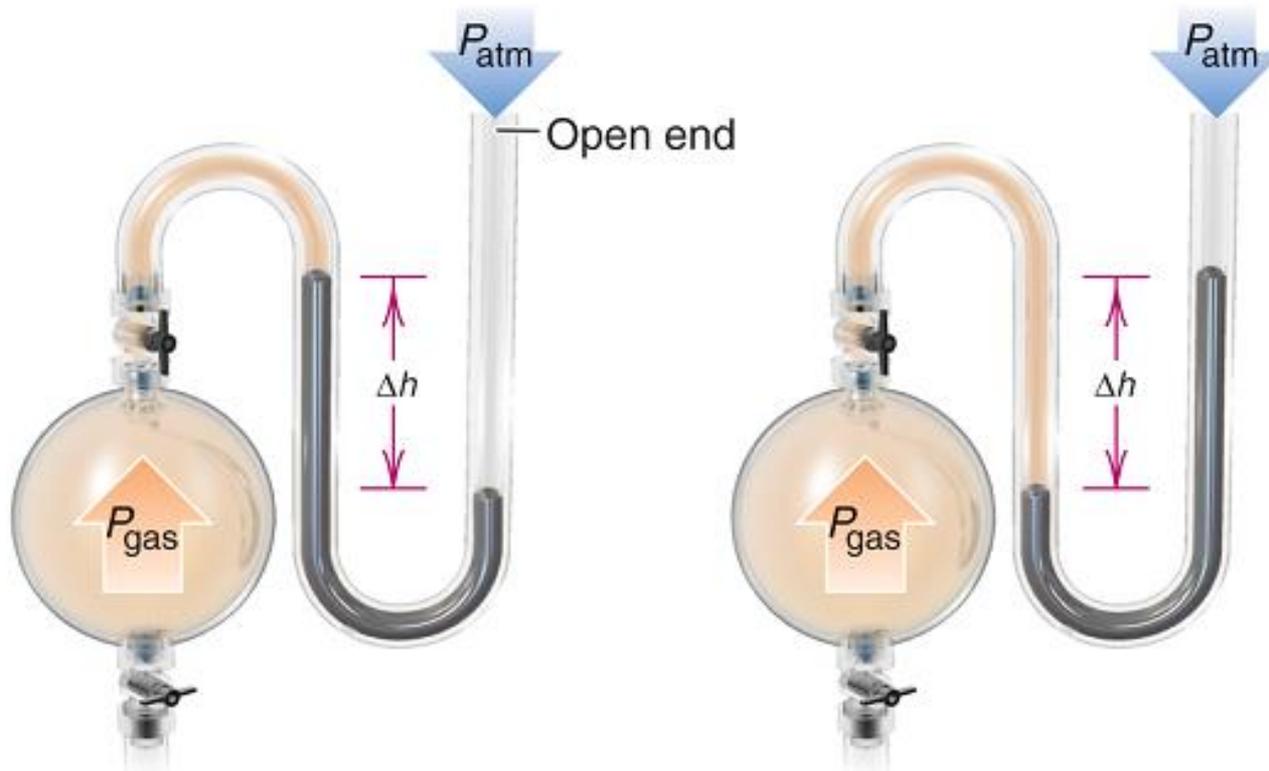
**The Hg levels are equal because both arms of the U tube are evacuated.**

**A gas in the flask pushes the Hg level down in the left arm.**

**The difference in levels,  $\Delta h$ , equals the gas pressure,  $P_{\text{gas}}$ .**

**Figure 5.4 A**

# Open-end manometer



When  $P_{gas}$  is less than  $P_{atm}$ ,  
subtract  $\Delta h$  from  $P_{atm}$ .

$$P_{gas} < P_{atm}$$

$$P_{gas} = P_{atm} - \Delta h$$

When  $P_{gas}$  is greater than  
 $P_{atm}$ , add  $\Delta h$  to  $P_{atm}$ .

$$P_{gas} > P_{atm}$$

$$P_{gas} = P_{atm} + \Delta h$$

Figure 5.4 B

# 5.2 Gas Pressure & its Measurements

## Common Units of Pressure

Unit	Normal Atmospheric Pressure at Sea Level and 0°C
pascal (Pa); kilopascal (kPa)	$1.01325 \times 10^5$ Pa; 101.325 kPa
atmosphere (atm)	1 atm*
millimeters of mercury (mmHg)	760 mmHg*
torr	760 torr*
pounds per square inch (lb/in <sup>2</sup> or psi)	14.7 lb/in <sup>2</sup>
bar	1.01325 bar

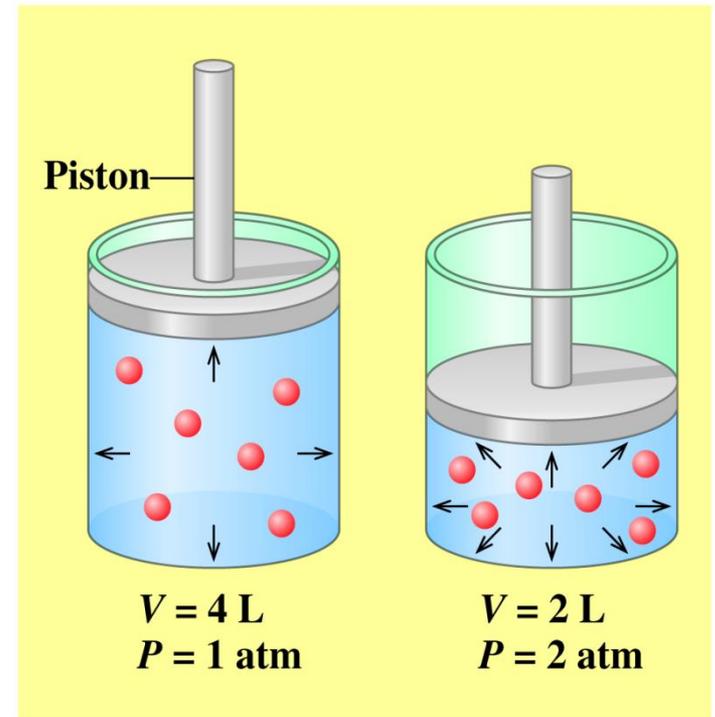
\*This is an exact quantity; in calculations, we use as many significant figures as necessary.

