

## Kinetic Molecular Theory – The Algebra

### A. Three assumptions

1. Gas molecules behave like point masses and have no appreciable volume.
2. Gas molecules are in motion, and their average speed,  $u$ , is constant.
3. The collisions between molecules and the walls of a container are elastic.

### B. The derivation (only consider x-axis initially)

1. Newton's 2<sup>nd</sup> law,  $F = m\Delta v/\Delta t$   
Force applied by a particle colliding with wall is  $2mu_x/\Delta t$
2. Distance traveled by the average molecule = (speed)(time) =  $u_x\Delta t$   
So all molecules within a distance of  $u_x\Delta t$  of the wall will hit it within  $\Delta t$ .
3. If a wall has an area  $A$ , then the volume containing those particles =  $Au_x\Delta t$   
All particles in that volume will strike in  $\Delta t$ .
4. If we have one mole of molecules ( $N$ ) in a volume ( $V$ ), then density is  $N/V$   
Number of particles in the volume =  $(N/V)Au_x\Delta t$
5. That means we can calculate total force applied in  $\Delta t$ :  
Total force = (force applied by one particle)(total # of particles hitting)

$$F = \frac{2mu_x}{\Delta t} \cdot \frac{NAu_x\Delta t}{V} = \frac{2NmA(u_x)^2}{V}$$

6. Remember that pressure =  $F/A$ , so

$$P = \frac{F}{A} = \frac{2NmA\langle v_x^2 \rangle}{AV} = \frac{2Nm\langle v_x^2 \rangle}{V}$$

7. I lied.

If particles are traveling at  $v_x$ , only half are headed towards the wall.

The other half are headed in the other direction! Pressure reduced by  $1/2$ .

$$P = \frac{1}{2} \cdot \frac{2Nm\langle v_x^2 \rangle}{V} = \frac{Nm\langle v_x^2 \rangle}{V}$$

8. Now we need to get into three dimensions

First off, particle is moving in three dimensions, so total speed is

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

$v_{\text{rms}} = \langle v \rangle$ , root mean square speed, average speed in 3 directions.

If we assume that speed in all directions is, on average, the same:

$$\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

Subbing into the equation for pressure (step 7) we get:

$$P = \frac{Nm\langle v^2 \rangle}{3V}$$

9. And now, recognizing that  $Nm = M$  (the molar mass of the gas) and  
The kinetic energy of one mole of gas =  $\frac{1}{2}M\langle v^2 \rangle$

$$P = \frac{N2\left(\frac{1}{2}m\langle v^2 \rangle\right)}{3V} = \frac{2\left(\frac{1}{2}M\langle v^2 \rangle\right)}{3V} = \frac{2}{3} \frac{\langle E_k \rangle}{V}$$

Cross-multiply with  $V$ , and we get

$$PV = \frac{2}{3} \langle E_k \rangle, \text{ and because } PV = RT \text{ when } n=1,$$

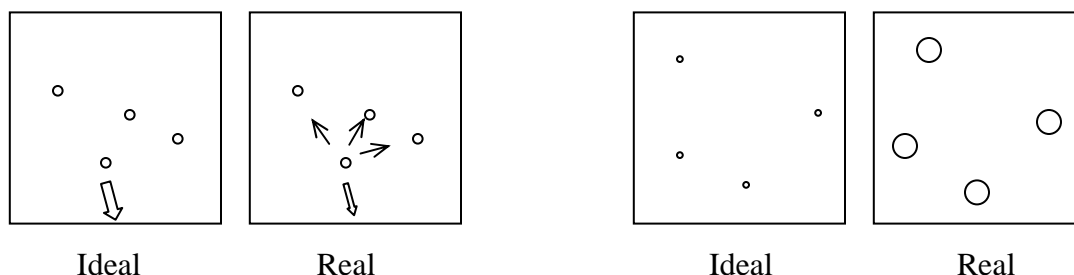
$$\langle E_k \rangle = \frac{3}{2} RT$$

## Real Gases

Unlike ideal gas molecules, *real gas* molecules have some finite size and there exists intermolecular forces between the molecules. What are the consequences of this?

A real gas will liquefy if cooled sufficiently. There are two competing factors: kinetic energy and intermolecular forces. At low temperatures, the minimal amount of average kinetic energy that maintains the constant rapid motion of gas molecules cannot overcome the intermolecular forces that enable the molecules to stick together. Intermolecular forces win out and the gas will condense to a liquid.

Due to the intermolecular forces, which cause individual molecules to attract each other, the observed pressure of a real gas will be less than that of an ideal gas. Also, because real gas molecules occupy some space, the observed volume of a real gas will be greater than an ideal gas. These cases are compared in Figure 1 below.



**Figure 1.** The differences between ideal and real gases. Note that the reduced pressure is dependent upon the concentration of the gas and the strength of attraction while the increased volume is dependent upon the amount of gas and the actual size of the molecules.

The most well-known attempt to modify the ideal gas law to describe real gases is summarized by the van der Waals equation of state:

$$(P + a(n/v)^2) \cdot (V - nb) = n R T$$

where  $P$ ,  $V$ ,  $R$ , and  $T$  represent the usual quantities and where  $a$  and  $b$  are correction factors for intermolecular forces and non-zero volume, respectively. These parameters, experimentally determined, are shown in Table 1 for some different gases. Note that the intermolecular force corrections are more significant than the volume corrections as values of  $a$  are generally larger than  $b$ . Note also that if both  $a$  and  $b$  are zero (an ideal gas), then the van der Waals equation reduces to the ideal gas law.

**Table 1.** Some van der Waals correction factors.

	<u>He</u>	<u>H<sub>2</sub></u>	<u>N<sub>2</sub></u>	<u>H<sub>2</sub>O</u>	<u>ideal</u>
a	0.035	0.245	1.37	5.537	0
b	0.0238	0.0265	0.0387	0.0305	0

Under moderate conditions, the ideal gas law describes real gases reasonably well. However, under the conditions of high pressures and low temperatures, the assumptions of zero volume and zero intermolecular forces undertaken by kinetic molecular theory are not valid.