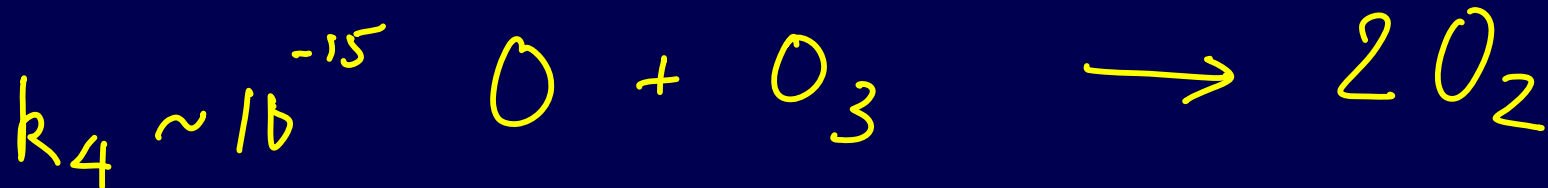
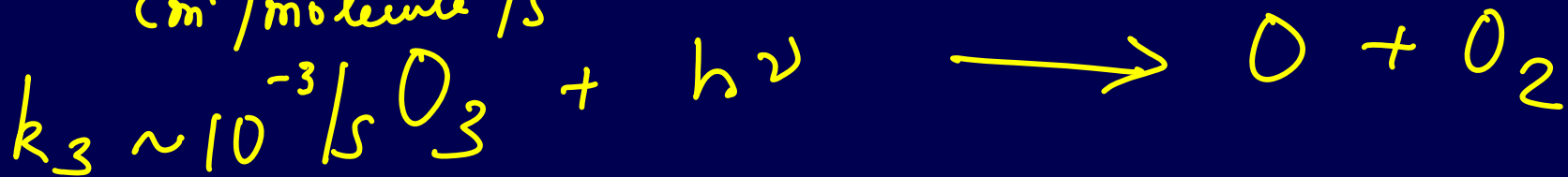
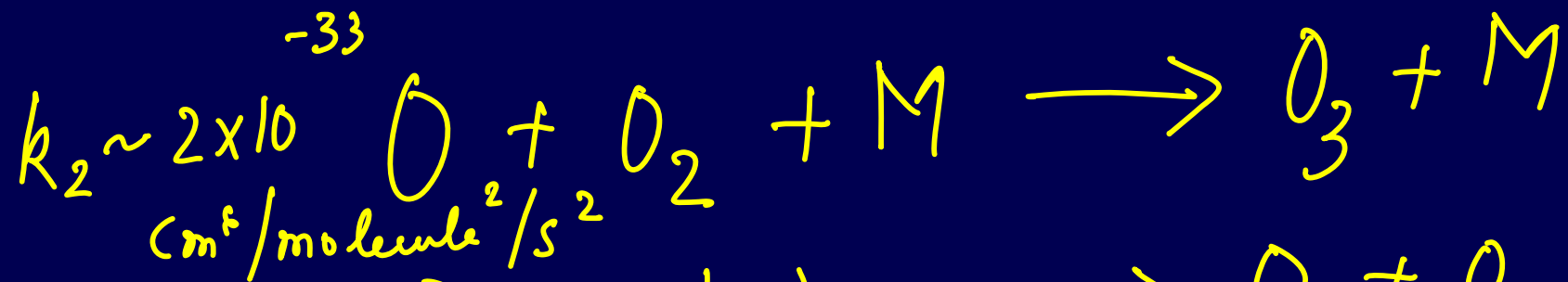
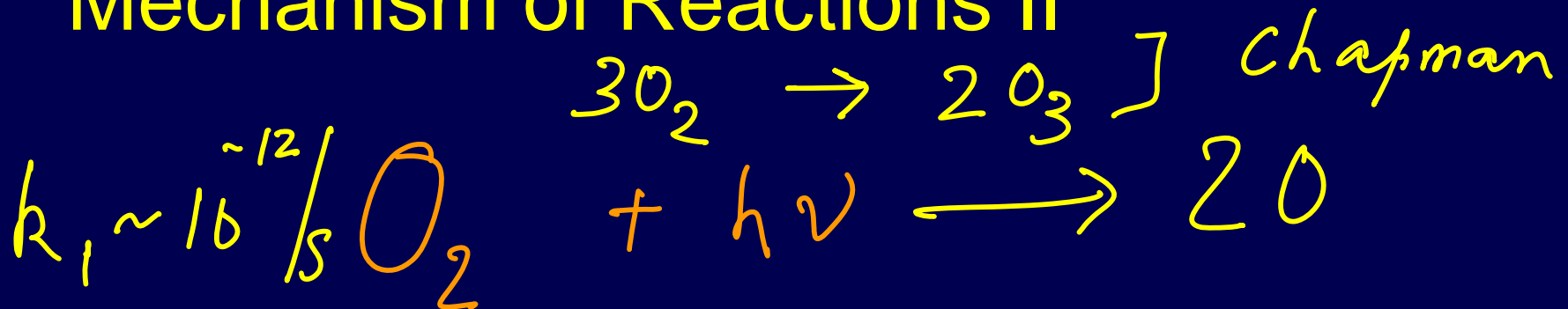


