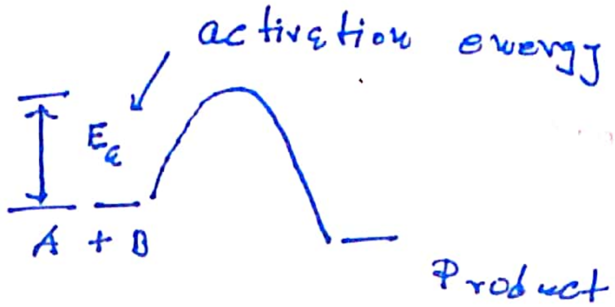
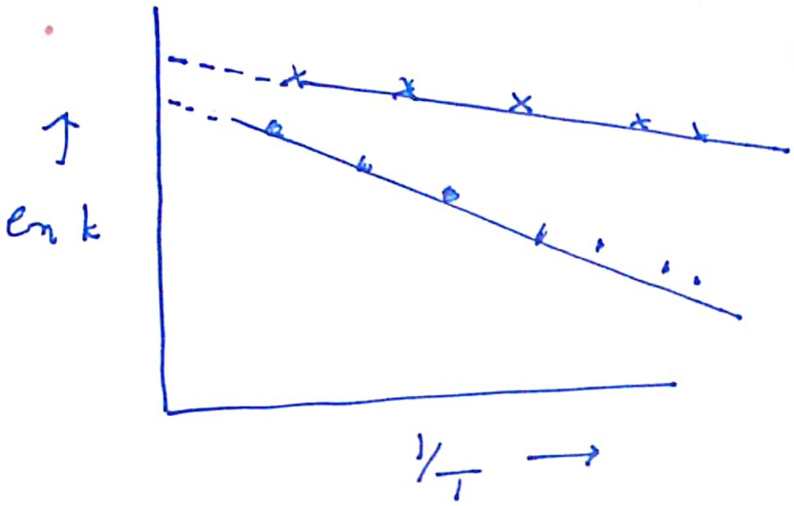
$$\text{Rate} = \underline{\underline{k}}\,[A]\,[B]$$



Arrhenius



$$\ln k \propto \frac{1}{T}$$

$$= \underbrace{\ln A}_{} - \underbrace{\frac{E_a}{R}}_{} \times \frac{1}{T}$$

$$y = c - m \times x$$

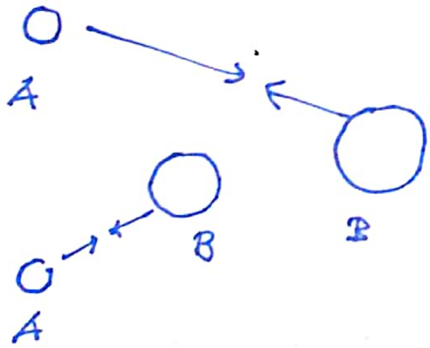
$$\boxed{k = A\,e^{-E_a/RT}}$$

$k = f(T)$?

→ 1) how many # of collisions ?

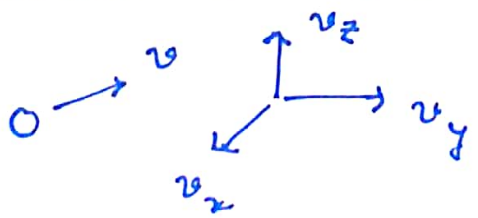
→ 2) distribution of <u>relative</u> speed at T ?

→ 3) collisions which are more energetic



Distribution of atomic/molecular speed:

Maxwell - Boltzmann distribution



n_4 —— 4ϵ

n_3 —— 3ϵ

n_2 —— 2ϵ

n_1 —— ϵ

n_0 —— 0

$4 = N$

$3\epsilon = E$

<u>Ergodicity</u>

$$\left.\begin{aligned} N &= \sum n_i = \text{constant} \\ E &= \sum \epsilon_i \times n_i = \text{constant} \end{aligned}\right\}$$

