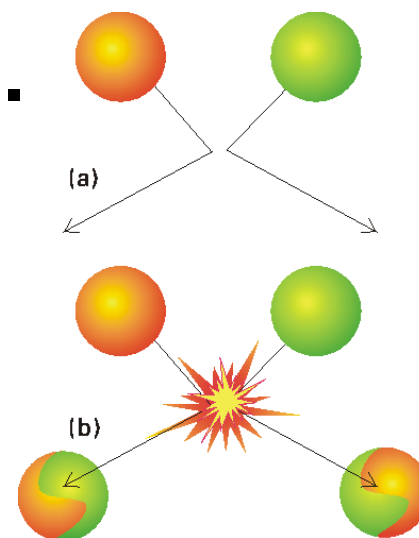


# Kinetika Kimia (Chemical Kinetics)

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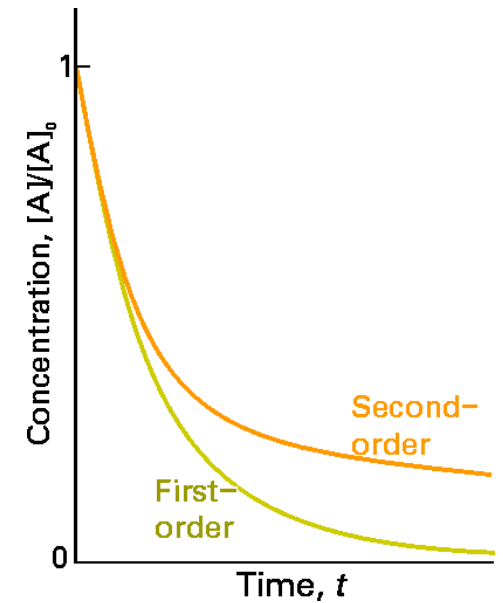
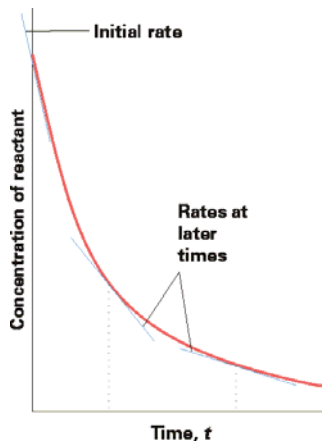


# Course Summary.

- Dependence of rate on concentration.
- Experimental methods in reaction kinetics.
- Kinetics of multistep reactions.
- Dependence of rate on temperature.

# Recommended reading.

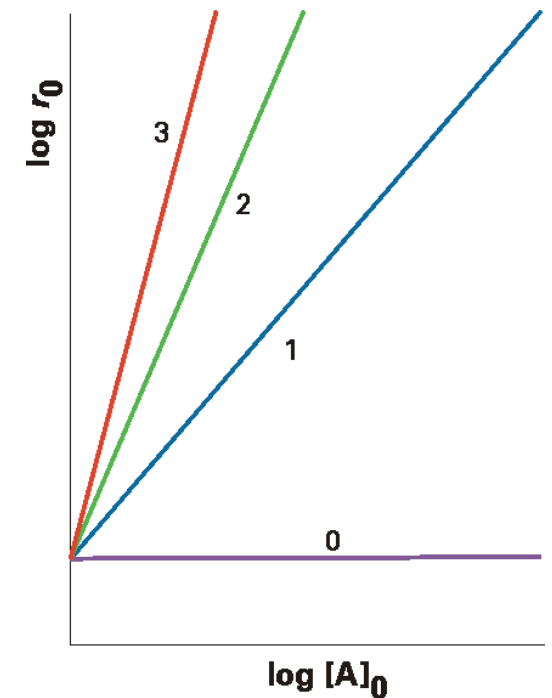
1. P.W. Atkins, Kimia Fisika (terjemahan), jilid 2, edisi keempat, Jakarta: Erlangga, 1999.
2. P.W. Atkins, Physical Chemistry, 5th ed., Oxford: Oxford University Press, 1994
3. Gordon M. Barrow, Physical Chemistry
4. Arthur M. Lesk, Introduction to Physical Chemistry



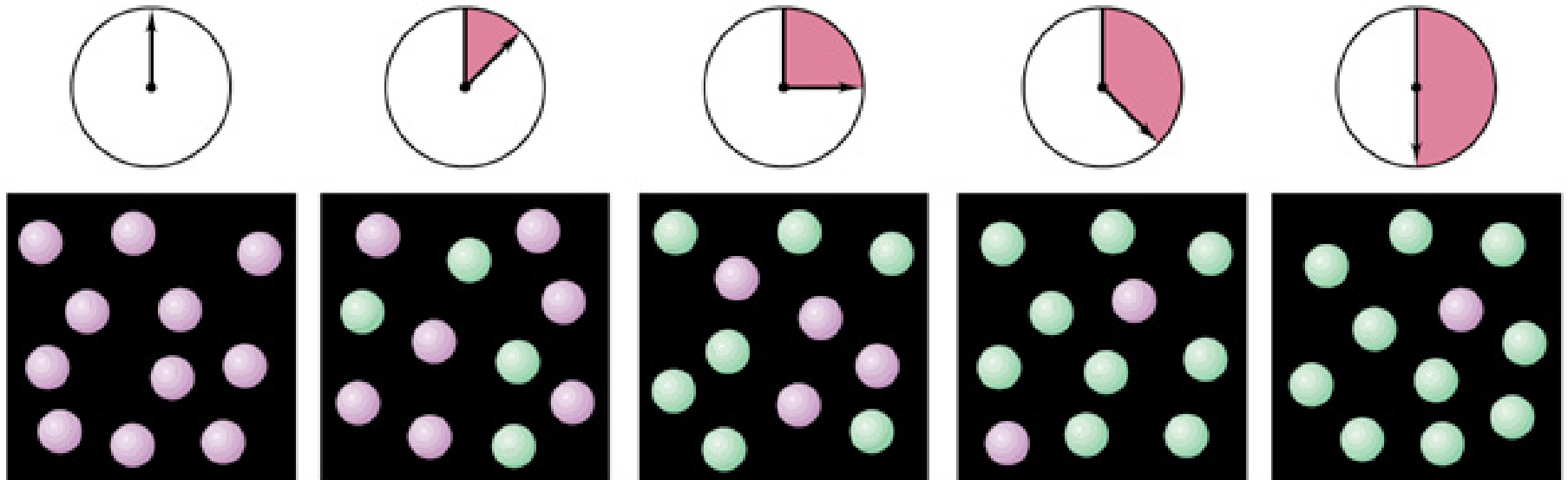
# Chemical Kinetics.

## Lecture 1.

### Review of Basic concepts.



# Reaction Rate: The Central Focus of Chemical Kinetics

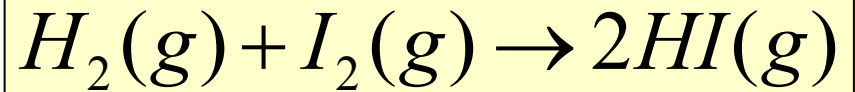


# Chemical reaction kinetics.

- Chemical reactions involve the forming and breaking of chemical bonds.
- Reactant molecules ( $H_2$ ,  $I_2$ ) approach one another and collide and interact with appropriate energy and orientation. Bonds are stretched, broken and formed and finally product molecules ( $HI$ ) move away from one another.
- How can we describe the rate at which such a chemical transformation takes place?

reactants

products



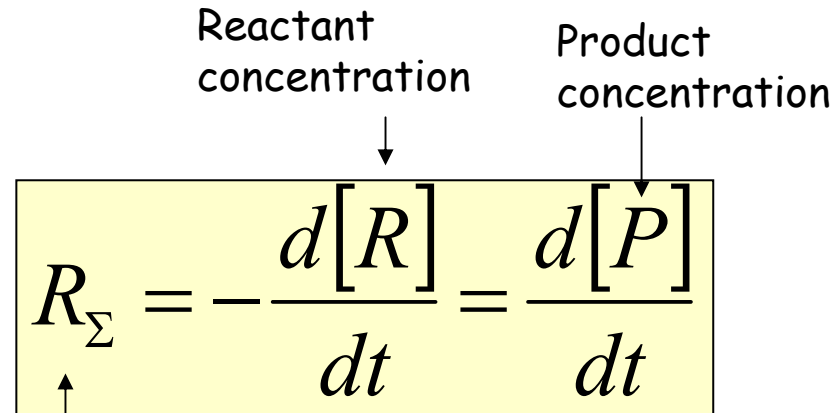
- Thermodynamics tells us all about the energetic feasibility of a reaction : we measure the Gibbs energy  $\Delta G$  for the chemical Reaction.
- Thermodynamics does not tell us how quickly the reaction will proceed : it does not provide kinetic information.

# Basic ideas in reaction kinetics.

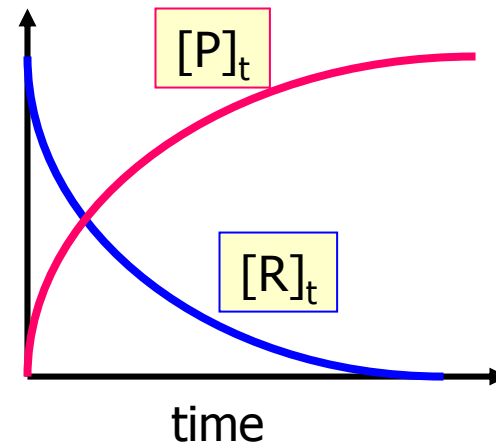
- Chemical reaction kinetics deals with the rate of **velocity** of chemical reactions.
- We wish to quantify
  - The **velocity** at which reactants are transformed to products
  - The detailed molecular pathway by which a reaction proceeds (the **reaction mechanism**).
- These objectives are accomplished using experimental measurements.
- Chemical reactions are said to be **activated** processes : energy (usually thermal (heat) energy) must be introduced into the system so that chemical transformation can occur. Hence chemical reactions occur more rapidly when the temperature of the system is increased.
- In simple terms an **activation energy barrier** must be overcome before reactants can be transformed into products.

# Reaction Rate.

- What do we mean by the term reaction rate?
  - The term rate implies that something changes with respect to something else.
- How may reaction rates be determined?
  - The reaction rate is quantified in terms of the change in concentration of a reactant or product species with respect to time.
  - This requires an experimental measurement of the manner in which the concentration changes with time of reaction. We can monitor either the concentration change directly, or monitor changes in some physical quantity which is directly proportional to the concentration.
- The reactant concentration decreases with increasing time, and the product concentration increases with increasing time.
- The rate of a chemical reaction depends on the concentration of each of the participating reactant species.
- The manner in which the rate changes in magnitude with changes in the magnitude of each of the participating reactants is termed the **reaction order**.



Net reaction rate  
Units : mol dm<sup>-3</sup> s<sup>-1</sup>

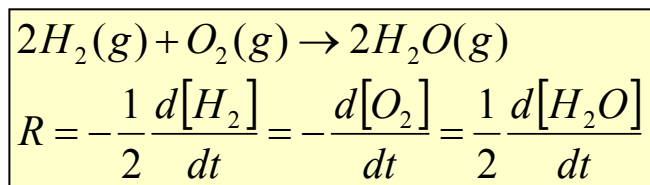




## Rate, rate equation and reaction order : formal definitions.

- The reaction rate (reaction velocity)  $R$  is quantified in terms of changes in concentration  $[J]$  of reactant or product species  $J$  with respect to changes in time. The magnitude of the reaction rate changes as the reaction proceeds.

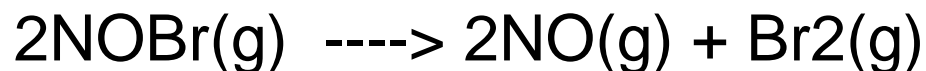
$$R_J = \frac{1}{\nu_J} \lim_{\Delta t \rightarrow 0} \frac{\Delta[J]}{\Delta t} = \frac{1}{\nu_J} \frac{d[J]}{dt}$$



- Note** : Units of rate :- concentration/time , hence  $R_J$  has units  $\text{mol dm}^{-3}\text{s}^{-1}$  .  $\nu_J$  denotes the **stoichiometric coefficient** of species  $J$ . If  $J$  is a reactant  $\nu_J$  is negative and it will be positive if  $J$  is a product species.
- Rate of reaction is often found to be proportional to the molar concentration of the reactants raised to a simple power (which need not be integral). This relationship is called the **rate equation**. The manner in which the reaction rate changes in magnitude with changes in the magnitude of the concentration of each participating reactant species is called the **reaction order**.

## Problem Example:

The rate formation of NO in the reaction:



was reported as  $1.6 \times 10^{-4} \text{ mol}/(\text{L s})$ .

What is the rate of reaction and the rate of consumption of NOBr ?

# Measuring Rate Laws: Isolation

For instance:  $A + B \rightarrow \text{Products}$

$$R = \frac{1}{\nu_A} \frac{d[A]}{dt} = \frac{1}{\nu_B} \frac{d[B]}{dt} = \frac{1}{\nu_Z} \frac{d[Z]}{dt}$$

form of rate law :  $v(t) = k[A]^\alpha [B]^\beta$

Choose conditions :  $[A] \gg [B]$

$\therefore [A] - d[A] \approx [A]$  (Method of isolation)

$$R = k[A]^\alpha [B]^\beta \approx k'[B]^\beta \quad k' = k[A]^\alpha$$

if  $[A] \ll [B]$ :  $R \approx k''[A]^\alpha \quad k'' = k[B]^\beta$

# Measuring Rate Laws: Initial Rates

F'r instance:  $A + B \rightarrow \text{Products}$        $R = k[A]^\alpha [B]^\beta$

$$R = \frac{1}{\nu_A} \frac{d[A]}{dt} = k[A]^\alpha [B]^\beta \approx \frac{1}{\nu_A} \frac{\Delta[A]}{\Delta t} \quad \Delta t \rightarrow dt$$

measure  $R_1$  @  $[B]_1$ ,  $R_2$  @  $[B]_2$ , etc.

$$[A]_0 - d[A] \approx [A]_0; \quad [B]_j - d[B] \approx [B]_j \quad (\Delta t \rightarrow dt)$$

$$R_1 = k[A]_0^\alpha [B]_1^\beta \approx \frac{1}{\nu_A} \left( \frac{\Delta[A]}{\Delta t} \right)_1 \quad \text{1st measurement}$$

$$R_2 = k[A]_0^\alpha [B]_2^\beta \approx \frac{1}{\nu_A} \left( \frac{\Delta[A]}{\Delta t} \right)_2 \quad \text{2nd measurement}$$

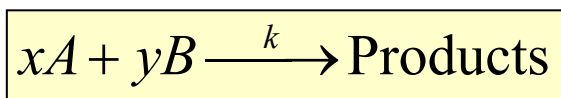
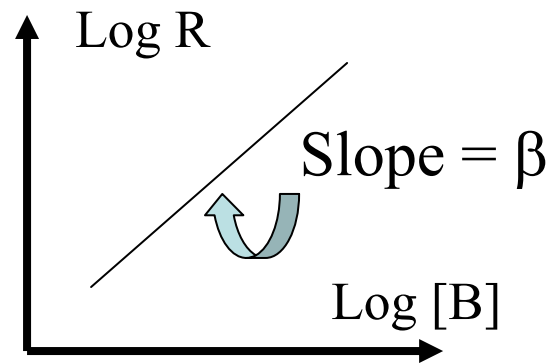
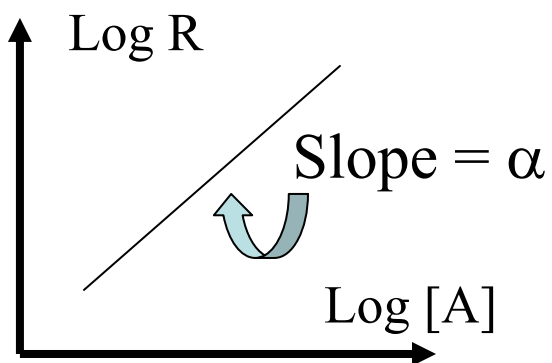
# Measuring Rate Laws: Initial Rates

$$R_1 = k[A]_0^\alpha [B]_1^\beta \approx \frac{1}{\nu_A} \left( \frac{\Delta[A]}{\Delta t} \right)_1 \quad \text{1st measurement}$$

$$R_2 = k[A]_0^\alpha [B]_2^\beta \approx \frac{1}{\nu_A} \left( \frac{\Delta[A]}{\Delta t} \right)_2 \quad \text{2nd measurement}$$

$$\frac{R_1}{R_2} = \frac{k[A]_0^\alpha [B]_1^\beta}{k[A]_0^\alpha [B]_2^\beta} = \left( \frac{[B]_1}{[B]_2} \right)^\beta \quad \therefore \beta = \frac{\ln(R_1/R_2)}{\ln([B]_1/[B]_2)}$$

$$\frac{R_3}{R_4} = \frac{k[A]_3^\alpha [B]_0^\beta}{k[A]_4^\alpha [B]_0^\beta} = \left( \frac{[A]_3}{[A]_4} \right)^\alpha \quad \therefore \alpha = \frac{\ln(R_3/R_4)}{\ln([A]_3/[A]_4)}$$