## Mechanism of Reactions II



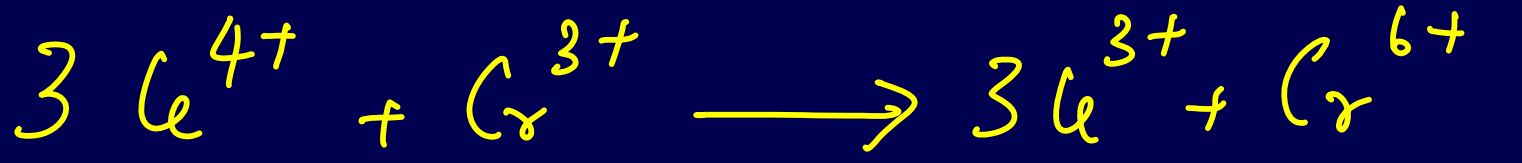
Reactive  
intermediate  $\rightarrow$   $\frac{d[O]}{dt} = 0$  and solve for  $[O]_{ss}$

$$\frac{d[O_3]}{dt} = 0$$

this is a product and normally SSA is not applied. In the atmosphere  $[O_3]$  is in steady state so  $\frac{d[O_3]}{dt} = 0$

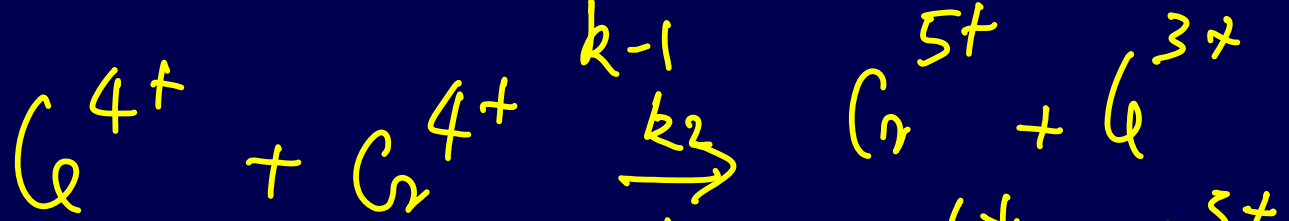
$[O_3]_{ss}$   $\rightarrow$   $\left\{ \begin{array}{l} \text{Experimental measurement by} \\ \text{Sherwood \& Molina showed that} \\ \text{it is less than expected. Attributed} \\ \text{to Chlorofluorocarbons (CFC)} \end{array} \right.$   
O<sub>3</sub> hole

In-class  
example of  
pre equilibrium



observed rate  $\left( \frac{d[\text{Cr}^{6+}]}{dt} = k_{\text{ex}} \frac{[\text{Cr}^{3+}][\text{Ce}^{4+}]^2}{[\text{Ce}^{3+}]} \right)$

Mech:



$$\frac{d[\text{Gr}^{5+}]}{dt} = k_2 [\text{Ce}^{4+}][\text{Gr}^{4+}] - k_3 [\text{Ce}^{4+}][\text{Gr}^{5+}]$$

$$0 = \frac{d[\text{Gr}^{4+}]}{dt} = k_1 [\text{Ce}^{4+}][\text{Gr}^{3+}] - k_{-1} [\text{Gr}^{4+}][\text{Ce}^{3+}] - k_2 [\text{Ce}^{4+}][\text{Gr}^{4+}] + k_3 [\text{Ce}^{4+}][\text{Gr}^{5+}]$$

$$\Rightarrow [\text{Gr}^{4+}]_{ss} = \frac{k_1 [\text{Ce}^{4+}][\text{Gr}^{3+}] - k_2 [\text{Ce}^{4+}][\text{Gr}^{4+}]}{k_{-1} [\text{Ce}^{3+}] + k_2 [\text{Ce}^{4+}]}$$

$$\frac{d[\text{Cr}^{6+}]}{dt} = k_3 \cdot [\text{U}^{4+}] [\text{Cr}^{5+}] = \cancel{k_3} [\text{U}^{4+}] \cdot \frac{k_2 [\text{Cr}^{4+}]_{ss}}{\cancel{k_3}}$$

