

# Physical Chemistry (Chem 132A)

---



## Lecture 24 Monday, December 4

**Homework 9 Due on Saturday, December 9**  
**Last homework of the quarter**

**Reminder: FINAL EXAM, DEC. 15,**  
**8—10AM**



---

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



## Steady State Approximation

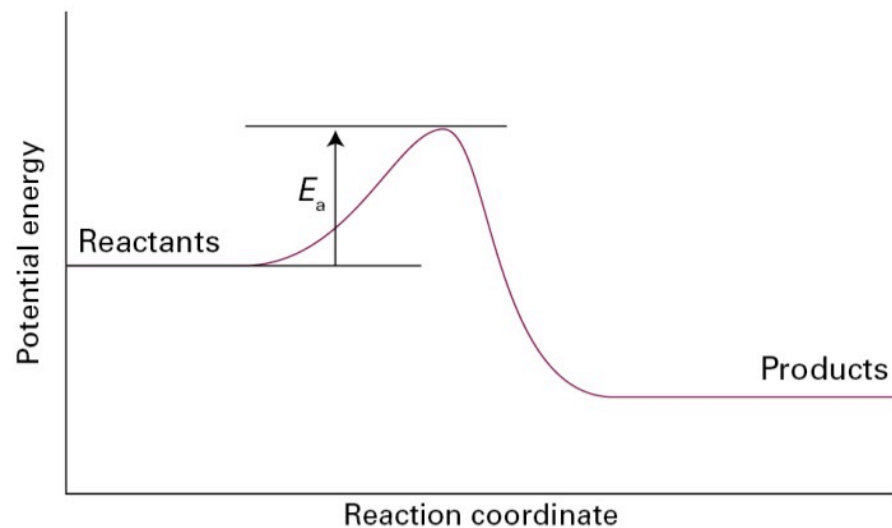
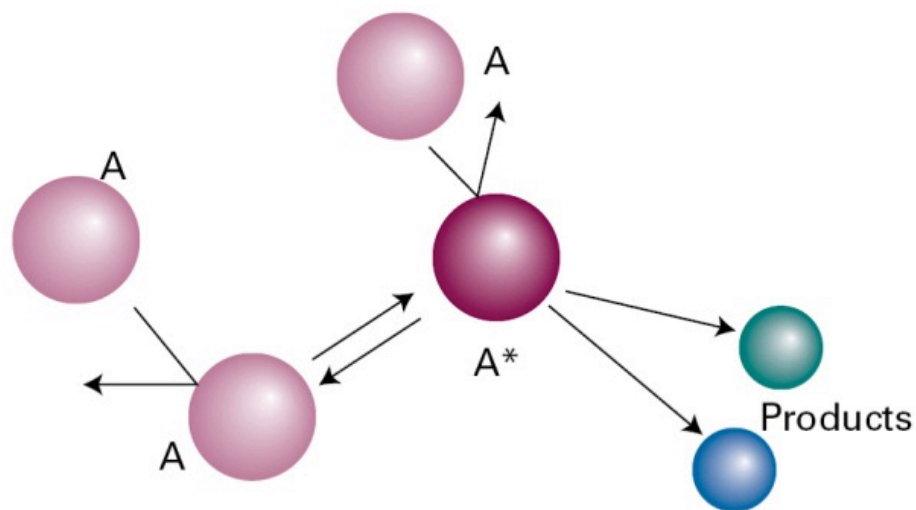
**The rate of formation of an intermediate is set equal to the rate it is used up by a subsequent reaction**

