Most probable speed
Mean speed, $\bar{c}$
Root mean square (rms) speed, c

Number of molecules

0   Speed, s

Values for N_2(g) at 273 K
most probable speed = 403 m s⁻¹
mean speed, $\bar{c}$ = 454 m s⁻¹
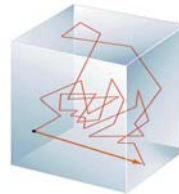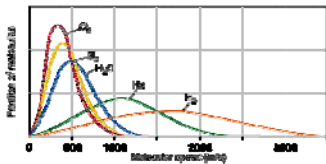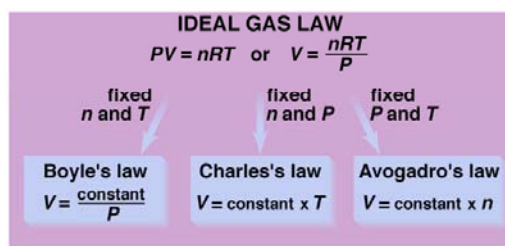rms speed, c = 493 m s⁻¹

Lecture 2-3.

Kinetic Molecular Theory of Ideal Gases

Last Lecture ....

Martin S. Silberberg, Chemistry: The Molecular Nature of Matter and Change, 2ⁿᵈ Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

Relationship between the Ideal Gas Law and the Individual Gas Laws

IDEAL GAS LAW

$$PV = nRT \quad \text{or} \quad V = \frac{nRT}{P}$$

fixed n and T | fixed n and P | fixed P and T

Boyle's law	Charles's law	Avogadro's law
$V = \dfrac{constant}{P}$	$V = constant \times T$	$V = constant \times n$

IGL is a purely empirical law - solely the consequence of experimental observations
Explains the behavior of gases over a limited range of conditions.
IGL provides a macroscopic explanation. Says nothing about the microscopic behavior of the atoms or molecules that make up the gas.

Today ….the Kinetic Molecular Theory (KMT) of gases.

KMTG starts with a set of assumptions about the microscopic behavior of matter at the atomic level.
KMTG Supposes that the constituent particles (atoms) of the gas obey the laws of classical physics.
Accounts for the random behavior of the particles with statistics, thereby establishing a new branch of physics - statistical mechanics.
Offers an explanation of the macroscopic behavior of gases.
Predicts experimental phenomena that suggest new experimental work (Maxwell-Boltzmann Speed Distribution).

Kotz, Section 11.6, pp.532-537
Chemistry[3], Section 7.4, pp.316-319
Section 7.5, pp.319-323.

Kinetic Molecular Theory (KMT) of Ideal Gas

- Gas sample composed of a large number of molecules (> 10^{23}) in continuous random motion.
- Distance between molecules large compared with molecular size, i.e. gas is dilute.
- Gas molecules represented as point masses: hence are of very small volume so volume of an individual gas molecule can be neglected.
- Intermolecular forces (both attractive and repulsive) are neglected. Molecules do not influence one another except during collisions. Hence the potential energy of the gas molecules is neglected and we only consider the kinetic energy (that arising from molecular motion) of the molecules.
- Intermolecular collisions and collisions with the container walls are assumed to be elastic.
- The dynamic behaviour of gas molecules may be described in terms of classical Newtonian mechanics.
- The average kinetic energy of the molecules is proportional to the absolute temperature of the gas. This statement in fact serves as a definition of temperature. At any given temperature the molecules of all gases have the same average kinetic energy.
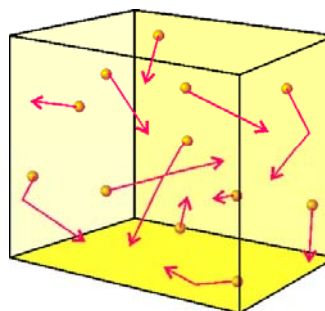
Air at normal conditions:

~ 2.7×10^{19} molecules in 1 cm^3 of air

Size of the molecules ~ $(2-3) \times 10^{-10}$ m,

Distance between the molecules ~ 3×10^{-9} m

The average speed - 500 m/s

The mean free path - 10^{-7} m (0.1 micron)

The number of collisions in 1 second - 5×10^9

Random trajectory of individual gas molecule.
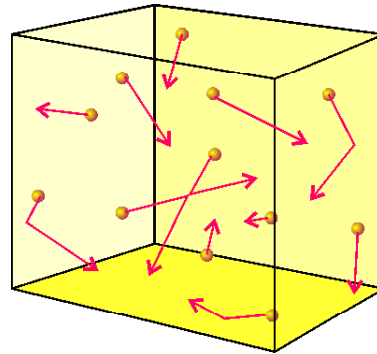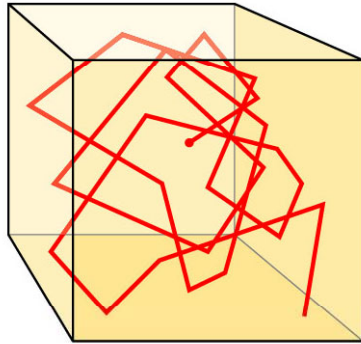
Assembly of ca. 10^{23} gas molecules Exhibit distribution of speeds.