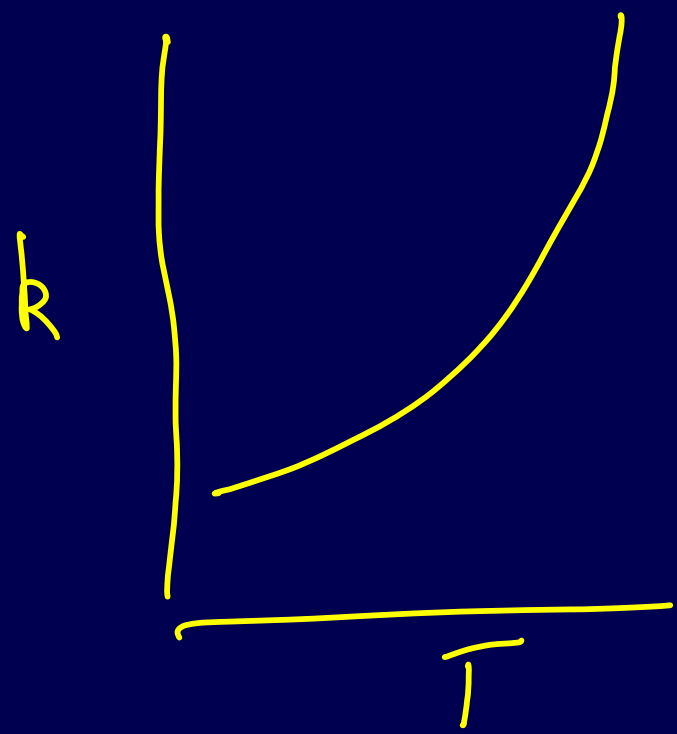
$$= \frac{k_1 k_2 [\text{U}^{4+}]^2 [\text{Cr}^{3+}]}{k_{-1} [\text{U}^{3+}] + k_2 [\text{U}^{4+}]}$$

If  $k_2 [\text{U}^{4+}] \ll k_{-1} [\text{U}^{3+}]$ , get the observed rate law

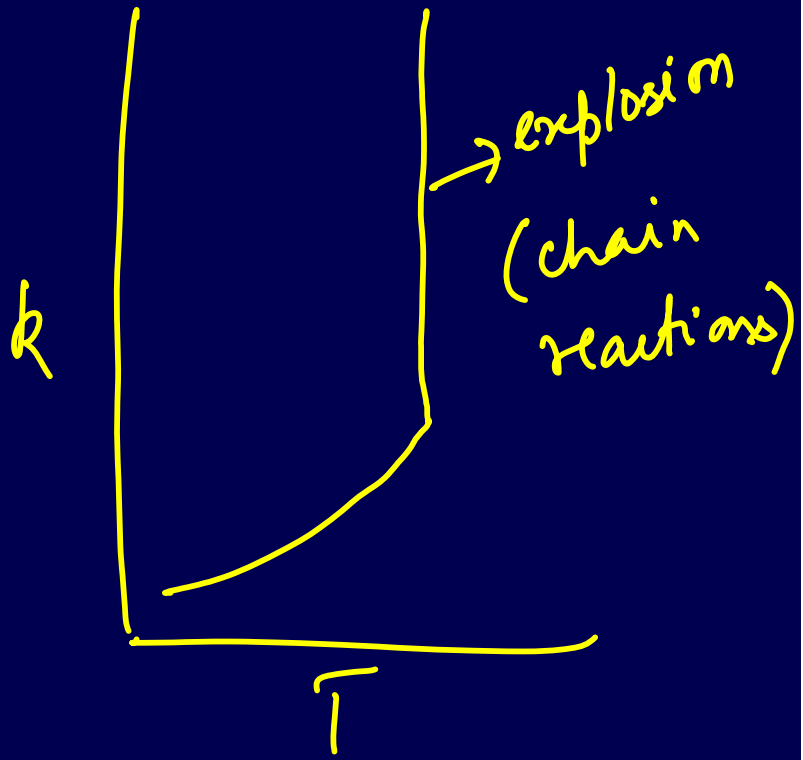
Note: 3<sup>rd</sup> step does not figure in the rate law  
(after the 2<sup>nd</sup> slow step)