# Unimolecular Reactions

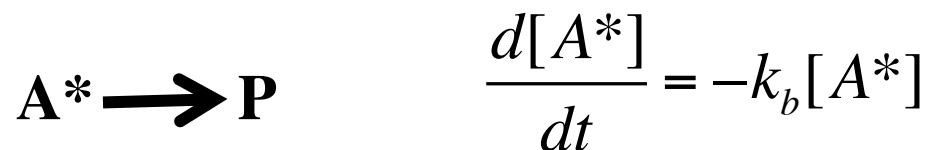
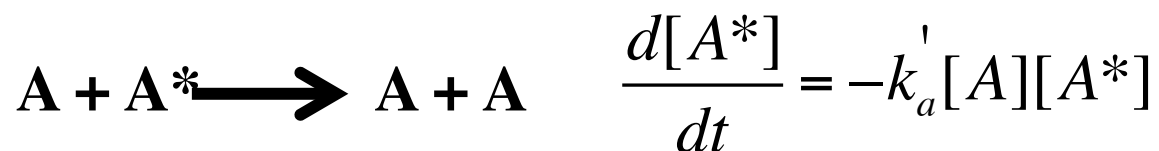
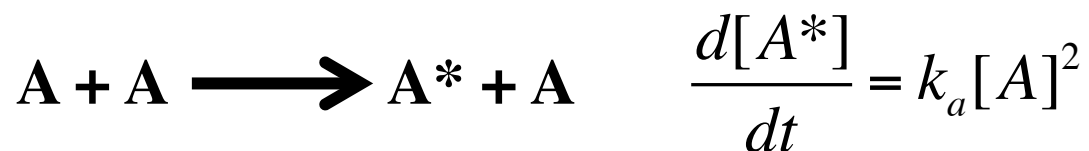
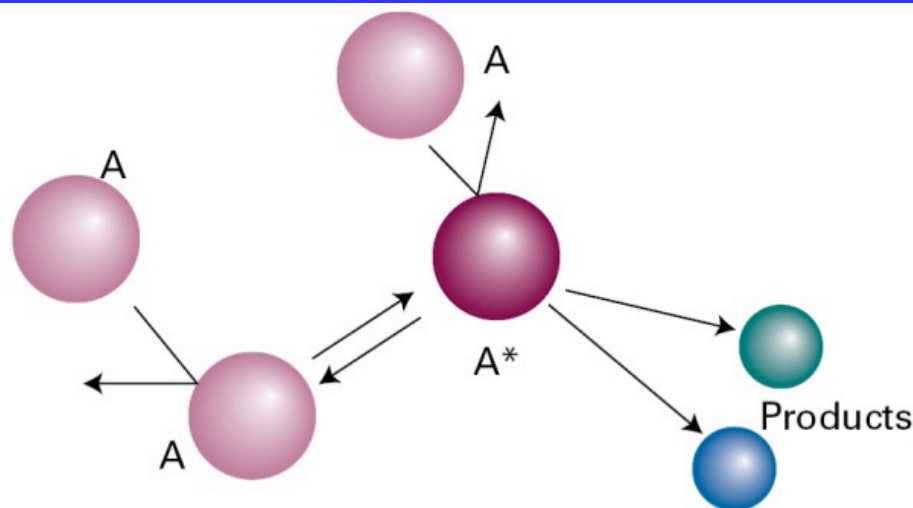


$$\text{Rate} = k_r[\text{cyclo-C}_3\text{H}_6] \text{---observation}$$

How does this reaction occur?



# Lindemann–Hinshelwood Mechanism





## 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:**

$$k'_a[A][A^*] > k_b[A^*]$$

$$k'_a[A] > k_b$$

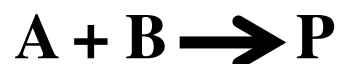
$$\frac{d[P]}{dt} = \frac{k_a k_b}{k'_a} [A] = k_r [A]$$

**So it looks like it is First Order**

# Simple Collision Theory Picture



**For a Bimolecular Reaction:**



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

**# collisions  $\sim v_{\text{mean}} \sim (T/M)^{1/2}$**

**Should also be proportional to cross section  $\sigma$**

**And the number densities of A and B**

**Rate  $\sim \sigma (T/M)^{1/2} [A][B]$**

**Also expect there to be a positive activation energy**

**So: Rate  $\sim \sigma (T/M)^{1/2} e^{-E'/RT} [A][B]$**

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

**Also expect a “steric factor”  $k \sim P \sigma (T/M)^{1/2} e^{-E'/RT}$**



$$k \sim \underset{\text{Steric factor}}{P} \underset{\text{encounter rate}}{\sigma (T/M)^{1/2}} \underset{\text{collision energy dependence}}{e^{-E'/RT}}$$

