The Kinetic-Molecular Theory of Gases

kinetic-molecular theory of gases

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

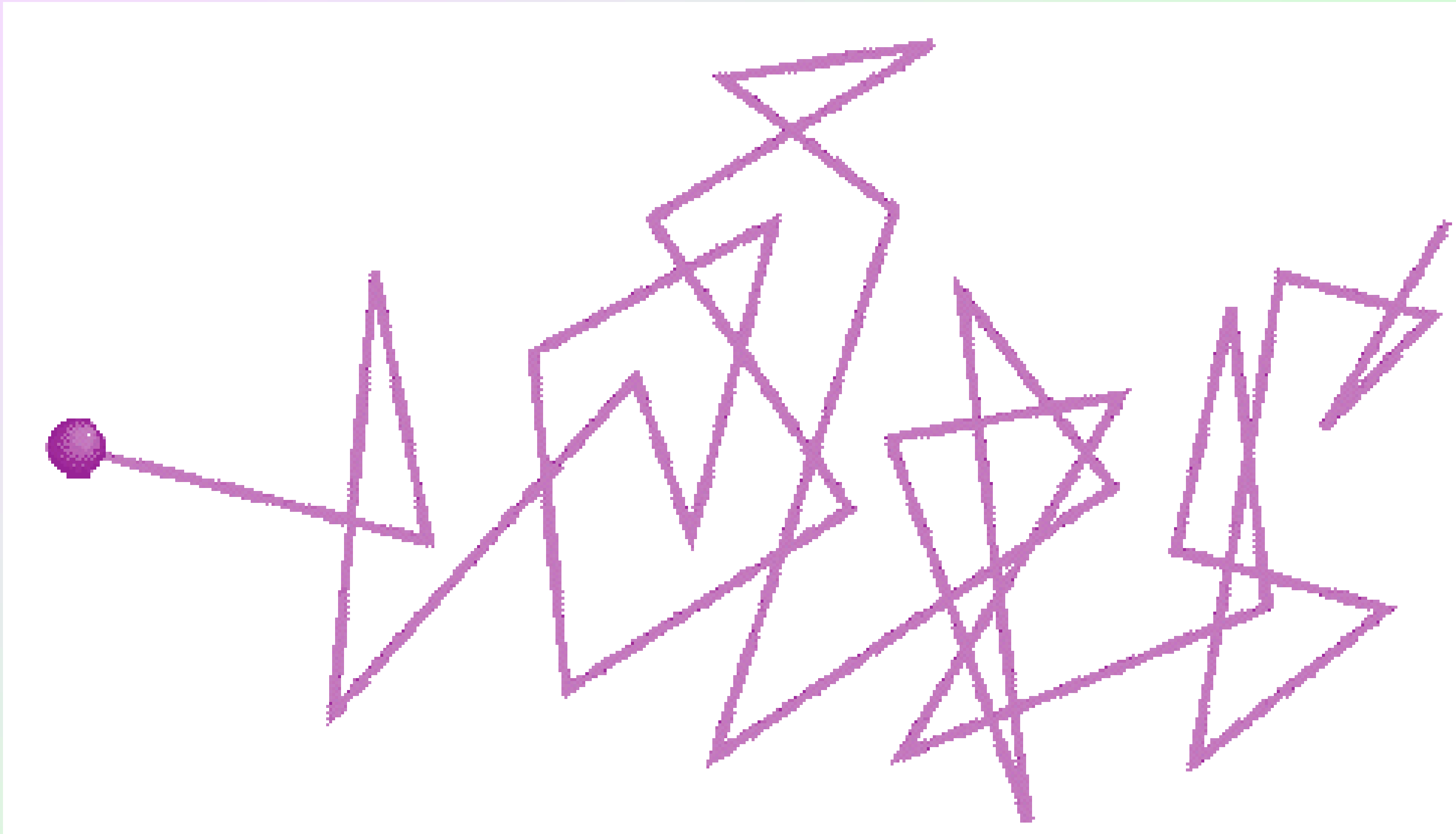
Explains gas behavior on the basis of the motion of individual particles

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.