# 5.3 The Gas Laws & Their Experimental Foundations

- **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.

# Boyle's Law

- The pressure of a gas is inversely related to its volume when  $T$  and  $n$  are constant.
- If the pressure increases, volume decreases.
- The product  $P \times V$  is constant as long as  $T$  and  $n$  do not change.



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$$PV = \text{constant} \quad \text{or} \quad P_1 V_1 = P_2 V_2$$

# Familiar Applications of Boyle's Law

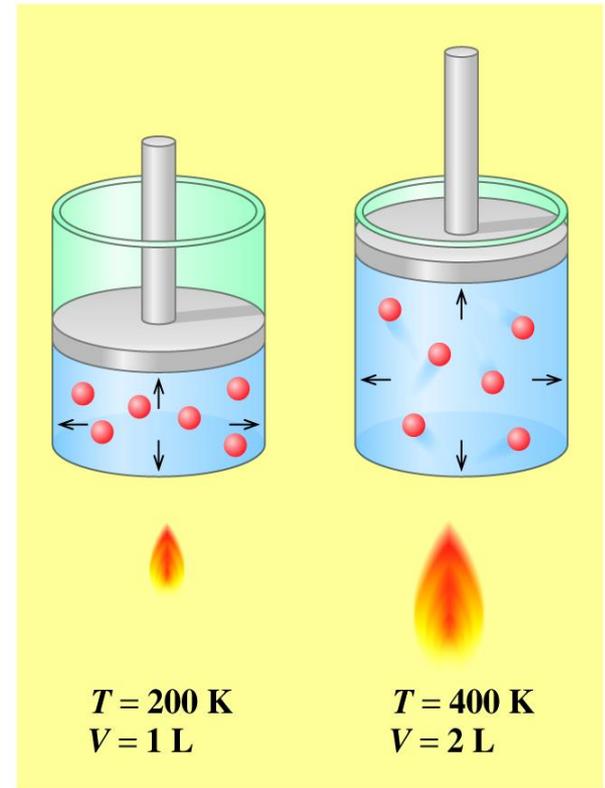
**A bicycle pump: As the volume of the air trapped in the pump is reduced, its pressure goes up, and air is forced into the tire.**



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# Charles' Law

- The Kelvin temperature of a gas is directly related to the volume.
- **P and n are constant.**
- When the temperature of a gas increases, its volume increases.



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$$\frac{V}{T} = \text{a constant} \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$



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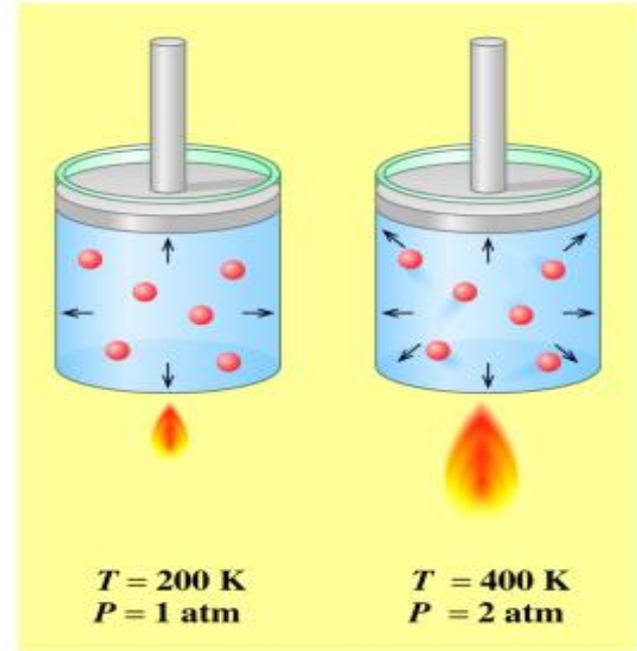
# Familiar Applications of Charles's Law



**Balloons immersed in liquid  $N_2$  (at  $-196\text{ }^\circ\text{C}$ ) will shrink as the air cools (and is liquefied).**

# Gay-Lussac's Law

- The pressure exerted by a gas is directly related to the Kelvin temperature.
- $V$  and  $n$  are constant.



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$$\frac{P}{T} = \text{a constant} \quad \text{or} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

# Problem

- 1) If a sample of helium gas has a volume of 120 mL and a pressure of 850 mm Hg, what is the new volume if the pressure is changed to 425 mm Hg?
- 2) A sample of oxygen gas has a volume of 420 mL at a temperature of 18°C. At what temperature (in °C) will the volume of the oxygen be 640 mL (P and n constant)?
- 3) A gas has a pressure of 645 mm Hg at 128°C. What is the temperature in Celsius if the pressure increases to 824 mm Hg (n and V remain constant)?

# Combining Gas Law

- The combined gas law uses Boyle's Law, Charles' Law (**n is constant**).

$$\frac{PV}{T} = \text{a constant} \quad \text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

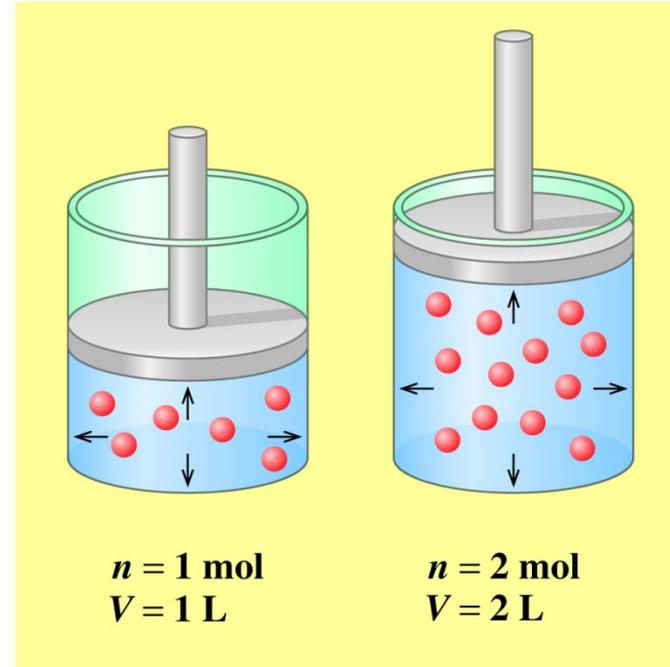
**Problem:** A gas has a volume of 675 mL at 35°C and 0.850 atm pressure. What is the volume (mL) of the gas at -95°C and a pressure of 802 mm Hg (n constant)?