↑ ↑  
stoichiometric  
coefficients

*empirical rate  
equation (obtained  
from experiment)*

$$R = -\frac{1}{x} \frac{d[A]}{dt} = -\frac{1}{y} \frac{d[B]}{dt} = k[A]^\alpha [B]^\beta$$

rate constant  $k$

$\alpha, \beta =$  *reaction  
orders for the  
reactants (got  
experimentally)*

**Rate equation can not in general be inferred from the stoichiometric equation for the reaction.**

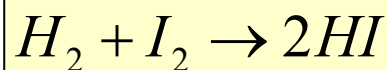
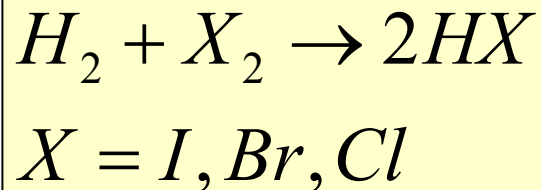
# Limits to methods of isolation and initial rates

- Assumed reactants can be mixed in any proportion desired
- Reaction rate can be measured
- Mixing time ( $\sim 1$ ms) vs. reaction time

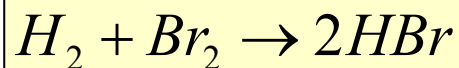
Other approaches:

- Relaxation methods (e.g. temperature jump)
- Time resolved methods

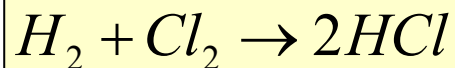
Different rate equations  
imply different mechanisms.



$$R = \frac{d[HI]}{dt} = k[H_2][I_2]$$



$$R = \frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + \frac{k'[HBr]}{[Br_2]}}$$



$$R = \frac{d[HCl]}{dt} = k[H_2][Cl_2]^{1/2}$$

- *The rate law provides an important guide to reaction mechanism, since any proposed mechanism must be consistent with the observed rate law.*
- *A complex rate equation will imply a complex multistep reaction mechanism.*
- *Once we know the rate law and the rate constant for a reaction, we can predict the rate of the reaction for any given composition of the reaction mixture.*
- *We can also use a rate law to predict the concentrations of reactants and products at any time after the start of the reaction.*



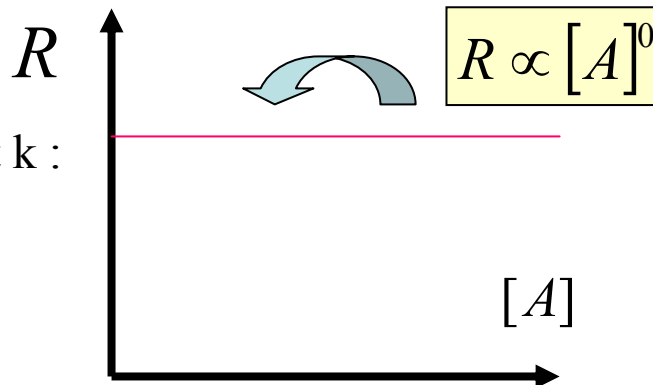
**Zero order kinetics.** The reaction proceeds at the same rate  $R$  regardless of concentration.

Rate equation :

$$R = -\frac{da}{dt} = k$$

$$a = a_0 \text{ when } t = 0$$

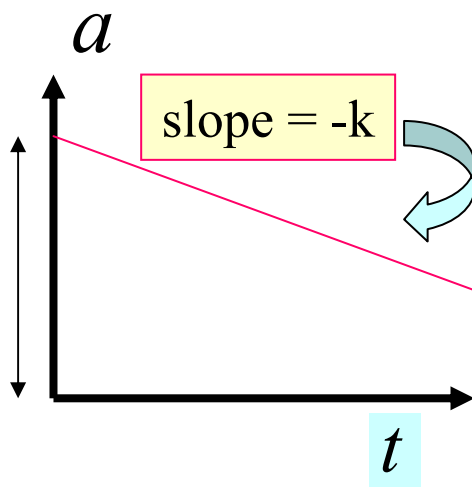
units of rate constant  $k$  :  
 $\text{mol dm}^{-3} \text{ s}^{-1}$



integrate  
using initial  
condition

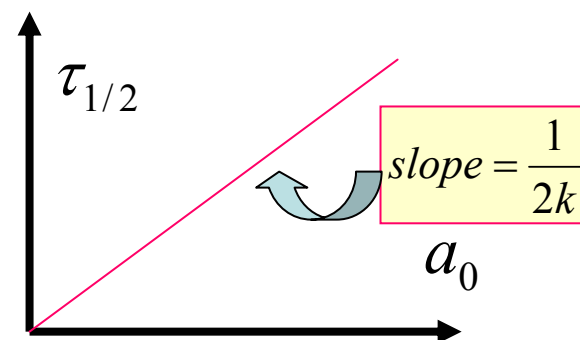
$$a(t) = -kt + a_0$$

diagnostic  
plot

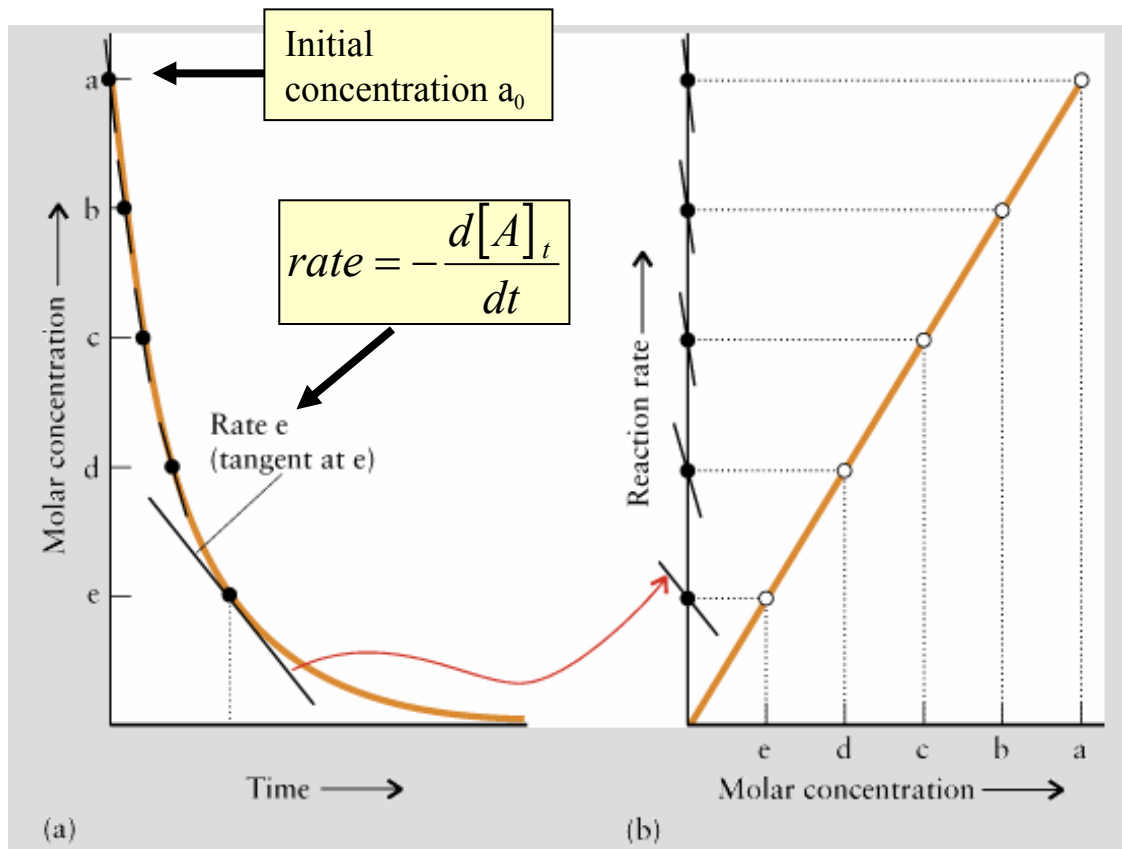
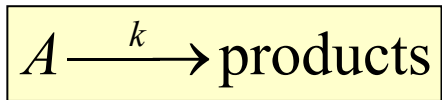


half life :  $t = \tau_{1/2}$  when  $a = \frac{a_0}{2}$

$$\tau_{1/2} = \frac{a_0}{2k} \quad \tau_{1/2} \propto a_0$$



# First order kinetics.



First order differential rate equation.

$$-\frac{da}{dt} = ka$$

Initial condition

$$t = 0 \quad a = a_0$$

Solve differential equation

Separation of variables

For a first order reaction the relationship:

$$(rate)_t \propto [A]_t$$

$$(rate)_t = k[A]_t$$

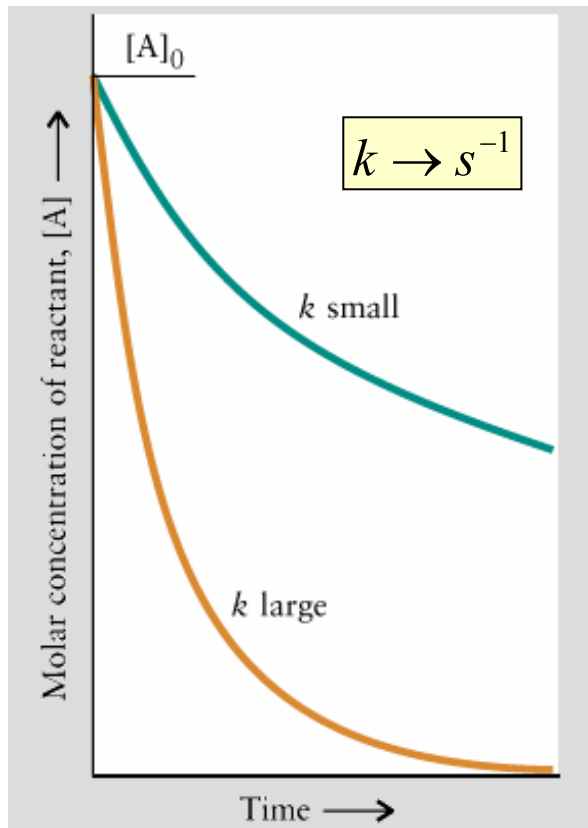
is valid generally for any time  $t$ .

$k$  is the first order rate constant, units:  $s^{-1}$

$$a(t) = a_0 e^{-kt} = a_0 \exp[-kt]$$

Reactant concentration as function of time.

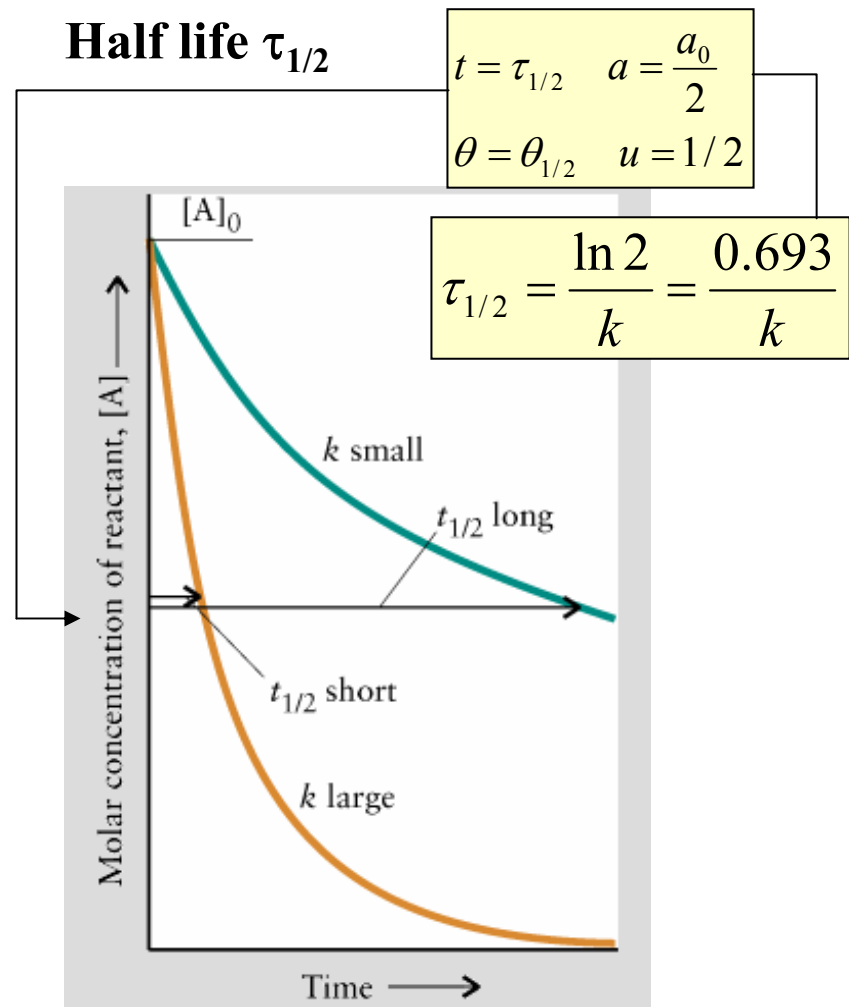
# First order kinetics.