Gas pressure derived from KMT analysis.

The pressure of a gas can be explained by KMT as arising from the force exerted by gas molecules impacting on the walls of a container (assumed to be a cube of side length L and hence of Volume L^3).

We consider a gas of N molecules each of mass m contained in cube of volume $V = L^3$.
When gas molecule collides (with speed v_x) with wall of the container perpendicular to x co-ordinate axis and bounces off in the opposite direction with the same speed (an elastic collision) then the momentum lost by the particle and gained by the wall is Δp_x.
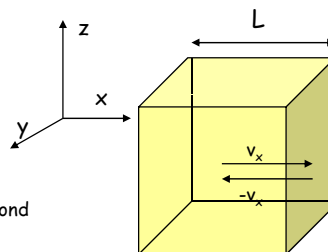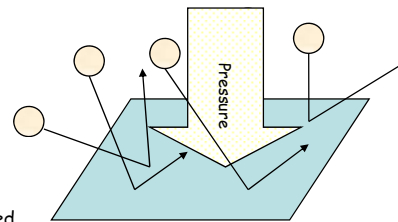
$$\Delta p_x = mv_x - (-mv_x) = 2mv_x$$

The particle impacts the wall once every $2L/v_x$ time units.

$$\Delta t = \frac{2L}{v_x}$$

The force F due to the particle can then be computed as the rate of change of momentum wrt time (Newtons Second Law).

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}$$

Force acting on the wall from all N molecules can be computed by summing forces arising from each individual molecule j.

$$F = \frac{m}{L}\sum_{j=1}^{N} v_{x,j}^2$$

The magnitude of the velocity v of any particle j can also be calculated from the relevant velocity components v_x, v_y, and v_z.

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

The total force F acting on all six walls can therefore be computed by adding the contributions from each direction.

$$F = 2\frac{m}{L}\left\{\sum_{j=1}^{N} v_{x,j}^2 + \sum_{j=1}^{N} v_{y,j}^2 + \sum_{j=1}^{N} v_{z,j}^2\right\} = 2\frac{m}{L}\sum_{j=1}^{N}\left\{v_{x,j}^2 + v_{y,j}^2 + v_{z,j}^2\right\} = 2\frac{m}{L}\sum_{j=1}^{N} v_j^2$$

Assuming that a large number of particles are moving randomly then the force on each of the walls will be approximately the same.
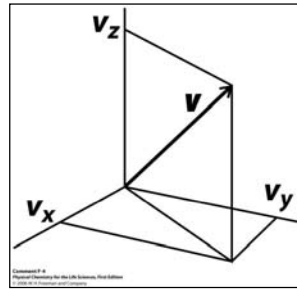
$$F = \frac{1}{6}\left\{2\frac{m}{L}\sum_{j=1}^{N} v_j^2\right\} = \frac{1}{3}\frac{m}{L}\sum_{j=1}^{N} v_j^2$$

The force can also be expressed in terms of the average velocity v_{rms}^2

$$\langle v^2 \rangle = v_{rms}^2 = \frac{1}{N}\sum_{j=1}^{N} v_j^2$$

Where v_{rms} denotes the root mean square velocity of the collection of particles.

$$F = \frac{Nmv_{rms}^2}{3L}$$

The pressure can be readily determined once the force is known using the definition P = F/A where A denotes the area of the wall over which the force is exerted.

$$P = \frac{F}{A} = \frac{Nmv_{rms}^2}{3AL} = \frac{Nmv_{rms}^2}{3V}$$

$$AL = V$$

The fundamental KMT result for the gas pressure P can then be stated in a number of equivalent ways involving the gas density ρ, the amount n and the molar mass M.

$$\rho = \frac{Nm}{V}$$

$$PV = \frac{1}{3}Nmv_{rms}^2 = \frac{2}{3}\left\{\frac{\rho v_{rms}^2}{2}\right\} = \frac{1}{3}N\left\{\frac{M}{N_A}\right\}v_{rms}^2 = \frac{1}{3}\left\{\frac{N}{N_A}\right\}Mv_{rms}^2 = \frac{1}{3}nMv_{rms}^2$$

$$m = \frac{M}{N_A}$$

Avogadro Number = 6×10^{23} mol^{-1}

Using the KMT result and the IGEOS we can derive a Fundamental expression for the root mean square Velocity v_{rms} of a gas molecule.