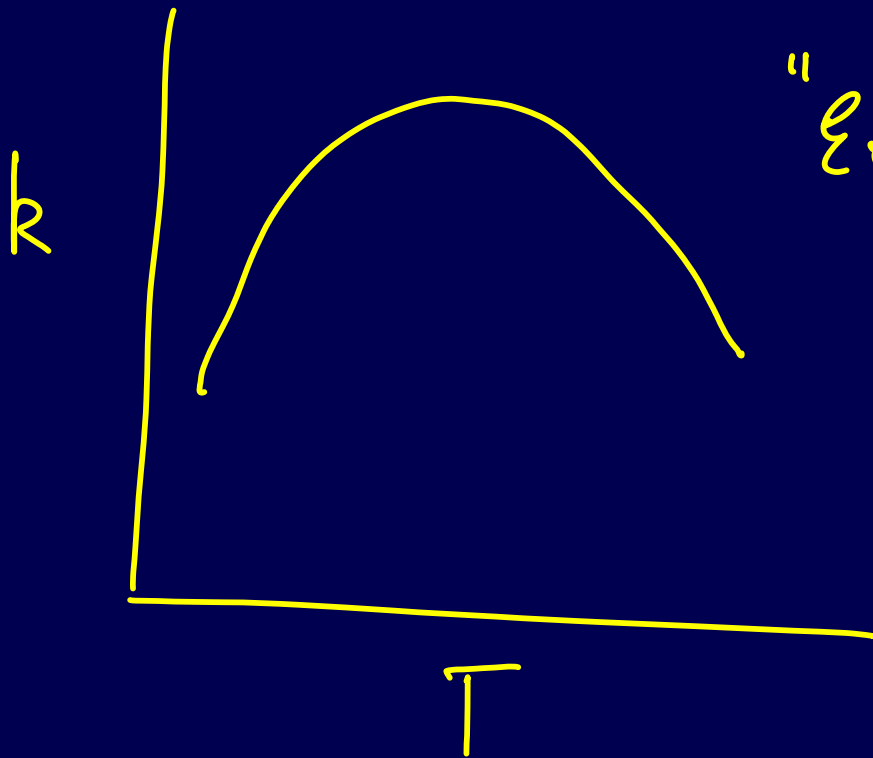
Rate law directly obtained by assuming  
first step is in equilibrium

