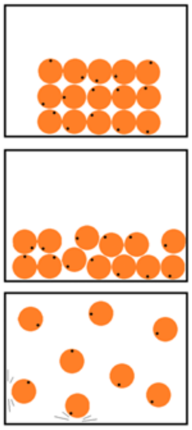
Kinetic Theory of Gases
Chapter 33

Kinetic Theory of Gases

Kinetic theory of gases envisions gases as a collection of atoms or molecules in motion. Atoms or molecules are considered as particles.

This is based on the concept of the particulate nature of matter, regardless of the state of matter.



A particle of a gas could be an atom or a group of atoms (molecule).

The Kinetic Theory relates the 'micro world' to the 'macro world'.

http://www.chemtutor.com/sta.htm#kin

For gases following the relationship, PV = nRT (IGL);

Observations	**KT Postulate**
Gas density is very low	Particles are far apart
Pressure is uniform in all directions	Particle motion is random
IGL is independent of particle type	Gas particles do not interact
Dalton’s Law of Partial Pressures	Gas particles do not interact

$$P = \frac{nRT}{V}$$

KT (IGL): Applicable when particle density is such that the inter-particle distance >> particle size (point masses).
Low pressures and high temperatures e.g 1atm and room temp.

Postulates

Gas particles are very far apart.

Gas particles in constant random motion.

Gas particles do not exert forces on each other due to their large intermolecular distances.

Pressure in a gas is due to particle collisions (elastic) with the walls of the container from translational motion - the microscopic explanation of pressure.

Collisions with the wall are elastic, therefore, *translational energy* of the particle is conserved with these collisions.

Each collision imparts a linear *momentum* to the wall, which *results the gaseous pressure*. In Newtonian mechanics force defined as the change of momentum, here, due to the collision; pressure is force per unit area.

In KT, the pressure arising from the collision of a single molecule at the wall is derived and then scaled up to the collection of molecules in the container, to obtain the ideal gas law (IGL);

$$PV = nRT$$

Gas kinetic theory derives the relationship between root-mean-squared speed and temperature.

The particle motions are *random*, therefore *velocities* along all directions are equivalent. Therefore the *average velocity* (vector) along any dimension/direction will be zero.

Now,
the root-mean-squared velocity = *root-mean-squared speed ; it is nonzero*.

A distribution of translational energies; therefore, many velocities would exist for a collection of gaseous particles.

What is the distribution of the particle velocities?

Velocity is a vector quantity (**v**). Speed is a scalar (v).

$$\mathbf{v}^2 = \mathbf{v}\bullet\mathbf{v} = v_x^2 + v_y^2 + v_z^2$$

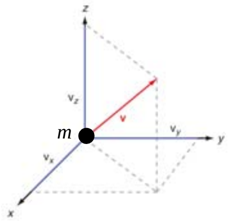
$$\mathbf{v}^2 = v^2 = v_x^2 + v_y^2 + v_z^2$$

$\langle \mathbf{v}^2\rangle = \langle v^2\rangle$; symbol $\langle x\rangle$ = average of x.

Most properties of gases depend on *molecular speeds*.

The translational movements of particles are amenable to treatment with classical Newtonian mechanics (Justification, later).

Root mean square velocity, translational energy:



$$v^2 = \mathbf{v}\cdot\mathbf{v} = v_x^2 + v_y^2 + v_z^2$$

$$\langle v^2\rangle^{1/2} = \langle v_x^2 + v_y^2 + v_z^2\rangle^{1/2}$$
$$= \langle 3v_x^2\rangle^{1/2}$$
$$= \left(\frac{3kT}{m}\right)^{1/2}$$

$$\varepsilon_{Tr} = \frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \varepsilon_{Tr_x} + \varepsilon_{Tr_y} + \varepsilon_{Tr_z}$$

Assume: $\frac{m\langle v_x^2\rangle}{2} = \frac{k_BT}{2}$ (Chapter 31) $\Rightarrow \langle v_x^2\rangle = \frac{k_BT}{m}$

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

$\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle$ ∵ random motion

Therefore,

$$\langle v^2\rangle = \langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle = \langle v_x^2\rangle + \langle v_x^2\rangle + \langle v_x^2\rangle$$
$$= 3\langle {v_x}^2\rangle = 3\langle v_y^2\rangle = 3\langle v_z^2\rangle$$