$$a(t) = a_0 e^{-kt} = a_0 \exp[-kt]$$

$$u = \frac{a(t)}{a_0} = \exp[-\theta]$$

$$\theta = kt$$



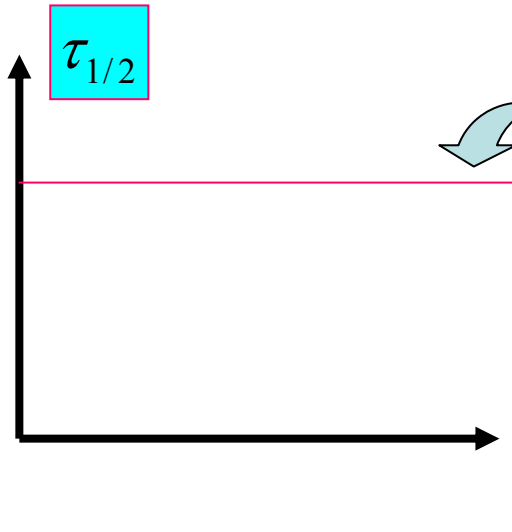
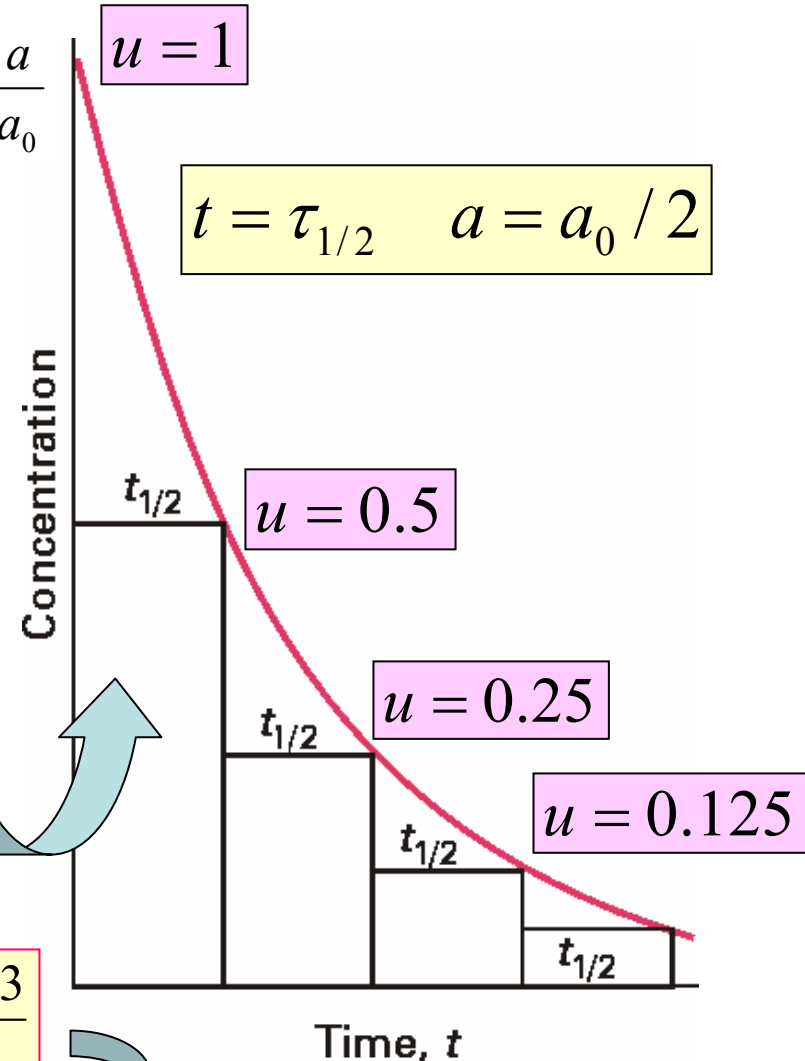
## Mean lifetime of reactant molecule

$$\tau = \frac{1}{a_0} \int_0^{\infty} a(t) dt = \frac{1}{a_0} \int_0^{\infty} a_0 e^{-kt} dt = \frac{1}{k}$$

# First order kinetics: half life.

$$u = \frac{a}{a_0}$$

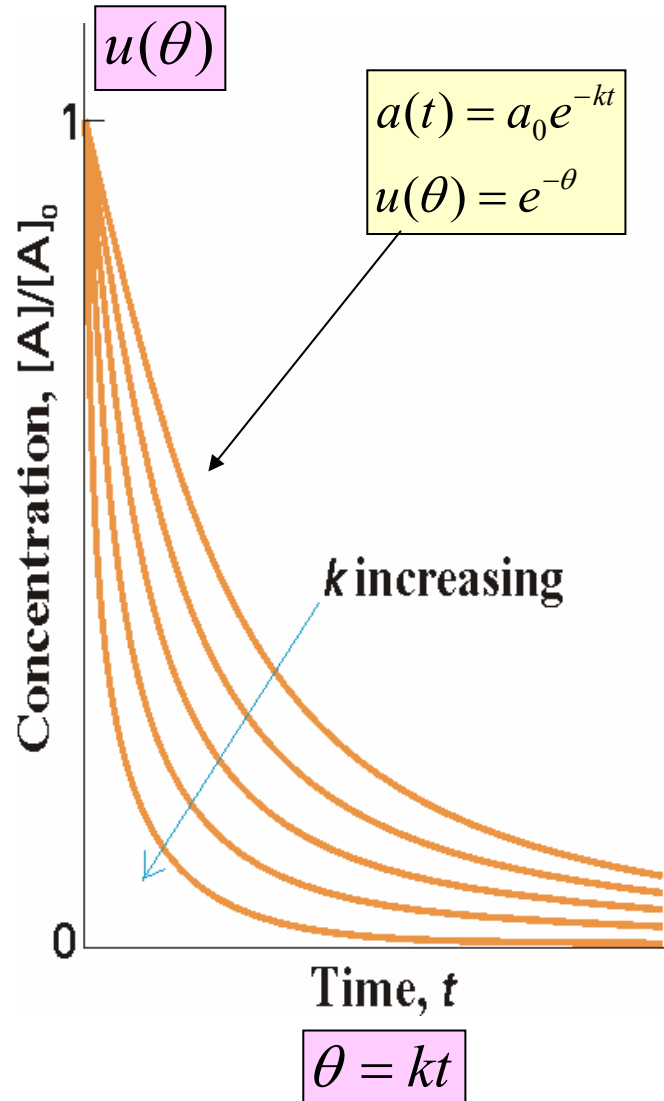
*In each successive period of duration  $\tau_{1/2}$  the concentration of a reactant in a first order reaction decays to half its value at the start of that period. After  $n$  such periods, the concentration is  $(1/2)^n$  of its initial value.*



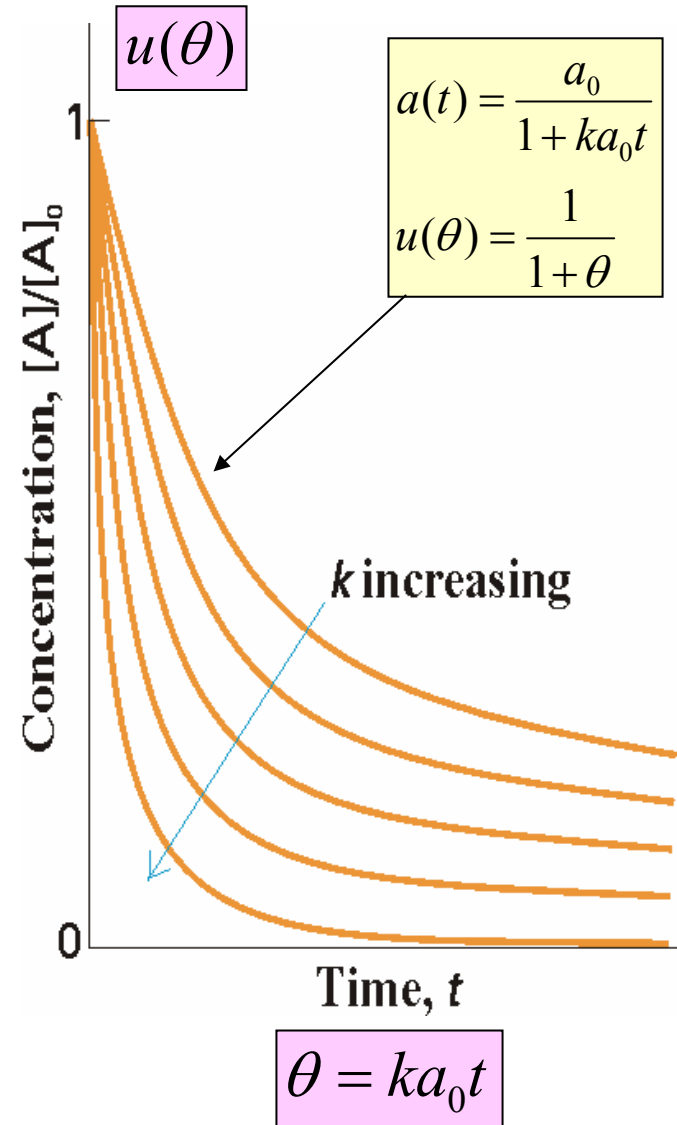
$$\tau_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

*half life independent of initial reactant concentration*

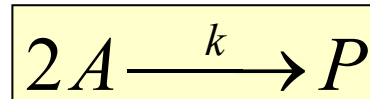
## 1st order kinetics



## 2nd order kinetics



Second order kinetics: equal reactant concentrations.



$\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$

slope = k

$$-\frac{da}{dt} = ka^2$$

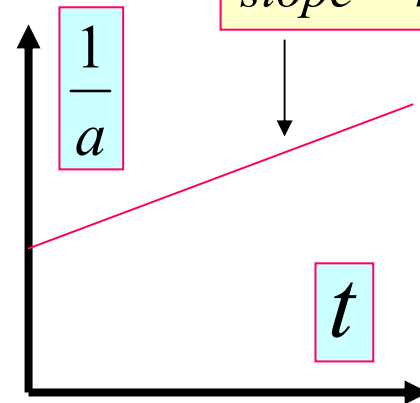
$t = 0 \quad a = a_0$

separate variables

integrate



$$\frac{1}{a} = kt + \frac{1}{a_0}$$



half life

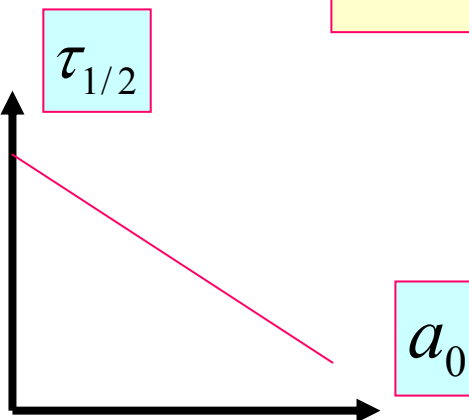
$$t = \tau_{1/2} \quad a = \frac{a_0}{2}$$

$$a(t) = \frac{a_0}{1 + ka_0t}$$

$$\tau_{1/2} = \frac{1}{ka_0}$$

$$\tau_{1/2} \propto \frac{1}{a_0}$$

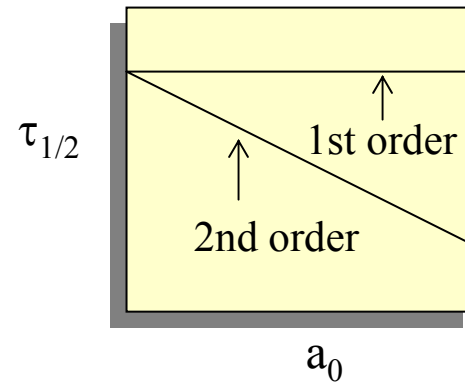
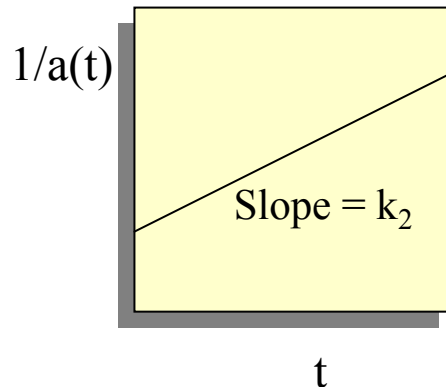
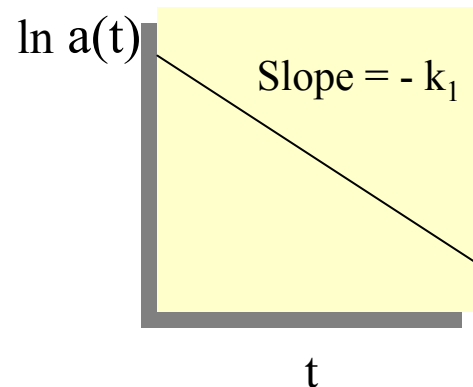
$\tau_{1/2} \downarrow$  as  $a_0 \uparrow$



rate varies as square of reactant concentration

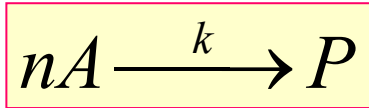
# 1st and 2nd order kinetics : Summary .

Reaction	Differential rate equation	Concentration variation with time	Diagnostic Equation	Half Life
$A \xrightarrow{k_1} \text{Products}$	$-\frac{da}{dt} = k_1 a$	$a(t) = a_0 \exp[-k_1 t]$	$\ln a(t) = -k_1 t + \ln a_0$	$\tau_{1/2} = \frac{\ln 2}{k_1}$
$2A \xrightarrow{k_2} \text{Products}$	$-\frac{da}{dt} = k_2 a^2$	$a(t) = \frac{a_0}{1 + k_2 a_0 t}$	$\frac{1}{a(t)} = k_2 t + \frac{1}{a_0}$	$\tau_{1/2} = \frac{1}{k_2 a_0}$



**Diagnostic Plots .**

n th order kinetics: equal reactant concentrations.



$$-\frac{da}{dt} = ka^n$$

$t = 0 \quad a = a_0$

separate variables  
integrate

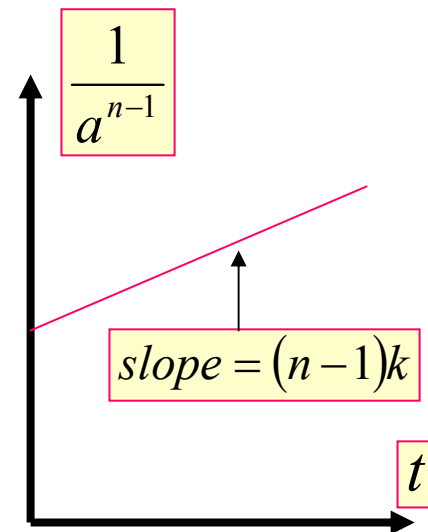


$$n \neq 1$$

$$\frac{1}{a^{n-1}} = (n-1)kt + \frac{1}{a_0^{n-1}}$$

$$n = 0, 2, 3, \dots$$

rate constant  $k$   
obtained from slope



## Half life

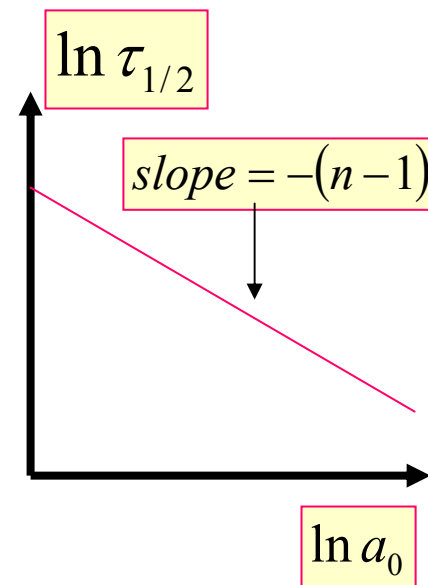
$$\tau_{1/2} = \frac{2^{n-1} - 1}{(n-1)ka_0^{n-1}}$$

$$\ln \tau_{1/2} = \ln \left\{ \frac{2^{n-1} - 1}{(n-1)k} \right\} - (n-1) \ln a_0$$

$$\tau_{1/2} \propto a_0^{1-n}$$

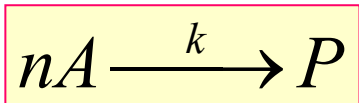
$n > 1 \quad \tau_{1/2} \downarrow \text{ as } a_0 \uparrow$   
 $n < 1 \quad \tau_{1/2} \uparrow \text{ as } a_0 \uparrow$

reaction order  $n$  determined  
from slope





# Summary of kinetic results.



$$t = 0 \quad a = a_0$$

$$t = \tau_{1/2} \quad a = \frac{a_0}{2}$$

Rate equation

Reaction Order	$R = -\frac{da}{dt}$	Integrated expression	Units of k	Half life $\tau_{1/2}$
0	$k$	$a(t) = -kt + a_0$	$\text{mol dm}^{-3}\text{s}^{-1}$	$\frac{a_0}{2k}$
1	$ka$	$\ln\left\{\frac{a_0}{a(t)}\right\} = kt$	$\text{s}^{-1}$	$\frac{\ln 2}{k}$
2	$ka^2$	$\frac{1}{a(t)} = kt + \frac{1}{a_0}$	$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$\frac{1}{ka_0}$
3	$ka^3$	$\frac{1}{a(t)^2} = 2kt + \frac{1}{a_0^2}$	$\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$	$\frac{3}{2ka_0^2}$
n	$ka^n$	$\frac{1}{a^{n-1}} = (n-1)kt + \frac{1}{a_0^{n-1}}$		$\frac{1}{n-1} \left\{ \frac{2^{n-1} - 1}{ka_0^{n-1}} \right\}$

## Problem Examples:

1. A first order reaction is 40% complete at the end of 1 h.  
What is the value of the rate constant?  
In how long will the reaction be 80 % complete ?
2. The half-life of the radioactive disintegration of radium is 1590 years. Calculate the decay constant. In how many years will three-quarters of the radium have undergone decay ?
3. Derive the rate equation for reaction whose orders are:  
(a). one-half, (b). three and a-half, (c). 4, and (d).  $n$  !