1

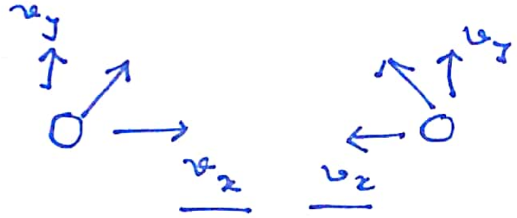
① In each direction, velocity distribution must be <u>even</u>

v_x to $v_x + dv_x$ 100 km/s to 110 km/s

$-v_x$ to $-(v_x + dv_x)$ -100 km/s to -110 km/s

$$f(-x) = f(x) \qquad \begin{array}{l|} f = ax^2 \\ f = ax^4 \end{array}$$

② v_x and v_y — uncorrelated



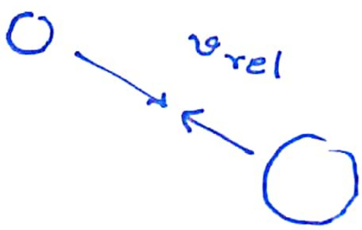
$$f(v_x) \equiv f(v_y) \equiv f(v_z)$$

③ very high / low v_x, $f \to 0$

$v_x \to +\infty$ $v_x \to 0$

$$f(v_x) \propto e^{-bv_x^2} = A e^{-bv_x^2}$$

④



$$\underline{v}^2 = \underline{v}_x^2 + \underline{v}_y^2 + \underline{v}_z^2$$

$$\underbrace{c \equiv v}_{\text{speed}} \equiv \underbrace{|\underline{v}|}_{\text{velocity}}$$

$$\underbrace{f(v^2)}_{\substack{\text{fraction of molecules} \\ \text{having a specific velocity} \\ \text{range}}} = f(v_x) \times f(v_y) \times f(v_z)$$

$\left.\begin{array}{l} v_x \text{ to } v_x + dv_x \\ v_y \text{ to } v_y + dv_y \\ \ldots \end{array}\right\}$ $= A e^{-b\underline{v}_x^2} \times A e^{-b\underline{v}_y^2} \times \ldots$

$$= A^3 e^{-bv^2} \qquad ②$$

$$f(v) \times dv_x dv_y dv_z = f(v_x) \times f(v_y) \times f(v_z) \times \underline{dv_x \times dv_y \times dv_z}$$

probability = probability density × volume

$$|\psi|^2 \times \underbrace{dV}_{\underline{dx \times dy \times dz}}$$

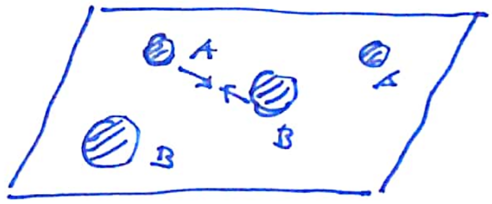
$$f(v)\, \underbrace{dv_x dv_y dv_z}_{dv} = \underbrace{A^3}\, \underbrace{e^{-bv^2}}\, \underbrace{dv_x dv_y dv_z}$$

$$\left.\begin{matrix} v_x + dv_x \\ v_y + dv_y \\ v_z + dv_z \end{matrix}\right\}$$