# Avogadro's Law: Volume and Moles

The volume of a gas is directly related to the number of moles ( $n$ ) of gas.

- $T$  and  $P$  are constant.

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$



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At fixed temperature and pressure, equal volumes of any ideal gas contain equal numbers of particles (or moles).

# Problem

If 0.75 mole helium gas occupies a volume of 1.5 L, what volume will 1.2 moles helium occupy at the same temperature and pressure?



# Gas Behavior at Standard Conditions

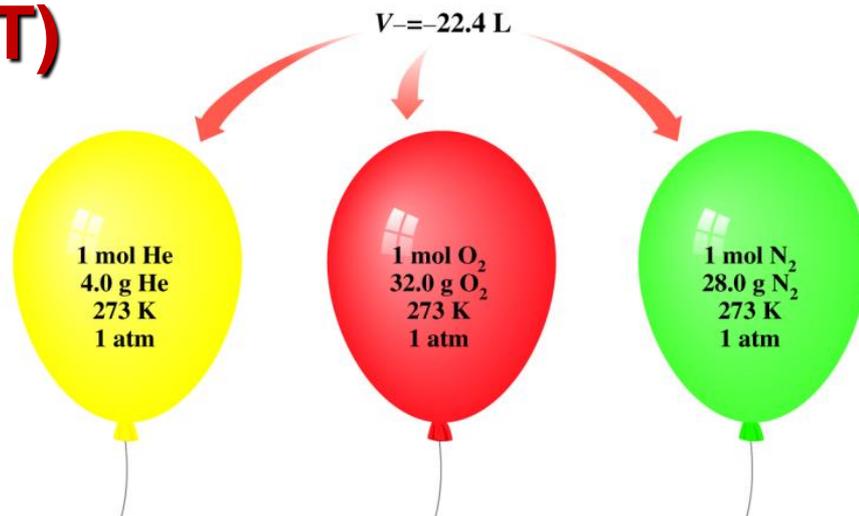
**STP** (Standard Temperature and Pressure)

Standard temperature (T)

0°C or 273 K

Standard pressure (P)

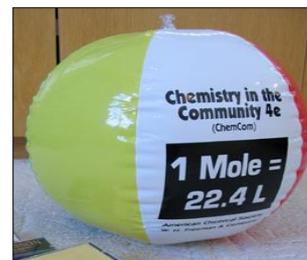
1 atm (760 mm Hg)



The volumes of gases can be compared at when they are at STP.

**Standard Molar Volume:**

**22.4 L for 1.00 mol of any gas at STP**



# Problems

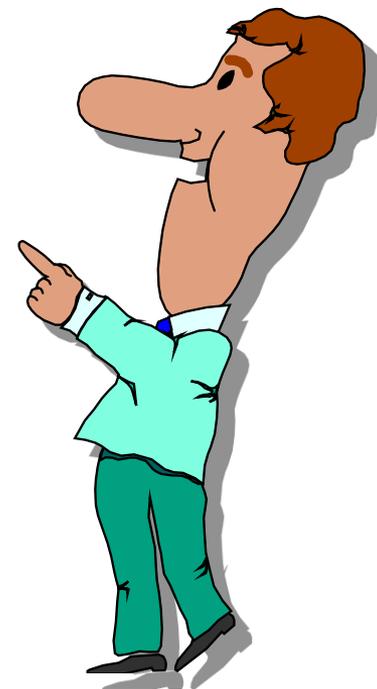
- A. What is the volume at STP of 4.00 g of  $\text{CH}_4$ ?
- B. How many grams of He are present in 8.00 L of He at STP?

# The IDEAL GAS LAW

$$P V = n R T$$

How much  $N_2$  is required to fill a small room with a volume of 960 cubic feet (27,000 L) to  $P = 745$  mm Hg at  $25\text{ }^\circ\text{C}$ ?

$$R = 0.082057 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol}$$



# The individual gas laws as special cases of the ideal gas law<sup>21</sup>

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## IDEAL GAS LAW

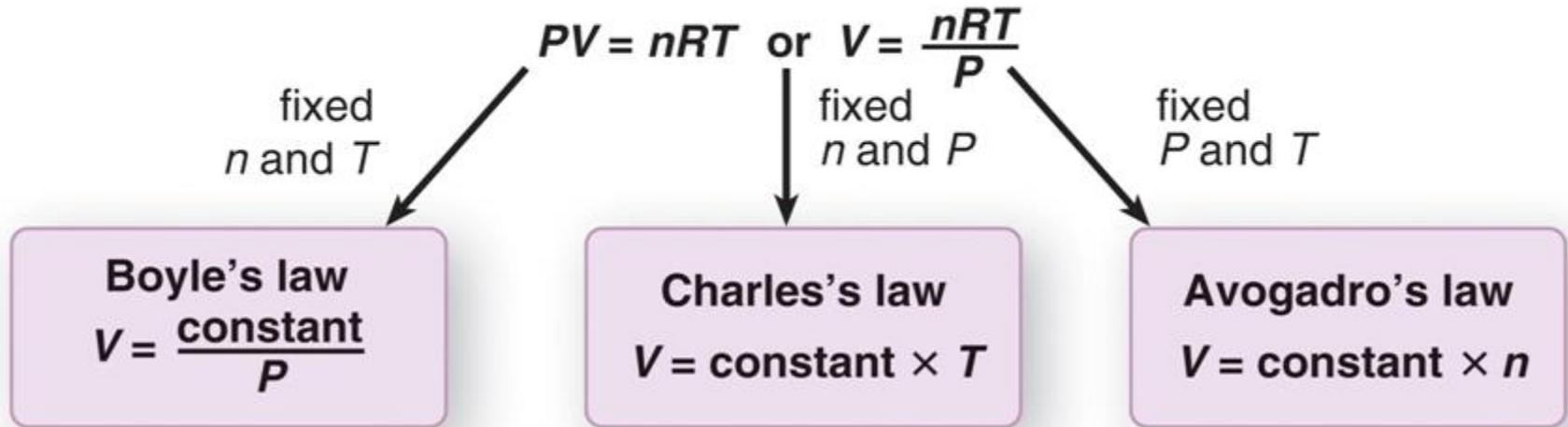


Figure 5.11

# 5.4 Rearrangements of the IDEAL GAS LAW

## DENSITY of a GAS

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

← d and M proportional

The density (d) of air at 15 °C and 1.00 atm is 1.23 g/L. What is the molar mass (M) of air?