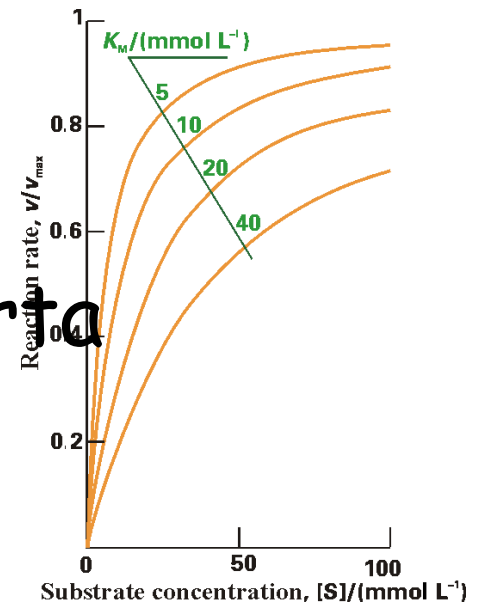
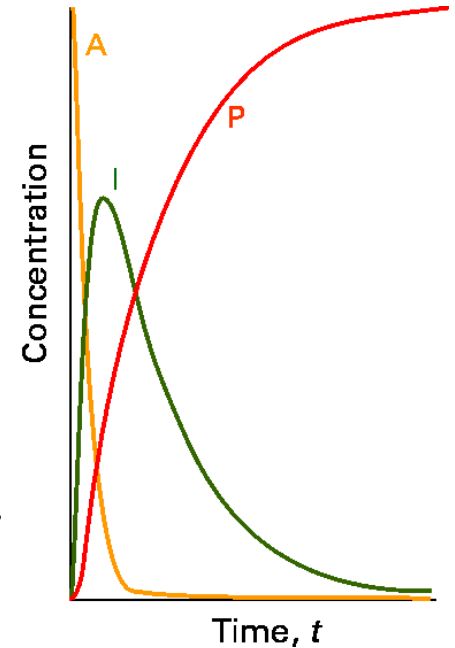
# Chemical Kinetics

## Lecture 2. Kinetics of more complex reactions.

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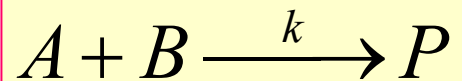
## Tujuan Perkuliahan:

1. Menurunkan Rate Law dari Kinetika Reaksi yang lebih Kompleks,
2. Menjelaskan Consecutive Reactions:
  - a. Rate Determining Steps,
  - b. Steady State Approximation.

## Reference:

1. P.W. Atkins, Physical Chemistry, 5th ed, Oxford: 1994
2. Ira N. Levine, Physical Chemistry

**Second order kinetics:  
Unequal reactant concentrations.**



*rate equation*

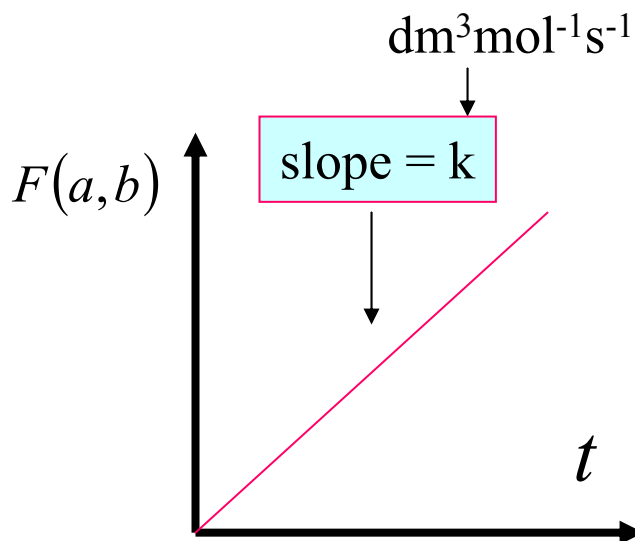
$$R = -\frac{da}{dt} = -\frac{db}{dt} = \frac{dp}{dt} = kab$$

*initial conditions*

$$t = 0 \quad a = a_0 \quad b = b_0 \quad a_0 \neq b_0$$

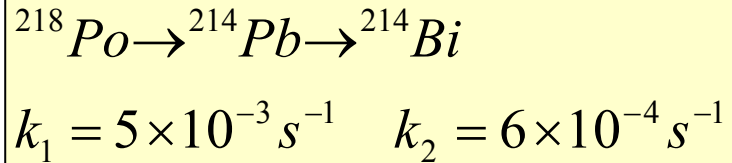
↓  
*integrate using  
partial fractions*

$$F(a, b) = \frac{1}{b_0 - a_0} \left\{ \ln \left( \frac{b/b_0}{a/a_0} \right) \right\} = kt$$



# Consecutive Reactions .

- Mother / daughter radioactive decay.



3 coupled LDE's define system :



$$\frac{da}{dt} = -k_1 a$$
$$\frac{dx}{dt} = k_1 a - k_2 x$$
$$\frac{dp}{dt} = k_2 x$$



Mass balance requirement:

$$p = a_0 - a - x$$



The solutions to the coupled equations are :

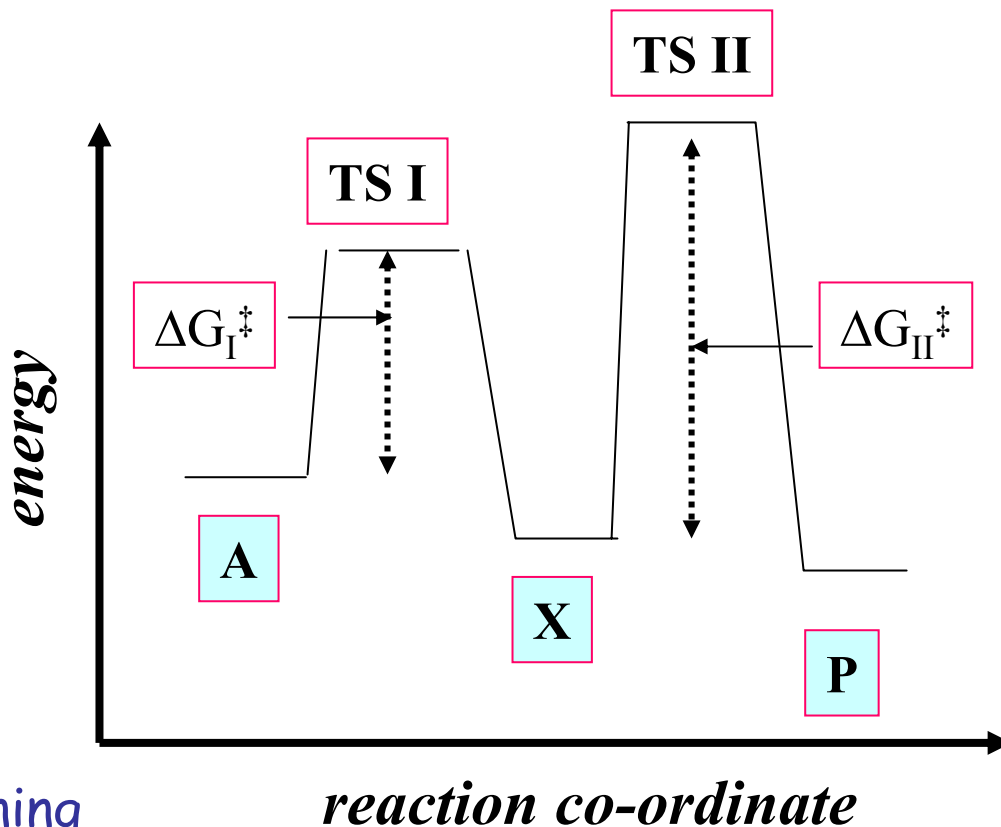
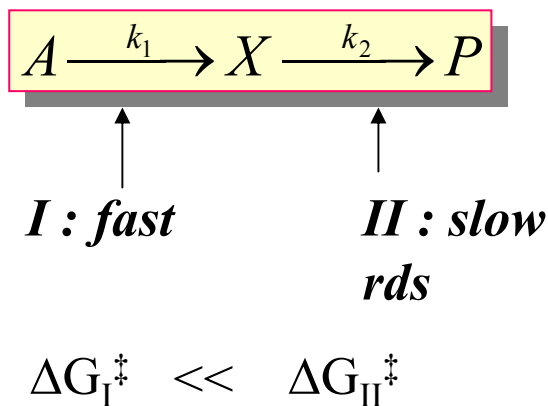
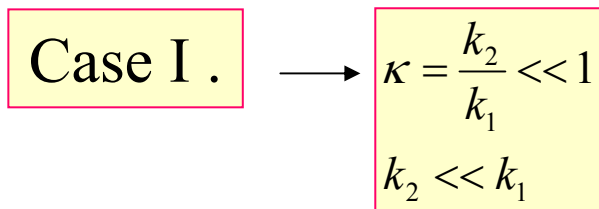


$$a(t) = a_0 \exp[-k_1 t]$$
$$x(t) = \frac{k_1 a_0}{k_2 - k_1} \{ \exp[-k_1 t] - \exp[-k_2 t] \}$$
$$p(t) = a_0 - a_0 \exp[-k_1 t] - \frac{k_1 a_0}{k_2 - k_1} \{ \exp[-k_1 t] - \exp[-k_2 t] \}$$

We get different kinetic behaviour depending on the ratio of the rate constants  $k_1$  and  $k_2$

## Consecutive reaction : Case I.

Intermediate formation fast, intermediate decomposition slow.



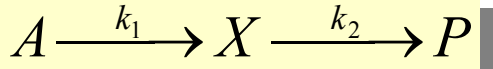
Step II is rate determining since it has the highest activation energy barrier.

The reactant species A will be more reactive than the intermediate X.

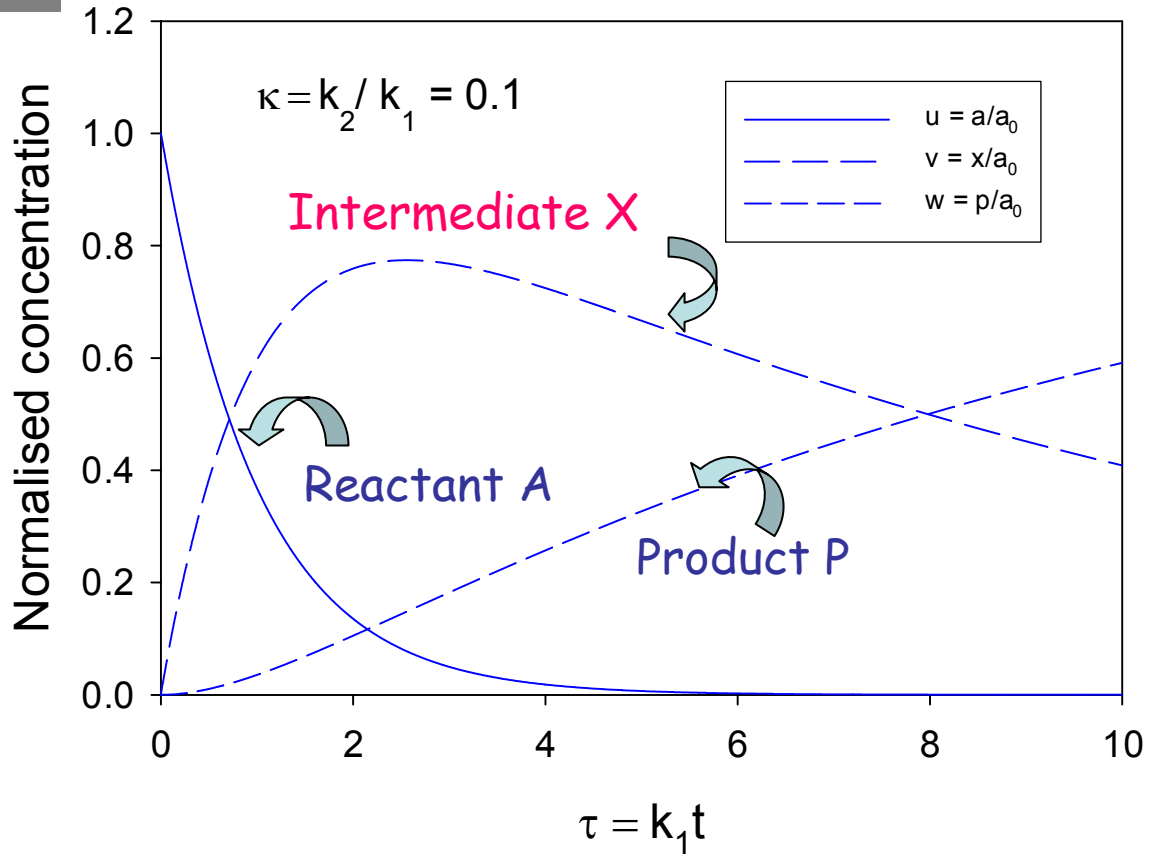
Case I .

$$\kappa = \frac{k_2}{k_1} \ll 1$$

$$k_2 \ll k_1$$



$$u = \frac{a}{a_0}$$
$$v = \frac{x}{a_0}$$
$$w = \frac{p}{a_0}$$



Initial reactant A more reactive than intermediate X .

Concentration of intermediate significant over time course of reaction.



## Consecutive reactions Case II:

Intermediate formation slow, intermediate decomposition fast.

$$K = \frac{k_2}{k_1}$$

Case II .

$$K = \frac{k_2}{k_1} \gg 1$$

$$k_2 \gg k_1$$



key parameter

Intermediate X fairly reactive.  
[X] will be small at all times.

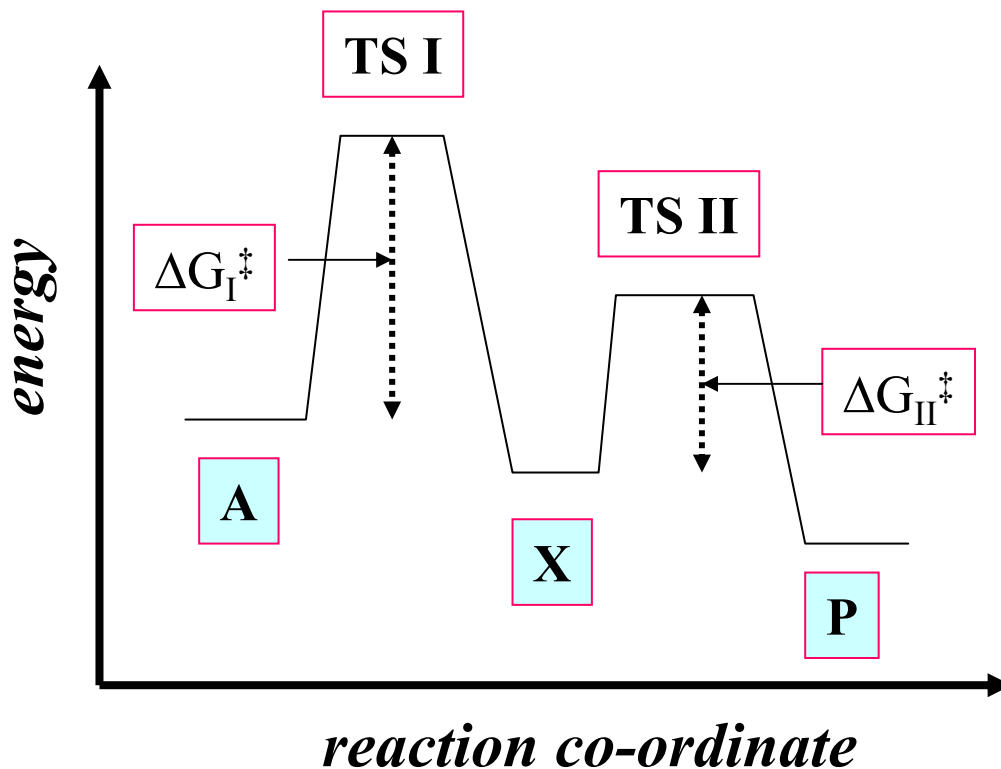


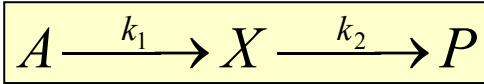
I : slow rds

II : fast

$$\Delta G_{I^\ddagger} \gg \Delta G_{II^\ddagger}$$

Step I rate determining  
since it has the highest  
activation energy barrier.



