# The Kinetic-Molecular Theory of Gases

# kinetic-molecular theory of gases

**Originated with Ludwig Boltzman and James Clerk Maxwell in the 19th century**

**Explains gas behavior on the basis of the motion of individual particles**

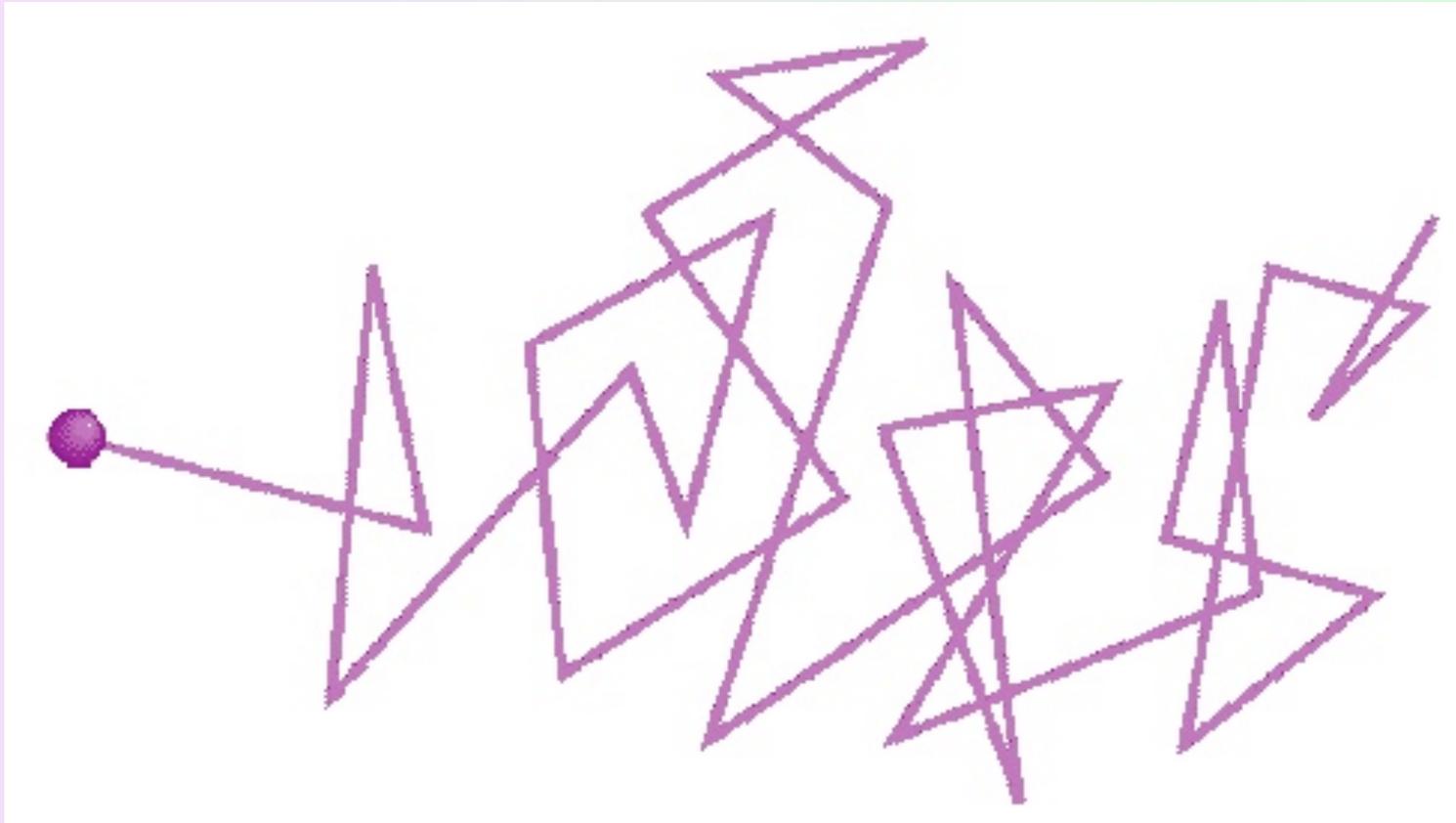**Is based on the following assumptions:**

**(1) A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions.**

(2)  Gas molecules are in constant motion in random directions, and they frequently collide with one another.

the collisions are completely elastic.