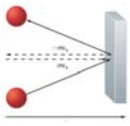
Using $\frac{m\langle v_x^2\rangle}{2} = \frac{k_BT}{2}$ remember $m\langle v_x^2\rangle = k_BT$

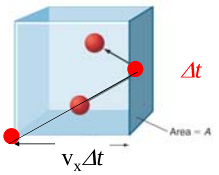
$m\langle v^2\rangle = m\cdot 3\langle v_x^2\rangle = 3k_BT$ (last slide)

$m\langle v^2\rangle = 3k_BT;$ $\sqrt{\langle v^2\rangle} = \sqrt{\frac{3k_BT}{m}} = \left(\frac{3kT}{m}\right)^{1/2}$

For a gas sample of n moles occupying a volume V (cube), with an area of each side A. Consider a single particle of mass m, velocity v.

Particle collides with the wall.
(elastic collisions)





Change of momentum Δp =

$$mv - (-mv) = 2mv$$

$$mv_x - (-mv_x) = 2mv_x$$

Number density of particles = $\tilde{N} = \frac{nN_A}{V}$

where N_A = Avagadro Number

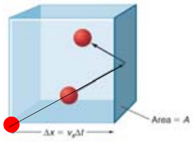
Half of the molecules moving on x axis with a (velocity component in the x direction) within the volume $v_x\Delta t$ collides with one surface in the x direction.

$$N_{coll} = \tilde{N} \times (Av_x\Delta t)\left(\frac{1}{2}\right) = \frac{nN_A}{V}(Av_x\Delta t)\left(\frac{1}{2}\right)$$

N_{coll} = number of collisions on the wall of area A in time Δt.

Change of momentum on a surface during Δt =

$$\Delta p_{Total} = (2m\text{v}_x)(N_{coll})$$



Force on the surface = Rate of change of momentum =

$$F = \frac{\Delta p_{Total}}{\Delta t} = \frac{nN_A}{V} Am\langle \text{v}_x^2 \rangle$$

Pressure = Force per unit area =

$$P = \frac{F}{A} = \frac{nN_A}{V} m\langle \text{v}_x^2 \rangle$$

Pressure arises because of the molecular motion of gases; microscopic/molecular model of pressure.

$$P = \frac{nN_A}{V} m\langle \text{v}_x^2 \rangle$$

using $m\left\langle \text{v}_x^2 \right\rangle = k_B T = kT$

$$P = \frac{nN_A}{V} m\langle \text{v}_x^2 \rangle = \frac{nN_A}{V} kT = \frac{nRT}{V}$$

$PV = nRT$ Ideal gas law- IGL

Pressure: microscopic/empirical model.

Thus the kinetic theory describes the pressure of an ideal gas using a classical description of the motion of a single molecular collision with the walls and then scaling this result up to macroscopic proportions.

The fact that component velocities of all molecules are not the same, necessitates the definition of an average in each direction.

Thus $\langle \text{v}_j \rangle$ arises because of a probability distribution of v_j values $f(\text{v}_j)$ in each direction ($j = x, y, z$)

$$\Omega(\text{v}_x, \text{v}_y, \text{v}_z) = f(\text{v}_x) f(\text{v}_y) f(\text{v}_z)$$

↑
velocity distribution function

Being a probability function; $\int_{all\ \text{v}_j} f(\text{v}_j) d\text{v}_j = 1$

Derivation of distribution functions $f(\text{v}_j)$

$$\Omega(\text{v}_x, \text{v}_y, \text{v}_z) = f(\text{v}_x) f(\text{v}_y) f(\text{v}_z)$$

$$\ln \Omega(v_x, v_y, v_z) = \ln f(v_x) + \ln(v_y) + \ln(v_z)$$

$$v \leftrightarrow \text{v} \Leftrightarrow (\text{v}_x, \text{v}_y, \text{v}_z)$$

$$\left(\frac{\partial \ln \Omega(\nu)}{\partial \text{v}_x} \right)_{\text{v}_y, \text{v}_z} = \frac{d \ln f(\text{v}_x)}{d\text{v}_x}$$

$$\left(\frac{d \ln \Omega(\nu)}{d\nu} \right) \left(\frac{\partial \nu}{\partial \text{v}_x} \right)_{\text{v}_y, \text{v}_z} = \frac{d \ln f(\text{v}_x)}{d\text{v}_x}$$ Chain rule

