RECAP.

RATE LAW. $aA + bB \to cC$

$$\text{Rate} = \frac{-dA}{a\,dt} = -\frac{dB}{b\,dt} = \frac{dC}{dt} = k\,[A]^n[B]^m$$

rate constant (k), order (n)

units of $k \Rightarrow$ overall order s^{-1}, $\frac{L}{mol\text{-}s}$ etc.

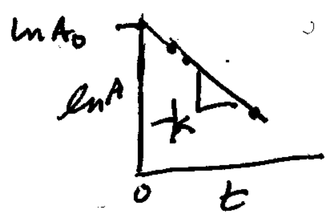
Method of initial rates $\Rightarrow$ order of reax

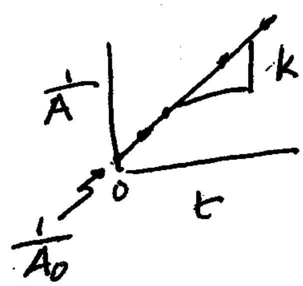
Need elementary steps to deduce order.

Integrated Rate Law : How much after time t?

$$-\frac{\partial A}{\partial t} = kA; \quad \int \frac{\partial A}{A} = \int k\,dt; \quad A = A_0 e^{-kt}; \quad \ln\frac{A}{A_0} = -kt$$

$$-\frac{\partial A}{\partial t} = kA^2; \quad \int \frac{\partial A}{A^2} = \int -k\,dt; \quad \frac{1}{A} - \frac{1}{A_0} = +kt$$



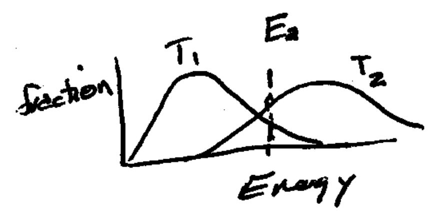


Graphs can determine order.

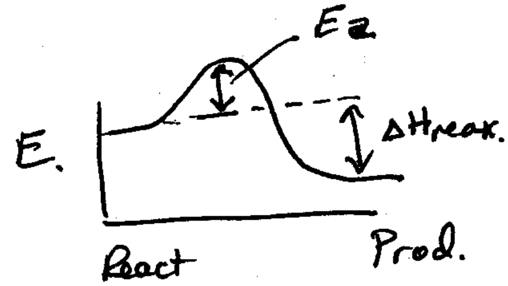
Collision Theory : - need energy (E_a) and orientation (A).
- depends on T

Arrhenius eq.

$$k = A\exp\left(-\frac{E_a}{k_B T}\right)$$



Activated Complex

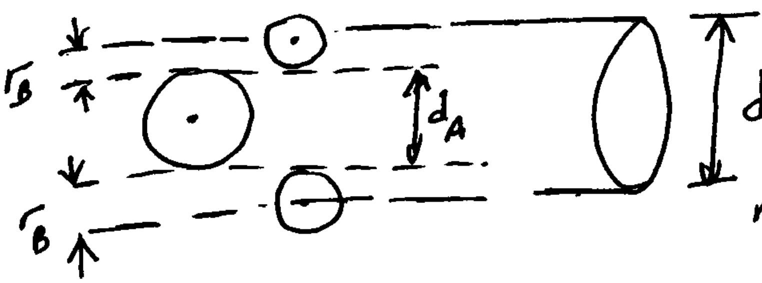


Molecular theories of reaction

what to do! $A + B \rightarrow$

① Rate $\propto$ # collisions. (Z, s^{-1})

Correction from class notes!



$d = d_A + d_B$

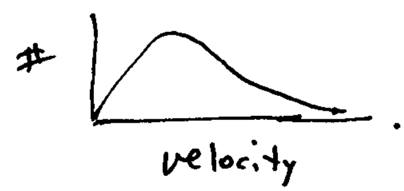
$r = \frac{1}{2}(d_A + d_B)$

length $= \bar{u} \cdot t$ (e.g., $t = 1s$) Rate $\propto \pi r^2 \cdot \bar{u}$

velocity

② Rate $\propto \left(\frac{N_A}{V}\right), \left(\frac{N_B}{V}\right)$

③ $R \propto \bar{u}$ ← AVG velocity.



$\bar{u} \propto \sqrt{\frac{k_B T}{\pi m}}$ for A & B.

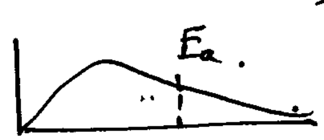
mass. reduced mass, μ.

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}.$$

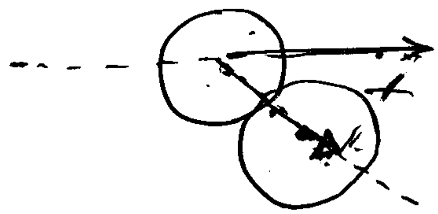
④ Acct for min collision Energy (i.e., E_a).

$\frac{f(\varepsilon)}{}$ →

M-B dist.



Must account for:



So....

$$\boxed{k = \underbrace{\sigma_c \sqrt{\frac{8 k_B T}{\pi \mu}}}\ \exp\left(\frac{-E_a}{k_B T}\right) P}$$

collision cross section

steric factor. (for orientation)

$$k = A \exp\left(-E_a/k_B T\right).$$

$$k = A' \exp\left(-E_a/RT\right)$$

Transition State Theory.

Based on Eyring-Polani equation.

$$k = \frac{k_B T}{h} K^{\dagger} \leftarrow \text{Equilib. for activated state.}$$

h ← Plank const

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta G^{o\dagger}}{RT}\right).$$

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta H^{\dagger}}{RT}\right) \exp\left(\frac{\Delta S^{\dagger}}{R}\right).$$

$$k = \frac{k_b T}{h} \exp\left(\frac{\Delta S^{\dagger}}{R}\right) \exp\left(\frac{-\Delta H^{\dagger}}{RT}\right).$$

$$k = \underbrace{K \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\dagger}}{R}\right)} \exp\left(\frac{-\Delta H^{\dagger}}{RT.}\right) \quad E_a.$$

$$k = A \exp\left(\frac{-\Delta H^{\dagger}}{RT.}\right)$$