# Collisions of Gas Particles
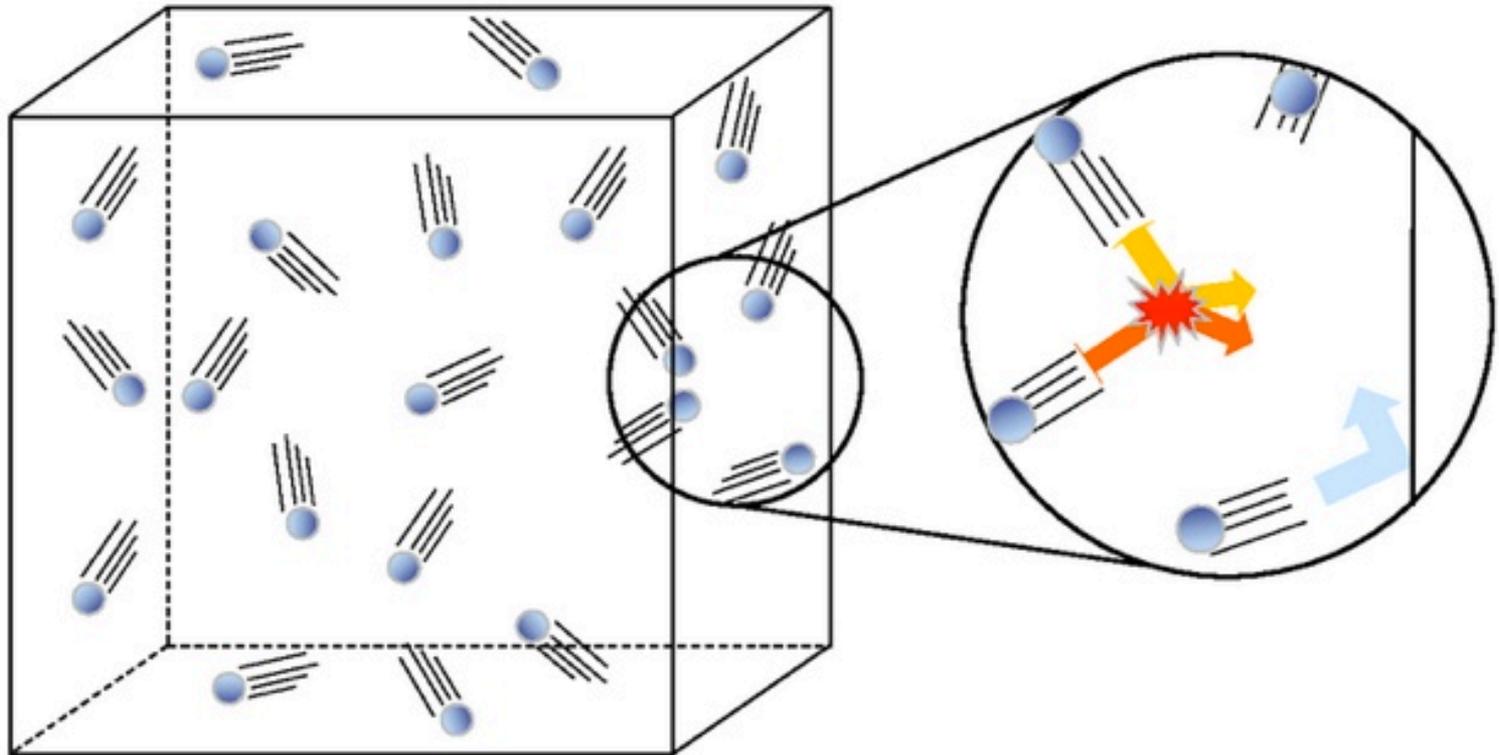
**The distances traveled by a single gas molecule between successive collisions. Each change in direction indicates a collision with another molecule.**

**(3)  Gas molecules exert neither attractive nor repulsive forces on one another.**

**(4)  The average kinetic energy of the molecules is proportional to the temperature of the gas in kelvins.**

# Application to the Gas Laws

- **Compressibility of gases**

- **Boyle's law**

- **Charles's law**

- **Avogadro's law**

- **Dalton's law of partial pressure**

# • **Compressibility of gases**

**Recall assumption 1 :**

**(1)  A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions.**

**Since molecules in the gas phase are separated by large distances, the main result of a decrease in the volume available to them is merely an increase in the rate at which they collide with each other**

- **Boyle's law**

**Pressure is inversely proportional to volume**

> gas pressure is the result of collisions between molecules and the walls of the container

> a decrease in volume causes an increase in the frequency of collisions between the gas molecule and the container