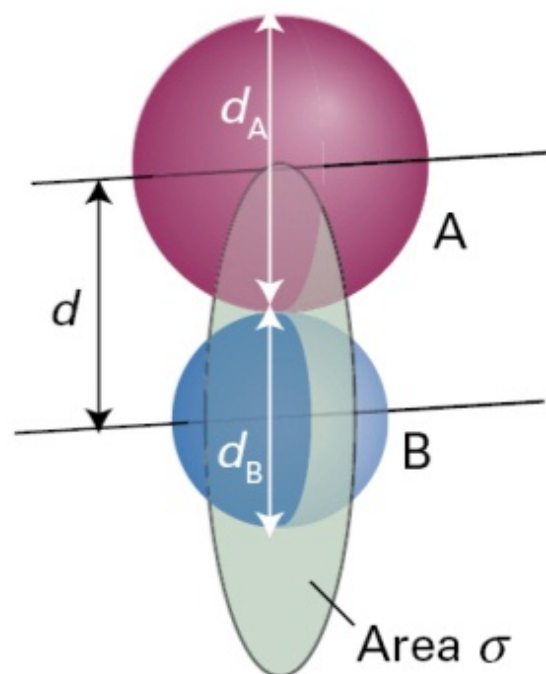
## Gas collision rate

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

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

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

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





# Energy Dependence

---



**Write the cross section  $\sigma$  as an energy dependent quantity**

**$\sigma(E) = 0$  if the “collision energy”  $<$  threshold value**



# Energy Dependence of Reaction

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

**Energy Requirement for reaction**

$$\sigma = \sigma(E)$$

**And  $\sigma(E) = 0$  if  $E < E_a$**

**$\sigma(E) = \text{geometrical } \sigma \text{ for } E \geq E_a$**

$$\frac{d[A]}{dt} = -\sigma(E) v_{rel} N_A [A][B]$$

**Assume Boltzmann distribution of energies**

$$\frac{d[A]}{dt} = - \left\{ \int_0^{\infty} \sigma(E) v_{rel} f(E) dE \right\} N_A [A][B]$$

$$k_r = \left\{ \int_0^{\infty} \sigma(E) v_{rel} f(E) dE \right\} N_A$$



$$k_r = \left\{ \int_0^{\infty} \sigma(E) v_{rel} f(E) dE \right\} N_A$$

$$f(v)dv = 4\pi \left( \frac{\mu}{2\pi kT} \right)^{3/2} v^2 e^{-\mu v^2 / kT} dv$$

**Change variables using  $E = 1/2\mu v^2$**

$$f(E)dE = 2\pi \left( \frac{\mu}{2\pi kT} \right)^{3/2} E^{1/2} e^{-E/kT} dE$$

$$k_r = \left\{ \int_0^{\infty} \sigma(E) v_{rel} 2\pi \left( \frac{\mu}{2\pi kT} \right)^{3/2} E^{1/2} e^{-E/kT} dE \right\} N_A$$

$$k_r = \left\{ \int_0^{\infty} \sigma(E) \left( \frac{2E}{\mu} \right)^{1/2} 2\pi \left( \frac{\mu}{2\pi kT} \right)^{3/2} E^{1/2} e^{-E/kT} dE \right\} N_A$$



$$k_r = \left\{ \int_0^{\infty} \sigma(E) \left( \frac{2E}{\mu} \right)^{1/2} 2\pi \left( \frac{\mu}{2\pi kT} \right)^{3/2} E^{1/2} e^{-E/kT} dE \right\} N_A$$

$$k_r = \left( \frac{8}{\pi\mu kT} \right)^{1/2} \left( \frac{1}{kT} \right) \int_0^{\infty} E \sigma(E) e^{-E/kT} dE$$

**$\sigma = 0$  unless  $E > E_a$**

$$k_r = \left( \frac{8}{\pi\mu kT} \right)^{1/2} \left( \frac{1}{kT} \right) \int_{E_a}^{\infty} E \sigma(E) e^{-E/kT} dE$$

$$k_r = \sigma N_A \left( \frac{8kT}{\pi\mu} \right)^{1/2} e^{-E_a/kT}$$

**There are various approximations for the functional form of  $\sigma(E)$**



$$k_r = \sigma N_A \left( \frac{8kT}{\pi\mu} \right)^{1/2} e^{-E_a/kT}$$

	$A/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$		$E_a/(\text{kJ mol}^{-1})$
	Experiment	Theory	
$2 \text{ NOCl} \rightarrow 2 \text{ NO} + 2 \text{ Cl}$	$9.4 \times 10^9$	$5.9 \times 10^{10}$	102
$2 \text{ ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	$6.3 \times 10^7$	$2.5 \times 10^{10}$	0
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	$1.24 \times 10^6$	$7.4 \times 10^{11}$	180
$\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$	$1.0 \times 10^{12}$	$2.1 \times 10^{11}$	0

