Physical Chemistry (Chem 132A)

Lecture 23
Friday, December 1

Homework Due on Saturday, December 2

Last homework of the quarter will be available Saturday evening. Due on Saturday, December 9

Reminder: FINAL EXAM, DEC. 15, 8—10AM

Relationship between reaction mechanisms and rate laws when overall reaction is not an elementary step??

TWO STEP REACTION WITH SLOW FIRST STEP

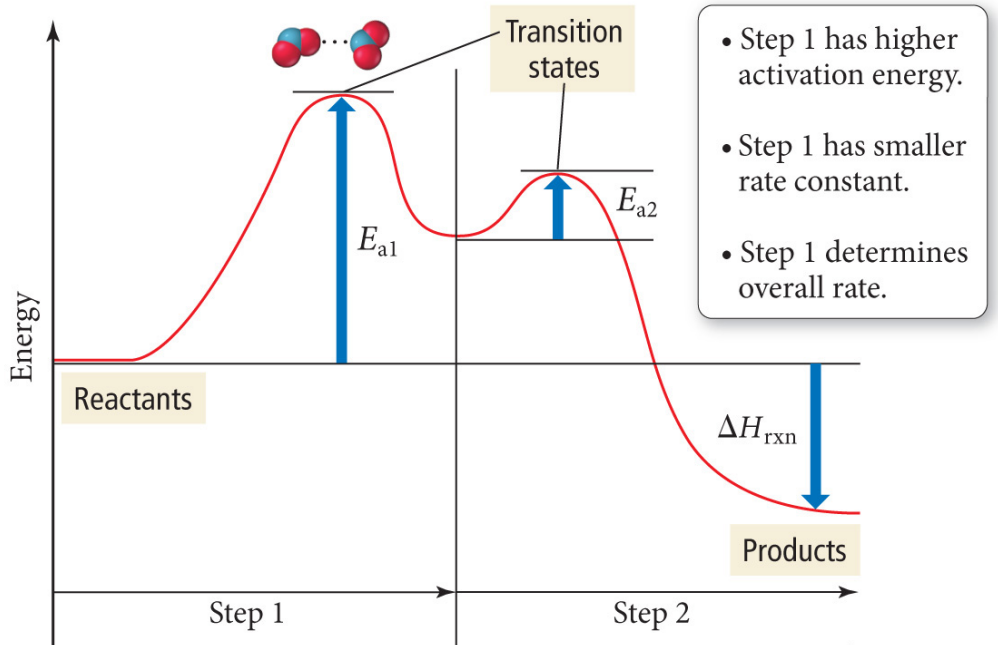
$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ overall reaction

Step 1 $NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)$ Slow

Step 2 $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ Fast

The slow first step controls the rate of the reaction

Rate = $k[NO_2]^2$



REACTION INTERMEDIATES

Intermediate---formed and used up in course of reaction.
In last example NO_3 is an intermediate.

What if the first elementary step is not SLOW?

$$2H_2(g) + 2NO(g) \longrightarrow 2H_2O(g) + N_2(g) \quad \text{overall rxn}$$

Mechanism

$$2NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O_2(g) \quad \text{FAST EQUILIBRIUM}$$

$$H_2(g) + N_2O_2(g) \xrightarrow{k_2} H_2O(g) + N_2O(g) \quad \text{SLOW}$$

$$N_2O(g) + H_2(g) \xrightarrow{k_3} N_2(g) + H_2O(g) \quad \text{FAST}$$

USE THE EQUILIBRIUM CONDITION

Rate = $k_2[H_2][N_2O_2]$ **Based on the SLOW STEP**

We don't want the N_2O_2 in the rate law since it isn't a reactant or product.

Since $2NO \longleftrightarrow N_2O_2$
Is at equilibrium----forward rate = reverse rate

$$k_1[NO]^2 = k_{-1}[N_2O_2]_{EQ}$$

$$[N_2O_2]_{EQ} = (k_1/k_{-1})[NO]^2$$

$$\text{Rate} = k_2[H_2](k_1/k_{-1})[NO]^2 = k[H_2][NO]^2$$

WHAT IF WE DON'T KNOW THAT STEP 2 IS SLOW? STEADY STATE APPROXIMATION

$$2H_2(g) + 2NO(g) \longrightarrow 2H_2O(g) + N_2(g) \quad \text{overall rxn}$$

Mechanism

$$2NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O_2(g)$$

$$H_2(g) + N_2O_2(g) \xrightarrow{k_2} H_2O(g) + N_2O(g)$$

$$N_2O(g) + H_2(g) \xrightarrow{k_3} N_2(g) + H_2O(g)$$

We might write: Rate = $\dfrac{d[N_2]}{dt} = k_3[N_2O][H_2]$

Intermediate

Steady State Approximation

The rate of formation of an intermediate is set equal to the rate it is used up by a subsequent reaction

