

Lecture #16 The Kinetic Theory of Gases /Thursday March 16

- I. Goals/Assumptions of the Kinetic Molecular Theory
 - II. Calculation of Pressure of a Gas
 - III. Molecular Speeds
 - IV. Graham's law of Effusion
 - V. Molecular Collisions
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I. Goals/Assumptions of the Kinetic Molecular Theory:

Previously ideal gases discuss with macroscopic par. P,V,T. Now more detailed molecular picture: start with gas composed of molecules possessing kinetic energy in terms of random motion with P & T as manifestations. 5 Postulates are: **1. Gas is composed of large # of particles in constant motion to allow statistical averaging to be done. 2. Intrinsic vol. of particles small compared to vol. of container. 3. Particles in random motion, have no mutual attraction. 4. Collision between particles and the wall are elastic® conservation of energy and momentum. 5. Average translational kinetic energy of particles is proportional to the absolute temperature.**

II. Calculation of Pressure of a Gas (see "Further Info #4" in the back of your textbook)

The following discussion will derive the relationship between gas pressure and rms speed (c) of gas sample:

$$P = \frac{1}{3} nM c^2$$

A particle of mass m travels with velocity u_1 in a box of length l . Thus the momentum is mu_1 , the time between collisions is $2l/u_1$ (collision freq. of one wall is $u_1/2l$).

$\Delta(\text{momentum}) = \text{momentum final} - \text{momentum initial} = -mu_1 - (mu_1) = -2mu_1$. $F=ma=m (du_1/dt) = d(mu_1)/dt$

The force acting on the particle by wall is equal to the change in momentum per unit time $= (-2mu_1 \text{ momentum change per collision}) \times (u_1/2l \text{ collision per unit time}) = -mu_1^2/l$, and by Newton's third law the force acting on the wall by the particle is mu_1^2/l . Thus the pressure acting on the wall is $mu_1^2/(Al) = mu_1^2/V$. If there are N particles of velocity $u_1, u_2, u_3, \dots, u_N$ then we obtain: the total pressure:

$$P = \frac{m(u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2)}{V} \quad (1)$$

The average of the squares of velocities, $\langle u^2 \rangle$ is:

$$\langle u^2 \rangle = \frac{(u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2)}{N} \quad (2)$$

$$P = \frac{Nm \langle u^2 \rangle}{V} \quad (3)$$

By definition we take c to be the average rms speed of the gas: $\langle u^2 \rangle + \langle v^2 \rangle + \langle w^2 \rangle = c^2$ where v and w are components orthogonal to u

Now we have no reason to expect any xyz directions average squared velocity to be larger than any other, thus $u^2 = v^2 = w^2$. Thus $\langle u^2 \rangle = (1/3)c^2$ inserting this into the 1-D equation yields:

$$P = \frac{\frac{1}{3} Nm c^2}{V} \quad (4)$$

Note: Nm (N = avogad #, m = mass of particle) = total mass = nM , thus

$$P = \frac{\frac{1}{3} nM c^2}{V}$$

III. Molecular Speeds

A. RMS speed

Now for ideal gas $PV = nRT$, inserting into $pV = 1/3 nMc^2$ yields: $nRT = 1/3 nMc^2$
so solving for c (r.m.s. speed): $c = (3RT/M)^{1/2}$

i.e. What is c for nitrogen gas at 25 C?

B. Maxwell Distribution of Speeds

The Boltzmann expression for the number of particles N in the i^{th} energy level:

$$N_i = A \exp[-E_i/RT]$$

This explains rotational, vibrational and electronic populations, i.e. at room temperature most molecules in the $v=0$ level, less in $v=1$, even less in $v=2$ level. (See Chapter 20 p. 476, Eq. 20.1)

Kinetic energy of a mole in 1-D is $\frac{1}{2} Ms^2$. Thus the probability of molecules having some kinetic energy $\frac{1}{2} Ms^2$ = the probability that it has 1-D (x-dir) speed s . Boltzmann Eqtn is:

$$p(s) = A e^{-\frac{m s^2}{2kT}} = A e^{-\frac{M s^2}{2RT}}$$

Normalizing this distribution $\sum p(s) = 1$

leads to the Maxwell distribution of speeds: fraction of molecules f with speed between s and $s+\Delta s$

$$f = 4p \left(\frac{M}{2pRT} \right)^{3/2} s^2 e^{-Ms^2/2RT} \Delta s$$

Example: What fraction of NO_2 gas particles are moving with speeds between 100 and 110 m

s^{-1} at 25 °C?