$$\underline{v} = \hat{i}\, v_x + \hat{j}\, v_y + \hat{z}\, v_z$$

$|\underline{v}|$ to $\underline{v + dv}$

$f(v)\, dv$



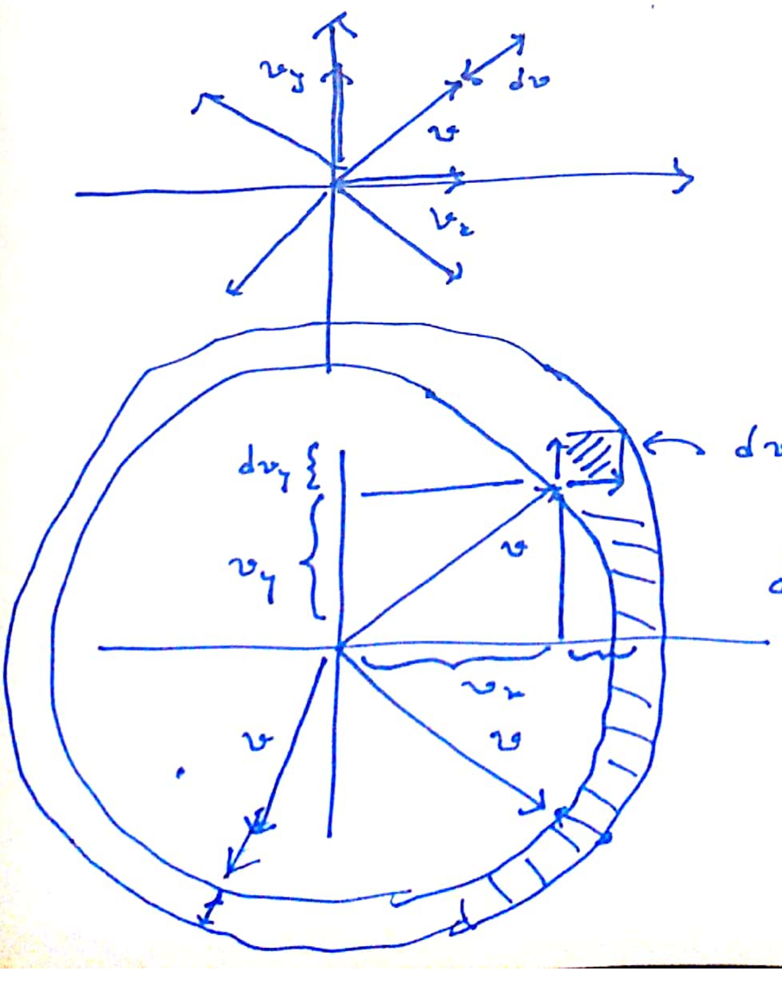
Speed distribution

v to $v + dv$

$$v \equiv |\underline{v}|$$

100 km/s to 110 km/s

__2D__



$dv_x dv_y$

↓

dv

$$\pi (v + dv)^2 - \pi v^2$$

$$= 2\pi v\, dv$$

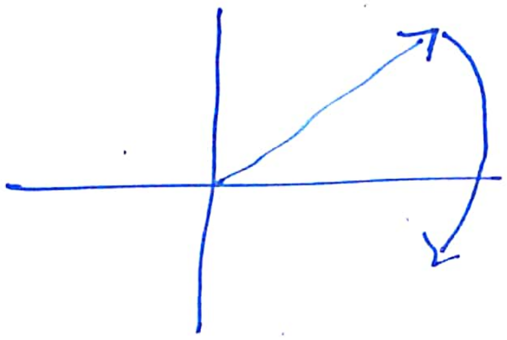
2D

$$f(v)\, dv_x dv_y dv_z = A^2 e^{-bv^2} dv_x dv_y dv_z$$

$$\downarrow$$

$$f(v)\, dv = A^2 e^{-bv^2} \times \iint dv_x dv_y$$

$$= A^2 e^{-bv^2} \times \underline{2\pi v\, dv}$$



$$= 2\pi A^2 e^{-bv^2} v\, dv$$

$$\boxed{f(v)\, dv = 2\pi A^2 e^{-bv^2} v\, dv}$$

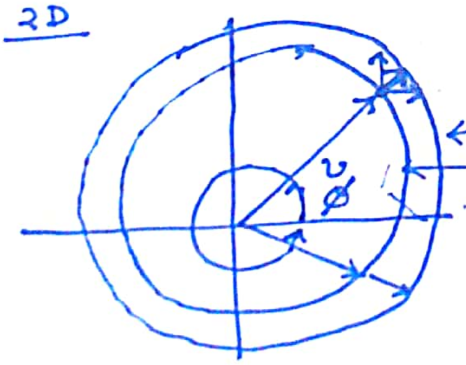
3D

$$\frac{4}{3}\pi (v+dv)^3 - \frac{4}{3}\pi v^3 \approx 4\pi v^2 dv$$

$$f(v)\, dv = A^3 e^{-bv^2} \times \underline{4\pi v^2 dv}$$

$$\boxed{f(v)\, dv = 4\pi A^3 e^{-bv^2} v^2 dv}$$

2D



3-different ways to get $2\pi v dv$

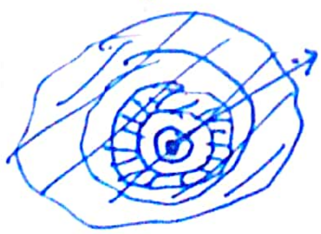
1) $\pi (v+dv)^2 - \pi v^2$

$= 2\pi v\, dv$

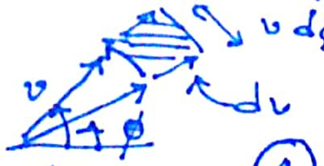
2) $d(\pi v^2) = 2\pi v\, dv$

3) $y = r\cos\phi$ | $v_y = v\cos\phi$

$x = r\sin\phi$ | $v_x = v\sin\phi$



$$\int_0^v 2\pi v\, dv = \pi v^2$$



$$\int^{2\pi} v\, d\phi\, dv = 2\pi v\, dv$$

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