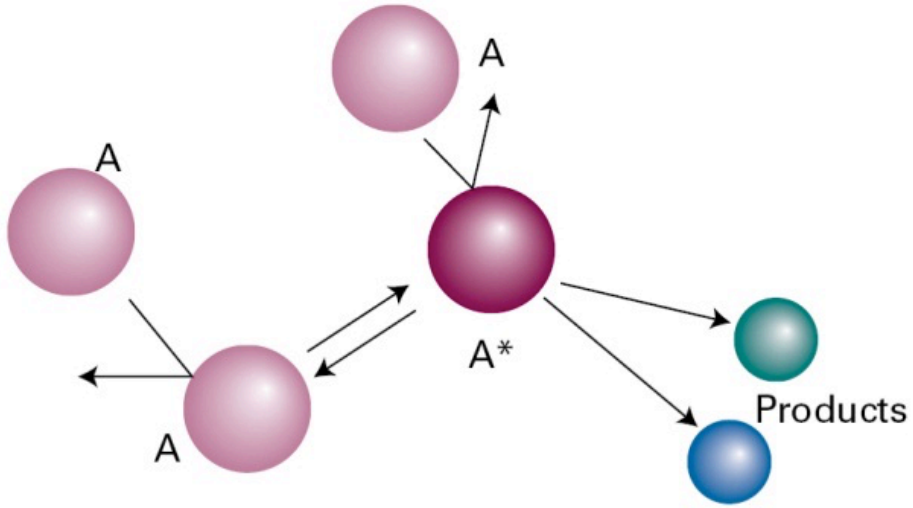
Unimolecular Reactions

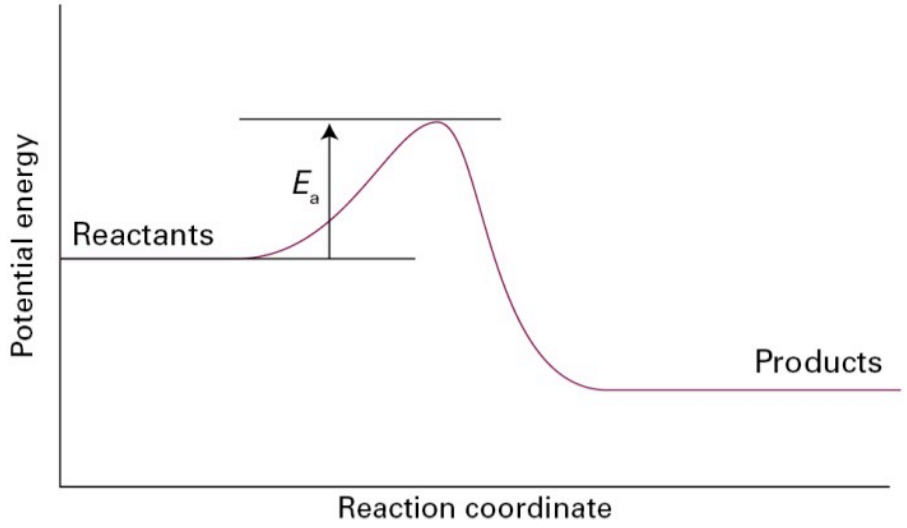
$$A \longrightarrow P$$

$$\text{Cyclo-}C_3H_6(g) \longrightarrow CH_3CH{=}CH_2(g)$$

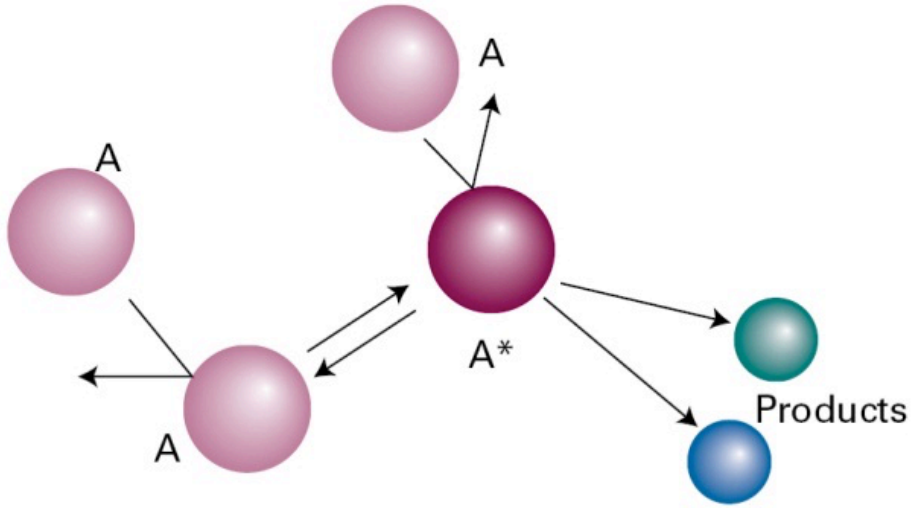
Rate = k_r[cyclo-C_3H_6]---observation

How does this reaction occur?





Lindemann–Hinshelwood Mechanism



$$\mathbf{A + A} \longrightarrow \mathbf{A^* + A} \qquad \frac{d[A^*]}{dt} = k_a[A]^2$$

$$\mathbf{A + A^*} \longrightarrow \mathbf{A + A} \qquad \frac{d[A^*]}{dt} = -k_a^{'}[A][A^*]$$

$$\mathbf{A^*} \longrightarrow \mathbf{P} \qquad \frac{d[A^*]}{dt} = -k_b[A^*]$$

Use Steady State Approximation on [A*]

$$\frac{d[A^*]}{dt} = k_a[A]^2 - k_a^{'}[A][A^*] - k_b[A^*]_{ss} = 0$$

$$[A^*]_{ss} = \frac{k_a[A]^2}{k_b + k_a^{'}[A]}$$

$$\frac{d[P]}{dt} = k_b[A^*]_{ss} = \frac{k_a k_b[A]^2}{k_b + k_a^{'}[A]}$$

If the decay of A* to P is the slow step then:

k_a' [A][A*] > k_b[A*]

k_a'[A] > k_b

$$\frac{d[P]}{dt} = \frac{k_a k_b}{k_a^{'}}[A] = k_r[A]$$

So it looks like it is First Order