Answer: $s = 100 \text{ ms}^{-1}$, $\Delta s = 10 \text{ ms}^{-1}$, $M = 0.046 \text{ Kg mol}^{-1}$, $R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 25 + 273.15 = 298.15 \text{ K}$,

$$\begin{aligned}
 f &= 4p \left(\frac{0.046 \text{ kg mol}^{-1}}{2p \times 8.31451 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \right)^{3/2} (100 \text{ ms}^{-1})^2 \\
 &\times \exp \left[- \frac{0.046 \text{ kg mol}^{-1} \times (100 \text{ ms}^{-1})^2}{2 \times 8.31451 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \right] \times 10 \text{ ms}^{-1} \\
 &= 4p \left(\frac{0.046 \text{ kg mol}^{-1}}{2p \times 8.31451 \text{ J} \frac{\text{kg m}^2 \text{ s}^{-2}}{1 \text{ J}} \text{ K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \right)^{3/2} 1 \times 10^4 \text{ m}^2 \text{ s}^{-2} \\
 &\times \exp \left[- \frac{0.046 \text{ kg mol}^{-1} \times (100 \text{ ms}^{-1})^2}{2 \times 8.31451 \text{ J} \frac{\text{kg m}^2 \text{ s}^{-2}}{1 \text{ J}} \text{ K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \right] \times 10 \text{ ms}^{-1} \\
 &= 4p \times 5.075 \times 10^{-9} \text{ m}^{-3} \text{ s}^3 \times 10^4 \text{ m}^2 \text{ s}^{-2} \times \exp(-0.09278) \times 10 \text{ ms}^{-1} \\
 &= 5.8 \times 10^{-3} = 0.58\%
 \end{aligned}$$

IV. Graham's law of Effusion

Escape of gas through hole = effusion

Effusion rate of gas 1 ÷ Effusion rate of gas 2 = $c_1/c_2 = (3RT/M_1)^{1/2} / (3RT/M_2)^{1/2} = (M_2/M_1)^{1/2}$

Example: What is the effusion rate ratio of N_2 to NO_2 ? $M(\text{N}_2) = 28 \text{ g mol}^{-1}$, $M(\text{NO}_2) = 46 \text{ g mol}^{-1}$,

1 , Thus rate of N_2 to $\text{NO}_2 = \sqrt{\frac{46}{28}} = 1.28$

In terms of mass of gas per unit time, which gas's mass is depleted faster?

V. Molecular Collisions

By carrying out molecular scattering experiments, one can essentially use Beer's law: $I = I_0 \exp[-\sigma n l]$ where I_0 is initial flux of particles, σ is the collision cross section, $n = \#$ density.

The effective diameter "d" of molecules is determined from: $\sigma = \pi d^2$

$c = l z$ where l = the mean free path, z = collision frequency (average # of collisions experienced by one particle).

$$l = \frac{RT}{\sqrt{2} N_A s p} \quad z = \frac{\sqrt{2} N_A s c p}{RT}$$

If we want to know the total collision frequency for all molecules in the container, we should sum up all Z values and divide by 2 to avoid counting same collisions twice.

For like molecules, i.e. A, the collision frequency per unit volume = $Z_{AA} = ?$ $r Z_A$ where Z_A is the collision frequency per molecule A (same as Z above), ρ = no. of A molecules per unit volume = number density. Thus to find the total # of collisions in a container: $V \cdot Z_{AA}$

Thus for homework problem #23 The total number of collisions per second for all molecules within a given volume may be determined as follows:

Total # collisions per second = (# collisions per molecule per second) \cdot (# molecules per L) \cdot volume \cdot 2