# Temperature dependence of reaction rates



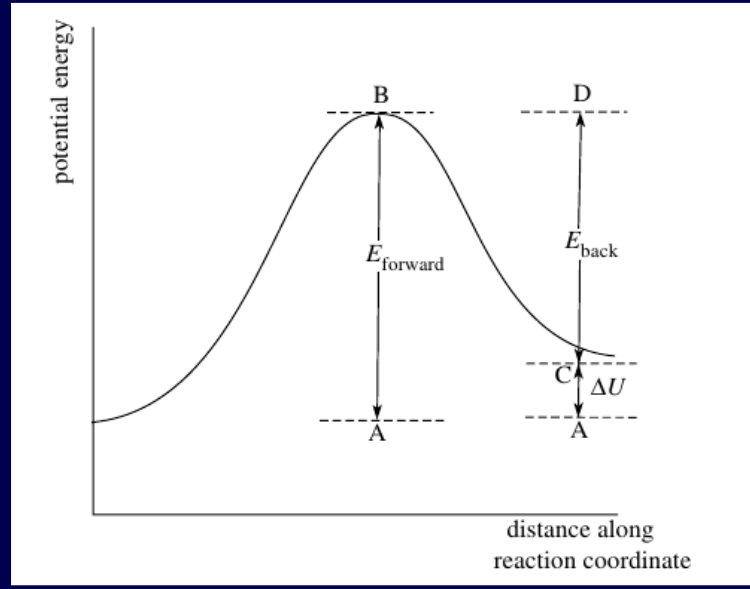
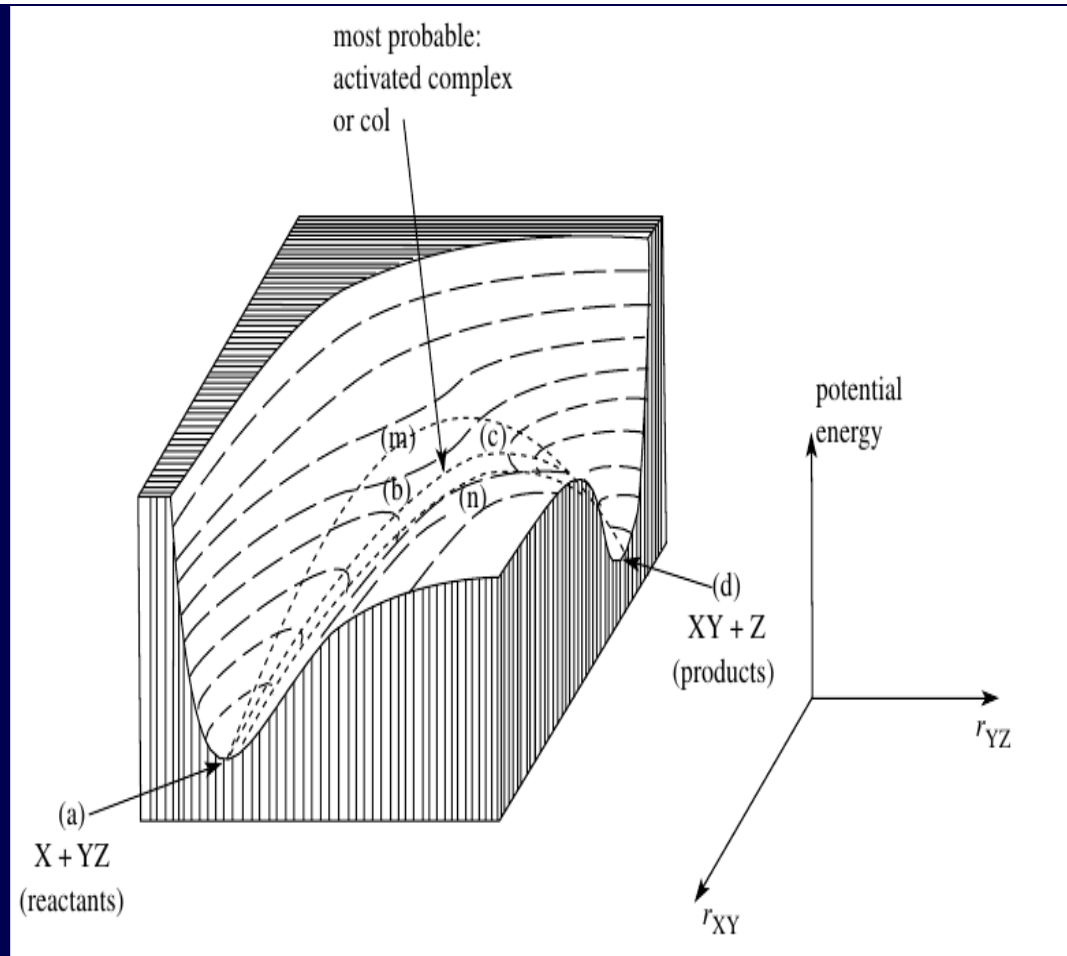
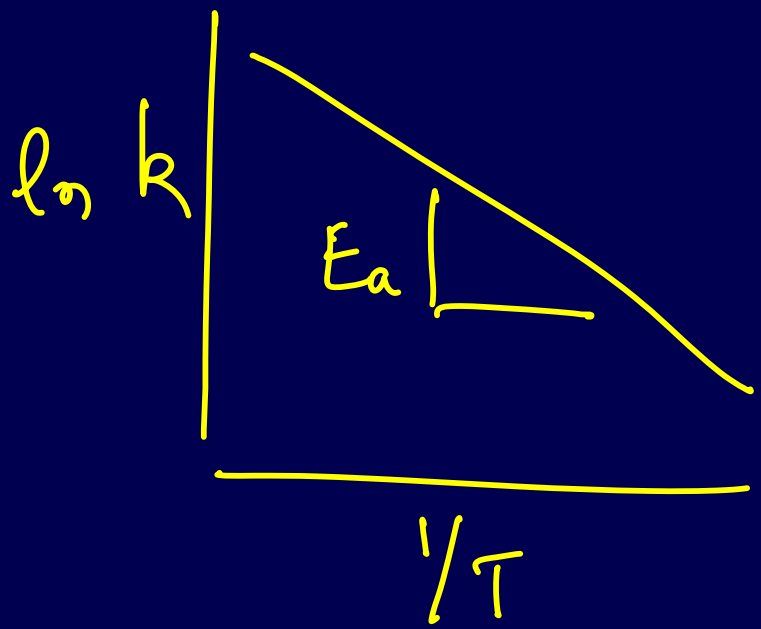
Arrhenius behavior  
(common but not universal)