Math supplement

also from another relationship

$v^2 = \text{v}_x^2 + \text{v}_y^2 + \text{v}_z^2$ for a molecule

$v = [\text{v}_x^2 + \text{v}_y^2 + \text{v}_z^2]^{1/2}$

$$\left(\frac{\partial \nu}{\partial \text{v}_x} \right)_{\text{v}_y, \text{v}_z} = \left(\frac{\partial}{\partial \text{v}_x} (\text{v}_x^2 + \text{v}_y^2 + \text{v}_z^2)^{1/2} \right)_{\text{v}_y, \text{v}_z}$$
$$= \frac{1}{2}(2\text{v}_x)(\text{v}_x^2 + \text{v}_y^2 + \text{v}_z^2)^{-1/2}$$
$$= \frac{\text{v}_x}{\nu}$$

$$\left(\frac{d\ln\Omega(\nu)}{d\nu}\right)\left(\frac{\partial\nu}{\partial \mathrm{v}_x}\right)_{\mathrm{v}_y,\mathrm{v}_z} = \frac{d\ln f(\mathrm{v}_x)}{d\mathrm{v}_x}$$

$$\left(\frac{d\ln\Omega(\nu)}{d\nu}\right)\left(\frac{\mathrm{v}_x}{\nu}\right) = \frac{d\ln f(\mathrm{v}_x)}{d\mathrm{v}_x}$$

$$\frac{d\ln\Omega(\nu)}{\nu\, d\nu} = \frac{d\ln f(\mathrm{v}_x)}{\mathrm{v}_x d\mathrm{v}_x}$$

Similarly

$$\frac{d\ln\Omega(\nu)}{\nu\, d\nu} = \frac{d\ln f(\mathrm{v}_y)}{\mathrm{v}_y d\mathrm{v}_y}$$

$$\frac{d\ln\Omega(\nu)}{\nu\, d\nu} = \frac{d\ln f(\mathrm{v}_z)}{\mathrm{v}_z d\mathrm{v}_z}$$

In general $\dfrac{d\ln f(\mathrm{v}_j)}{\mathrm{v}_j d\mathrm{v}_j} = \dfrac{df(\mathrm{v}_j)}{\mathrm{v}_j f(\mathrm{v}_j)\,d\mathrm{v}_j} = \underset{?}{-\gamma}$ for $j = x, y, z$

Because derivatives of three independent variables are equal, the derivatives must be constant, say = -γ ;(γ>0).

Upon rearrangement and integration,

$$\int \frac{df(\mathrm{v}_j)}{f(\mathrm{v}_j)} = -\int \gamma \mathrm{v}_j\, d\mathrm{v}_j$$

$$\ln f(\mathrm{v}_j) = -\frac{1}{2}\gamma \mathrm{v}_j^2$$

$$\boxed{f(\mathrm{v}_j) = Ae^{-\gamma \mathrm{v}_j^2/2}}$$

where *A* = integration constant

Note the distribution (probability) function!

Evaluating A:

$$\int_{-\infty}^{\infty} f(\mathrm{v}_j)\, d\mathrm{v}_j = 1 = \int_{-\infty}^{\infty} Ae^{-\gamma \mathrm{v}_j^2/2} d\mathrm{v}_j$$

$$1 = 2A\int_{0}^{\infty} e^{-\gamma \mathrm{v}_j^2/2} d\mathrm{v}_j$$

even function

$$1 = A\sqrt{\frac{2\pi}{\gamma}}$$

$$\sqrt{\frac{\gamma}{2\pi}} = A$$

Math supplement

$$f(\mathrm{v}_j) = \left(\frac{\gamma}{2\pi}\right)^{1/2} e^{-\gamma \mathrm{v}_j^2/2}$$

Distribution function: probability of a gas particle having a velocity within a given range, e.g. v_x and $\mathrm{v}_x + d\mathrm{v}_x$.