IGEOS → $$PV = nRT$$

KMT result → $$PV = \frac{1}{3}Nmv_{rms}^2 = \frac{1}{3}nMv_{rms}^2$$

$$\frac{1}{3}nMv_{rms}^2 = nRT$$
$$Mv_{rms}^2 = 3RT$$
$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

Gas	10^3 M/kg mol^{-1}	V_{rms}/ms^{-1}
H_2	2.0158	1930
H_2O	18.0158	640
N_2	28.02	515
O_2	32.00	480
CO_2	44.01	410

Internal energy of an ideal gas

We now derive two important results.
The first is that the gas pressure P is proportional to the average kinetic energy of the gas molecules.
The second is that the internal energy U of the gas, i.e. the mean kinetic energy of translation (motion) of the molecules is directly proportional to the temperature T of the gas.
This serves as the molecular definition of temperature.

Average kinetic Energy of gas molecule

$$\langle E \rangle = \frac{1}{2}mv_{rms}^2$$

$$P = \frac{Nmv_{rms}^2}{3V} = \frac{2N}{3V}\left\{\frac{1}{2}mv_{rms}^2\right\} = \frac{2N}{3V}\langle E \rangle$$

Boltzmann Constant

$$n = \frac{N}{N_A}$$

$$k_B = \frac{R}{N_A} = \frac{8.314 \text{J mol}^{-1}\text{ K}^{-1}}{6.02 \times 10^{23}\text{mol}^{-1}} = 1.38 \times 10^{-23}\text{J K}^{-1}$$

$$nR = Nk_B$$

$$P = \frac{nRT}{V} = \frac{NRT}{N_AV} = \frac{Nk_BT}{V}$$

$$\frac{2N}{3V}\langle E \rangle = \frac{Nk_BT}{V}$$

$$\langle E \rangle = \frac{3}{2}k_BT$$

$$U = N\langle E \rangle = \frac{3}{2}Nk_BT = \frac{3}{2}nRT$$
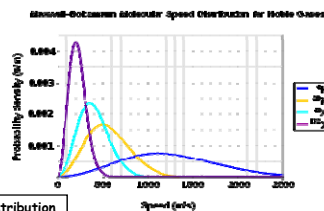
Maxwell-Boltzmann velocity distribution

- In a real gas sample at a given temperature T, all molecules do not travel at the same speed. Some move more rapidly than others.
- We can ask : what is the distribution (spread) of molecular velocities in a gas sample ? In a real gas the speeds of individual molecules span wide ranges with constant collisions continually changing the molecular speeds.
- Maxwell and independently Boltzmann analysed the molecular speed distribution (and hence energy distribution) in an ideal gas, and derived a mathematical expression for the speed (or energy) distribution f(v) and f(E).
- This formula enables one to calculate various statistically relevant quantities such as the average velocity (and hence energy) of a gas sample, the rms velocity, and the most probable velocity of a molecule in a gas sample at a given temperature T.

James Maxwell
1831-1879

$$F(v) = 4\pi v^2 \left\{ \frac{m}{2\pi k_B T} \right\}^{3/2} \exp\left[-\frac{mv^2}{2k_B T} \right]$$

$$F(E) = 2\sqrt{\frac{E}{\pi (k_B T)^3}} \exp\left[-\frac{E}{k_B T} \right]$$

Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases

http://en.wikipedia.org/wiki/Maxwell_speed_distribution

http://en.wikipedia.org/wiki/Maxwell-Boltzmann_distribution

Ludwig Boltzmann
1844-1906

Maxwell-Boltzmann velocity Distribution function

$$F(v) = 4\pi v^2 \left\{ \frac{m}{2\pi k_B T} \right\}^{3/2} \exp\left[-\frac{mv^2}{2k_B T} \right]$$

m = particle mass (kg)
k_B = Boltzmann constant
= 1.38×10^{-23} J K^{-1}

$F(v)$

- The velocity distribution curve has a very characteristic shape.
- A small fraction of molecules move with very low speeds, a small fraction move with very high speeds, and the vast majority of molecules move at intermediate speeds.
- The bell shaped curve is called a Gaussian curve and the molecular speeds in an ideal gas sample are Gaussian distributed.
- The shape of the Gaussian distribution curve changes as the temperature is raised.
- The maximum of the curve shifts to higher speeds with increasing temperature, and the curve becomes broader as the temperature increases.
  - A greater proportion of the gas molecules have high speeds at high temperature than at low temperature.

Gas molecules exhibit a spread or distribution of speeds.

v

Properties of the Maxwell-Boltzmann Speed Distribution.

