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Course 565/665 Lecture Number ____ Date 4/28/03

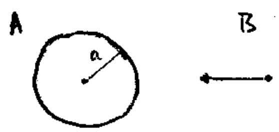
Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

Last Time

① Translational Diffusion Driven by conc. gradients (passive diffusion).

② Diffusion of molecules through a sphere.

Fixed



If B disappears upon collision, we have a "rxn."

$A + B \longrightarrow$ Products.

If collision is all that matters.

$$I_a = k_a C_\infty$$

- I_a ↑ Rate of Reaction (*)
- k_a ← Rate Constant (Coefficient)
- C_∞ ← Bulk concentration of Reactant B.

(*) # of molecules colliding w/ sphere per unit time.

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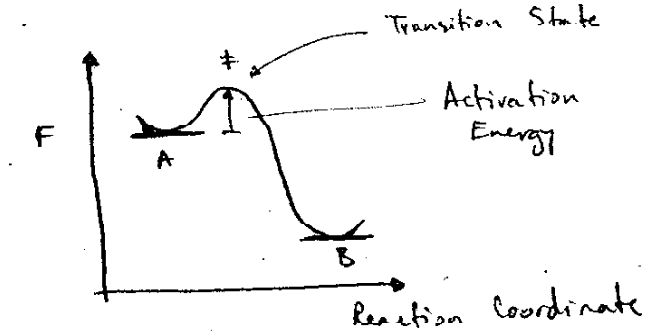
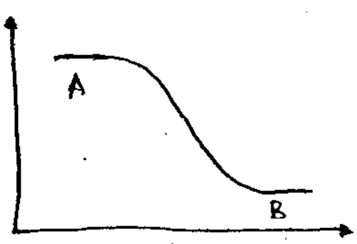
Sometimes Collisions are Not Enough to get reactions to go...

$A \xrightarrow{k_1} B$



Diffusion Controlled Reactions:



No reaction barrier
(Activation Energy = 0 J)

Thus, even if B is a lower energy state than A, (and therefore thermodynamically favored), it must still overcome the reaction barrier to do this. If this barrier is very high, A may never go to B.

In general, for activated reactions,

$$k_{a,act} \ll k_{a,diff}$$

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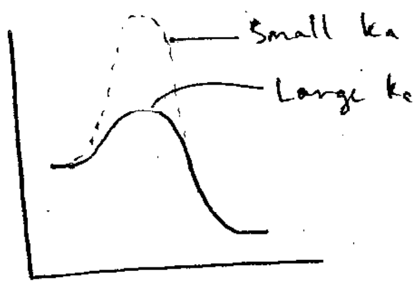
$A \xrightarrow{k_1} B$

$$\text{Rate} \equiv \left(\begin{array}{c}\#\text{ of molecules converted}\\ \text{to product per second}\end{array}\right) = \frac{d[A]}{dt} = -k_1[A] = -\frac{d[B]}{dt}$$



- How does [A] change with time?
- Away from equilibrium.

$$\frac{d[A]}{dt} = -k_1[A]$$

$$\int_{A_0}^{A(t)} \frac{d[A]}{[A]} = -k_1\int_0^t dt$$

$$\ln[A]\Big|_{A_0}^{A(t)} = -k_1 t$$

$$\boxed{A(t) = A_0 e^{-k_1 t}}$$

Also,

$$\frac{d[B]}{dt} = k_1[A_1] = k_1(A_0 - [B])$$

since $[B] = A_0 - [A]$

$[A] = A_0 - [B]$

(Assuming 1:1 reaction).

....

$$\boxed{[B] = A_0\left(1 - e^{-k_1 t}\right)}$$

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What is a landscape?

A hypersurface!

E (degrees of freedom)

↑ Potential Energy

↖ Dihedral Angles