Distribution function →

$$f(\mathrm{v}_j) = \left(\frac{\gamma}{2\pi}\right)^{1/2} e^{-\gamma \mathrm{v}_j^2/2}$$

$$\langle \mathrm{v}_x^2 \rangle = \frac{kT}{m}$$

(Assumption slide 9)

Mean/average

$$\langle \mathrm{v}_x^2 \rangle = \frac{kT}{m} = \int_{-\infty}^{\infty} \mathrm{v}_x^2 f(\mathrm{v}_x)\, d\mathrm{v}_x$$

averaging

$$= \int_{-\infty}^{\infty} \mathrm{v}_x^2 \sqrt{\frac{\gamma}{2\pi}} e^{-\gamma \mathrm{v}_x^2/2} d\mathrm{v}_x$$

$$= \sqrt{\frac{\gamma}{2\pi}} \int_{-\infty}^{\infty} \mathrm{v}_x^2 e^{-\gamma \mathrm{v}_x^2/2} d\mathrm{v}_x$$

use tables

Math supplement

$$= \sqrt{\frac{\gamma}{2\pi}}\left(\frac{1}{\gamma}\sqrt{\frac{2\pi}{\gamma}}\right)$$

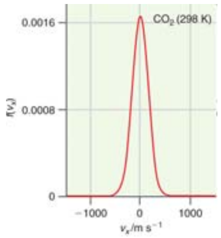
$$= \frac{1}{\gamma}$$

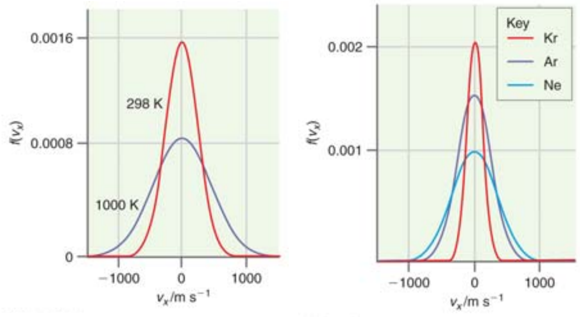
$$\boxed{\frac{m}{kT} = \gamma}$$

Now, $f(\mathrm{v}_j) = \left(\dfrac{\gamma}{2\pi}\right)^{1/2} e^{-\gamma \mathrm{v}_j^2/2}$ where $\gamma = \dfrac{m}{kT}$

Substituting for γ in $f(\mathrm{v}_j)$;

$$f(\mathrm{v}_j) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{(-m\mathrm{v}_j^2/2kT)} = \left(\frac{M}{2\pi RT}\right)^{1/2} e^{(-M\mathrm{v}_j^2/2RT)}$$





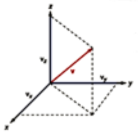
velocity distribution function

$$F(v) = \boxed{f(v_x)f(v_y)f(v_z)}\,dv_x\,dv_y\,dv_z$$

$$= \left[\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}\right]\left[\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_y^2/2kT}\right]$$

$$\times \left[\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_z^2/2kT}\right] dv_x\,dv_y\,dv_z$$

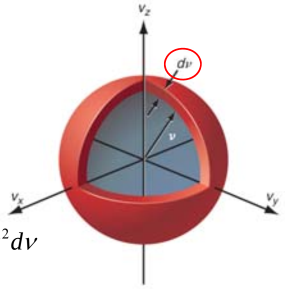
$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{[-m(v_x^2+v_y^2+v_z^2)]/2kT}\,dv_x\,dv_y\,dv_z$$



Deriving the distribution function for *v*

$$v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$$

Changing the 'volume' element (in *Cartesian*) to variable *v*, *spherical coordinates.*



replace $dv_x dv_y dv_z$ by $4\pi v^2 dv$

and $v_x^2 + v_y^2 + v_z^2$ by v^2

$$F(v)\,dv = f(v_x)f(v_y)f(v_z)\,dv_x\,dv_y\,dv_z$$

$$= \left[\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}\right]\left[\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_y^2/2kT}\right]$$

$$\times \left[\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_z^2/2kT}\right] dv_x\,dv_y\,dv_z$$

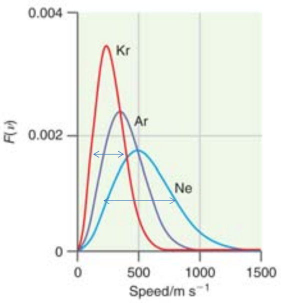
$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{[-m\underbrace{(v_x^2+v_y^2+v_z^2)}_{}]/2kT}\,\underbrace{dv_x\,dv_y\,dv_z}_{}$$

$$F(v)\,dv = \underbrace{4\pi}_{}\left(\frac{m}{2\pi kT}\right)^{3/2}\underbrace{v^2}_{}e^{-m\underbrace{v^2}_{}/2kT}\,\underbrace{dv}_{}$$

$$F(v)\,dv = \underline{4\pi}\left(\frac{m}{2\pi kT}\right)^{3/2}\underline{v^2}e^{-m\underline{v}^2/2kT}\,\underline{dv}$$