- **Charles's law**

**recall assumption 4 :**

**(4) The average kinetic energy of the molecules is proportional to the temperature of the gas in kelvins.**

**raising the temperature raises the average kinetic energy**

**Greater effect on pressure**

**the frequency of collisions increases**

**the force of collisions increases**

# • Avogadro's law

**recall assumption 1:**

**(1)  A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions.**

**Equal volumes of gases (at the same temperature and pressure) contain equal numbers of molecules**

## • Dalton's law of partial pressure

**recall assumption 3 :**

**(3) Gas molecules exert neither attractive nor repulsive forces on one another.**

**Therefore, the pressure exerted by one type of molecule is unaffected by the presence of another gas.**

**Therefore, the total pressure is given by the sum of the individual gas pressures.**

# Root -mean-square speed

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

## Where M is the molar mass

Root -mean-square speed is directly proportional to the square root kelvin temperature and inversely proportional to the square root of the molar mass (molecular weight)
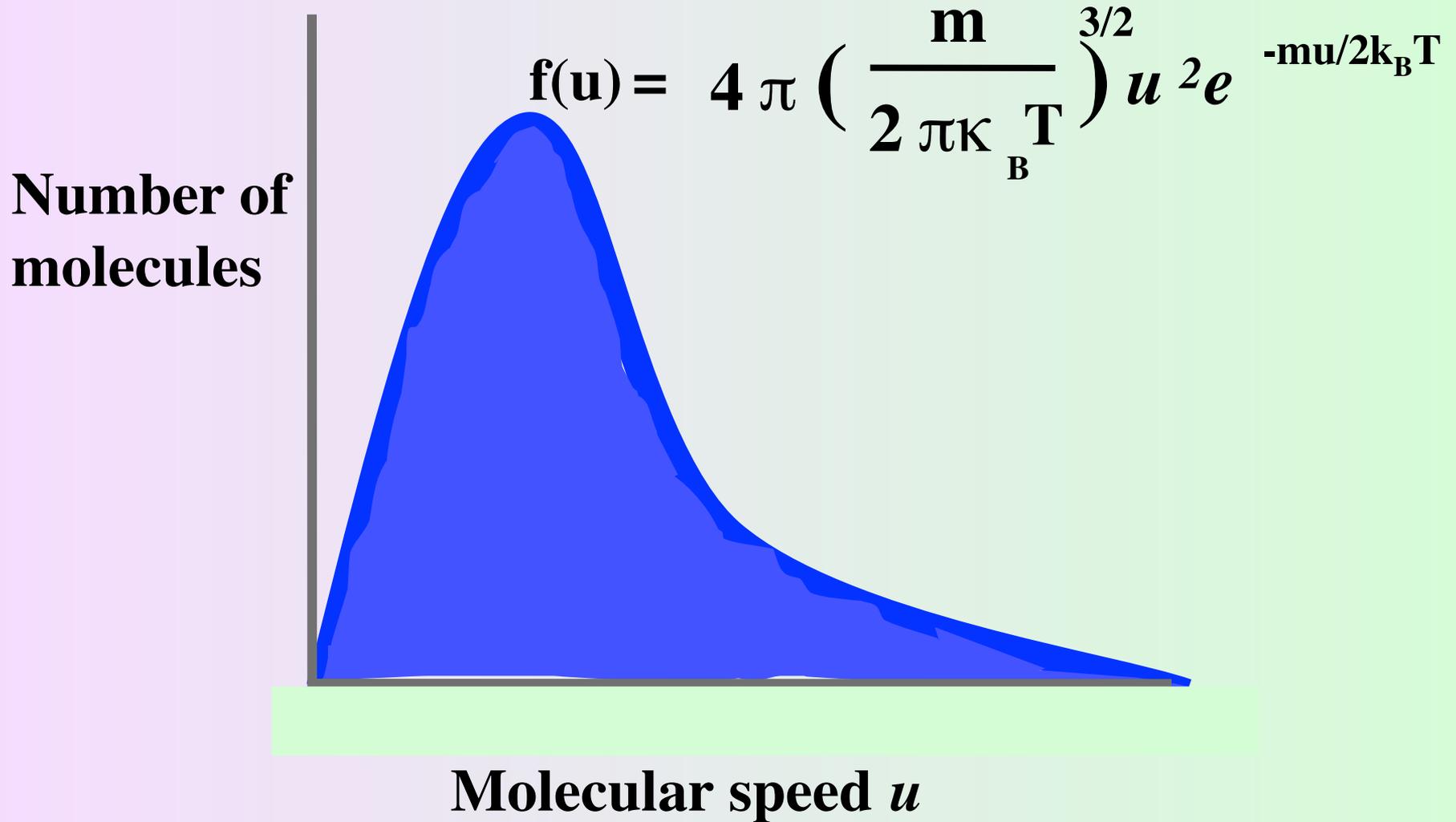
# Distribution of Molecular Speeds

exhibits what is called a "Maxwell-Boltzmann"

- not all molecules move at same speed

- most of the molecules have speeds close to a "most probable speed"