# 5.4 Rearrangements of the IDEAL GAS LAW

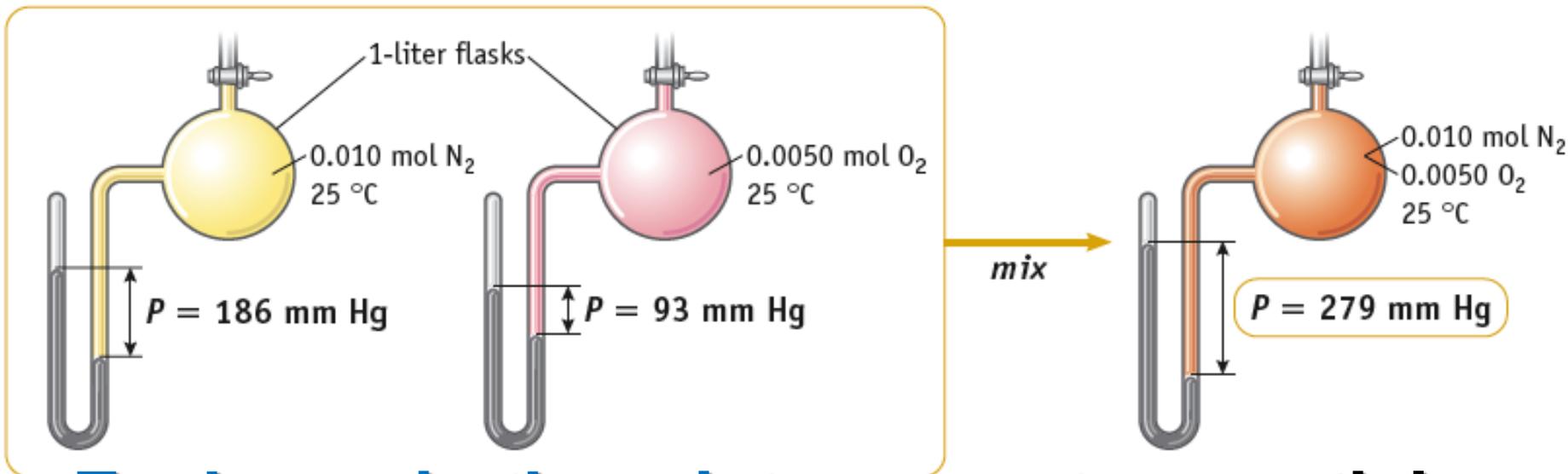
## MOLAR MASS of a GAS

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



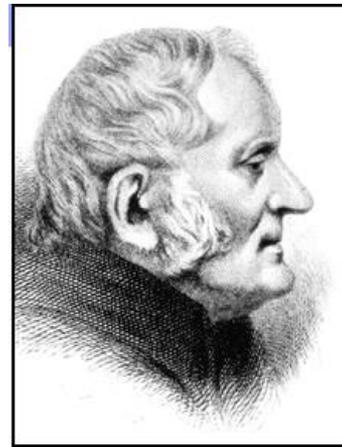
**Problem:** What is the molar mass of a 149-mL gas at 95 °C and 740 torr if it weighs 0.225 g?

# The Partial Pressure of each Gas in a Mixture

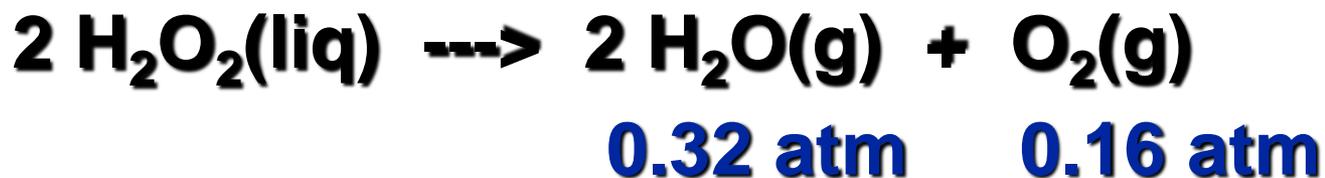


**Each gas in the mixture exerts a partial pressure equal to the pressure it would exert by itself.**

**John Dalton**  
1766-1844



# Dalton's Law of Partial Pressures<sup>25</sup>



What is the total pressure in the flask?

$$P_{\text{total}} \text{ in gas mixture} = P_A + P_B + \dots$$

Therefore,

$$P_{\text{total}} = P(\text{H}_2\text{O}) + P(\text{O}_2) = 0.48 \text{ atm}$$

**Dalton's Law: total P is sum of**  
**PARTIAL pressures.**

# Dalton's Law of Partial Pressures



What is the partial pressure of  $\text{O}_2$  if total pressure is 0.48 atm?