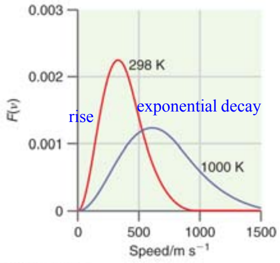
$$F(v)\,dv = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}\,dv$$

rise exponential decay



Notice the shape, blue.

v_{ave}'s of Xe, H_2, He ?
Earth and Jupiter (×300)



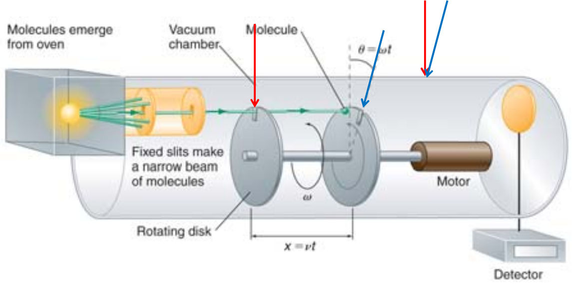
Notice the shape, blue.

v_{ave}'s of Xe, H_2, He ?
Earth and Jupiter (×300)

x and θ fixed
ω varied

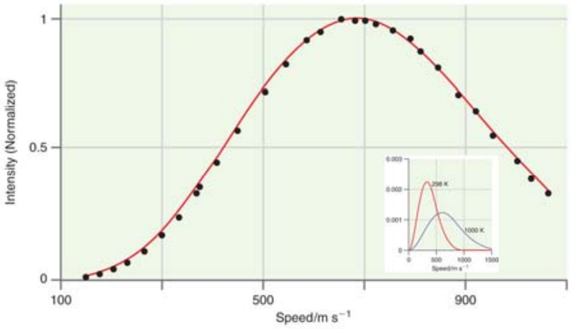
$t = \frac{\theta}{\omega}$

$v = \frac{x}{t} = \frac{x}{\theta}\omega$



At lower angular velocities slower moving molecules go through the second slit.

Detector signal proportional to the number of particles reaching the detector.



Notice the shape.

Most probable velocity v_{mp}

$$F(v)\,dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\,dv$$

$$F(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

Most probable velocity v_{mp}: differentiate $F(v)$, set to zero.

$$2v_{mp} - \frac{mv_{mp}^3}{kT} = 0$$

$$v_{mp} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}}$$

Mean (average) velocity:

$$v_{ave} = \langle v\rangle = \int_0^\infty vF(v)\,dv$$

$$= \int_0^\infty v\left(4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\right)dv$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^3 e^{-mv^2/2kT}\,dv$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\frac{1}{2}\left(\frac{2kT}{m}\right)^2$$

$$v_{ave} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

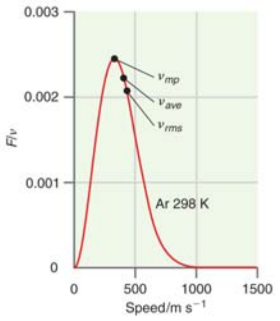
Root mean square velocity:

Using: $\langle v_x^2\rangle = \frac{kT}{m}$ (Assumption slide 4)

and $\because \langle v^2\rangle = \langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle = 3\langle v_x^2\rangle$

$$\sqrt{\langle v^2\rangle} = \sqrt{3\langle v_x^2\rangle} = v_{rms}$$

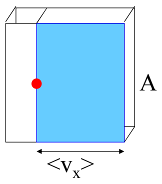
$$v_{rms} = \left[\langle v^2\rangle\right]^{1/2} = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2}$$



Number of collisions per unit time on the wall of area A:

average x component of velocity $\langle v_x \rangle = \int_0^\infty v_x f(v_x)\, dv_x$

molecules in 'light blue volume' of the cube colliding per unit time = $\underbrace{\tilde{N} A \int_0^\infty v_x f(v_x)\, dv_x}$



N_c = number of particles colliding.