Most molecules in a gas move at speeds around the average value in the middle of the range

Some molecules in the gas move at low speed

Some molecules in the gas move at high speed

Most probable speed

Mean speed, $\bar{c}$

Root mean square (rms) speed, c

Values for N_2(g) at 273K
most probable speed = 403 ms^{-1}
mean speed, $\bar{c}$ = 454 ms^{-1}
rms speed, c = 493 ms^{-1}

(a)
M (Xe) = 131 $g\,mol^{-1}$
M (Ar) = 40 $g\,mol^{-1}$
M (Ne) = 20 $g\,mol^{-1}$

For gases with higher molar mass the average speed is lower and the distribution of speeds is less broad

(b)
T = 100 K
T = 300 K
T = 700 K

At higher temperatures, a gas has a higher average speed and a broader distribution of speeds

Low temperature or high molecular mass

Intermediate temperature or molecular mass

High temperature or low molecular mass

Maxwell Boltzmann (MB) Velocity Distribution

$v_{max} = v_P$

Ar M = 39.95 kg mol^{-1}

v_P (300K) = 353.36 ms^{-1}
v_{rms} (300K) = 432.78 ms^{-1}
$\langle v \rangle$ (300K) = 398.74 ms^{-1}

T = 300 K
T = 400 K
T = 500 K
T = 600 K
T = 700 K
T = 800 K
T = 900 K
T = 1000K

Features to note:
The most probable speed is at the peak of the curve.
The most probable speed increases as the temperature increases.
The distribution broadens as the temperature increases.

Relative mean speed (speed at which one molecule approaches another.

$$v_{rel} = \sqrt{2}\langle v \rangle$$

MB Velocity Distribution Curves : Effect of Molar Mass

T = 300 K

F(v)

He	M = 4.0 kg/mol
Ne	M = 20.18 kg/mol
Ar	M = 39.95 kg/mol
Xe	M = 131.29 kg/mol

v / ms^{-1}
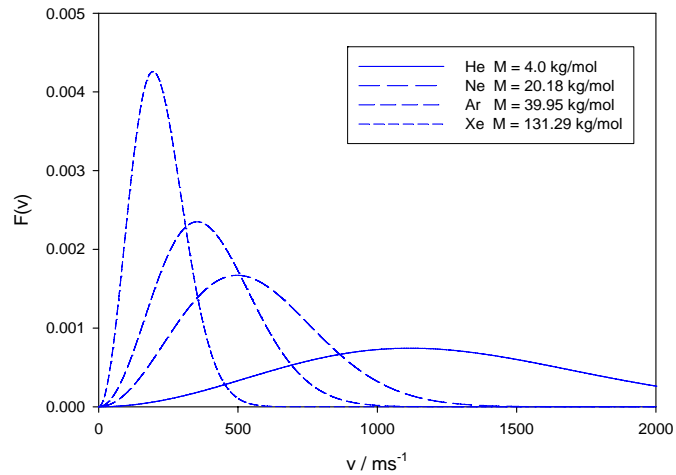
Determining useful statistical quantities from MB Distribution function.

Average velocity of a gas molecule

$$\langle v \rangle = \int_0^\infty v\, F(v)\,dv$$

$$F(v) = 4\pi\, v^2 \left\{ \frac{m}{2\pi\, k_B T} \right\}^{3/2} \exp\left[-\frac{mv^2}{2k_B T} \right]$$

MB distribution of velocities enables us to statistically estimate the spread of molecular velocities in a gas

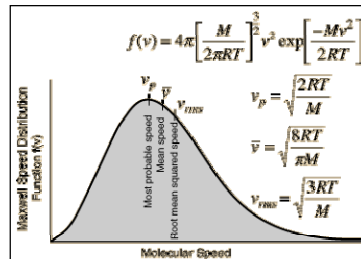Derivation of these formulae Requires knowledge of Gaussian Integrals.

Some maths !

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi\, m}} = \sqrt{\frac{8RT}{\pi M}}$$

Molar mass

Maxwell-Boltzmann velocity Distribution function

Mass of molecule

$$v_P < \langle v \rangle < v_{rms}$$

Most probable speed, v_{max} or v_P derived from differentiating the MB distribution function and setting the result equal to zero, i.e. $v = v_{max}$ when $dF(v)/dv = 0$.

$$v_{max} = v_P = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}$$

Root mean square speed   **Yet more maths!**

$$v_{rms} = \left\{ \int_0^\infty v^2 F(v)\,dv \right\}^{1/2} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

$$f(v) = 4\pi \left[\frac{M}{2\pi RT} \right]^{\frac{3}{2}} v^2 \exp\left[\frac{-Mv^2}{2RT} \right]$$

Maxwell Speed Distribution Function f(v)