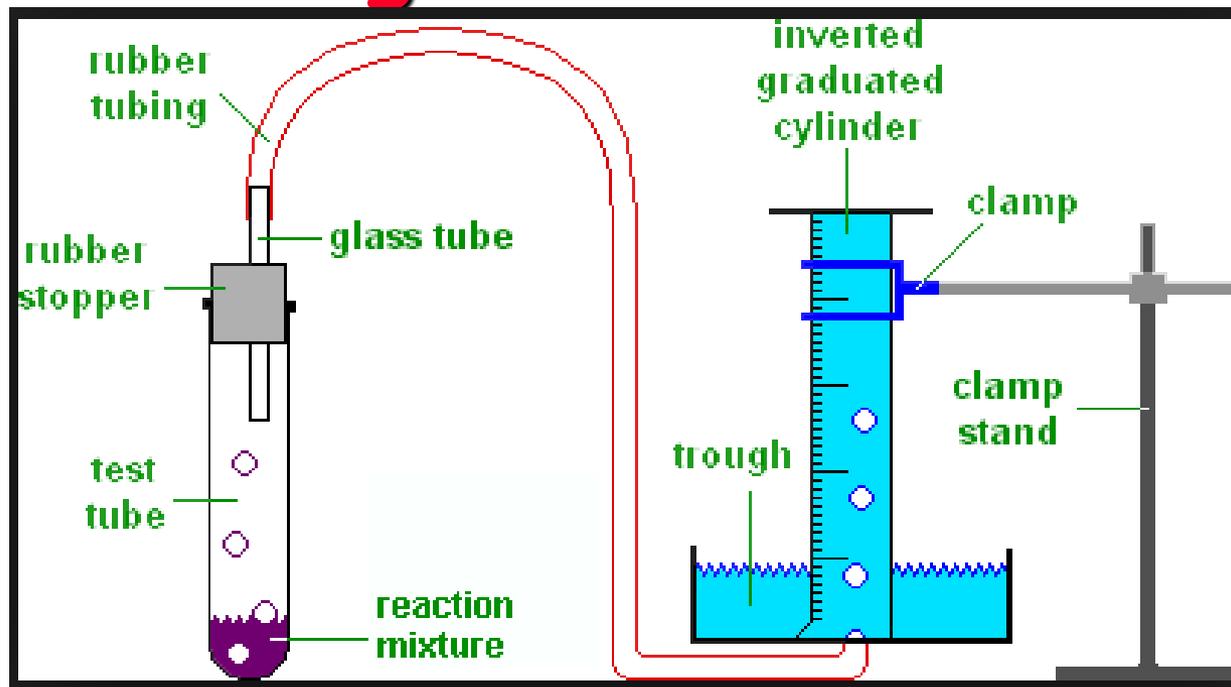
$$P_A = \left( \frac{n_A}{n_{total}} \right) P_{total} = \chi_A P_{total}$$

$\chi_A$  is mole fraction of A

$$P_{\text{O}_2} = \left( \frac{1 \text{ mol O}_2}{1 \text{ mol O}_2 + 2 \text{ mol H}_2\text{O}} \right) (0.48 \text{ atm}) = 0.16 \text{ atm}$$

# Applications of Dalton's Law: Collecting a Gas over Water

27



- As the gas is created, it will displace water from the bottle. The volume of gas can be determined by the amount of water that was displaced by the gas.
- During the collection, the water level in the container will adjust so that the pressure inside and outside the container are the same. Because of this, if we know the atmospheric pressure, we also know the pressure of the gas inside the bottle.

# Vapor Pressure of Liquid Water at Different Temperatures

Temp. (°C)	Vapor Pressure (mm Hg)	Temp. (°C)	Vapor Pressure (mm Hg)	Temp. (°C)	Vapor Pressure (mm Hg)
0.0	4.58	15.0	12.8	30.0	31.8
1.0	4.93	16.0	13.6	31.0	33.7
2.0	5.29	17.0	14.5	32.0	35.7
3.0	5.69	18.0	15.5	33.0	37.7
4.0	6.10	19.0	16.5	34.0	39.9
5.0	6.54	20.0	17.5	35.0	42.2
6.0	7.01	21.0	18.7	40.0	55.3
7.0	7.51	22.0	19.8	50.0	92.5
8.0	8.05	23.0	21.1	60.0	149.4
9.0	8.61	24.0	22.4	70.0	233.7
10.0	9.21	25.0	23.8	80.0	355.1
11.0	9.84	26.0	25.2	90.0	525.8
12.0	10.5	27.0	26.7	100.0	760.0
13.0	11.2	28.0	28.3		
14.0	12.0	29.0	30.0		

# Applications of Dalton's Law: Collecting a Gas over Water

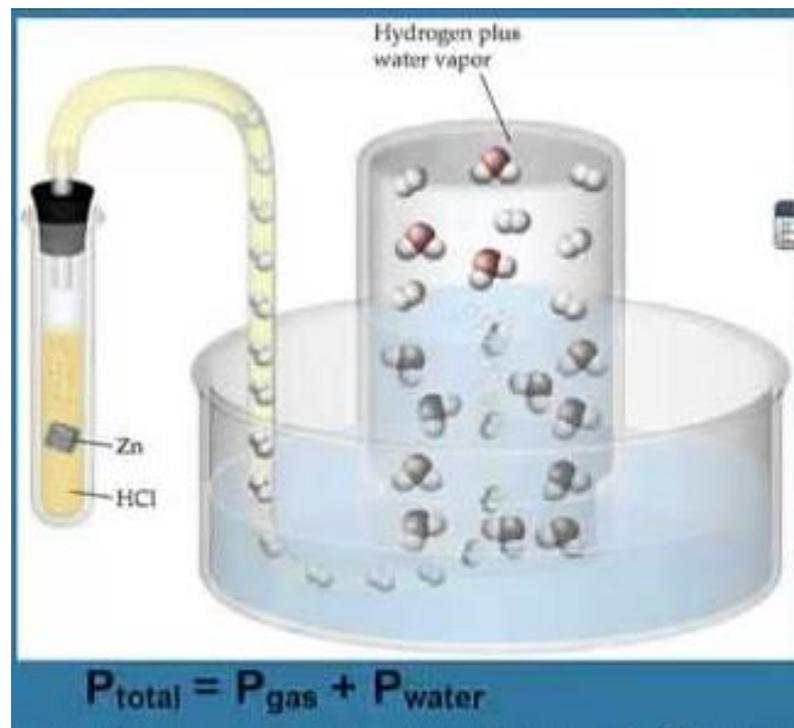
**Problem:** A small piece of zinc reacts with dilute hydrochloric acid to form hydrogen gas, which is collected over water at 16 °C into a large flask. The total pressure is adjusted to barometer pressure of 752 torr, and the volume is 1495 mL. Calculate the partial pressure and mass of hydrogen gas.