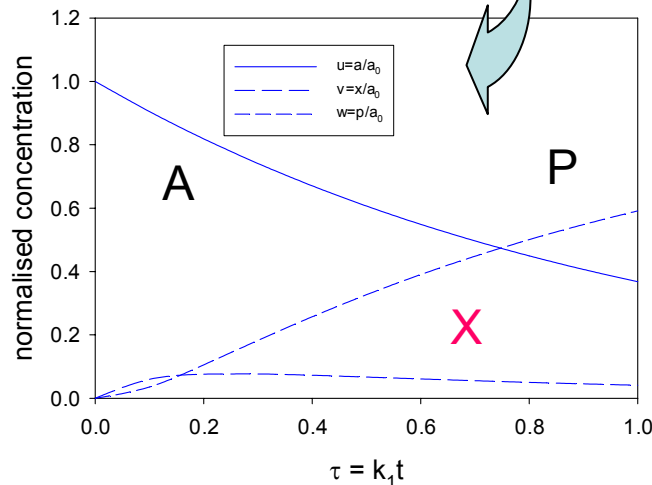
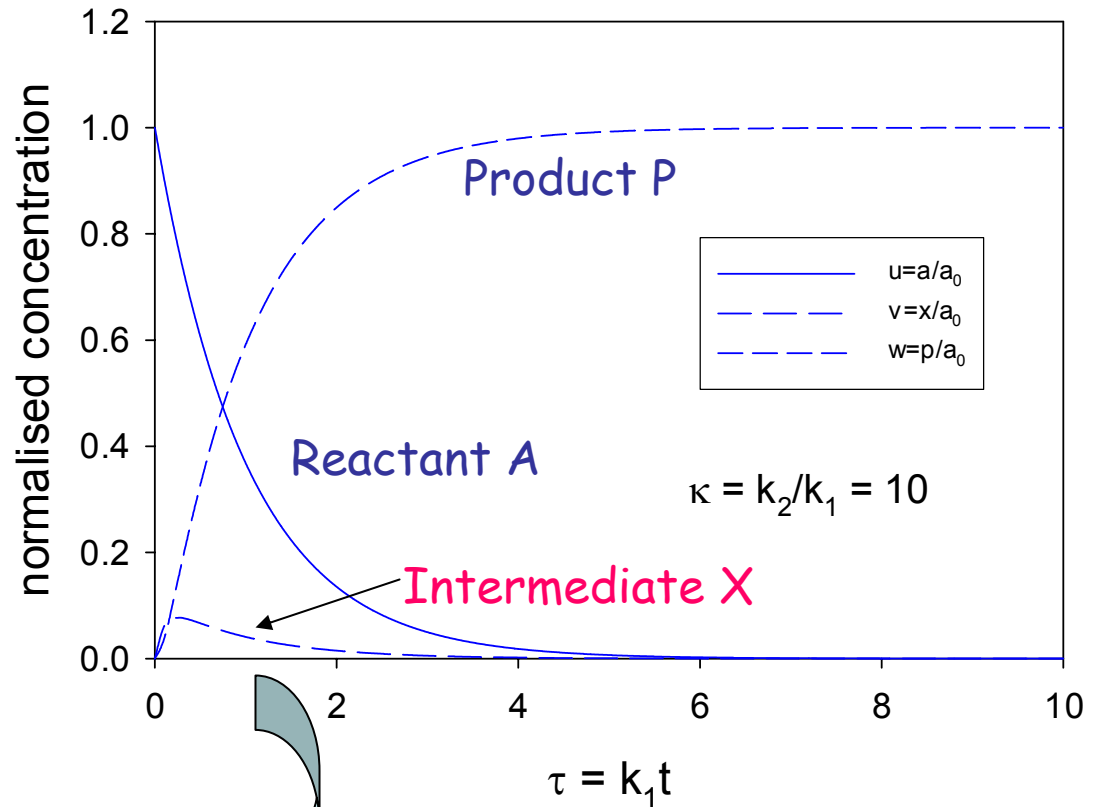


Case II.

$$\kappa = \frac{k_2}{k_1} \gg 1$$

$$k_2 \gg k_1$$

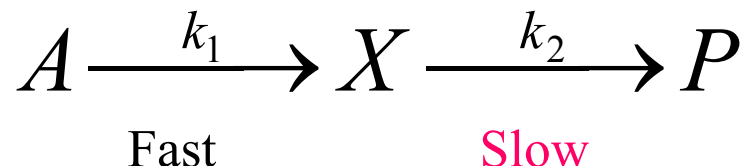
Intermediate X is fairly reactive. Concentration of intermediate X will be small at all times.



Intermediate concentration is approximately constant after initial induction period.

$$k_1 \gg k_2$$

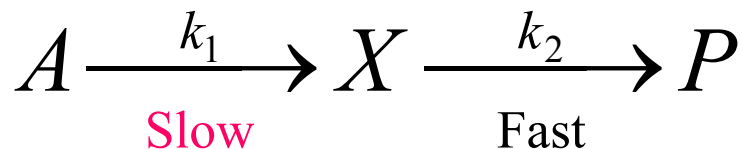
Rate Determining Step



- Reactant A decays rapidly, concentration of intermediate species X is high for much of the reaction and product P concentration rises gradually since X  $\rightarrow$  P transformation is slow .

$$k_2 \gg k_1$$

Rate Determining Step



- Reactant A decays slowly, concentration of intermediate species X will be low for the duration of the reaction and to a good approximation the net rate of change of intermediate concentration with time is zero. Hence the intermediate will be formed as quickly as it is removed. This is the *quasi steady state approximation* (QSSA).

## Parallel reaction mechanism.

- We consider the kinetic analysis of a concurrent or parallel reaction scheme which is often met in real situations.

- A single reactant species can form two distinct products.

We assume that each reaction exhibits 1<sup>st</sup> order kinetics.

- Initial condition :  $t = 0, a = a_0 ; x = 0, y = 0$

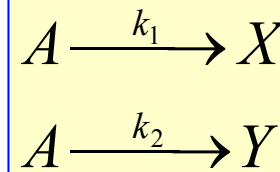
- Rate equation:

$$R = -\frac{da}{dt} = k_1 a + k_2 a = (k_1 + k_2) a = k_{\Sigma} a$$

$$a(t) = a_0 \exp[-k_{\Sigma} t] = a_0 \exp[-(k_1 + k_2) t]$$

- Half life: 
$$\tau_{1/2} = \frac{\ln 2}{k_{\Sigma}} = \frac{\ln 2}{k_1 + k_2}$$

- All of this is just an extension of simple 1<sup>st</sup> order kinetics.



$k_1, k_2 = 1^{\text{st}}$  order rate constants

We can also obtain expressions for the product concentrations  $x(t)$  and  $y(t)$ .

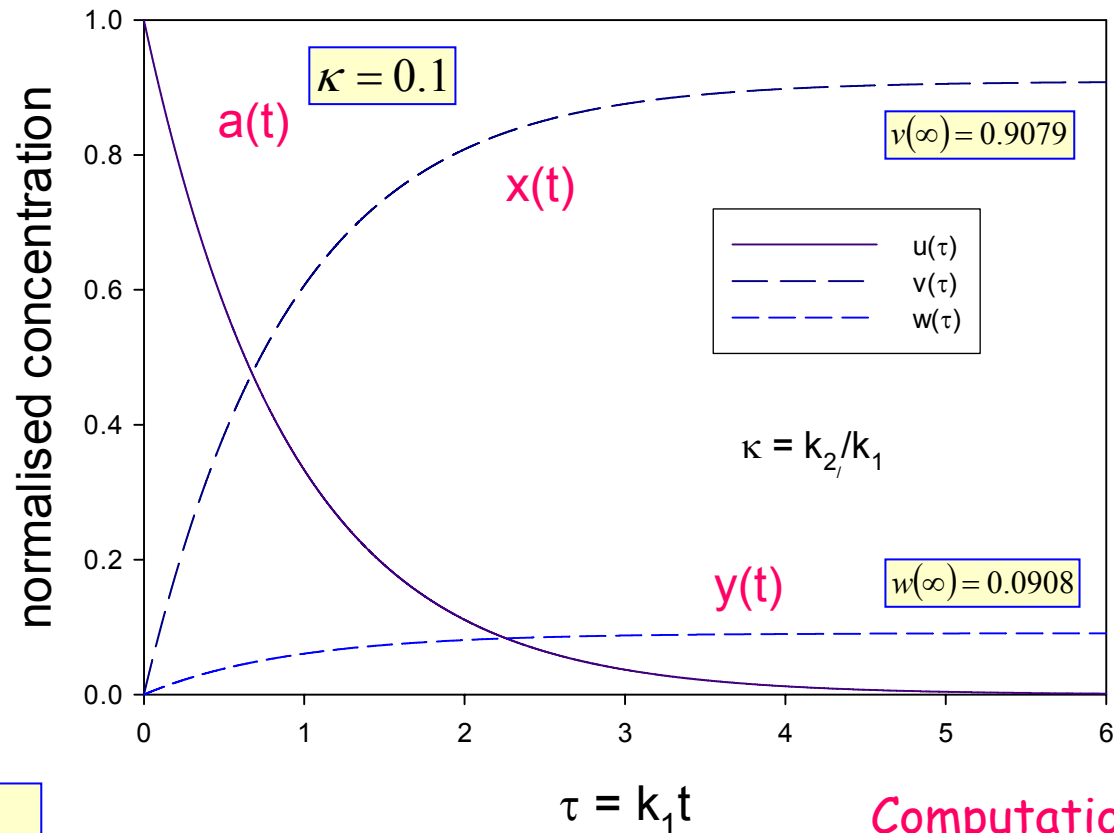
$$\begin{aligned} \frac{dx}{dt} &= k_1 a = k_1 a_0 \exp[-(k_1 + k_2) t] \\ x(t) &= k_1 a_0 \int_0^t \exp[-(k_1 + k_2) t] dt \\ x(t) &= \frac{k_1 a_0}{k_1 + k_2} \{1 - \exp[-(k_1 + k_2) t]\} \end{aligned}$$

$$\begin{aligned} \frac{dy}{dt} &= k_2 a = k_2 a_0 \exp[-(k_1 + k_2) t] \\ y(t) &= k_2 a_0 \int_0^t \exp[-(k_1 + k_2) t] dt \\ y(t) &= \frac{k_2 a_0}{k_1 + k_2} \{1 - \exp[-(k_1 + k_2) t]\} \end{aligned}$$

Final product analysis yields rate constant ratio.

