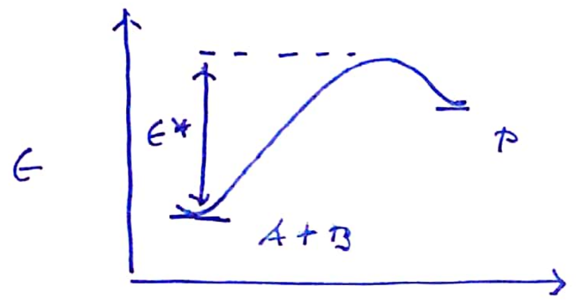
$$f(v)\,dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT}\, v^2\, dv$$

$$\epsilon = \frac{1}{2} m v^2 \Rightarrow v = \left(\frac{2\epsilon}{m}\right)^{1/2} \quad dv = \left(\frac{2}{m}\right)^{1/2} \frac{1}{2} \frac{d\epsilon}{\epsilon^{1/2}}$$

$$g(\epsilon)\,d\epsilon = 2\pi\left(\frac{1}{\pi k_B T}\right)^{3/2} e^{-\epsilon/k_BT}\, \epsilon^{1/2}\, d\epsilon$$

fraction of no of molecules having energy between ϵ to $\epsilon + d\epsilon$



Reaction coordinate

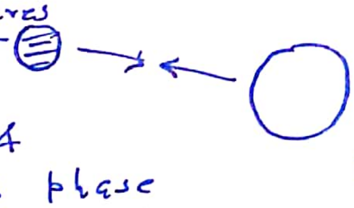
$$\boxed{k(T) = A\, e^{-E_a/kT}}$$

$$\left.\begin{array}{l} A + B \rightleftharpoons I \\ I \longrightarrow P \end{array}\right\}$$

Rate $= k\,[\ ]\,[\ ]$

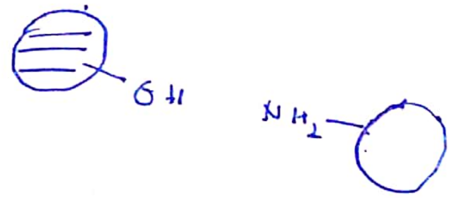
A + B + ... → C + D + ...