Most probable speed v_P
Mean speed $\bar{v}$
Root mean squared speed v_{rms}

$$v_P = \sqrt{\frac{2RT}{M}}$$

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

Molecular Speed

$v_P < \langle v \rangle < v_{rms}$

Gas	$10^3 M/$ kg mol^{-1}	v_{rms}/ms^{-1}	$\langle v \rangle/ms^{-1}$	V_{rel}/ms^{-1}	v_P/ms^{-1}
H_2	2.0158	1930	1775	2510	1570
H_2O	18.0158	640	594	840	526
N_2	28.02	515	476	673	421
O_2	32.00	480	446	630	389
CO_2	44.01	410	380	537	332
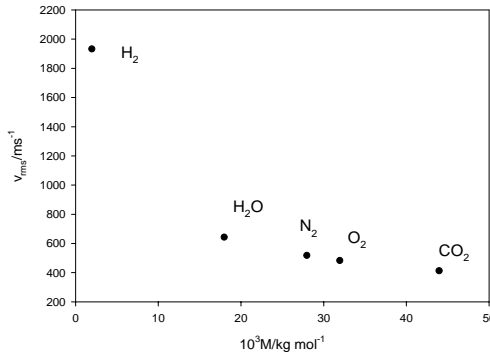
Typical molecular velocities
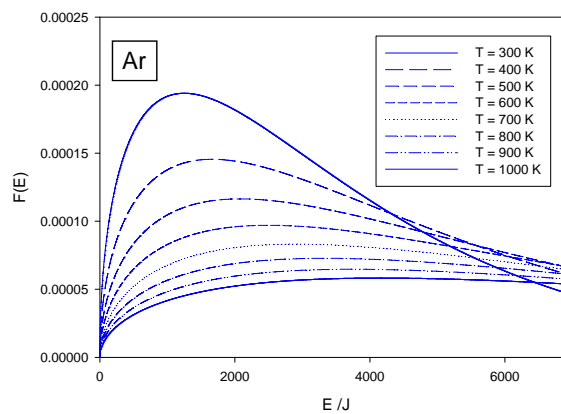Extracted from MB distribution
At 300 K for common gases.

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi\, m}} = \sqrt{\frac{8RT}{\pi M}}$$

$$v_{max} = v_P = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}$$

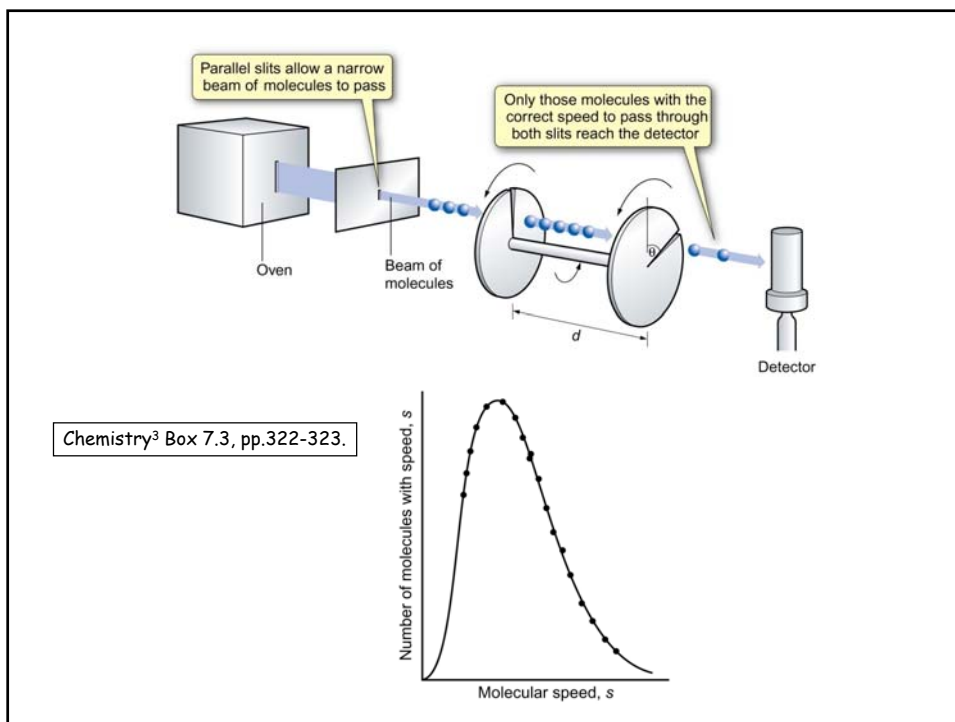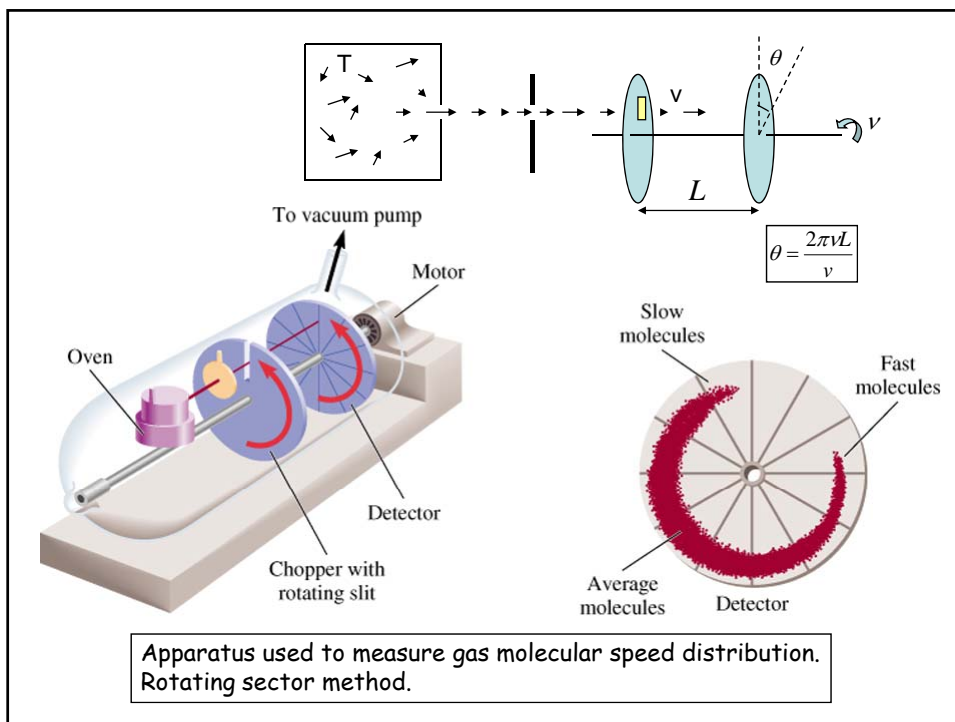$$v_{rms} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

