Postulates of Kinetic Molecular Theory

1. ***A gas is made up of vast number of particles, and these particles are in constant random motion***

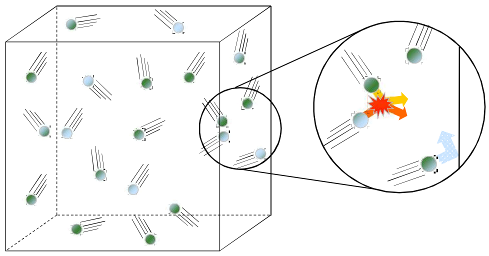


Image source: http://www.docstoc.com/docs/113002286/Kinetic-Molecular-Theory

Postulates of Kinetic Molecular Theory

2. ***Particles in a gas are infinitely small, they occupy no volume***

Volumeless - ***Most of the volume occupied by a gas is empty space***

- **Accounts for lower density compared to solid and liquids.**
- **Accounts for compressibility of gases.**

Postulates of Kinetic Molecular Theory

3. ***Particles in a gas move in straight lines except when they collide with other molecules or with the walls of the container. All collisions are elastic, so that the total kinetic energy of the particles is conserved***

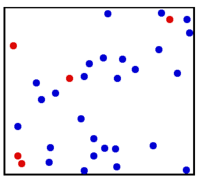


Image source: http://en.wikipedia.org/wiki/Kinetic_theory

Postulates of Kinetic Molecular Theory

4. ***Particles in a gas interact with each other only when collisions occur.***

- **Assumes no force of attraction/repulsin between gas particles**

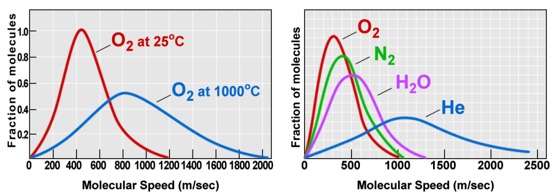
Postulates of Kinetic Molecular Theory

5. ***The average kinetic energy of the particles in a gas is proportional to the absolute temperature of the gas and does not depend on the identity of the gas***

The average Kinetic Energy of gas particles depends on Temperature of the gas:

$$KE_{av} \propto T$$

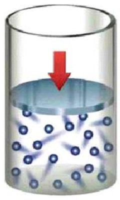
Maxwell-Boltzmann Speed Distributions



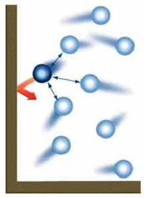
Deviations from Ideality - “Real” Gases

(a) At high pressure

(b) At low temperature



At high pressure



At low temperature

İmage source: http://wps.prenhall.com/wps/media/objects/3311/3391331/blb1009.html

van der Waals Equation

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

Van der Waals constants for several common gases

Gas	a (atm L² mol⁻²)	b (L mol⁻¹)
Ammonia, NH_3	4.170	0.03707
Argon, Ar	1.345	0.03219
Carbon dioxide, CO_2	3.592	0.04267
Helium, He	0.034	0.0237
Hydrogen, H_2	0.2444	0.02661
Hydrogen fluoride, HF	9.433	0.0739
Methane, CH_4	2.253	0.04278
Nitrogen, N_2	1.390	0.03913
Oxygen, O_2	1.360	0.03183
Sulfur dioxide, SO_2	6.714	0.05636
Water, H_2O	5.464	0.03049

The magnitude of the deviations from ideal gas behavior can be illustrated by comparing the results of calculations using the ideal gas equation and the van der Waals equation

Sumup exercise

a) Calculate the pressure for 1.00 mole of CO_2 at 0°C in a container of 22.4 L volume.

According to the ideal gas equation,

$$P = \frac{nRT}{V} = \frac{(1.00mol)(0.08206\frac{Latm}{molK})(273K)}{22.4L} = 1.00atm$$

Substituting what we know about CO_2 into the van der Waals equation,

$$\left[P + \frac{\left(3.592\frac{L^2atm}{mol^2}\right)(1.00mol)^2}{(22.4L)^2}\right]\left[22.4L - (1.00mol)(0.04267\frac{L}{mol})\right]$$

$$= (1.00mol)(0.08206\frac{Latm}{molK})(273K) = 0.995atm$$

Percentage correction : 0.5%

b) Let's now repeat this calculation, assuming that the gas is compressed so that it fills a container that has a volume of only 0.200 liters.

According to the ideal gas equation, the pressure

$$P = \frac{nRT}{V} = \frac{(1.00mol)(0.08206\frac{Latm}{molK})(273K)}{0.200L} = 112atm$$

The van der Waals equation, however, predicts that the pressure

$$\left[P + \frac{\left(3.592\frac{L^2atm}{mol^2}\right)(1.00mol)^2}{(0.200L)^2}\right]\left[0.200L - (1.00mol)(0.04267\frac{L}{mol})\right]$$

$$= (1.00mol)(0.08206\frac{Latm}{molK})(273K) = 52.6atm$$

Percentage correction: $\frac{112 - 52.6}{112} \times 100\% = 53\%$

A conceptual question

- ***van der Waals equation provides a much better fit with the behavior of a “real” gas than the “ideal” gas equation, but with a cost! What do you think the cost is?***

  Answ. : *Loss in generality!*