- small number of molecules have very low speeds

- small number have very high speeds

- distribution flattens as temperature increases

- most probable speed increases as temperature increases

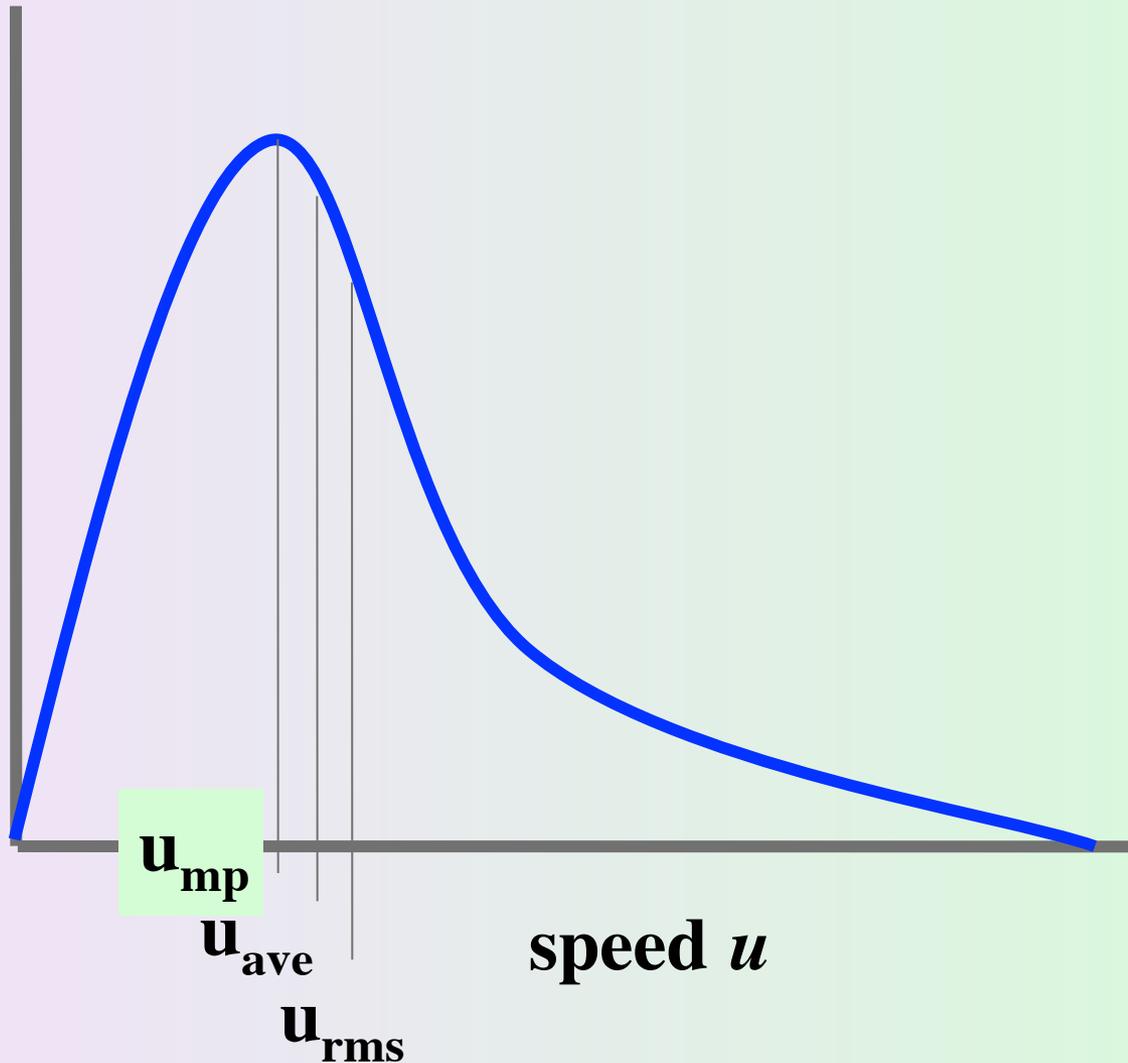# Distribution of molecular speeds as a function of temperature.
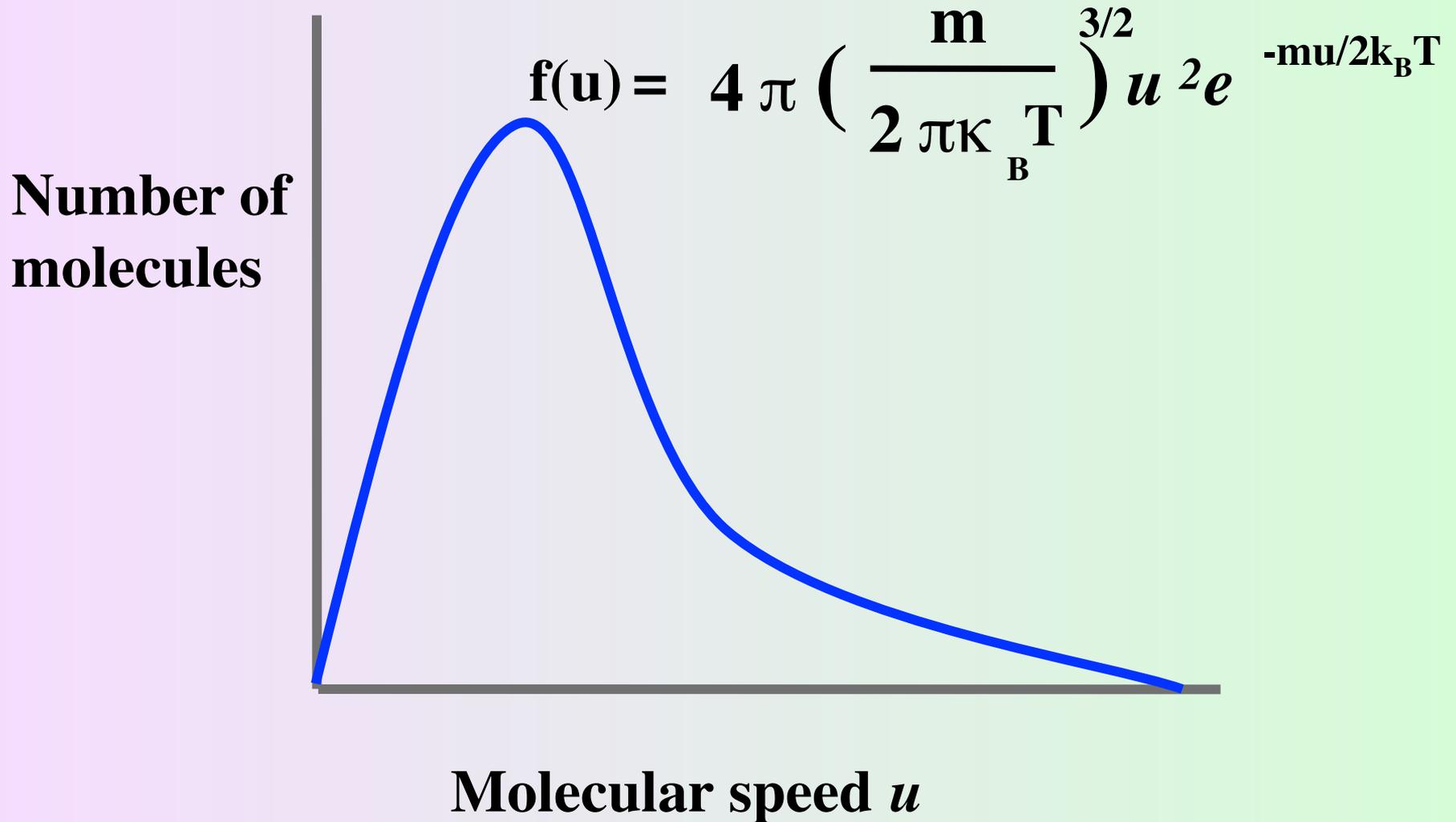
$$f(u) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} u^2 e^{-mu/2k_B T}$$