$$v_{rel} = \sqrt{2}\langle v \rangle$$

(Graph: v_{rms}/ms^{-1} vs $10^3 M/$kg mol^{-1} with points labeled H_2, H_2O, N_2, O_2, CO_2)

Maxwell Boltzmann Energy Distribution

Ar

Legend:
T = 300 K
T = 400 K
T = 500 K
T = 600 K
T = 700 K
T = 800 K
T = 900 K
T = 1000 K

(Graph: F(E) vs E /J)

$$F(E) = \frac{2}{\sqrt{\pi}}(k_B T)^{-3/2} E^{1/2} \exp\left[-\frac{E}{k_B T}\right]$$

$$\langle E \rangle = \int_0^\infty E\, F(E)\, dE = \frac{2}{\sqrt{\pi}}(k_B T)^{-3/2} \int_0^\infty E^{3/2} \exp\left[-\frac{E}{k_B T}\right] dE = \frac{3}{2}k_B T$$

9

$$\theta = \frac{2\pi vL}{v}$$

Apparatus used to measure gas molecular speed distribution.
Rotating sector method.

Parallel slits allow a narrow
beam of molecules to pass

Only those molecules with the
correct speed to pass through
both slits reach the detector

Oven

Beam of
molecules

Detector

d

Chemistry[3] Box 7.3, pp.322-323.

Number of molecules with speed, s

Molecular speed, s

Further aspects of KMT Ideal Gases.
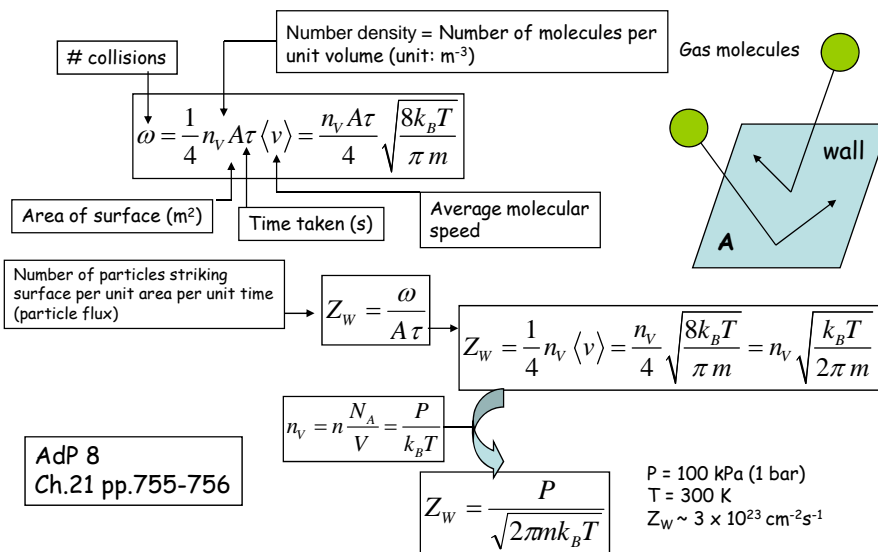
The KMT of ideal gases can be developed further to derive a number of further very useful results.

1. It is used to develop expressions for the mean free path λ (the distance travelled by a gas molecule before it collides with other gas molecules).

2. The number of molecules hitting a wall per unit area per unit time can be derived.

3. The rate of effusion of gas molecules through a hole in a wall can be determined.

4. The number of collisions per unit time (collision frequency) between two molecules (like or unlike molecules) can also be readily derived. This type of expression is useful in describing the microscopic theory of chemical reaction rates involving gas phase molecules (termed the Simple Collision Theory (SCT)).

5. The transport properties of gases (diffusion, thermal conductivity, viscosity) can also be described using this model. The KMT proposes expressions for the diffusion coefficient D, thermal conductivity κ and viscosity coefficient η which can be compared directly with experiment and so it is possible to subject the KMT to experimental test.