Hard spheres

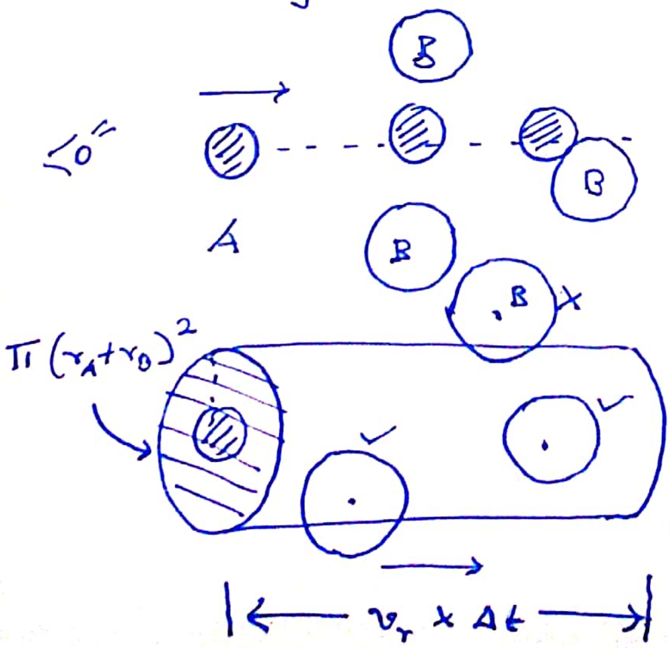


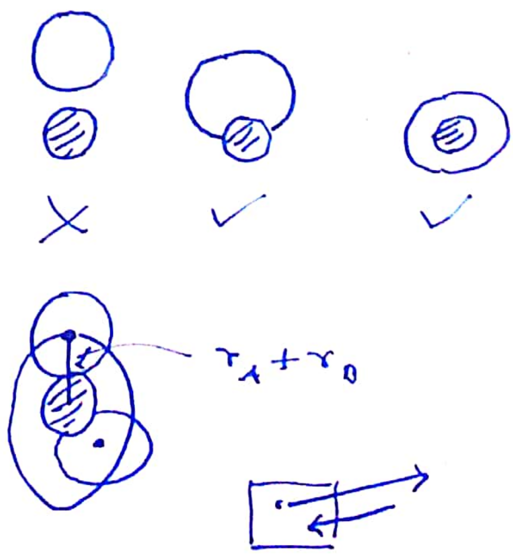
Gas phase

$\frac{1}{V}\frac{d\xi}{dt}$



How many collisions happen per unit time per unit volume?





# of collisions per unit time per unit volume

$$= \frac{\pi (r_A + r_B)^2 \times v_r \Delta t \times n_B \times n_A}{\Delta t}$$

$$= \sigma_{total} \times v_r \times n_B \times n_A$$

↑

collision cross-section

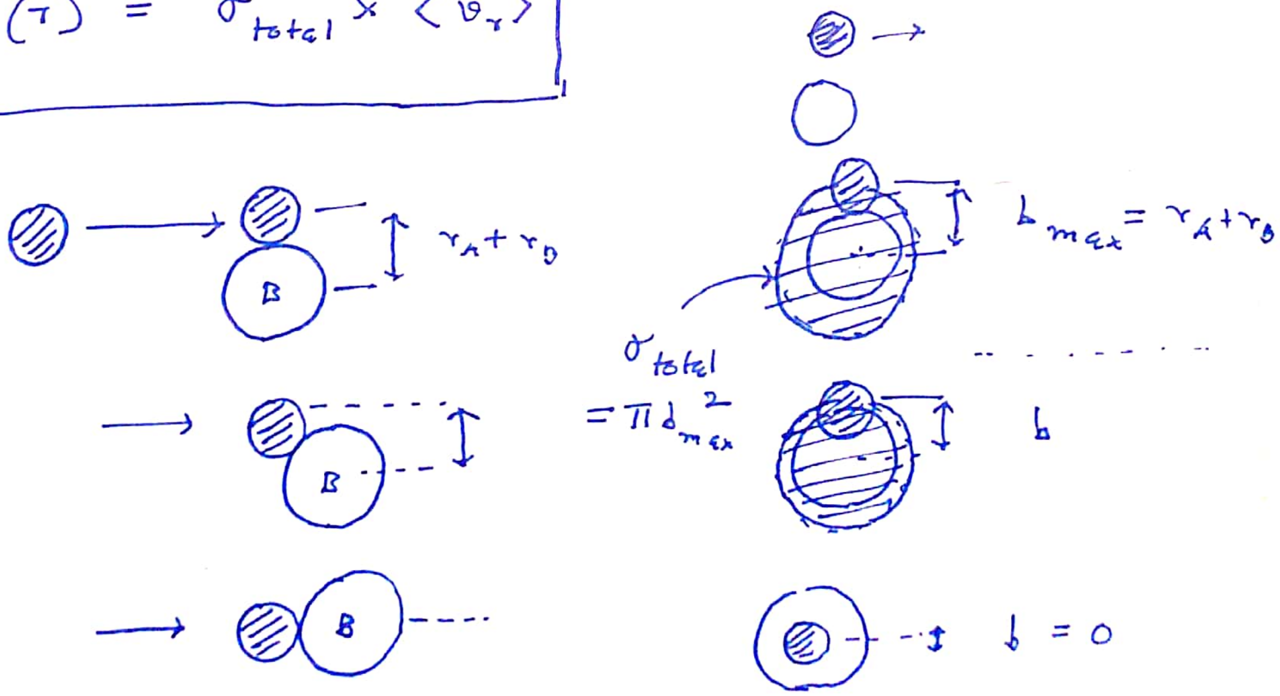
$$\text{Rate} = \sigma_{total} \times \int f(v)\, v_r \, dv_r \times n_A \times n_B$$

$$= \underbrace{\sigma_{total} \times \langle v_r \rangle}_{} \times n_A \times n_B$$