**Number of molecules**

**Molecular speed** *u*

**Distribution of molecular speeds as a function of temperature.**

$$f(u) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} u^2 e^{-mu/2k_B T}$$

**Number of molecules**

**Molecular speed *u***

**Distribution of molecular speeds as a function of temperature.**

Number of molecules

speed $u$

$u_{mp}$

$u_{ave}$

$u_{rms}$

Distribution of molecular speeds as a function of temperature.
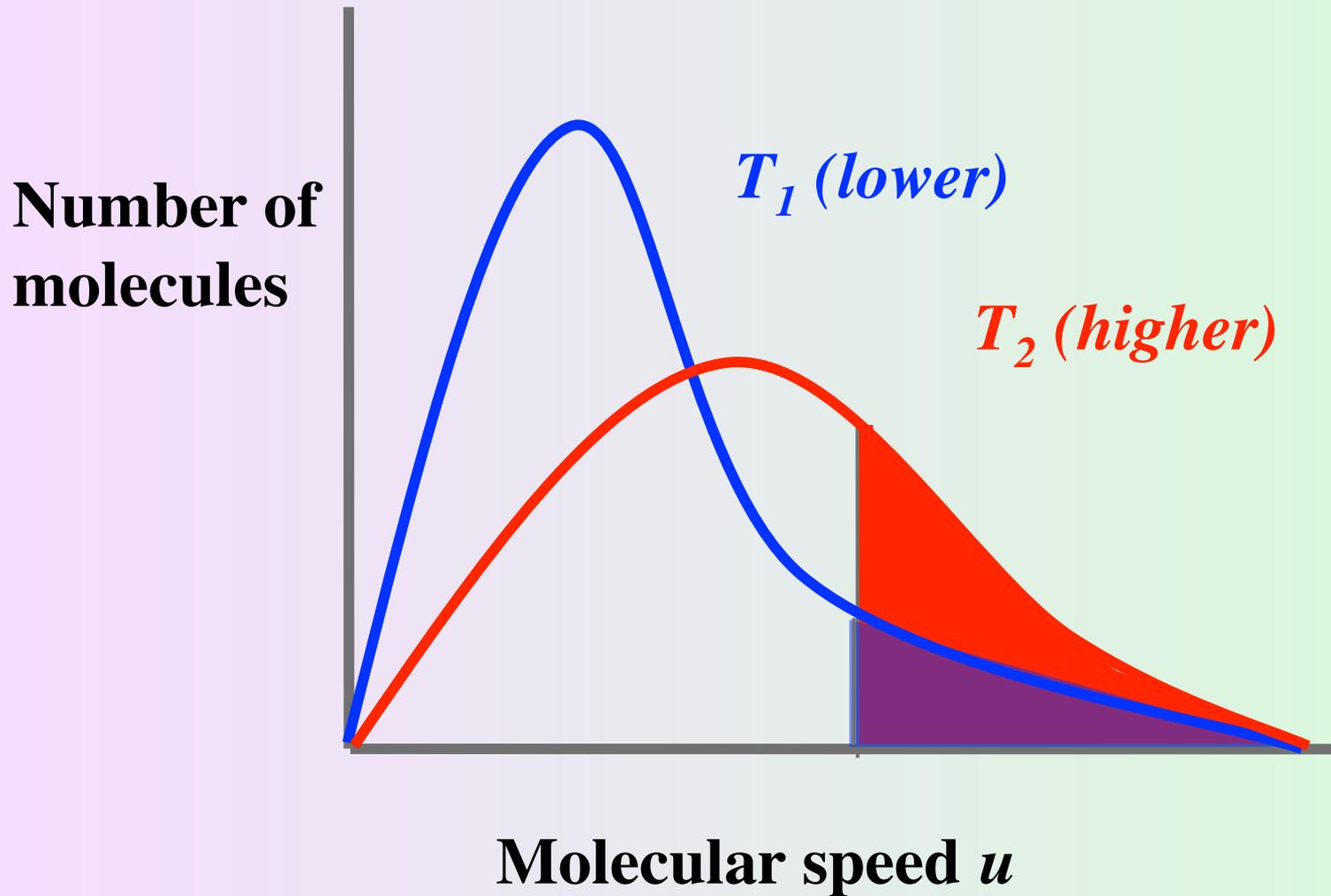
# Graham's Laws of Diffusion and Effusion