Rate of collisions on surface =

$$\frac{dN_c}{dt} = \tilde{N} A \int_0^\infty v_x f(v_x)\, dv_x$$

$$\frac{dN_c}{dt} = \tilde{N} A \int_0^\infty v_x \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} dv_x$$

$$= \tilde{N} A \left(\frac{m}{2\pi kT}\right)^{1/2} \int_0^\infty v_x e^{-mv_x^2/2kT} dv_x$$

$$= \tilde{N} A \left(\frac{m}{2\pi kT}\right)^{1/2} \left(\frac{kT}{m}\right)$$

$$= \tilde{N} A \underbrace{\left(\frac{kT}{2\pi m}\right)^{1/2}}$$

$$\frac{dN_c}{dt} = \tilde{N} A \underbrace{\frac{1}{4} v_{ave}}$$

Collisional Flux Z_c:

Number of collisions on the wall *per unit time per unit area*.

$$Z_c = \frac{dN_c/dt}{A} = \frac{1}{4}\tilde{N} v_{ave} \quad \& \quad v_{ave} = \left(\frac{8kT}{\pi m}\right)^{1/2}$$

$$\tilde{N} = \frac{N}{V} = \frac{nN_A}{V} = \frac{P}{kT}$$

Substituting in Z_c;

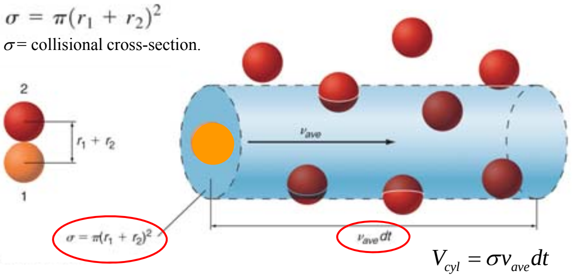
$$Z_c = \frac{P}{(2\pi m kT)^{1/2}} = \frac{PN_A}{(2\pi MRT)^{1/2}}$$

Particle collision rates: (Hard sphere model)

Particles interact when spheres attempt to occupy the same region of the phase. (consider one moving particle – orange, label 1; all other particles stationary are red – label 2

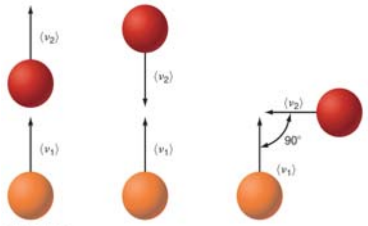
$\sigma = \pi(r_1 + r_2)^2$

σ = collisional cross-section.



$V_{cyl} = \sigma v_{ave} dt$

Because the collisional 'partners are moving too' in reality, an "effective speed", $\langle v_{12} \rangle$, of orange particle will be considered in the model to emulate the collisions the orange particle encounters;



$$\langle v_{12} \rangle = (\langle v_1 \rangle^2 + \langle v_2 \rangle^2)^{1/2}$$

Because the collisional 'partners are moving', an *effective speed* $<v_{12}>$ used to model the system;

$$\langle \nu_{12}\rangle = (\langle \nu_1\rangle^2 + \langle \nu_2\rangle^2)^{1/2} = \left[\left(\frac{8kT}{\pi m_1}\right) + \left(\frac{8kT}{\pi m_2}\right)\right]^{1/2}$$

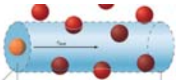
$$= \left[\frac{8kT}{\pi}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\right]^{1/2}$$

$$= \left(\frac{8kT}{\pi\mu}\right)^{1/2}$$

$$\uparrow$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}; \quad \text{reduced mass}$$

Collisional partner (red) density = $\frac{N_2}{V}$



Volume covered by orange in dt = V_{cyl}

$$V_{cyl} = \sigma v_{ave} dt$$

Collisions by it in time dt = $V_{cyl}\frac{N_2}{V}$

Particle collisional frequency of it = z_{12}

$$z_{12} = \frac{N_2}{V}\left(\frac{V_{cyl}}{dt}\right) = \frac{N_2}{V}\left(\frac{\sigma v_{ave} dt}{dt}\right) = \frac{N_2}{V}\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2}$$