Wall collision flux and effusion

KMT provides expressions for rate at which gas molecules strike an area (collision flux) and the rate of effusion through a small hole.

collisions

Number density = Number of molecules per unit volume (unit: m^{-3})

Gas molecules

$$\omega = \frac{1}{4} n_V A \tau \langle v \rangle = \frac{n_V A \tau}{4} \sqrt{\frac{8 k_B T}{\pi m}}$$

Area of surface (m^2)

Time taken (s)

Average molecular speed

wall

A

Number of particles striking surface per unit area per unit time (particle flux)

$$Z_W = \frac{\omega}{A \tau}$$

$$Z_W = \frac{1}{4} n_V \langle v \rangle = \frac{n_V}{4} \sqrt{\frac{8 k_B T}{\pi m}} = n_V \sqrt{\frac{k_B T}{2 \pi m}}$$

$$n_V = n \frac{N_A}{V} = \frac{P}{k_B T}$$

AdP 8
Ch.21 pp.755-756

$$Z_W = \frac{P}{\sqrt{2 \pi m k_B T}}$$

P = 100 kPa (1 bar)
T = 300 K
$Z_W \sim 3 \times 10^{23}$ $cm^{-2}s^{-1}$

This expression for Z_W also describes the rate of effusion f_E of molecules through a small hole of area A_0.

Confirms Grahame's experimental Law of Effusion that states that the molecular flux is inversely proportional to $M^{1/2}$.
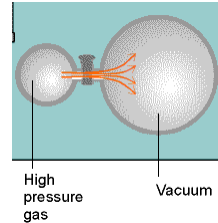
$$f_E = Z_W A_0 = \frac{pA_0}{\sqrt{2\pi m k_B T}} = \frac{PA_0 N_A}{\sqrt{2\pi MRT}}$$

Diffusion of a Gas Particle

Diffusion - One gas mixing into another gas, or gases, of which the molecules are colliding with each other, and exchanging energy between molecules.

Effusion - A gas escaping from a container into a vacuum. There are no other (or few) for collisions.

High pressure gas   Vacuum

Effusion of an Ideal Gas

- the process of a gas escaping through a small hole (a << l) into a vacuum – the collisionless regime.

High pressure gas   Vacuum

The number of molecules that escape through a hole of area A in 1 sec, N_h, in terms of $P(t)$, T.
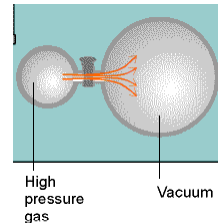
$$P = N_h \frac{\Delta p}{\Delta t} \frac{1}{A} = N_h \frac{2m\langle v_x\rangle}{\Delta t} \frac{1}{A} \qquad N_h = \frac{P\,A\,\Delta t}{2m\,\langle v_x\rangle} \qquad \langle v_x\rangle \;\Rightarrow\; \frac{1}{2}m\langle v_x^2\rangle = \frac{1}{2}k_B T, \quad \langle v_x\rangle \approx \sqrt{\langle v_x^2\rangle} = \sqrt{\frac{k_B T}{m}}$$

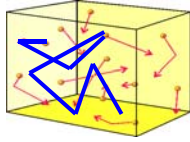$N_h = -\Delta N$, where N is the total # of molecules in a system

$$-\Delta N = \frac{P\,A\,\Delta t}{2m}\sqrt{\frac{m}{k_B T}} = \frac{Nk_B T}{V}\frac{A\Delta t}{2m}\sqrt{\frac{m}{k_B T}} = \frac{AN\Delta t}{2V}\sqrt{\frac{k_B T}{m}} \qquad \frac{\Delta N}{\Delta t} = -\frac{A}{2V}\sqrt{\frac{k_B T}{m}}N = -\frac{1}{\tau}N$$

$$N(t) = N(0)\exp\left(-\frac{t}{\tau}\right), \quad \tau = \frac{2V}{A}\sqrt{\frac{m}{k_B T}}$$

Depressurizing of a space ship, V - 50m³, A of a hole in a wall – 10^{-4} m²

$$\tau = \frac{2\times 50\,\text{m}^3}{10^{-4}\,\text{m}^2}\sqrt{\frac{30\times 1.7\cdot 10^{-27}\,\text{kg}}{1.38\cdot 10^{-23}\,\text{J/K}\times 30\,\text{K}}} \approx 10^6 \times 10^{-2} \times 0.3\,\text{s} = 3000\,\text{s}$$
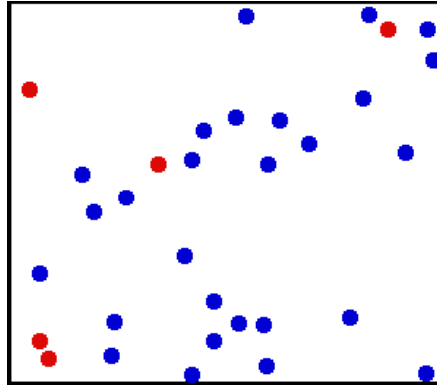
The Mean Free Path of Molecules

Energy, momentum, mass can be transported due to random thermal motion of molecules in gases and liquids.