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

Pressure increases

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.

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

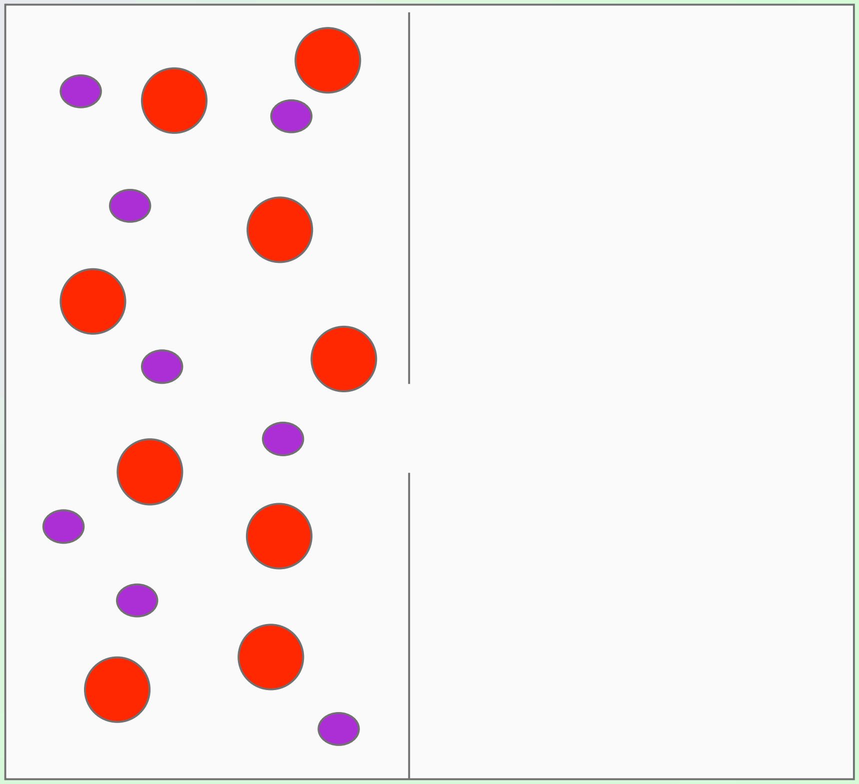
the process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening

Graham's Law of Effusion

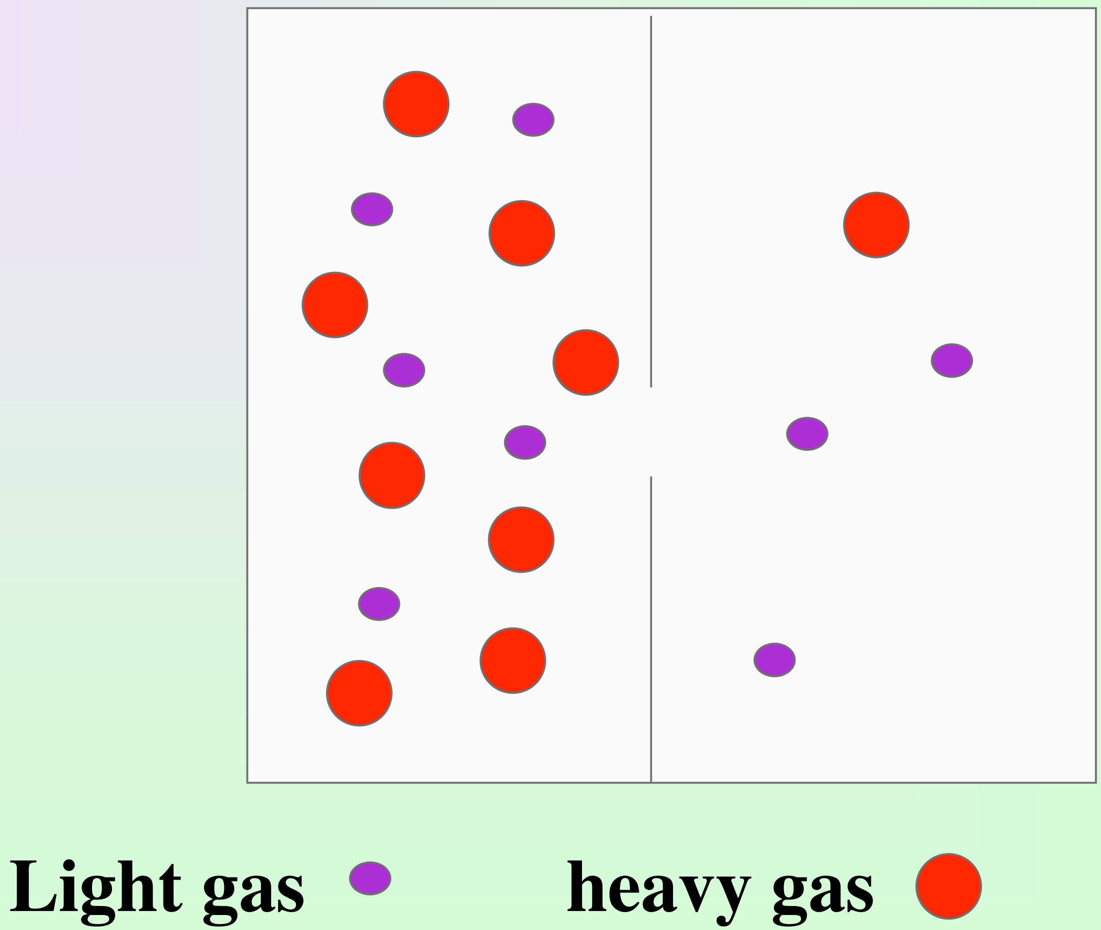
experimental

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

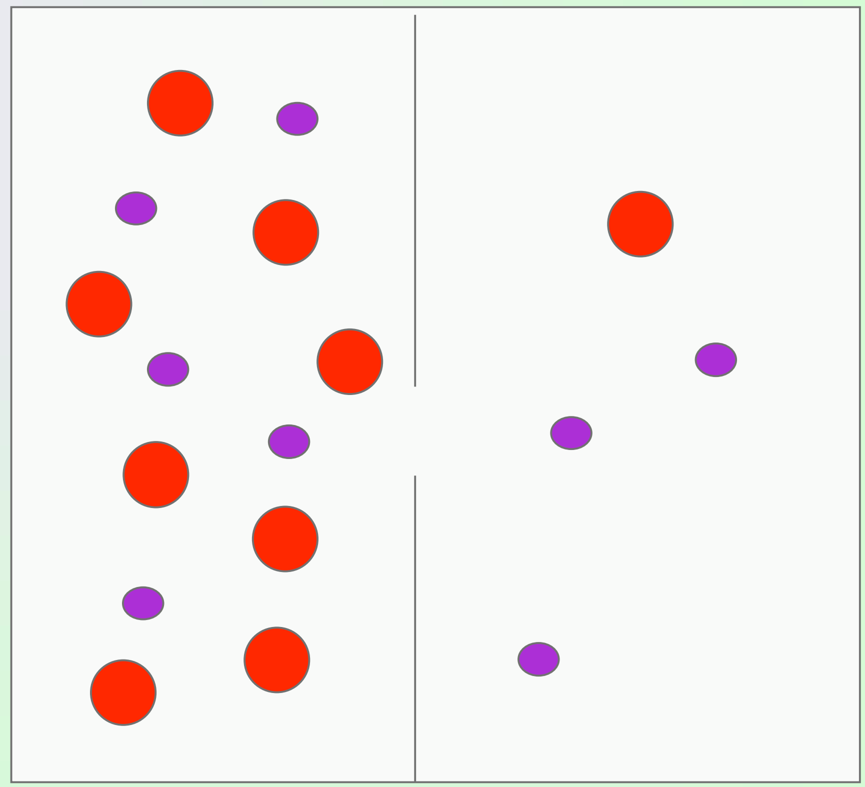
Gaseous effusion. Gas molecules move from a high-pressure region (left) to a low-pressure region through a pinhole.



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



Light 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 6.3×10^{-2} mol s^{-1}, what is the rate of effusion of the CCl_4?