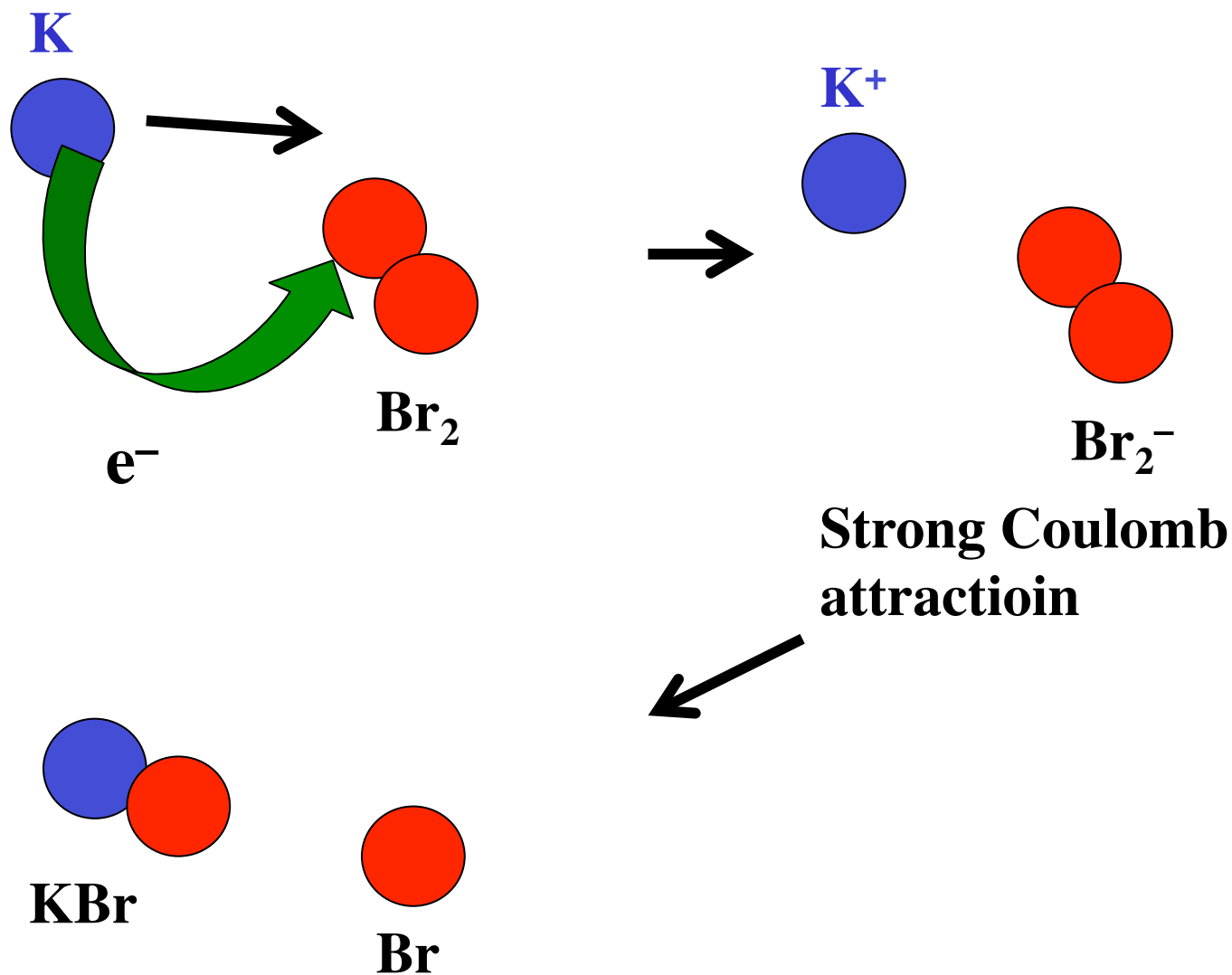


# Introduce the Steric Factor

$$k_r = P\sigma N_A \left( \frac{8kT}{\pi\mu} \right)^{1/2} e^{-E_a/kT}$$

	$A/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$		$E_a/(\text{kJ mol}^{-1})$	$P$
	Experiment	Theory		
$2 \text{ NOCl} \rightarrow 2 \text{ NO} + 2 \text{ Cl}$	$9.4 \times 10^9$	$5.9 \times 10^{10}$	102	0.16
$2 \text{ ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	$6.3 \times 10^7$	$2.5 \times 10^{10}$	0	$2.5 \times 10^{-3}$
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	$1.24 \times 10^6$	$7.4 \times 10^{11}$	180	$1.7 \times 10^{-6}$
$\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$	$1.0 \times 10^{12}$	$2.1 \times 10^{11}$	0	4.8