For a sample of <u>one type of gas</u>;

$$z_{11} = \overset{\downarrow}{\frac{N_1}{V}}\sigma\sqrt{2}\left(\frac{8kT}{\pi m_1}\right)^{1/2} = \frac{P_1 N_A}{RT}\sigma\sqrt{2}\left(\frac{8RT}{\pi M_1}\right)^{1/2}$$

<u>Total collisional frequency, two types of gases</u> Z_{12}:

Total number of collisions in the gaseous sample.

$$Z_{12} = \frac{N_1}{V} z_{12}$$

For a sample of one type of gas we have;

$$Z_{11} = \underset{\uparrow}{\frac{1}{2}}\frac{N_1}{V} z_{11} = \frac{1}{\sqrt{2}}\left(\frac{N_1}{V}\right)^2\sigma\left(\frac{8kT}{\pi m_1}\right)^{1/2} = \frac{1}{\sqrt{2}}\left(\frac{P_1 N_A}{RT}\right)^2\sigma\left(\frac{8RT}{\pi M_1}\right)^{1/2}$$

Accounts for double counting

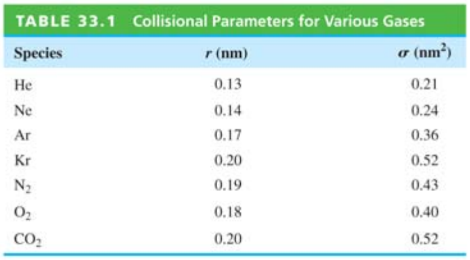


TABLE 33.1 Collisional Parameters for Various Gases

Species	r (nm)	σ (nm^2)
He	0.13	0.21
Ne	0.14	0.24
Ar	0.17	0.36
Kr	0.20	0.52
N_2	0.19	0.43
O_2	0.18	0.40
CO_2	0.20	0.52

<u>Mean Free Path</u>:

Average distance a particle would travel between two successive collisions two types of molecules , say 1 and 2.

$$\lambda = \frac{\nu_{ave}\, dt}{(z_{11} + z_{12})\, dt} = \frac{\nu_{ave}}{(z_{11} + z_{12})}$$

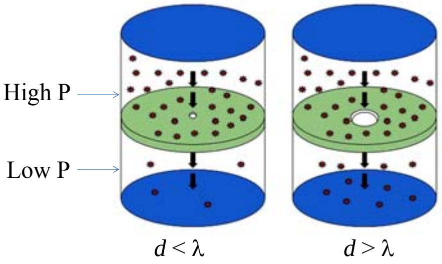
For one type of molecules,

$$\lambda = \frac{\nu_{ave}}{z_{11}} = \frac{\nu_{ave}}{\left(\frac{N_1}{V}\right)\sqrt{2}\sigma\nu_{ave}} = \left(\frac{RT}{P_1 N_A}\right)\frac{1}{\sqrt{2}\sigma}$$

<u>Effusion:</u>

Effusion is the process in which a gas escapes through a small aperture. This occurs if the *diameter of the aperture is considerably smaller than the* *<u>mean free path</u>* of the molecules (effusion rate = number of molecules that pass through the opening (aperture) per second). Once the particle passes through it generally wont come back because of the low partial pressure on the other side

Pressure of the gas and size of the aperture is such the molecules do not undergo collisions near or when passing through the opening.



Left – effusion; right - diffusion. Effusion occurs through an aperture (size *A*~*d*) smaller than the mean path of the particles in motion whereas diffusion occurs through an aperture through which many particles can flow through simultaneously.

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

Collisional Flux Z_C:

Z_C = number of collisions *per unit time per unit area*. *(by one type of molecule);* definition.

$$Z_c = \frac{dN_c/dt}{A} = \frac{1}{4}\tilde{N}v_{ave} \qquad v_{ave} = \left(\frac{8kT}{\pi m}\right)^{1/2}$$

Note: $\tilde{N} = \frac{N}{V} = \frac{nN_A}{V} = \frac{P}{kT}$;using IGL

Upon substitution for v_{ave}, $\tilde{N}$ and simplification;

$$Z_c = \frac{P}{(2\pi mkT)^{1/2}} = \frac{PN_A}{(2\pi MRT)^{1/2}}$$

Effusion rate decreases with time because of the reduction in gas pressure inside the container due to effusion/diffusion.

$$\frac{dP}{dt} = \frac{d}{dt}\left(\frac{NkT}{V}\right) = \frac{kT}{V}\frac{dN}{dt}$$