Simple Collision Theory Picture

For a Bimolecular Reaction:

$$A + B \rightarrow P$$

Rate = k_r[A][B] proportional to # collisions

 # collisions ~ v_{mean} ~ $(T/M)^{1/2}$
Should also be proportional to cross section σ
And the number densities of A and B

Rate ~ σ $(T/M)^{1/2}$[A][B]
Also expect there to be a positive activation energy

So: Rate ~ σ $(T/M)^{1/2}$ $e^{-E'/RT}$ [A][B]
k ~ σ $(T/M)^{1/2}$ $e^{-E'/RT}$

Also expect a "steric factor" k ~ P σ $(T/M)^{1/2}$ $e^{-E'/RT}$

$$k \sim P\,\sigma\,(T/M)^{1/2}\,e^{-E'/RT}$$

Steric factor **encounter rate** **collision energy dependence**

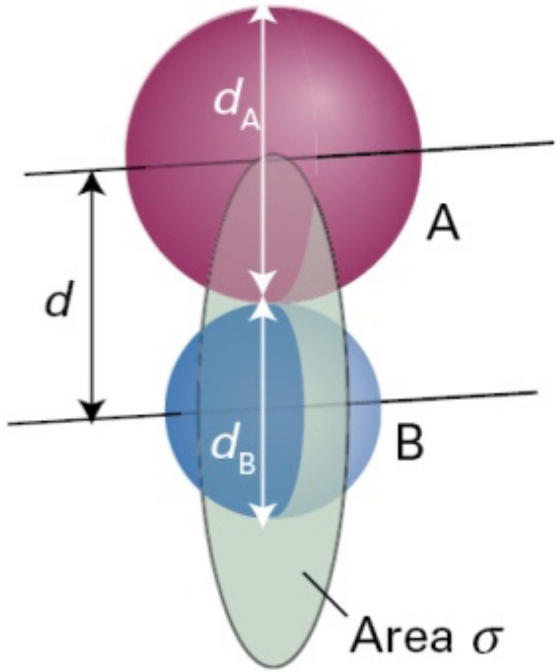
Gas collision rate

$$Z_{AB} = \sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A^2[A][B]$$

$$\sigma = \pi d^2$$

$$d = \frac{1}{2}\left(d_A + d_B\right)$$

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



Energy Dependence

Write the cross section σ as an energy dependent quantity

σ(E)
= 0 if the "collision energy" < threshold value

THE END

SEE YOU ON MONDAY

ONE MORE WEEK