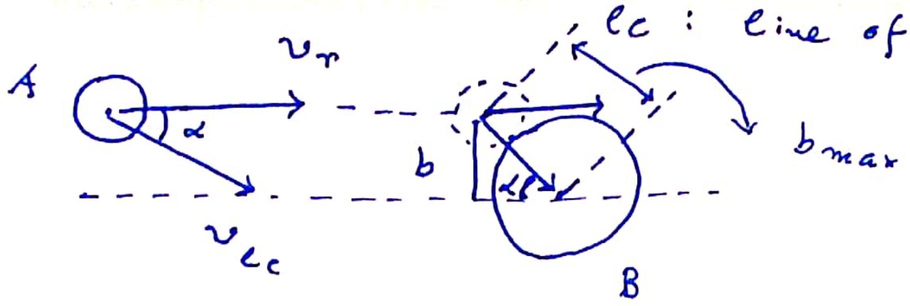
$$= k(T) \times [A] \times [B]$$

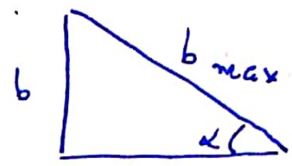
$$\qquad\qquad\quad n_A \times n_B$$

$$\boxed{k(T) = \sigma_{total} \times \langle v_r \rangle}$$



$\geq \epsilon^*$ $\qquad$ b = impact parameter





$$\epsilon_{lc} = \frac{1}{2}\mu v_{lc}^2 = \frac{1}{2}\mu v_r^2\cos^2\alpha = \frac{1}{2}\mu v_r^2(1-\sin^2\alpha)$$

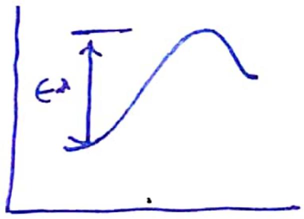
$$= \underbrace{\frac{1}{2}\mu v_r^2}\left(1-\frac{b^2}{b_{max}^2}\right) = \underbrace{\epsilon_r\left(1-\frac{b^2}{b_{max}^2}\right) \geq \epsilon^*}$$

$$\sigma(\epsilon_r) = \int_0^{b^*} 2\pi b\, db$$

$$b^2 \leq b_{max}^2\left(1-\frac{\epsilon^*}{\epsilon_r}\right)$$

$$\pi b^2 \leq \pi b_{max}^2\left(1-\frac{\epsilon^*}{\epsilon_r}\right)$$

$$\sigma(\epsilon_r) \leq \sigma_{total}\left(1-\frac{\epsilon^*}{\epsilon_r}\right)$$



reactive cross-section

$$k(T) = \int_{\epsilon^*}^{\infty} \sigma(\epsilon_r) \times v_r \times f(\epsilon_r)\, d\epsilon_r \quad \Big| \quad \frac{1}{2}\mu v_r^2 = \epsilon_r$$

$$= \sigma_{total} \times 2\pi\left(\frac{1}{\pi k_B T}\right)^{3/2} \times \int_{\epsilon^*}^{\infty}\left(1-\frac{\epsilon^*}{\epsilon_r}\right) \times \left(\frac{2\epsilon_r}{\mu}\right)^{1/2} \times \epsilon_r^{1/2} e^{-\epsilon_r/k_B T}\, d\epsilon_r$$

$$= (\quad) \times \int_{\epsilon^*}^{\infty}\left(\frac{\epsilon_r-\epsilon^*}{\cancel{\epsilon_r}}\right) \times \left(\frac{2}{\mu}\right)^{1/2} \times \cancel{\epsilon_r^{1/2}} \times \cancel{\epsilon_r^{1/2}}\, e^{-\epsilon_r/k_B T}\, d\epsilon_r$$

$$= (\,) \times e^{-\frac{\epsilon^*}{k_B T}} \times \left(\frac{2}{\mu}\right)^{1/2} \times \int_{\epsilon^*}^{\infty}(\epsilon_r-\epsilon^*)\, e^{-\frac{(\epsilon_r-\epsilon^*)}{k_B T}}\, d\epsilon_r$$