Graham's Law of Diffusion

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

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

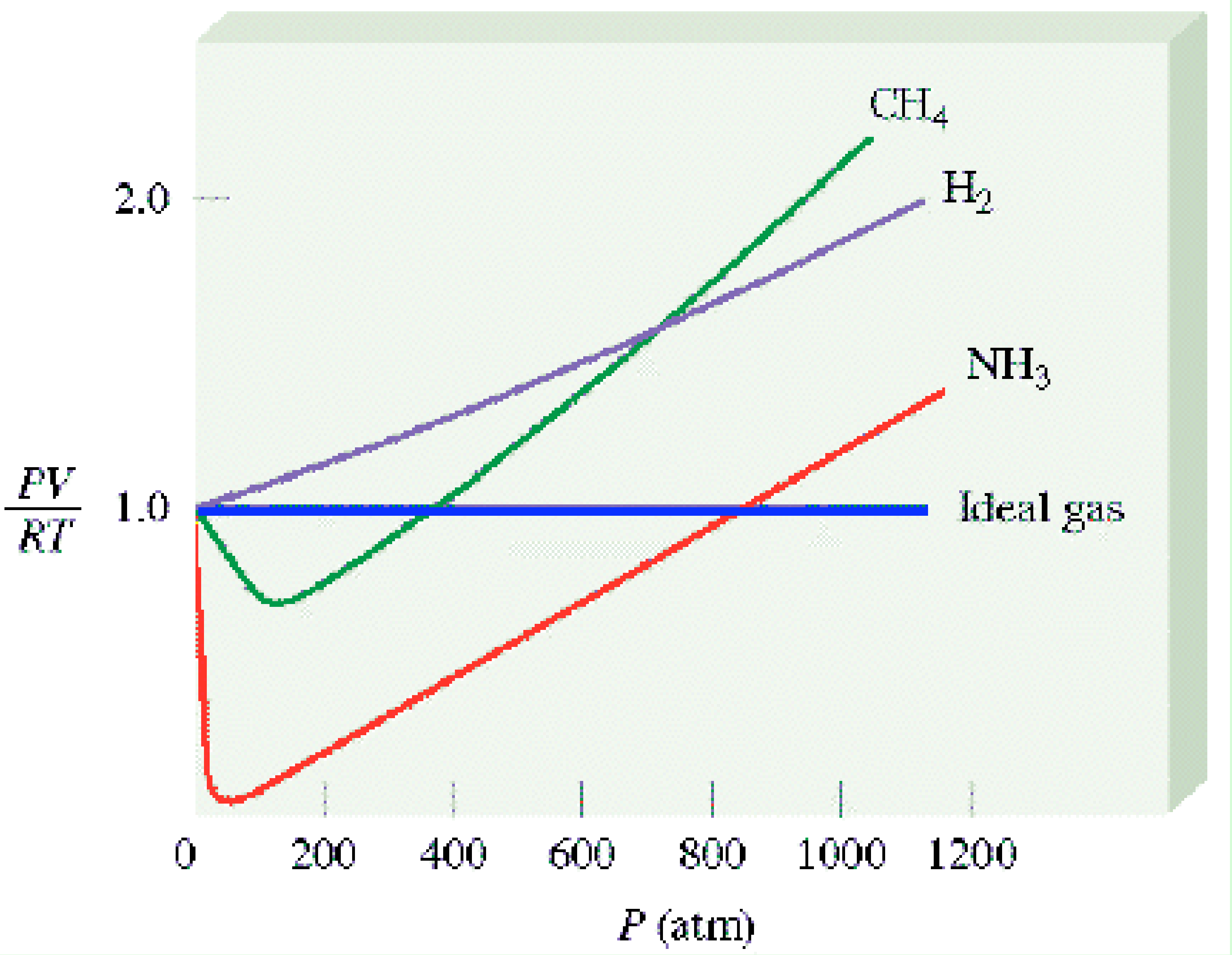
$$\frac{\text{rate of effusion of } CCl_4}{6.3 \times 10^{-2} \text{ mol/s}} = \frac{(44g)^{1/2}}{(153.8g)^{1/2}}$$

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

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

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

Deviation from Ideal Behavior



Plot of PV/RT versus P of 1 mole of a gas at 0˚C.