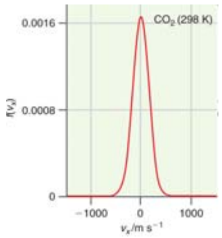
And rate of loss of molecules

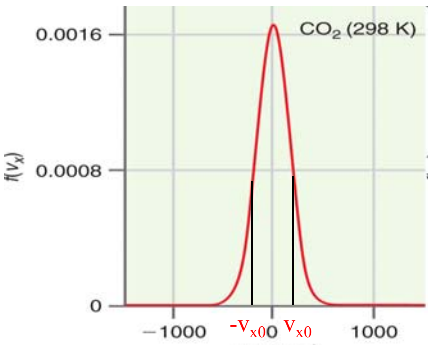
$$\frac{dN}{dt} = -Z_cA = \frac{-PA}{(2\pi mkT)^{1/2}}$$

Upon substitution $\frac{dP}{dt} = \frac{kT}{V}\left(\frac{-PA}{(2\pi mkT)^{1/2}}\right)$

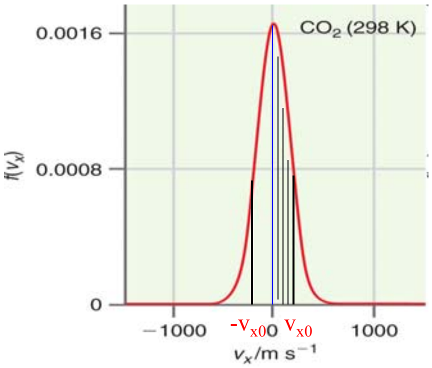
Integration yields; $P = P_0 \exp\left[-\frac{At}{V}\left(\frac{kT}{2\pi m}\right)^{1/2}\right]$

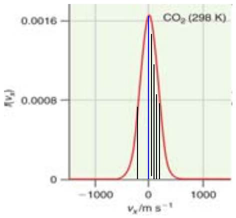
$$f(v_j) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{(-mv_j^2/2kT)} = \left(\frac{M}{2\pi RT}\right)^{1/2} e^{(-Mv_j^2/2RT)}$$





$$f(v_j) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{(-mv_j^2/2kT)}$$





$$\underbrace{f(\mathrm{v}_j) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{(-m\mathrm{v}_j^2/2kT)}}$$

$$f(-v_{x0} \le v_x \le v_{x0}) = \int_{-x0}^{xo} f(v_x)dv_x = \overset{\downarrow}{2}\underbrace{\int_0^{xo} \overbrace{f(v_x)}dv_x}$$

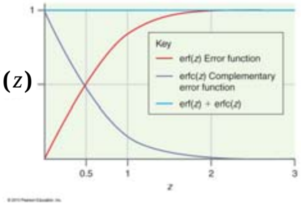
$$\xi^2 = \frac{mv_x^2}{2kT} \qquad \xi^2{}_0 = \frac{mv_{x0}^2}{2kT} \qquad \xi_0 = \sqrt{\frac{mv_{x0}^2}{2kT}}$$

$$f(-v_{x0} \le v_x \le v_{x0}) = \underbrace{\frac{2}{\sqrt{\pi}}\int_0^{\xi_0}} e^{-\xi^2} d\xi$$

$$f(-v_{x0} \le v_x \le v_{x0}) = \underbrace{\frac{2}{\sqrt{\pi}}\int_0^{\xi_0} e^{-\xi^2} d\xi}$$

$$erf(z) = \frac{2}{\sqrt{\pi}}\int_0^{z} e^{-x^2} dx \quad = f(-z \le v_x \le z)$$

$erf(z)$



$$\xi^2 = mv_x^2 / 2kT \qquad @\, v_x = v_{x0} = \sqrt{2kT/m}$$

$$\xi^2 = mv_{x0}^2 / 2kT = 1 \qquad \xi = 1$$

$$erf(z) = \frac{2}{\sqrt{\pi}}\int_0^{z} e^{-x^2} dx$$

$$erf(1) = \frac{2}{\sqrt{\pi}}\int_0^{1} e^{-x^2} dx$$

$= 0.8427$

covers $v_x \le \sqrt{2kT/m}$

probability $v_x > \sqrt{2kT/m}$**?**

$erf(z)$