# Diffusion

the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties

# Effusion

the process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening
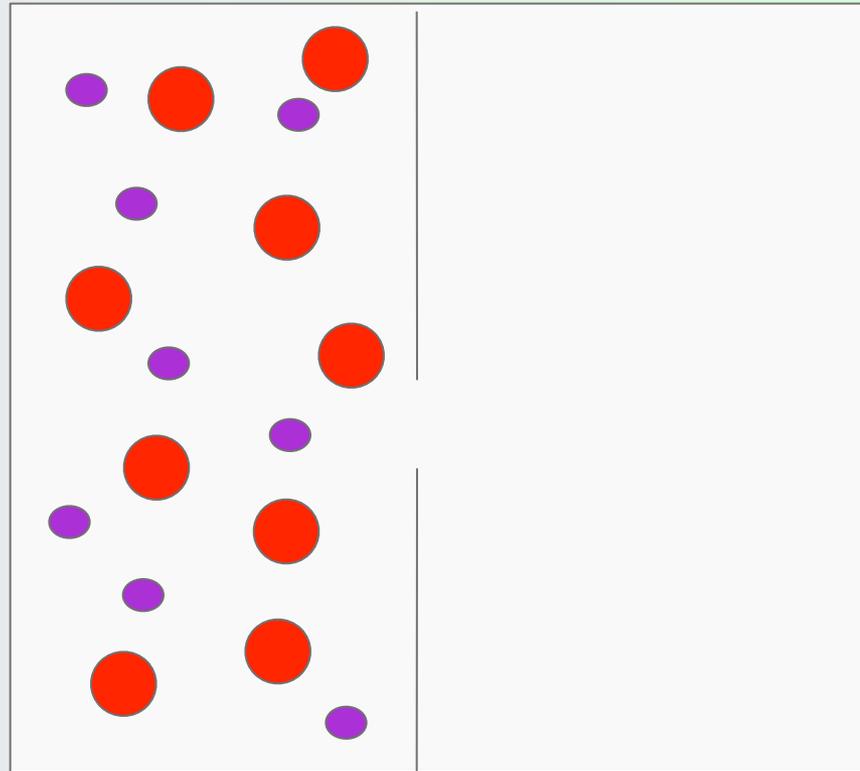
# Graham's Law of Effusion

*experimental*

$$\frac{\text{rate of effusion of gas 1}}{\text{rate of effusion of gas 2}} = \frac{(MW_2)^{1/2}}{(MW_1)^{1/2}}$$

**same expression can be derived from kinetic-molecular theory**

**Gaseous effusion. Gas molecules move from a high-pressure region (left) to a low-pressure region through a pinhole.**
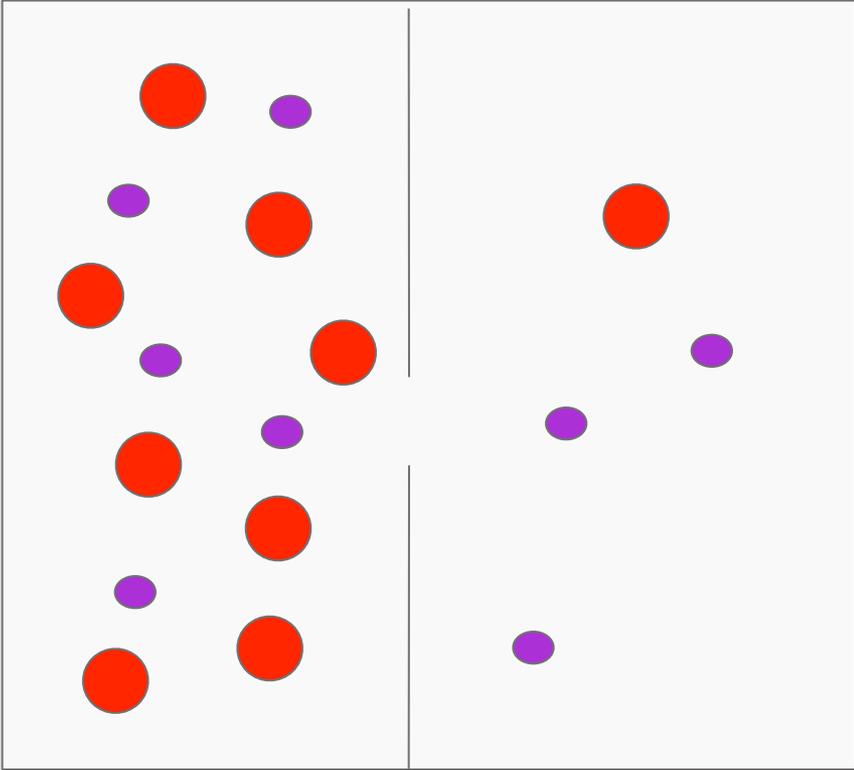
**Gaseous effusion. Gas molecules move from a high-pressure region (left) to a low-pressure region through a pinhole.**
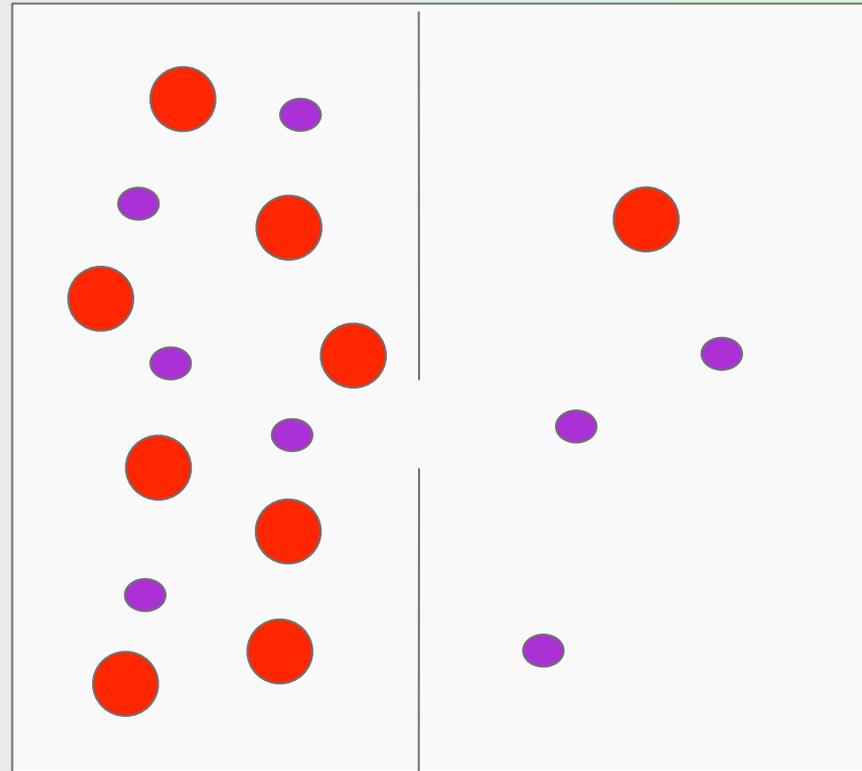


**Light gas** •       **heavy gas** 🔴

Light gases effuse more rapidly than heavy gases.