Modifications to Ideal gas law

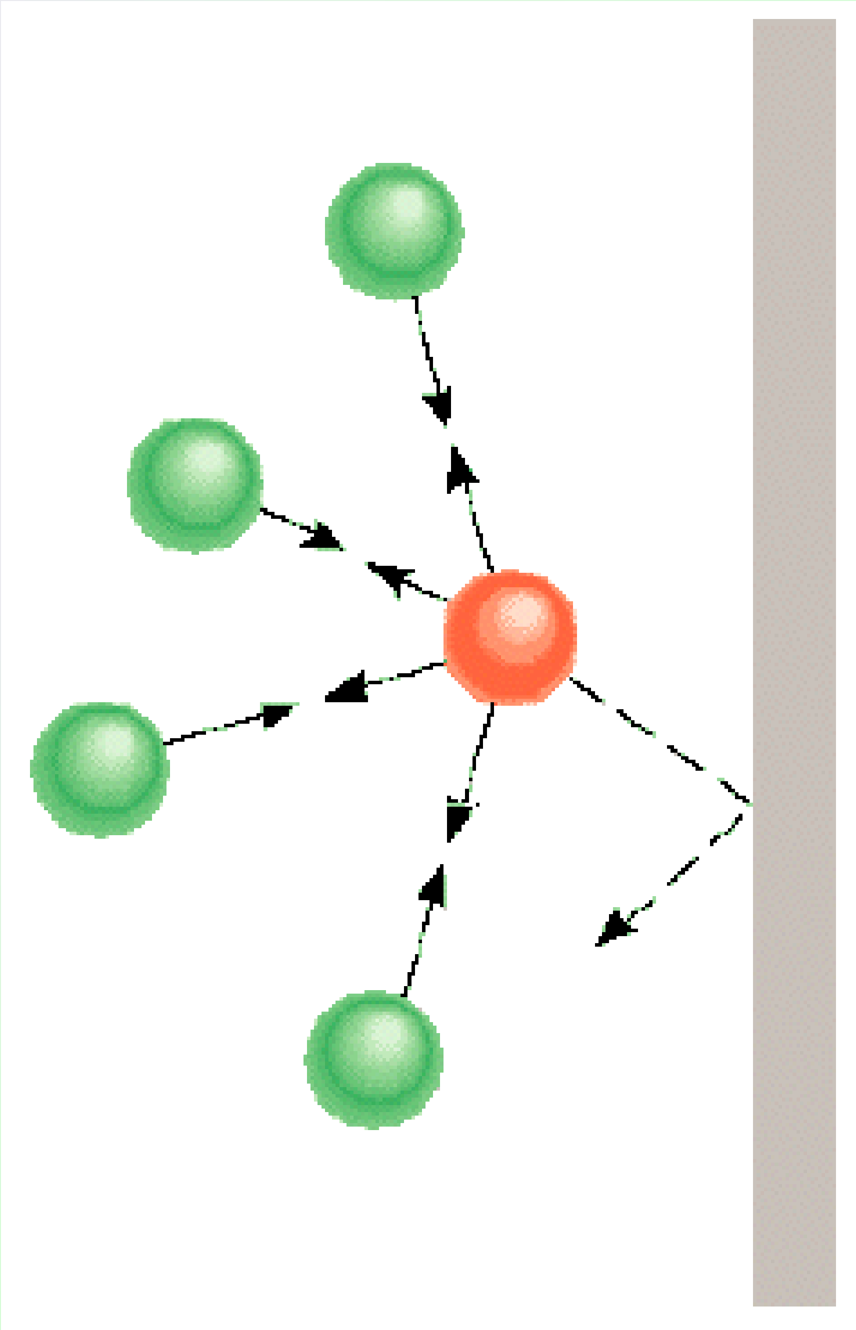
$$P_1 = \frac{nRT}{V}$$

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 $L\text{-}mol^{-1}$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
H_2O	5.46	0.0305