

## Introduction to Theoretical kinetics – modified 2009

Arrhenius empirical relation

$$k = (\text{const})e^{-\gamma/T} = Ae^{-E_a/RT}$$

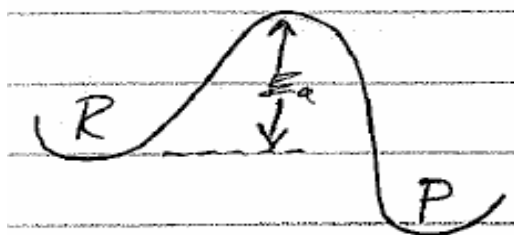
**$E_a$  – activation energy**

$E_a$  behave like barrier, if molecules have enough energy

can go over barrier – where  $T \Rightarrow$  average K.E.

Top of barrier—transition state - no lifetime

**A** – “**pre-exponential factor**” (T-independent)



For a mechanism, steps will bring added barriers/t.s.:

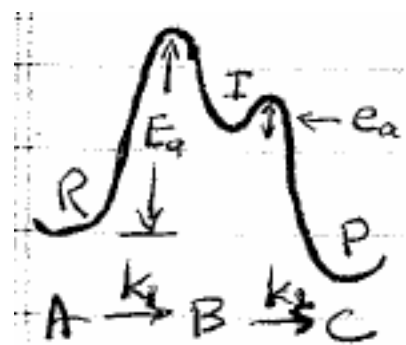
Bring ideas from reaction coordinate / energy diagram

1<sup>st</sup> step slow – big  $E_a$        $k_1 = A_1e^{-E_a/RT}$

2<sup>nd</sup> step fast – small  $e_a$        $k_2 = A_2e^{-e_a/RT}$

in this case reverse steps slow (big  $E_a$ )

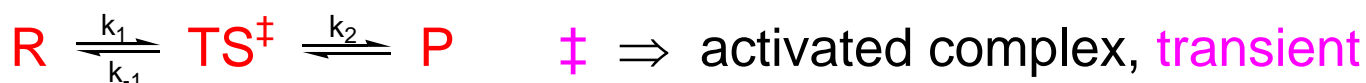
$\Rightarrow$  like steady state case (a)



Simple mechanism  $\rightarrow$  theoretical model

$E_a$  – barrier for  $R \rightarrow$  T.S. (**pseudo reaction**)

Imagine treat TS as intermediate (**but TS not isolatable**)



(reality –  **$TS^\ddagger$**  more like steady state – no population)

Then imagine have some equilibrium  $R \xrightleftharpoons{K_e^\ddagger} TS^\ddagger$   
 $K_e^\ddagger = e^{-\Delta G^\ddagger/RT}$  treat as if thermodynamic

Eyring model - developed for above kinetic mechanism –  
rate depend on:

$K_0^0$  – transmission coefficient – probability go onto P  
 i.e. at top of barrier have choice: R or P

$kT/h$  – (Boltzman's const/ Planck's const)•T →  
 microscale energy correction for T → frequency  
 relates to vibration,  $E=h\nu$ , oscillate on top barrier

$K_e^\ddagger$  → adds in the population of transition state

$k_{TS} = K_0^0 \cdot kT/h \cdot K_e^\ddagger$  → higher T – cross more probable  
 $= kT/h e^{-\Delta G^\ddagger/RT}$  and  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$   
 $= (kT/h) e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$  -- assumes  $K_0^0 = 1$  (max.)

Now has form of Arrhenius Equation:  $(kT/h e^{\Delta S^\ddagger/R}) \sim A$   
 $\Delta H^\ddagger \sim E_a$  -- more precisely (unimolec.):  $E_a = \Delta H^\ddagger - RT$   
 correct for RT →  $A \sim e(kT/h e^{\Delta S^\ddagger/R})$ :  $e^{-\Delta H^\ddagger/RT} = e^{-(E_a-RT)/RT} = e e^{-E_a/RT}$

Note: A no longer constant -- depend on  $\Delta S^\ddagger$  – entropy –  
 if T.S. more organized than R:  $\Delta S^\ddagger$  (–) and rxn slow  
 $\Delta H^\ddagger$  an energy term – bond break- faster / make - slower

### Microscopic (molecular level) picture

Have discussed multi step mechanisms

- Ideas
- rate determining step
  - steady state for reactive intermediate
  - fast equilibrium for buildup intermediate

## Collision Theory

All this sort of ignores how molecules act

→ need to come together in space to react

If reaction in gas phase  $A + B \rightarrow \text{Product}$

 collision frequency & energy govern rate

frequency  $\sim [A][B] \rightarrow 2^{\text{nd}}$  order --

Energy  $f = e^{-E_c/RT}$  fraction collision  $> E_c$  (probability)

$$r \approx R (e^{-E_c/RT}) [A][B]$$

now if  $E_c \sim E_a$  activation } → Arrhenius form  
 $R \sim \text{max rate} \sim A$  }

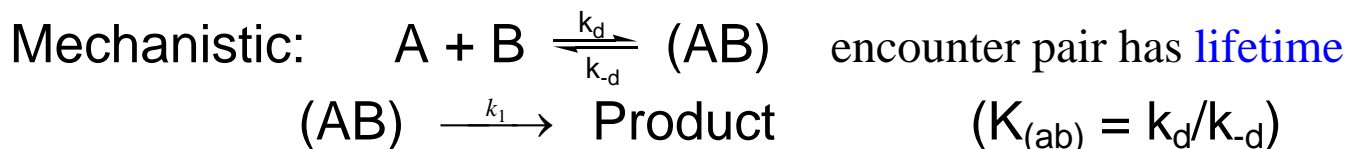
⇒ generally too high – add **steric factor** (mult. fraction)  
 to account for geometry [analogous to  $e^{\Delta S/R} \rightarrow$  entropy]

Solution → collision impeded by solvent

→ slows rate of  $A + B$  —

form non-bonded (weak interact) encounter pair

\* But also slow rate separation (→ intermediate lifetime)



Unless extremely viscous – (AB) short-lived → **mechanism**

**Steady state:**  $d(AB)/dt \cong 0 = k_d[A][B] - k_{-d}(AB) - k_1(AB)$

$$(AB) = \{k_d/(k_{-d} + k_1)\}[A][B]$$

rate:  $dP/dt = k_1(AB) = \{k_1k_d/(k_{-d} + k_1)\}[A][B]$

2<sup>nd</sup> order:  $r = k_2[A][B] \quad k_2 = k_1k_d/(k_{-d} + k_1)$

### Conditions:

a)  $k_{-d} \ll k_1$  As soon as (AB) forms goes on to product  
– encounter lasts some time, **rate limited by diffusion:**

Rate limit  $k_2 \sim k_1k_d/k_1 \sim k_d \rightarrow r \sim k_d [A][B]$

$k_d \sim D$  (Diffusion const.)  $\sim kT/a\eta$  -where  $\eta$  is viscosity

Diffusion Control – reaction only as fast as

A,B come together (like collision),  $\eta$  inc.,  $k_d$  dec.

reaction very fast  $k_d \approx 10^{10}$  L/mol • s

this will be a constraint on possible A values  
generally a property of small molecules

Large molecules have steric issue—not included

b)  $k_1 \ll k_{-d}$   $k_2 \sim k_1k_d/k_{-d} = k_1 (K_{en})$

break up faster

$k_1 \rightarrow$  Activation control – need many collisions in solvent cage-find energy

$$r \sim k_1(k) [A][B]$$