## Solution:

$$P_{\text{H}_2} = P_{\text{total}} - P_{\text{vapor}} = 738 \text{ mmHg} \\ = 0.971 \text{ atm}$$

$$n_{\text{H}_2} = 0.0612 \text{ mol H}_2 \text{ gas}$$

$$\text{Mass of hydrogen gas} = 0.123 \text{ g}$$

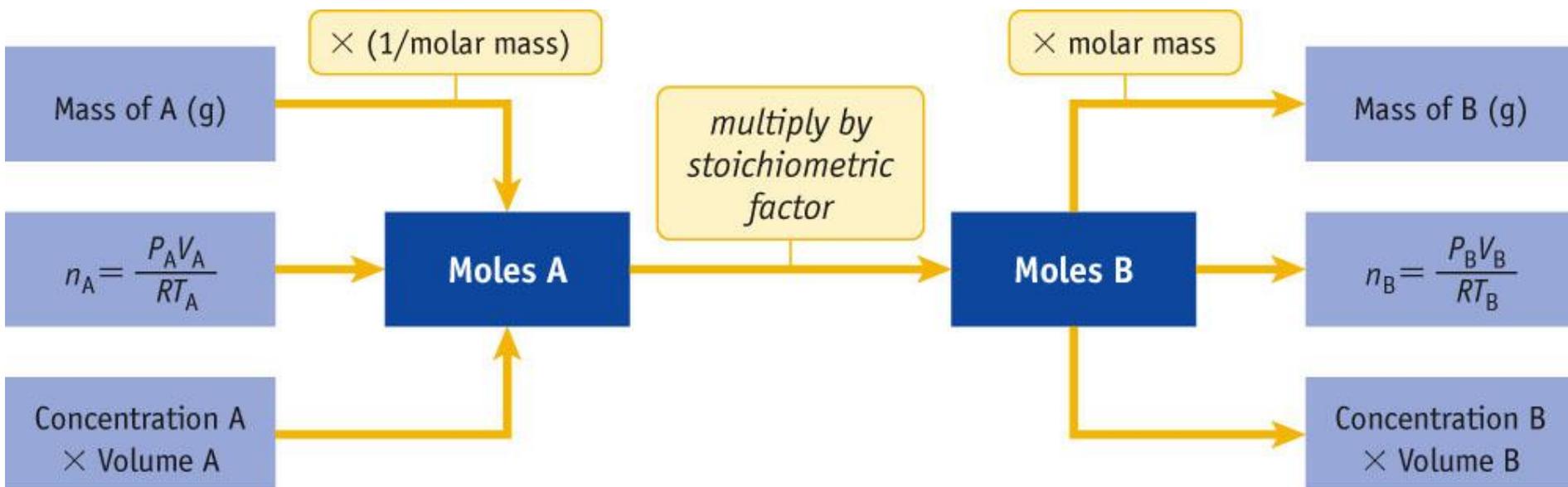


# The Ideal Gas Law & Reaction Stoichiometry



Decompose 1.1 g of  $\text{H}_2\text{O}_2$  in a flask with a volume of 2.50 L. What is the pressure of  $\text{O}_2$  at 25 °C? Of  $\text{H}_2\text{O}$ ?

**Strategy: (A is given, B is inquired)**



# Problem



Decompose 1.1 g of  $\text{H}_2\text{O}_2$  in a flask with a volume of 2.50 L. What is the pressure of  $\text{O}_2$  at 25 °C?  
Of  $\text{H}_2\text{O}$ ?

## Strategy:

Calculate moles of  $\text{H}_2\text{O}_2$  and then moles of  $\text{O}_2$  and  $\text{H}_2\text{O}$ .

Finally, calculate  $P$  from  $n$ ,  $R$ ,  $T$ , and  $V$ .

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

## Postulate 1:

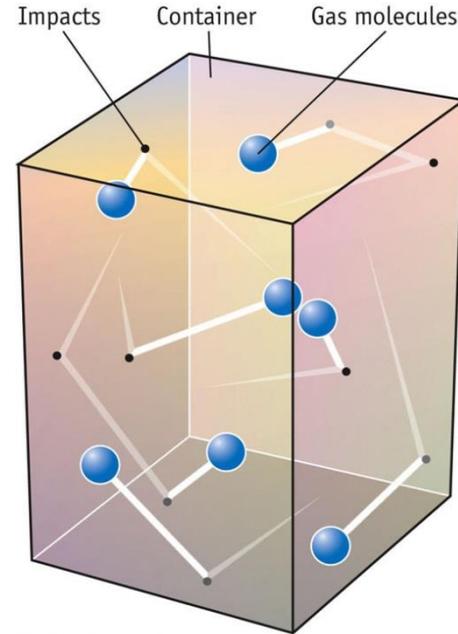
Gas particles are tiny with large spaces between them. The volume of each particle is so small compared to the total volume of the gas that it is assumed to be zero.

## 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.



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# Gases: Speed vs. Temperature

## $E_K$ vs. speed and temperature of gases

Because gas molecules are in motion, they have kinetic energy.