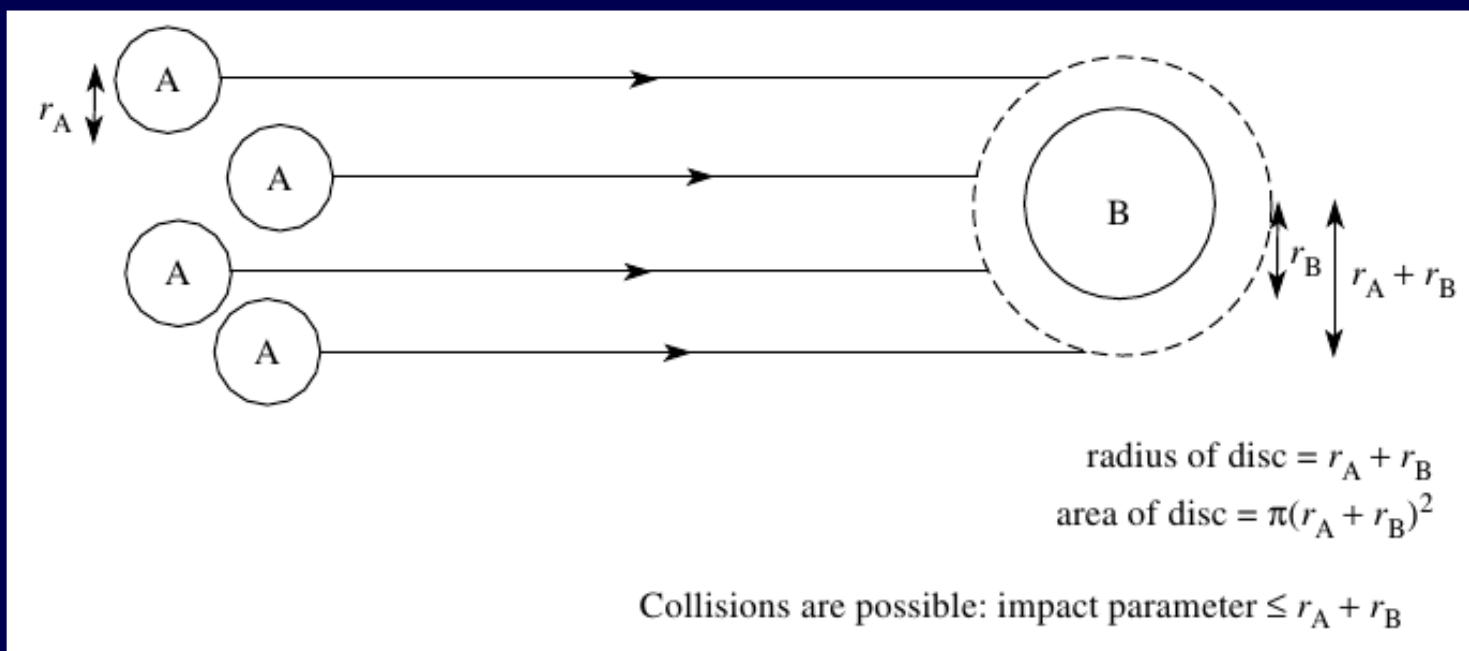


"Enzyme" catalyzed  
reactions

→ High temperatures  
not "good" for this  
enzyme - structure  
changed to inactive  
form at high T







$Z = \left( \frac{8\pi kT}{M} \right)^{3/2}$ 
 $k \propto (\# \text{ of collisions}) \times \text{Spatial factor} \times \text{fraction of collisions with sufficient energy}$

$\frac{1}{M} = \frac{1}{m_A} + \frac{1}{m_B}$

Boltzmann

from kinetic theory  
probability  $e^{-E_a/kT}$

$k \propto T^{1/2}$

$e^{-E_a/kT}$



$k = A T^m e^{-E_a/kT}$