Light gas ● heavy gas ●

# Example

Under identical conditions gaseous $CO_2$ and $CCl_4$ are allowed to effuse through a pinhole.  If the rate of effusion of the $CO_2$ is $6.3 \times 10^{-2}$ mol s$^{-1}$, what is the rate of effusion of the $CCl_4$?

# Graham's Law of Diffusion

$$\frac{\text{rate of effusion of gas 1}}{\text{rate of effusion of gas 2}} = \frac{(MW_2)^{1/2}}{(MW_1)^{1/2}}$$

$$\frac{\text{rate of effusion of } CCl_4}{\text{rate of effusion of } CO_2} = \frac{(44g)^{1/2}}{(153.8g)^{1/2}}$$

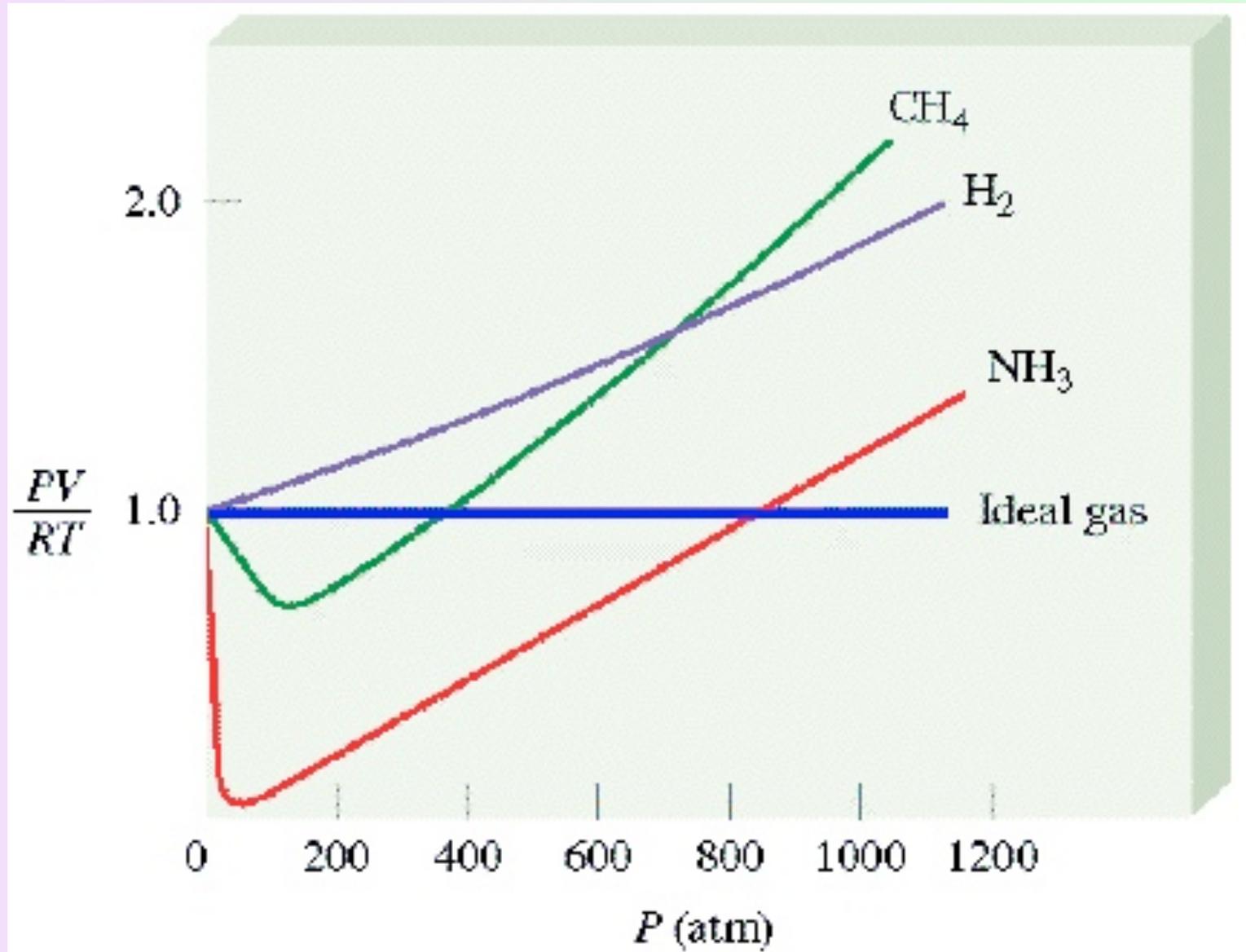$$\frac{\text{rate of effusion of } CCl_4}{6.3 \times 10^{-2} \text{ mol/s}} = \frac{(44g)^{1/2}}{(153.8g)^{1/2}}$$

