



CHEM 1035 – Lecture 17


Kinetic Molecular Theory of Gases

The pressure, volume, temperature relationships describe the macroscopic behavior of gases. We now need to relate these observed behaviors to some molecular description of matter. This Hypothesis is known as the Kinetic Molecular Theory of Gases.



Postulates of the Kinetic-Molecular Theory

1. A gas consists of a collection of individual particles. The volume of each particle is extremely small compared to the volume occupied by the gas.
2. Gas particles are in constant, random motion along straight line paths. The particles deviate from the straight line path only when they collide with other particles or the walls of the container.
3. Collisions are elastic (e.g. collisions involve the exchange of energy by not the loss of energy through friction).



Fundamental understanding of Pressure

Animation

1. Boyle's Law
2. Charles' Law
3. Dalton's Law of Partial Pressure
4. Avogadro's law

Pressure = (force)/area

Given this kinetic view of Gases, can we explain the gas laws with this Model?

Each collision of gas particles with the walls of the container exerts a force on the walls of the container. Many of these collisions results in the measured pressure. Therefore, the pressure is a function of the number of collisions. How can we rationalize the gas laws with this description?

Boyle's law?

Charles' law?

Avogadro's law?

Dalton's law of Partial pressure?

What happens if we increase the velocity of the gas particles? Then the frequency of collisions between the particles and the walls would increase, and the pressure would also increase.

What happens if we increase the number of gas particles? Then the frequency of the collisions with the wall would increase, and the pressure would also increase.

Force = mass x acceleration

So how to increase pressure? Increase the force (mass or acceleration)



Question

How can we explain that the identity of the gas substance does not influence the P, V, and T behavior?

E.G. Why do equal amount of H₂ and Ne have the same physical behavior as gases?

It would seem that the force that exists every time a collision occurs between the gas atoms/molecules and the container walls would depend on the mass of the colliding species? It does (Force = mass x acceleration) if we assume that each atom/molecule has the same velocity.

Since this is the case, then how can the same amount of different gases that have different mass (present at the same temperature and pressure) occupy the same volume?

It is related to the relationship between the gas mass and the kinetic energy of the gas. The kinetic energy ($E_k = 1/2mv^2$) for all the gases (at a given temperature, pressure, and volume) are the same. The atom/molecule average K.E. is directly proportional to the temperature of the system ($E_k = K \cdot T$).



Average Kinetic Energy

$$\bar{E}_{KE} = \frac{1}{2} m u^2$$

$$u_{rms} = \sqrt{\frac{3RT}{Molar\ Mass}}$$

RMS = root-mean square – this is the average speed of the molecules having average KE

We see that the gas particle velocity is related to the inverse square-root of the Molar mass. Therefore, heavier gas particles will have slower velocities than lighter gases that have the same kinetic energy. The heavier gas, therefore, will collide with the walls of the container fewer times than the lighter gas – but these collisions will have a greater force



Temperature

The kinetic energy of a gas particle is directly proportional to the temperature of the system. This is expressed by:

$$\overline{E}_{KE} = \frac{3}{2} \left(\frac{R}{N_A} \right) T$$



Rate of Gas Diffusion

Diffusion – the rate at which 2 gases mix

[Animation](#)



Gas Effusion

The process by which a gas escapes from a container through a small hole into evacuated space.

$$\text{Rate of Effusion} \propto \frac{1}{\sqrt{\text{Molar Mass}}}$$

The average velocity of a gas is inversely proportional to the square-root of the molar mass. The faster a molecule moves through space, the more likely it is to encounter the small hole and escape the container. The rate of effusion, therefore, is also inversely proportional to the inverse square-root of molar mass.



Example problem

What is the ratio of the effusion rates for O_2 and Kr?

Because the rate of effusion for a particular gas is inversely related to the molar mass, we simply take the ratio of $\{1/\text{square-root}(\text{molar Mass})\}$ for O_2 vs. Kr



Real gases

- Deviations from Ideal behavior

Atoms/Molecules are matter (e.g. have mass and occupy volume), so they don't satisfy the conditions of an "Ideal" gas. Similarly, in a mixture there will be interactions between the gas atoms/molecules.

Under ordinary conditions (relatively high temp and low pressure) gases exhibit "ideal" behavior; however, deviations from this ideal PVT behavior are seen and can be measured. If you go to high pressure, then the deviations become easily measurable.

Observed Deviations:

1. Moderate pressures 2-10 atmosphere – the observed PVT behavior is smaller than ideal – due to attractive forces between atoms/molecules
2. At very high pressures (100's-1000's atmospheres) the PVT behavior is larger than predicted by the ideal gas law. This is due to the finite volume occupied by the atoms/molecules.



Van der Waals Equation

- Corrected Gas equation

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

First term on left – corrected pressure for attractive interactions between gas particles (a term)

2nd term – corrected volume that accounts for molecular volume effects

a and b are van der Waals constants (a – accounts for attractive interactions, b accounts for volume)

Values of a and b are given in table 5.5 on page 209 of the chapter.