$$\lim_{t \rightarrow \infty} \frac{x(t)}{y(t)} = \frac{k_1}{k_2}$$

# Parallel Mechanism: $k_1 \gg k_2$



Theory

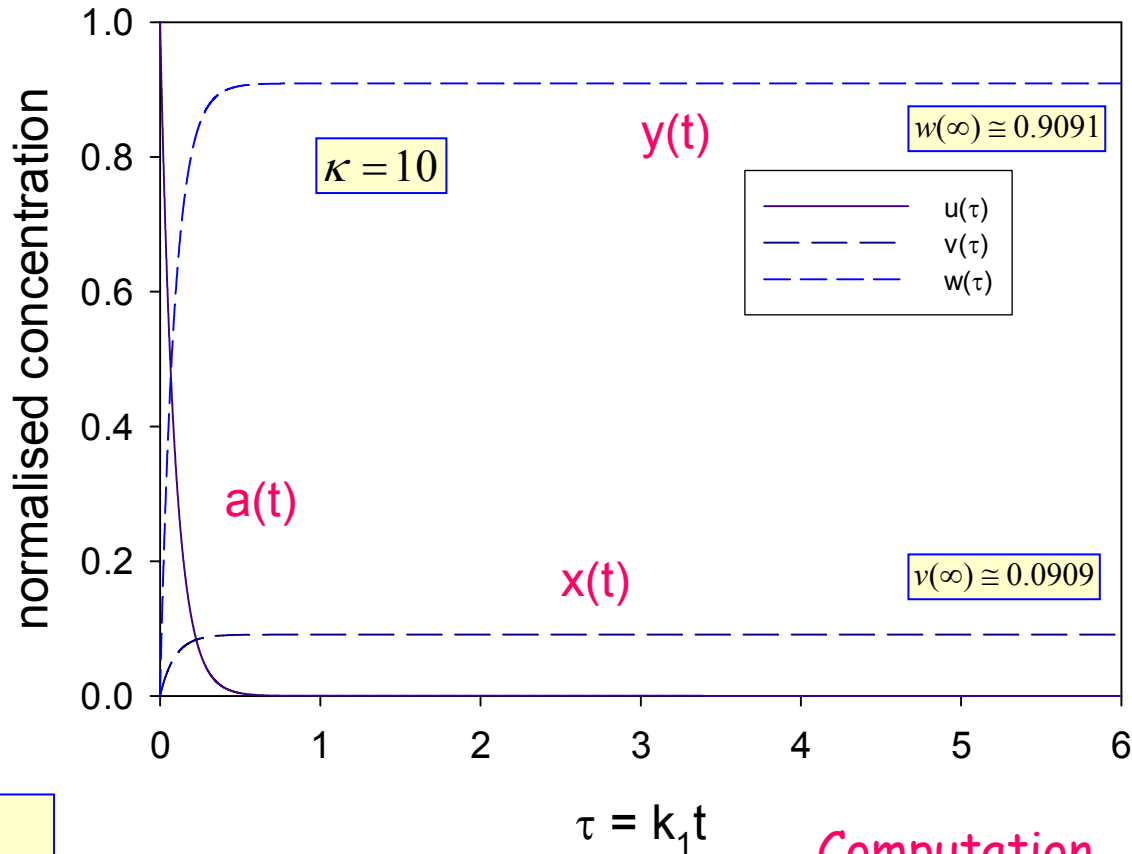
$$\kappa = \frac{k_2}{k_1} = 0.1$$

$$\frac{k_1}{k_2} = 10 = \frac{v(\infty)}{w(\infty)}$$

Computation

$$\frac{v(\infty)}{w(\infty)} \cong \frac{0.9079}{0.0908} = 9.9989$$

# Parallel Mechanism: $k_2 \gg k_1$



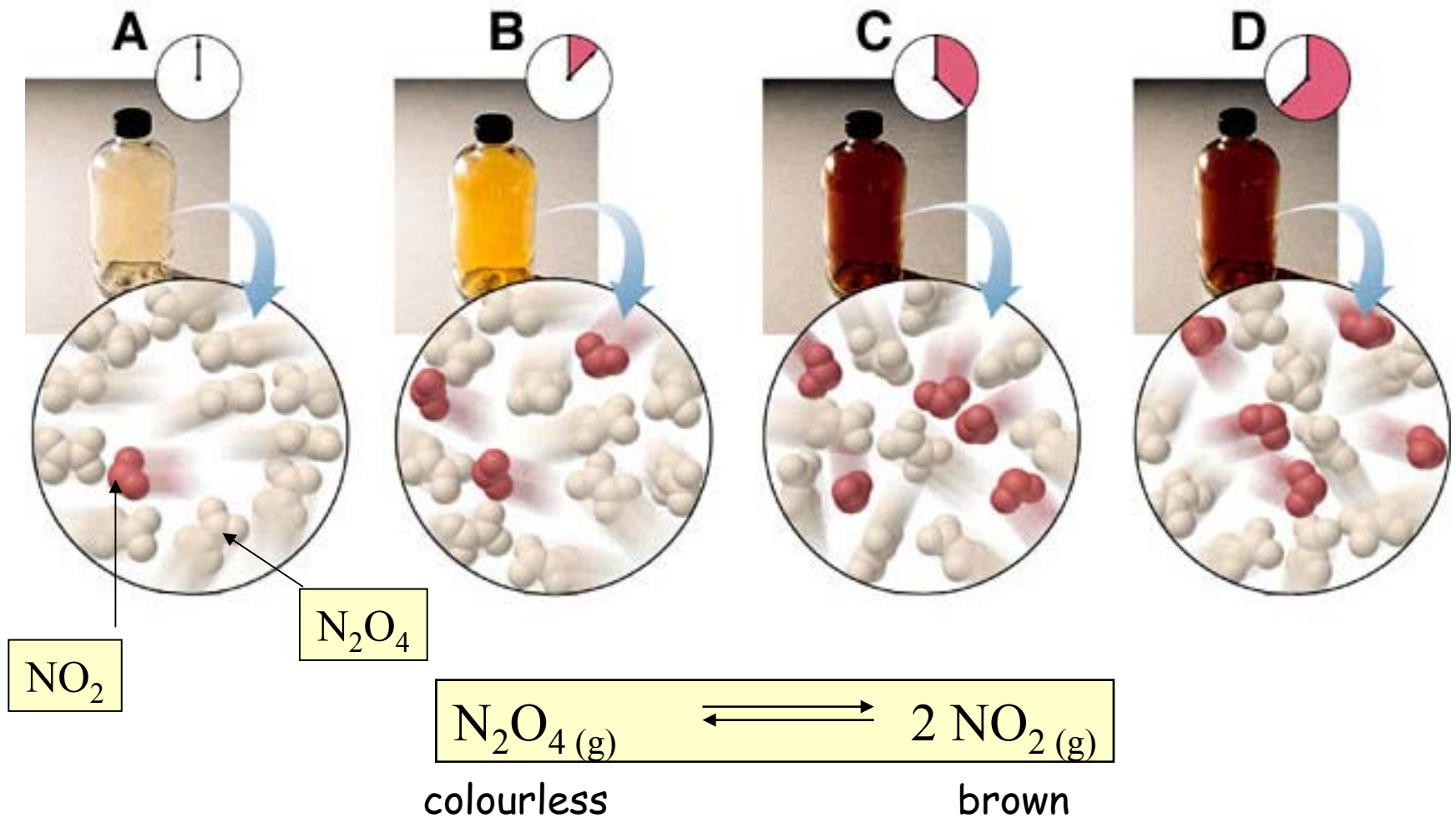
Theory

$$\kappa = \frac{k_2}{k_1} = 10$$
$$\frac{k_1}{k_2} = 0.1 = \frac{v(\infty)}{w(\infty)}$$

Computation

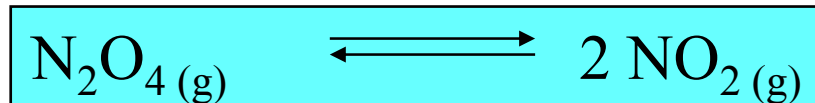
$$\frac{v(\infty)}{w(\infty)} \cong \frac{0.0909}{0.9091} = 0.0999$$

# Reaching Equilibrium on the Macroscopic and Molecular Level



# Chemical Equilibrium : a kinetic definition.

- Countless experiments with chemical systems have shown that in a state of equilibrium, the concentrations of reactants and products no longer change with time.
- This apparent cessation of activity occurs because under such conditions, all reactions are microscopically reversible.
- We look at the dinitrogen tetraoxide/nitrogen oxide equilibrium which occurs in the gas phase.



colourless

brown

Kinetic analysis.

$$\bar{R} = k[\text{N}_2\text{O}_4]$$

$$\bar{R} = k'[\text{NO}_2]^2$$

Valid for any time  $t$

Equilibrium:

$$t \rightarrow \infty$$

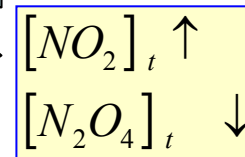
$$\bar{R} = \bar{R}$$

$$k[\text{N}_2\text{O}_4]_{eq} = k'[\text{NO}_2]_{eq}^2$$

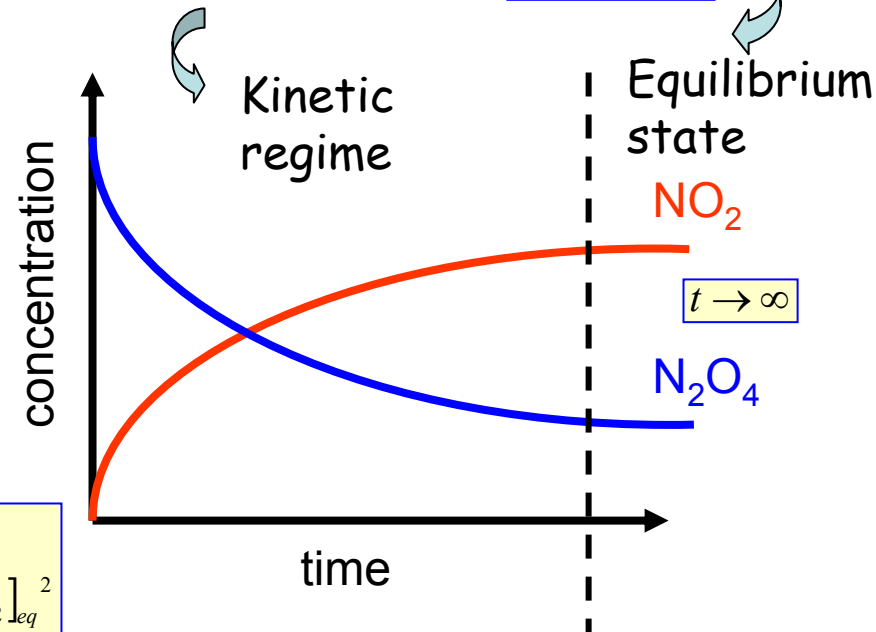
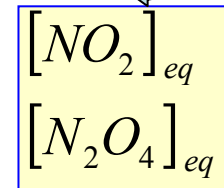
$$\frac{[\text{NO}_2]_{eq}^2}{[\text{N}_2\text{O}_4]} = \frac{k}{k'} = K$$

Equilibrium constant

Concentrations vary with time

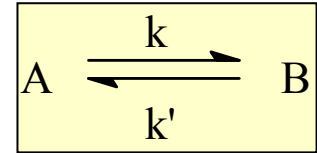


Concentrations time invariant





First order reversible reactions :  
understanding the approach to chemical equilibrium.



Rate equation

$$\frac{da}{dt} = -ka + k'b$$

$$u + v = 1$$

$$\tau = 0 \quad u = 1 \quad v = 0$$

Initial condition

$$t = 0 \quad a = a_0 \quad b = 0$$

Rate equation in normalised form

$$\frac{du}{d\tau} + u = \frac{1}{1 + \theta}$$

Mass balance condition

$$\forall t \quad a + b = a_0$$

Solution produces the concentration expressions

$$u(\tau) = \frac{1}{1 + \theta} \{1 + \theta \exp[-\tau]\}$$

$$v(\tau) = \frac{\theta}{1 + \theta} \{1 - \exp[-\tau]\}$$

Introduce normalised variables.

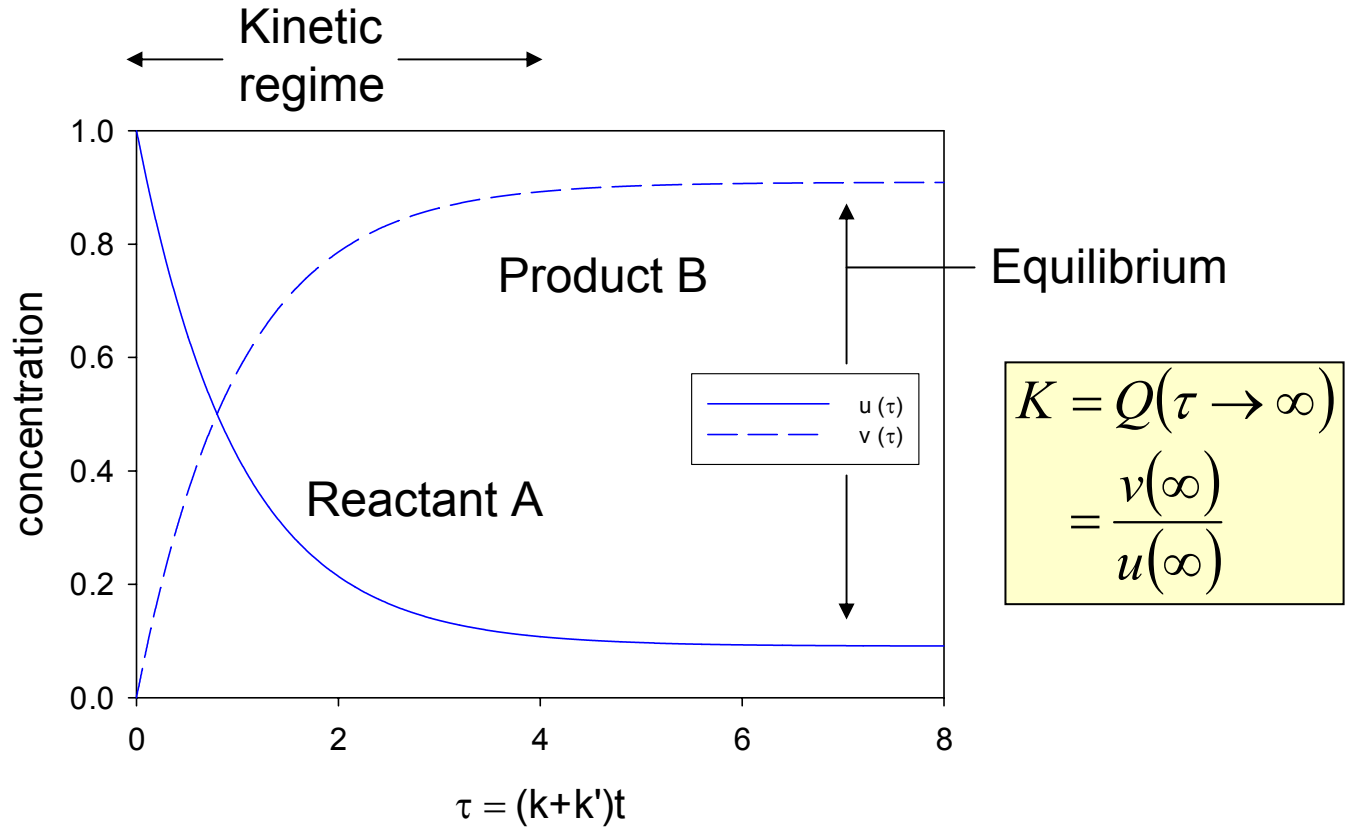
$$u = \frac{a}{a_0} \quad v = \frac{b}{a_0} \quad \tau = (k + k')t \quad \theta = \frac{k}{k'}$$



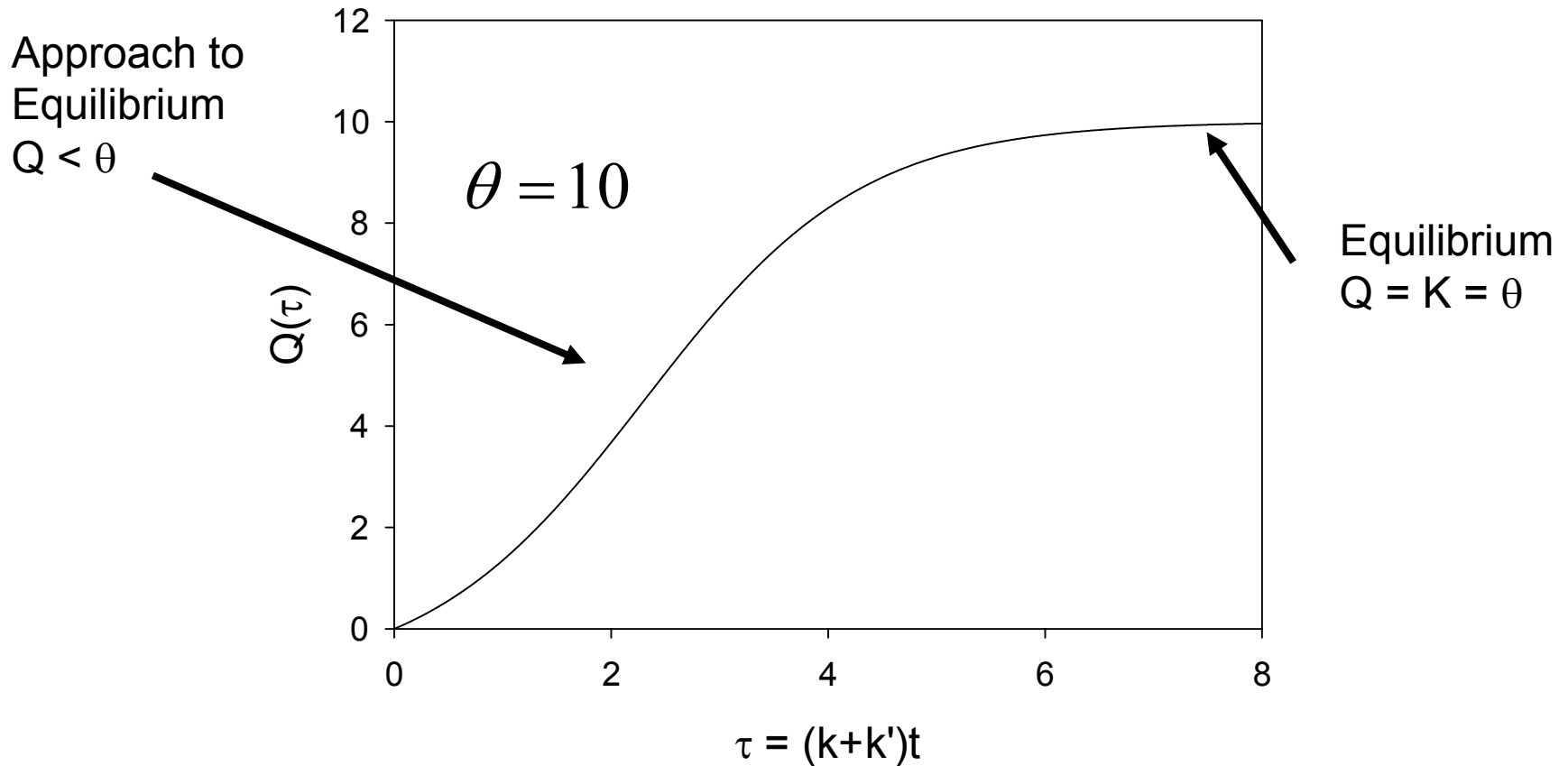
$$Q(\tau) = \frac{v(\tau)}{u(\tau)} = \theta \left\{ \frac{1 - \exp[-\tau]}{1 + \theta \exp[-\tau]} \right\}$$

Reaction quotient Q

# First order reversible reactions: approach to equilibrium.



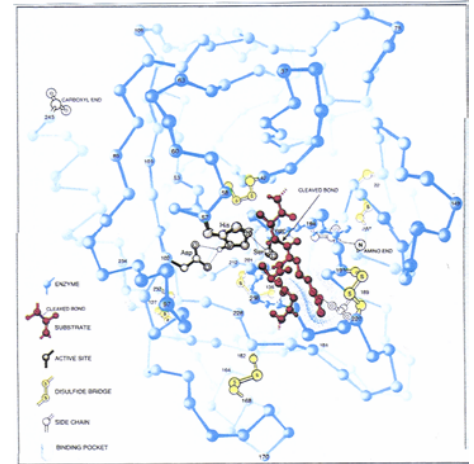
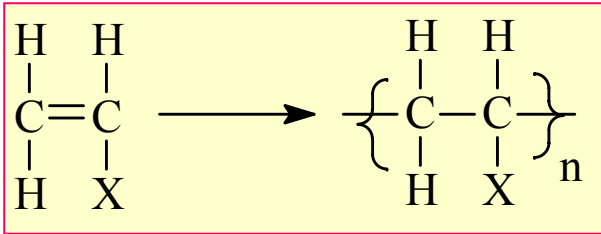
# Understanding the difference between reaction quotient $Q$ and Equilibrium constant $K$ .



$$Q(\tau) = \frac{v(\tau)}{u(\tau)} = \theta \left\{ \frac{1 - \exp[-\tau]}{1 + \theta \exp[-\tau]} \right\}$$

$$t \rightarrow \infty \quad Q \rightarrow K = \theta = \frac{k}{k'}$$

$$K = \frac{v(\infty)}{u(\infty)}$$



# Chemical Kinetics.

## Lecture 3/4.

Application of the Steady State Approximation: Macromolecules and Enzymes.