$$\frac{\text{rate of effusion of CCl}_4}{6.3 \times 10^{-2} \text{ mol/s}} = \frac{(44g)^{1/2}}{(153.8.g)^{1/2}}$$

$$\text{rate of effusion CCl}_4 = \frac{(44g)^{1/2}}{(153.8g)^{1/2}} \times 6.3 \times 10^{-2} \text{ mol/s}$$

$$= 3.4 \times 10^{-2} \text{ mol/s}$$

# Deviation from Ideal Behavior

**Plot of PV/RT versus P of 1 mole of a gas at 0°C.**
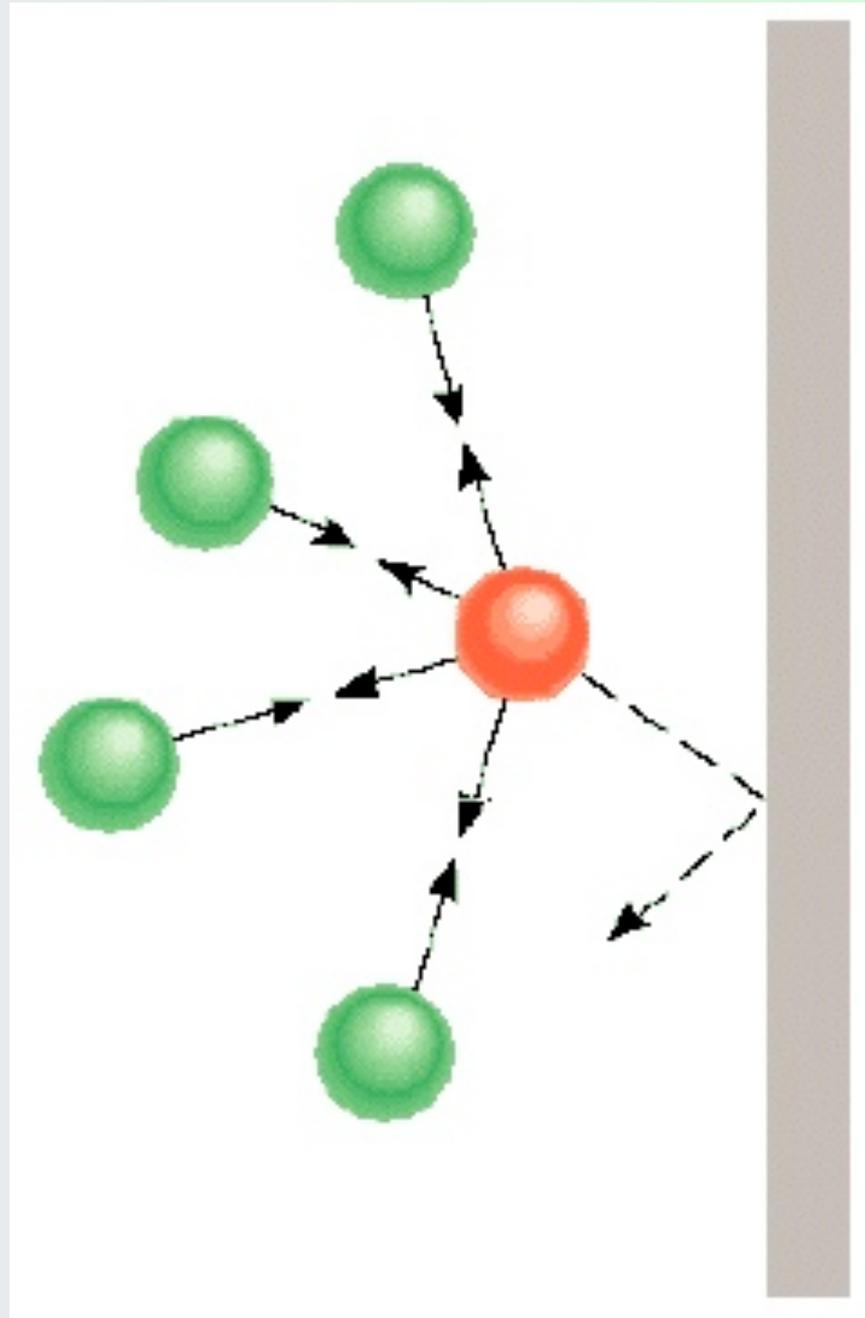
# Modifications to Ideal gas law

$$P_1 = \frac{nRT}{V}$$

**but volume available to the gas is smaller than V because gas molecules consume some of the space          ;  this makes the pressure exerted by the gas ($P_1$) larger than the ideal pressure**

$$P_1 = \frac{nRT}{V - nb}$$

**(b is a constant characteristic of a particular gas)**

**Effect of intermolecular forces exerted by a gas.**

# Modifications to ideal-gas law

**but attractive forces between gas molecules make the observed pressure less than that of an ideal gas; subtract a correction factor**

$$P_{obs} = \frac{nRT}{V - nb} - a\,\frac{n^2}{V^2}$$

**(a is a constant characteristic of a particular gas)**

**Van der Waal's equation**

# van der Waal's constants

| | a (atm-L$^2$-mol$^{-2}$) | b L-mol$^{-1}$ |
|---|---|---|
| He | 0.034 | 0.0237 |
| Ne | 0.211 | 0.0171 |
| Ar | 1.34 | 0.0322 |
| H$_2$O | 5.46 | 0.0305 |