The mean free path λ - the average distance traveled by a molecule btween two successive collisions.

Reference :
AdP 8
Ch.21, pp.752-755
Chemistry[3] Ch.7,
pp.326-330.

To evaluate the mean free path we examine how we describe collisions between molecules of like size in a gas.

We consider two molecules A and B approaching each other and assume initially that A is stationary and B is moving. The molecules will collide if the centre of one (B) comes within a distance of two molecular radii (a diameter) of molecule A. The area of the target for molecule B to hit molecule A is a circle with an area $\sigma = \pi d^2$. This area is called the _collision cross section_.
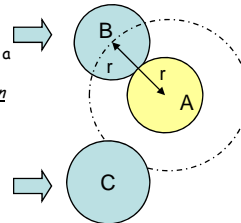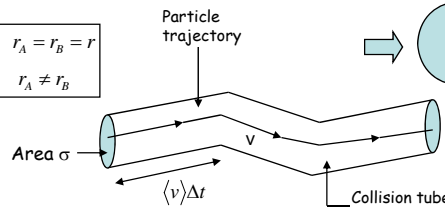
$$\sigma = \pi d^2 = 4\pi r^2 \quad r_A = r_B = r$$
$$\sigma = 4\pi(r_A + r_B)^2 \quad r_A \neq r_B$$

Particle trajectory

Number density
= # molecules N per unit volume V

$$n_V = \frac{N}{V}$$

Area σ

$\langle v \rangle \Delta t$

Collision tube

collisions in time $\Delta t = n_V \times (V_{tube})$
= $n_V \cdot \langle v \rangle \cdot \Delta t \cdot \sigma$

The average time interval between successive collisions
- **the collision time**:

$$\tau = \frac{\lambda}{\langle v \rangle}$$

$$\langle v_r \rangle = \sqrt{\frac{8 k_B T}{\pi \mu}}$$

collisions per unit time = $Z = n_v \langle v \rangle \sigma$

$$Z = \frac{\sqrt{2}\sigma \langle v \rangle P}{k_B T}$$

$$n_V = n\frac{N_A}{V} = \frac{P}{k_B T}$$

$$\lambda = \langle v \rangle \tau$$

$$\mu = \frac{m_A m_B}{m_A + m_B} = \frac{m}{2}$$

Mean free path λ = (total distance travelled in time Δt)/(# collisions in time Δt) = $\langle v \rangle \Delta t / n_V \langle v \rangle \sigma \Delta t$

$$\lambda = \frac{\langle v \rangle}{Z} = \frac{1}{n_V \sigma}$$

$$= \frac{k_B T}{P \sigma}$$

More generally all molecules move with An average speed $\langle v \rangle$.

MB speed distribution

$$\frac{\langle v_r \rangle}{\langle v \rangle} = \sqrt{2}$$

Average relative speed

$$\lambda = \frac{1}{(\langle v_r \rangle / \langle v \rangle) n_V \sigma} = \frac{1}{\sqrt{2}\,\sigma\, n_V} = \frac{k_B T}{\sqrt{2} P \sigma}$$

Some Numbers:

MFP inversely proportional to gas density, inversely proportional to gas pressure and directly proportional to gas temperature.

$$\lambda \propto \frac{1}{\sigma \, n_V}$$ $\Rightarrow$ for an ideal gas: $$PV = Nk_BT \qquad P = n_V k_B T$$ $\Rightarrow$ $$\lambda \propto \frac{1}{n_V} \propto \frac{T}{P}$$

air at norm. conditions: $$\frac{1}{n_V} = \frac{V}{N} = \frac{k_B T}{P} = \frac{1.38 \cdot 10^{-23} \, \text{J/K} \times 300 \text{K}}{10^5 \, \text{Pa}} \approx 4 \cdot 10^{-26} \, \text{m}^3$$

the intermol. distance $$d = \sqrt[3]{\frac{V}{N}} \sim 3 \cdot 10^{-9} \text{ m}$$

$P = 10^5$ Pa: $\lambda \sim 10^{-7}$ m - 30 times greater than d

$P = 10^{-2}$ Pa (10^{-4} mbar): $\lambda \sim 1$ m (size of a typical vacuum chamber)

 - at this P, there are still ~$2.5 \cdot 10^{12}$ molecule/cm³ **(!)** $$\frac{\lambda}{d} \propto n_V^{-2/3} \propto P^{-2/3}$$

The collision time at norm. conditions: $\tau \sim 10^{-7}$m / 500m/s = $2 \cdot 10^{-10}$ s

For H_2 gas in interstellar space, where the density is ~ 1 molecule/ cm³,

 $\lambda \sim 10^{13}$ m - ~ 100 times greater than the Sun-Earth distance (1.5 $\cdot 10^{11}$ m)