$$= (\quad) \times (k_B T)^2 \int_{\epsilon^*}^{\infty}\left(\frac{\epsilon_r-\epsilon^*}{k_B T}\right) e^{-\frac{(\epsilon_r-\epsilon^*)}{k_B T}}\, d\left(\frac{\epsilon_r-\epsilon^*}{k_B T}\right)$$

$$= \sigma_{total} \times \underbrace{2\pi \left(\frac{1}{\pi k_B T}\right)^{3/2} \times \left(\frac{2}{\mu}\right)^{1/2}}_{c} \times e^{-\epsilon^*/k_B T} \times \underbrace{(k_B T)^2}$$

$$\times \underbrace{\int_0^\infty x\, e^{-x}\, dx}_{\substack{\text{III} \\ 1}}$$

$$\frac{\epsilon_r - \epsilon^*}{k_B T} = x$$

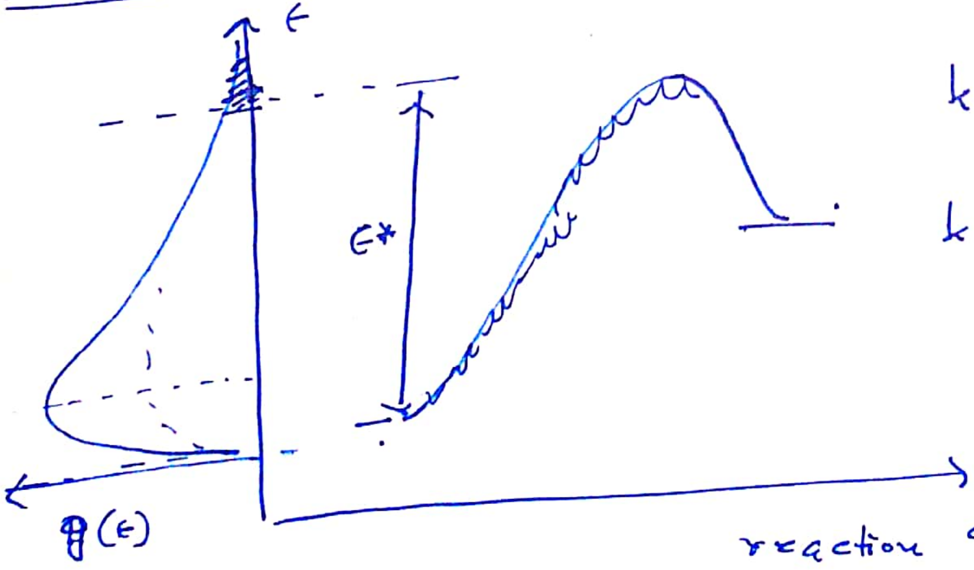
$\epsilon_r \to \epsilon^*, \quad x \to 0$

$\epsilon_r \to \infty, \quad x \to \infty$

$$= \sigma_{total} \times \frac{2^{3/2} \times (k_B T)^{1/2}}{\pi^{1/2} \times \mu^{1/2}} \times e^{-\epsilon^*/k_B T}$$

$$= \sigma_{total} \times \left(\frac{8 k_B T}{\pi \mu}\right)^{1/2} \times e^{-\epsilon^*/k_B T}$$

$$\boxed{k(T) = \sigma_{total} \times \langle v_r \rangle \times e^{-\epsilon^*/k_B T}}$$

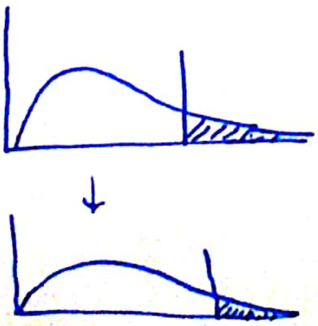


$k(T) = A\, e^{-E_a/RT}$

$k(T) = \sigma_{total} \times \langle v_r \rangle \times e^{-\epsilon^*/k_B T}$

$E_a \longleftrightarrow \epsilon^*$

$\frac{d \ln k}{dT} = ?$



$$E_a = \langle \epsilon_r \rangle_{\epsilon_r \geq \epsilon^*} - \langle \epsilon_r \rangle$$

$\uparrow$

Activation energy

$\epsilon^* \longleftarrow$ (energy of activation)

threshold energy