$$\overline{E_K} = \frac{1}{2} \left( \frac{R}{N_A} \right) T$$

R: Ideal gas constant,  $N_A$ : Avogadro number

**At the same T, all gases have the same average KE.**

**As T goes up for a gas, KE also increases — and so does speed.**

# Kinetic Molecular Theory

## Maxwell's equation: Speed vs. T and M of gas

$$\sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}$$

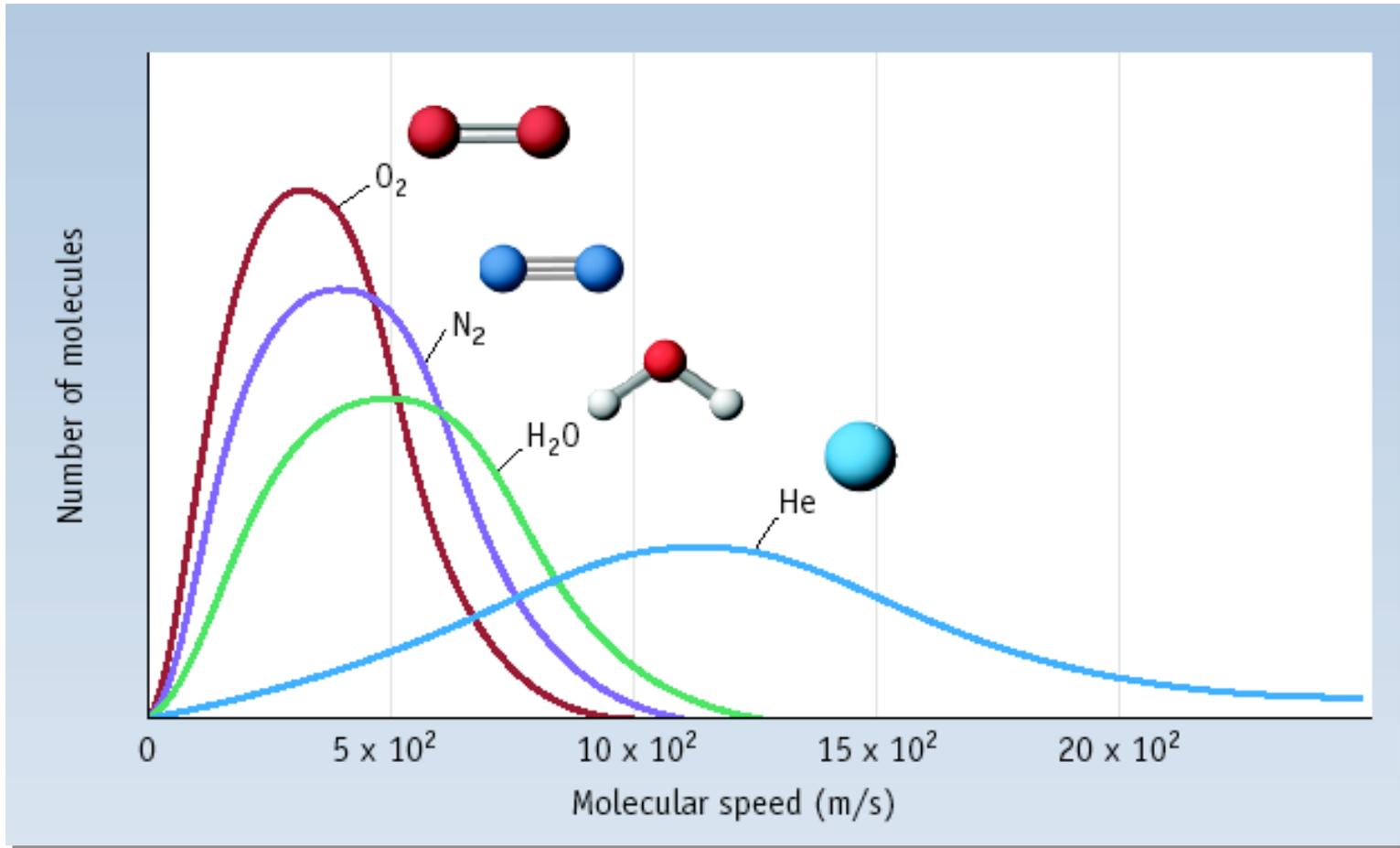
↑  
root mean square speed

where

- u** is the speed of gas (in m/s)
- M** is the molar mass (in **kg/mol**)
- R** = 8.3145 J/mol.K, the universal gas law constant

# Gases: Speeds vs. Molar Masses

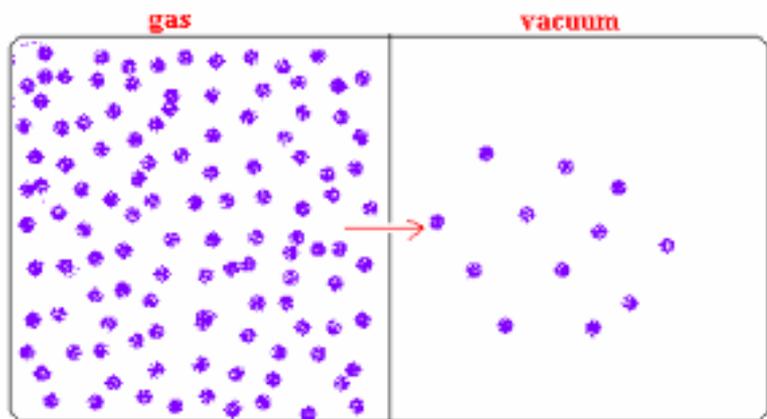
Average velocity decreases with increasing mass.



# GRAHAM'S LAW: GAS EFFUSION AND DIFFUSION

$$\frac{\text{Rate for A}}{\text{Rate for B}} = \sqrt{\frac{M \text{ of B}}{M \text{ of A}}}$$

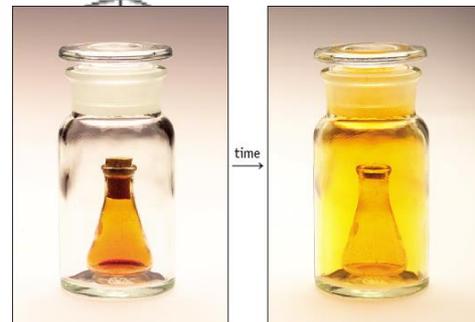
Rate of effusion and/or diffusion is inversely proportional to square root of molar mass.