## Quasi-Steady State Approximation. QSSA

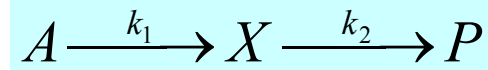
- Detailed mathematical analysis of complex reaction mechanisms is difficult. Some useful methods for solving sets of coupled linear differential rate equations include **matrix methods** and **Laplace Transforms**.
- In many cases utilisation of the **quasi steady state approximation** leads to a considerable simplification in the kinetic analysis.

*The QSSA assumes that after an initial induction period (during which the concentration  $x$  of intermediates  $X$  rise from zero), and during the major part of the reaction, the rate of change of concentrations of all reaction intermediates are negligibly small.*

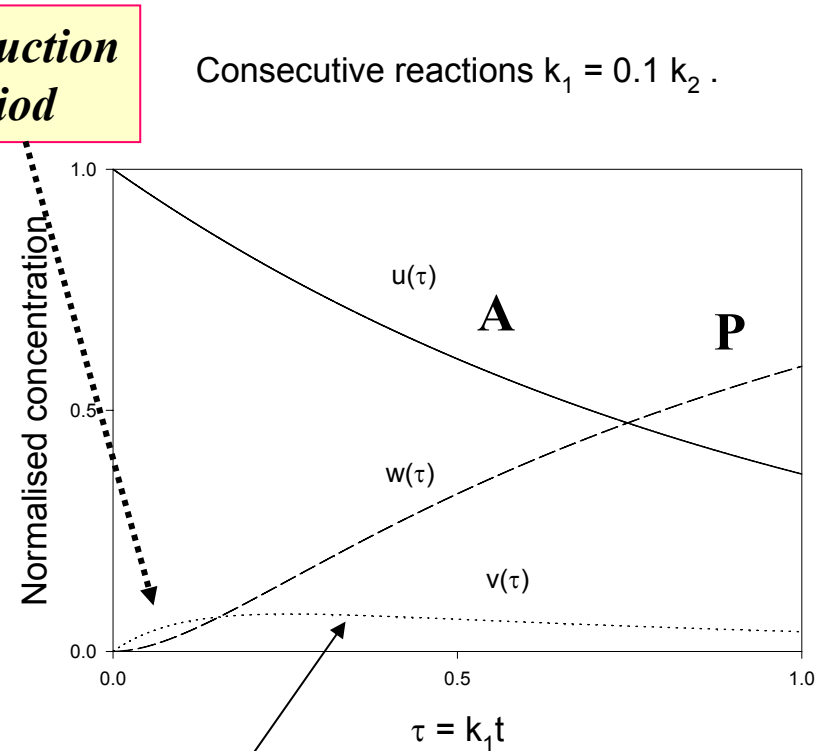
Mathematically, QSSA implies

$$\frac{dx}{dt} = R_{X \text{ formation}} - R_{X \text{ removal}} \cong 0$$

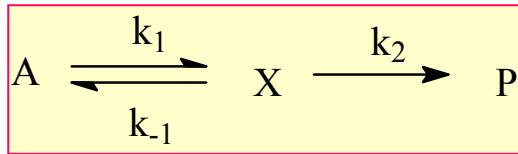
$$R_{X \text{ formation}} = R_{X \text{ removal}}$$



Consecutive reactions  $k_1 = 0.1 k_2$ .



## Consecutive reaction mechanisms.



Step I is reversible, step II is Irreversible.

Rate equations



$$\begin{aligned} \frac{du}{d\tau} &= -u + \kappa v \\ \frac{dv}{d\tau} &= u - (\kappa + \phi) v \\ \frac{dw}{d\tau} &= \phi v \end{aligned}$$

Coupled LDE's can be solved via Laplace Transform or other methods.

$$u(\tau) = \frac{1}{\beta - \alpha} \{ (\kappa + \phi - \alpha) \exp[-\alpha \tau] - (\kappa + \phi - \beta) \exp[-\beta \tau] \}$$

$$v(\tau) = \frac{1}{\beta - \alpha} \{ \exp[-\alpha \tau] - \exp[-\beta \tau] \}$$

$$w(\tau) = 1 - \frac{1}{\beta - \alpha} \{ \beta \exp[-\alpha \tau] - \alpha \exp[-\beta \tau] \}$$

$$u = \frac{a}{a_0} \quad v = \frac{x}{a_0} \quad w = \frac{p}{a_0}$$

$$\forall \tau \quad u + v + w = 1$$

$$\tau = 0 \quad u = 1 \quad v = w = 0$$

$$\kappa = \frac{k_{-1}}{k_1} \quad \phi = \frac{k_2}{k_1} \quad \tau = k_1 t$$

Note that  $\alpha$  and  $\beta$  are composite quantities containing the individual rate constants.

$$\alpha\beta = \phi$$

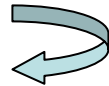
$$\alpha + \beta = 1 + \kappa + \phi$$

Definition of normalised variables and initial condition.



QSSA assumes that

$$\frac{dv}{d\tau} \cong 0$$



$$u_{ss} - (\kappa + \phi)v_{ss} = 0$$
$$v_{ss} \cong \frac{u_{ss}}{\kappa + \phi}$$



$$\frac{du_{ss}}{d\tau} = -\frac{\phi}{\kappa + \phi} u_{ss}$$
$$u_{ss} \cong \exp\left[-\frac{\phi}{\kappa + \phi} \tau\right]$$



$$v_{ss} \cong \frac{\exp\left[-\left(\frac{\phi}{\kappa + \phi}\right) \tau\right]}{\kappa + \phi}$$

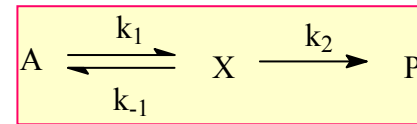
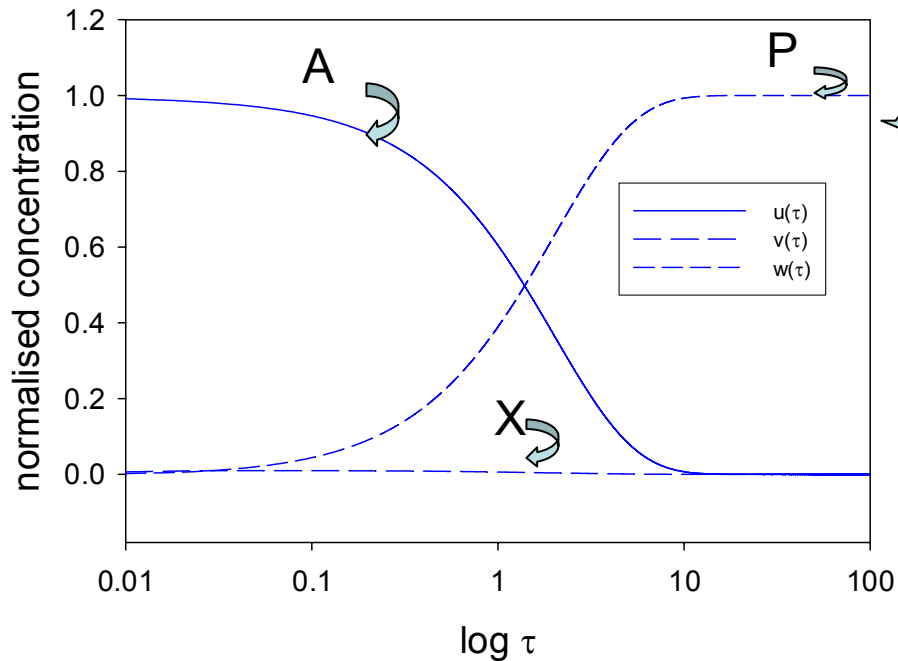


Using the QSSA we can develop more simple rate equations which may be integrated to produce approximate expressions for the pertinent concentration profiles as a function of time.

The QSSA will only hold provided that:

- **the concentration of intermediate is small and effectively constant,**
- and so :**
- **the net rate of change in intermediate concentration wrt time can be set equal to zero.**

$$\frac{dw_{ss}}{d\tau} \cong \phi v_{ss} = \frac{\phi}{\kappa + \phi} \exp\left[-\left(\frac{\phi}{\kappa + \phi}\right) \tau\right]$$
$$w_{ss} \cong \frac{\phi}{\kappa + \phi} \int_0^{\tau} \exp\left[-\left(\frac{\phi}{\kappa + \phi}\right) \tau\right] d\tau$$
$$= 1 - \exp\left[-\left(\frac{\phi}{\kappa + \phi}\right) \tau\right]$$



Concentration versus log time curves for reactant A, intermediate X and product P when full set of coupled rate equations are solved without any approximation.

$k_{-1} \gg k_1$ ,  $k_2 \gg k_1$  and  $k_{-1} = k_2 = 50$ .

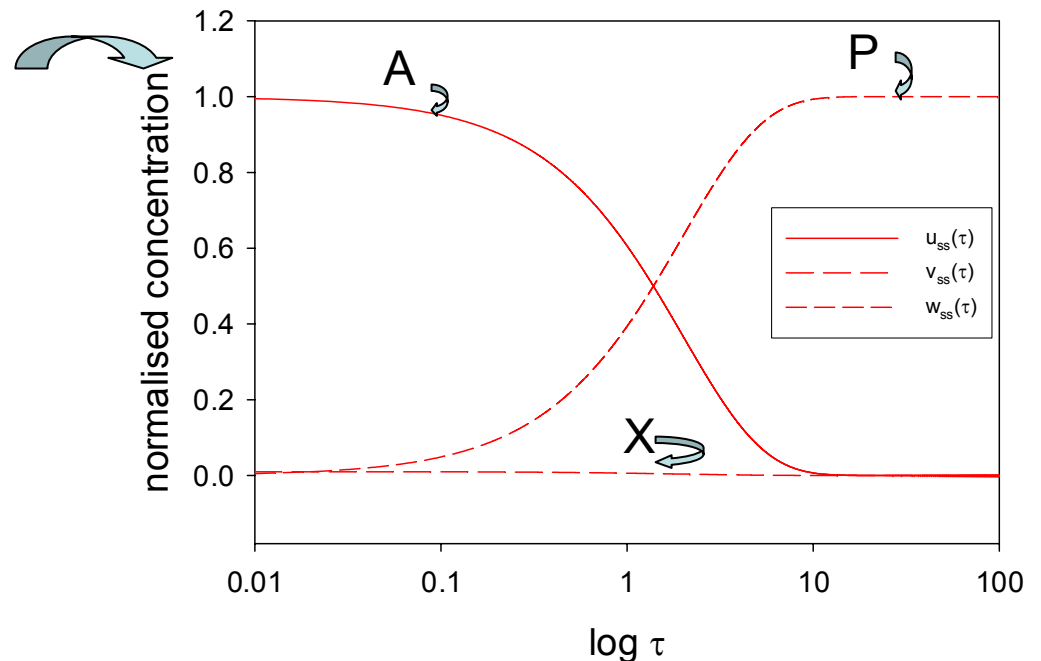
The concentration of intermediate X is very small and approximately constant throughout the time course of the experiment.

Concentration versus log time curves for reactant A, intermediate X, and product P when the rate equations are solved using the QSSA.

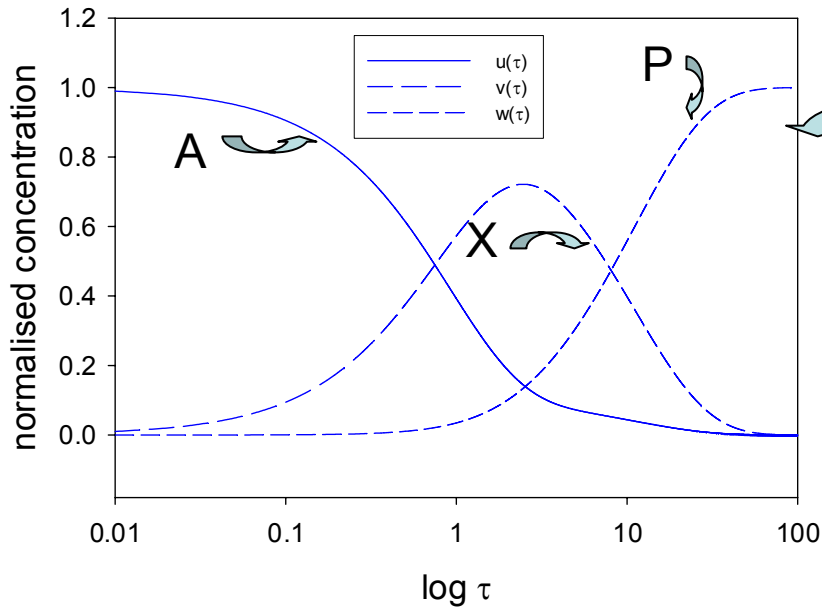
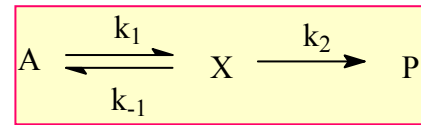
Values used for the rate constants are the same as those used above.

QSSA reproduces the concentration profiles well and is valid.

QSSA will hold when concentration of intermediate is **small** and **constant**. Hence the rate constants for getting rid of the intermediate ( $k_{-1}$  and  $k_2$ ) must be much larger than that for intermediate generation ( $k_1$ ).





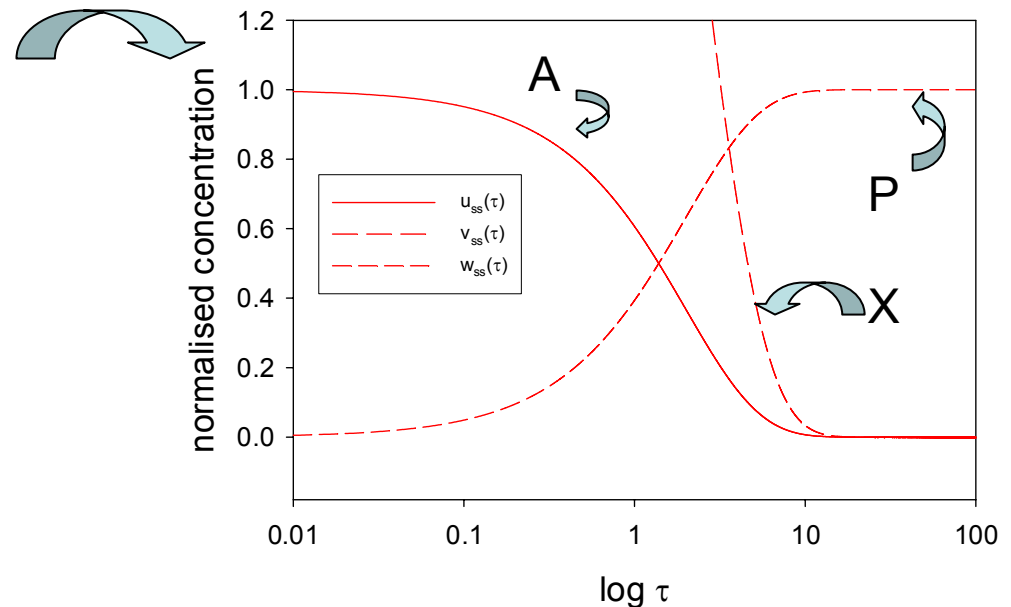


Concentration versus log time curves for reactant A, intermediate X and product P when full set of coupled rate equations are solved without any approximation.