# What's Going on with $\text{K} + \text{Br}_2 = \text{KBr} + \text{Br}$



# Diffusion Controlled Reactions In Solution



$$\frac{d[AB]}{dt} = k_d[A][B] - k'_d[AB] - k_a[AB] = 0 \quad \text{Steady State approximation}$$

$$[AB]_{ss} = \frac{k_d[A][B]}{k_a + k'_d}$$

$$\frac{dP}{dt} = k_a[AB] = \frac{k_a k_d}{k_a + k'_d} [A][B]$$





$$\frac{dP}{dt} = k_a[AB] = \frac{k_a k_d}{k_a + k'_d} [A][B]$$

**If  $k'_d \ll k_a$  called the diffusion controlled limit**

**And  $k_r = k_d$**

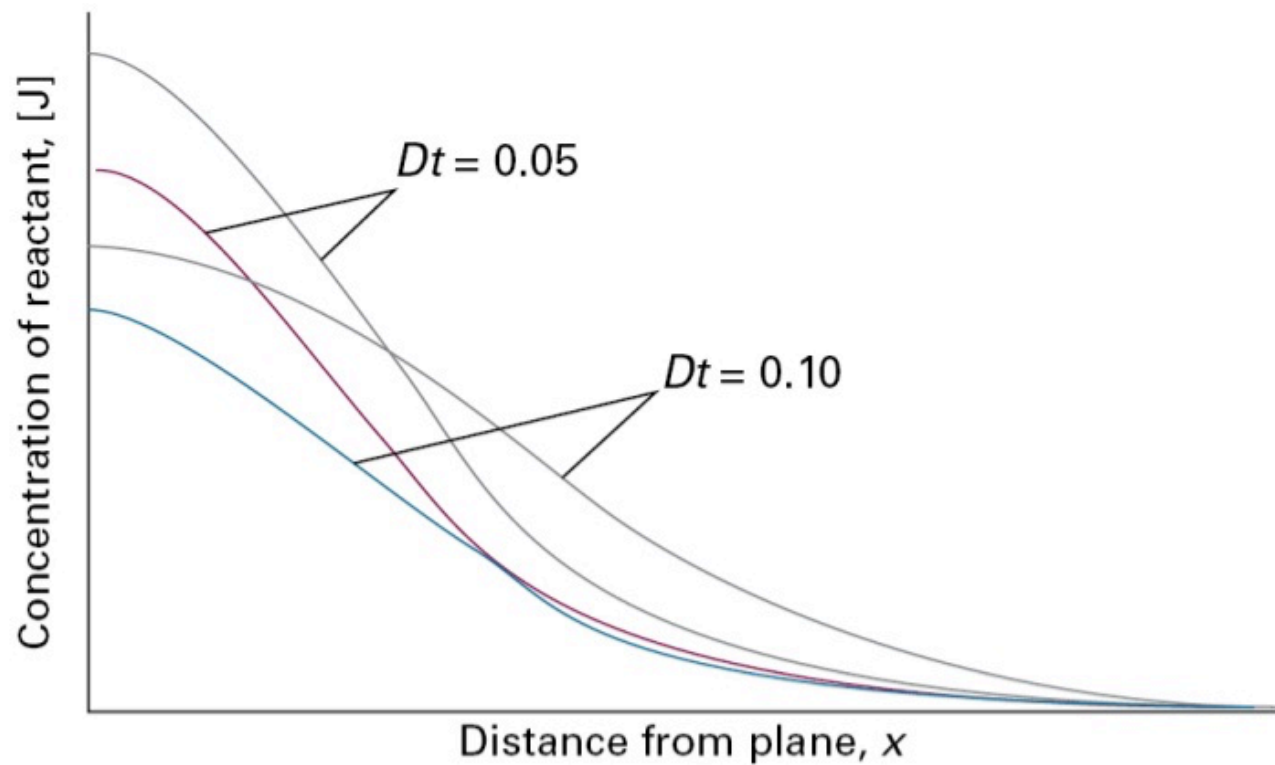
**For a diffusion controlled reaction in water**

**$k_r \sim 10^9 \text{ m}^3\text{mol}^{-1}\text{sec}^{-1}$**

**Assumes a reaction “distance” of  $\sim 100\text{nm}$**



## Concentration profile for a diffusing reacting system starting with reactant in the plane $x=0$



# Photochemistry



**Light is another way to initiate a reaction**



$$\nu = c/\lambda$$

$$\text{Energy} = h\nu$$

**UV light  $\sim 3.5 \text{ eV} = 337.7 \text{ kJ/mol}$**

**A few Bond enthalpies:**

**Br-CH<sub>3</sub> 293**

**O<sub>2</sub>N-NO<sub>2</sub> 54**

**H-CH<sub>3</sub> 435**

**H-OH 492**

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

$$RT = 337 \text{ kJ/mol at } T = 40,534 \text{ K}$$

**THE END**



**SEE YOU ON WEDNESDAY**