**Effusion**



**Diffusion**

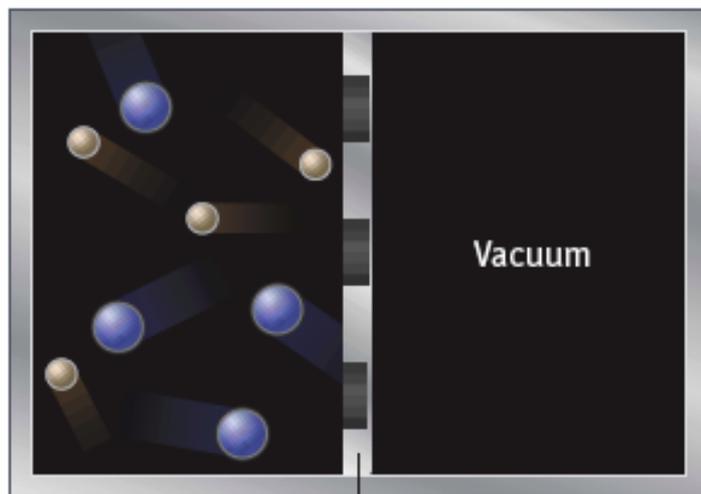


# GRAHAM'S LAW: GAS EFFUSION AND DIFFUSION

## Problem:

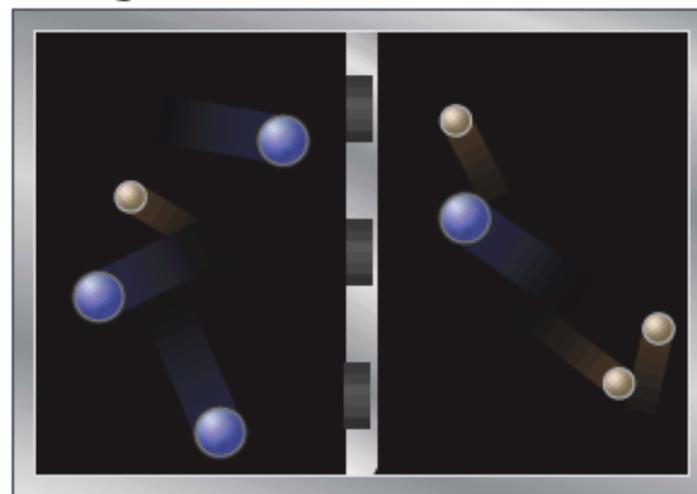
If it takes 1.25 min. for 0.010 mol of He to effuse, how long will it take for the same amount of ethane  $C_2H_6$  to effuse?

Before effusion



Porous barrier

During effusion



# 5.6 Real Gases: Deviations from Ideal Behavior

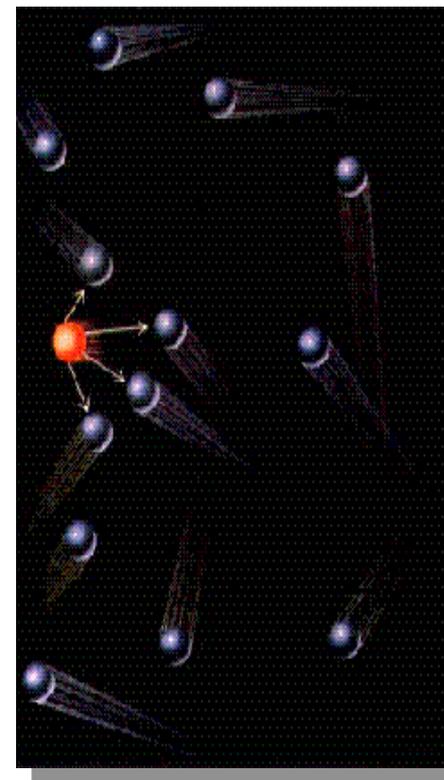
- The kinetic-molecular model describes the behavior of ideal gases. Real gases deviate from this behavior.
- **Real gas molecules have volume**

Gas particles are not points of mass, but have volumes determined by the sizes of their atoms and the bonds between them.

and **intermolecular forces.**

Otherwise a gas could not become a liquid.

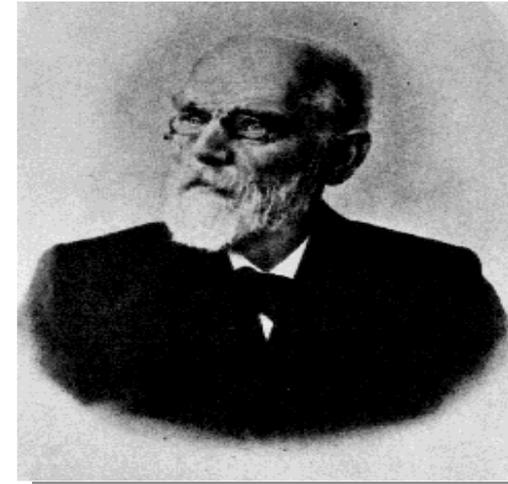
**Real gases deviate most from ideal behavior at *low temperature* and *high pressure*.**



# Non-Ideal Behavior: Real Gases 39

## VAN DER WAALS'S EQUATION:

Account for volume of gas molecules and intermolecular forces.



J. van der Waals,  
1837-1923,  
Professor of  
Physics,  
Amsterdam. Nobel  
Prize 1910.

Observed P                      Container V = V(ideal)

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

Correction for  
intermolecular forces

Correction for  
molecular volume

- At ordinary conditions (high T and low P), 1 mol of gas exerts  $PV/RT = 1$ : most real gases exhibit nearly ideal behavior
- $PV/RT > 1$ : intermolecular attractions predominate
- $PV/RT < 1$ : gas volumes predominate

---

**TABLE** van der Waals  
**Constants**

<b>Gas</b>	<b>a Values atm · L<sup>2</sup>/mol<sup>2</sup></b>	<b>b Values L/mol</b>
He	0.034	0.0237
Ar	1.34	0.0322
H <sub>2</sub>	0.244	0.0266
N <sub>2</sub>	1.39	0.0391
O <sub>2</sub>	1.36	0.0318
CO <sub>2</sub>	3.59	0.0427
Cl <sub>2</sub>	6.49	0.0562
H <sub>2</sub> O	5.46	0.0305

---

# Non-Ideal Behavior: Real Gases

Measured P

Measured V = V(ideal)

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

intermol. forces
vol. correction

Cl<sub>2</sub> gas has **a** = 6.49, **b** = 0.0562

For 8.0 mol Cl<sub>2</sub> in a 4.0 L tank at 27 °C.

**P (ideal) = nRT/V = 49.3 atm**

**P (van der Waals) = 29.5 atm**