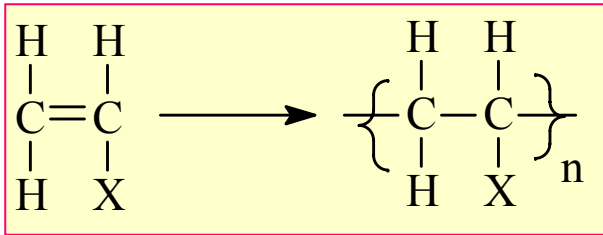
$k_{-1} \ll k_1, k_2, k_1$  and  $k_{-1} = k_2 = 0.1$   
 The concentration of intermediate is high and it is present throughout much of the duration of the experiment.

Concentration versus log time curves for reactant A, intermediate X and product P when the Coupled rate equations are solved using the quasi steady state approximation. The same values for the rate constants were adopted as above.

**The QSSA is not good in predicting how the intermediate concentration varies with time, and so it does not apply under the condition where the concentration of intermediate will be high and the intermediate is long lived.**



## Macromolecule Formation : Polymerization.



↑  
monomer  
vinyl halide

X = Cl, vinyl chloride

↑  
polymer  
poly(vinyl chloride)

Polymerization of vinyl halides occurs via a **chain growth addition polymerization** mechanism.

3 step process :

- *initiation*
- *propagation*
- *termination*

Polymer = large molar mass molecule  
(Macromolecule).

**Chain initiation** : highly reactive transient molecules or active centers (such as free radicals formed).

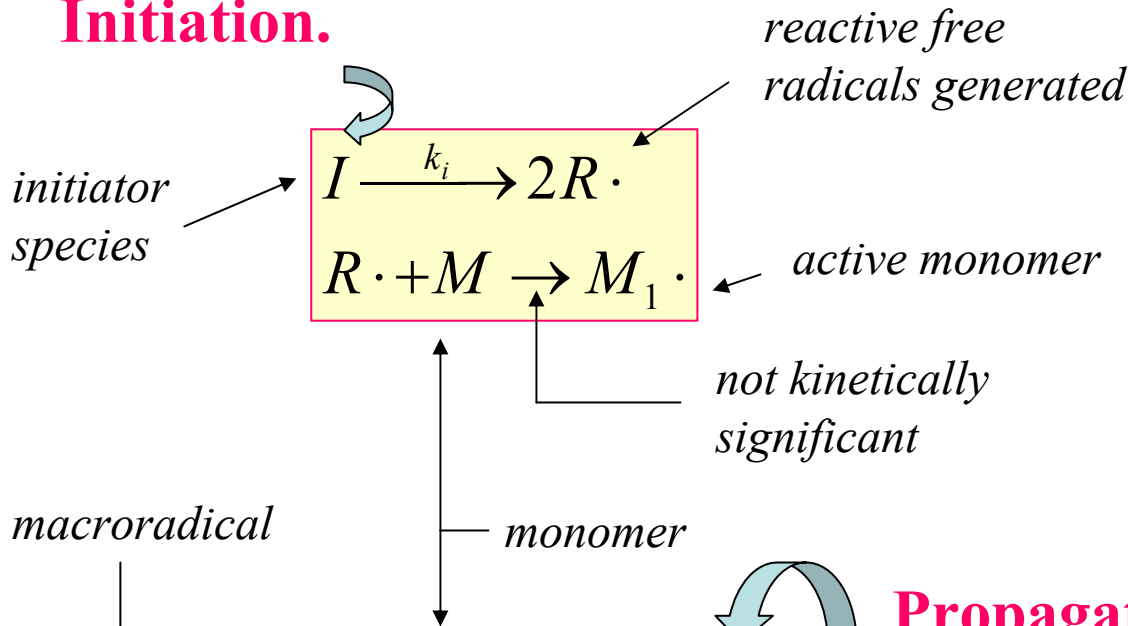
**Chain propagation** : addition of monomer molecules to active chain end accompanied by regeneration of terminal active site.

**Chain termination** : reaction in which active chain centers are destroyed.

We focus on radical addition polymerization . Kinetics of polymerization quantified via QSSA .

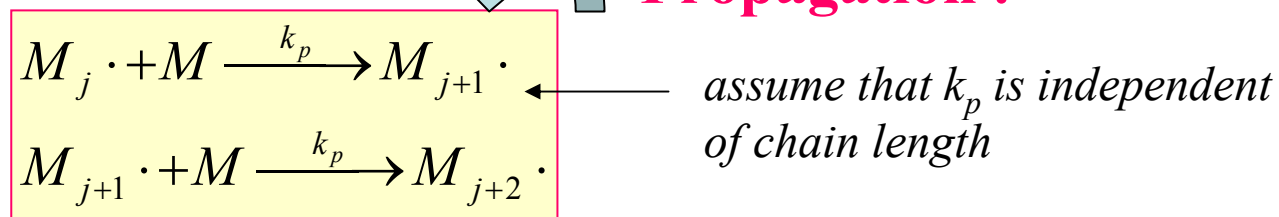
# Free Radical Addition Polymerization.

## Initiation.

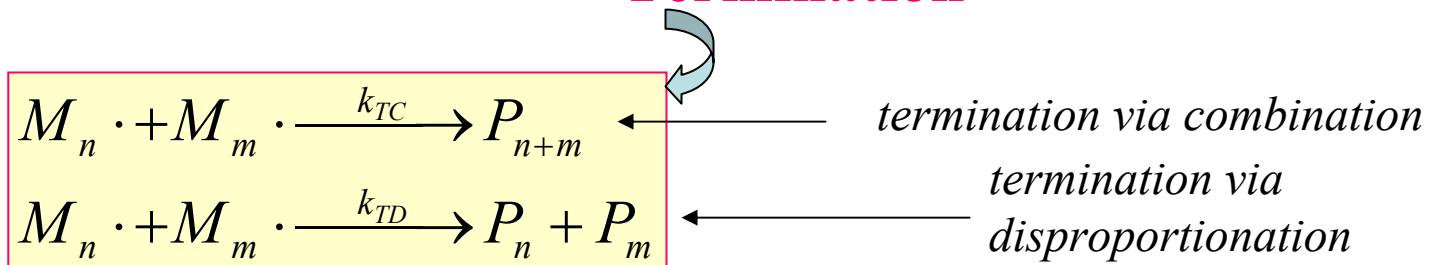


$k_i$  = initiation rate constant  
 $k_p$  = propagation rate constant  
 $k_T = k_{TC} + k_{TD}$   
= termination rate constant

## Propagation .



## Termination



# Free Radical Addition Polymerization.

## Analysis of the steady state kinetics.

polymerization rate = rate of chain propagation

$$R_P = -\frac{dm}{dt} = r_P = k_P mx$$

macroradical concentration

bimolecular propagation rate constant

monomer concentration

$$R_P = r_P = k_P mx$$

$$= k_P \left\{ \frac{r_i}{2k_T} \right\}^{1/2} m$$

$r_i$  can be left unspecified depends on initiation mechanism

$$r_i = 2k_T x^2$$

Propagating macroradical concentration will be small since they are very reactive so QSSA can be applied.

$$\frac{dx}{dt} \cong 0$$

$$\frac{dx}{dt} = r_{x \text{ formation}} - r_{x \text{ removal}} \cong 0$$

$$r_{x \text{ formation}} = r_{x \text{ removal}}$$

initiation rate  $r_i$

$$r_i = r_T$$

termination rate  $r_T$

$$r_T = 2k_T x^2$$

2 macroradicals disappear for each incidence of termination

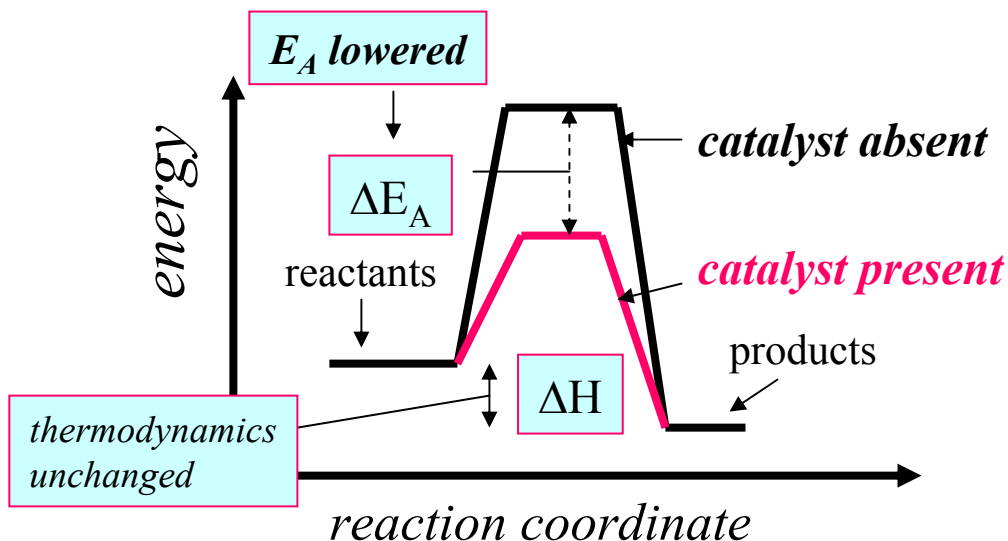
$$x = \sqrt{\frac{r_i}{2k_T}}$$

# Application of QSSA. Kinetics of enzyme reactions.

Enzymes are very specific biological catalysts.

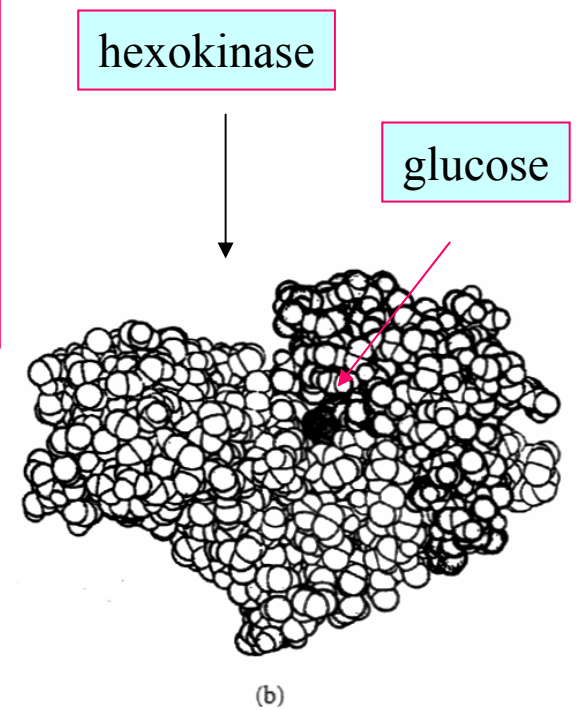
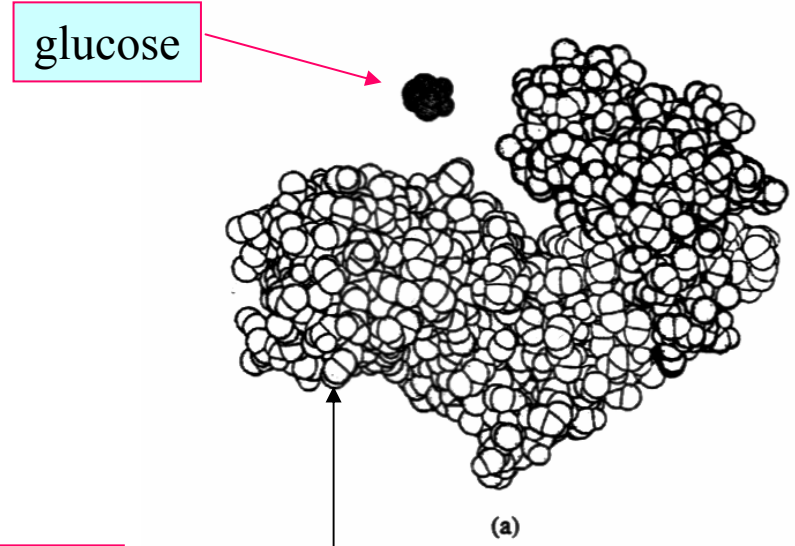
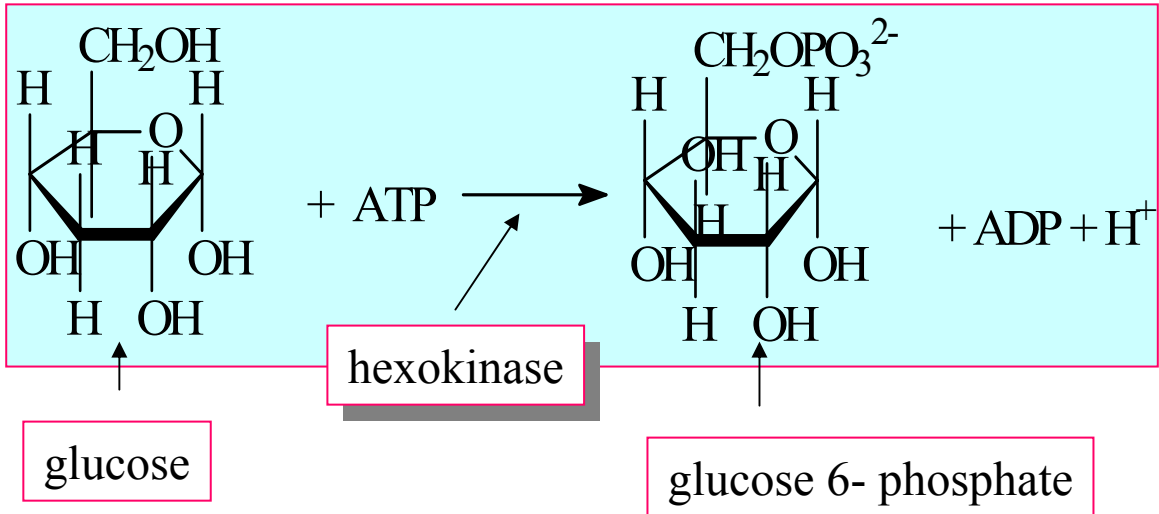
A catalyst is a substance that increases the rate of a reaction without itself being consumed by the process.

- A catalyst lowers the Gibbs energy of activation  $\Delta G^\ddagger$  by providing a different mechanistic pathway by which the reaction may proceed. This alternative mechanistic path enhances the rate of both the forward and reverse directions of the reaction.
- The catalyst forms an intermediate with the reactants in the initial step of the reaction (a binding reaction), and is released during the product forming step.
- Regardless of the mechanism and reaction energetics a catalyst does not effect  $\Delta H$  or  $\Delta G$  of the reactants and products. Hence catalysts increase the rate of approach to equilibrium, but cannot alter the value of the thermodynamic equilibrium constant.



A reactant molecule acted upon by an enzyme is termed a substrate. The region of the enzyme where the substrate reacts is called the active site. Enzyme specificity depends on the geometry of the active site and the spatial constraints imposed on this region by the overall structure of the enzyme molecule.

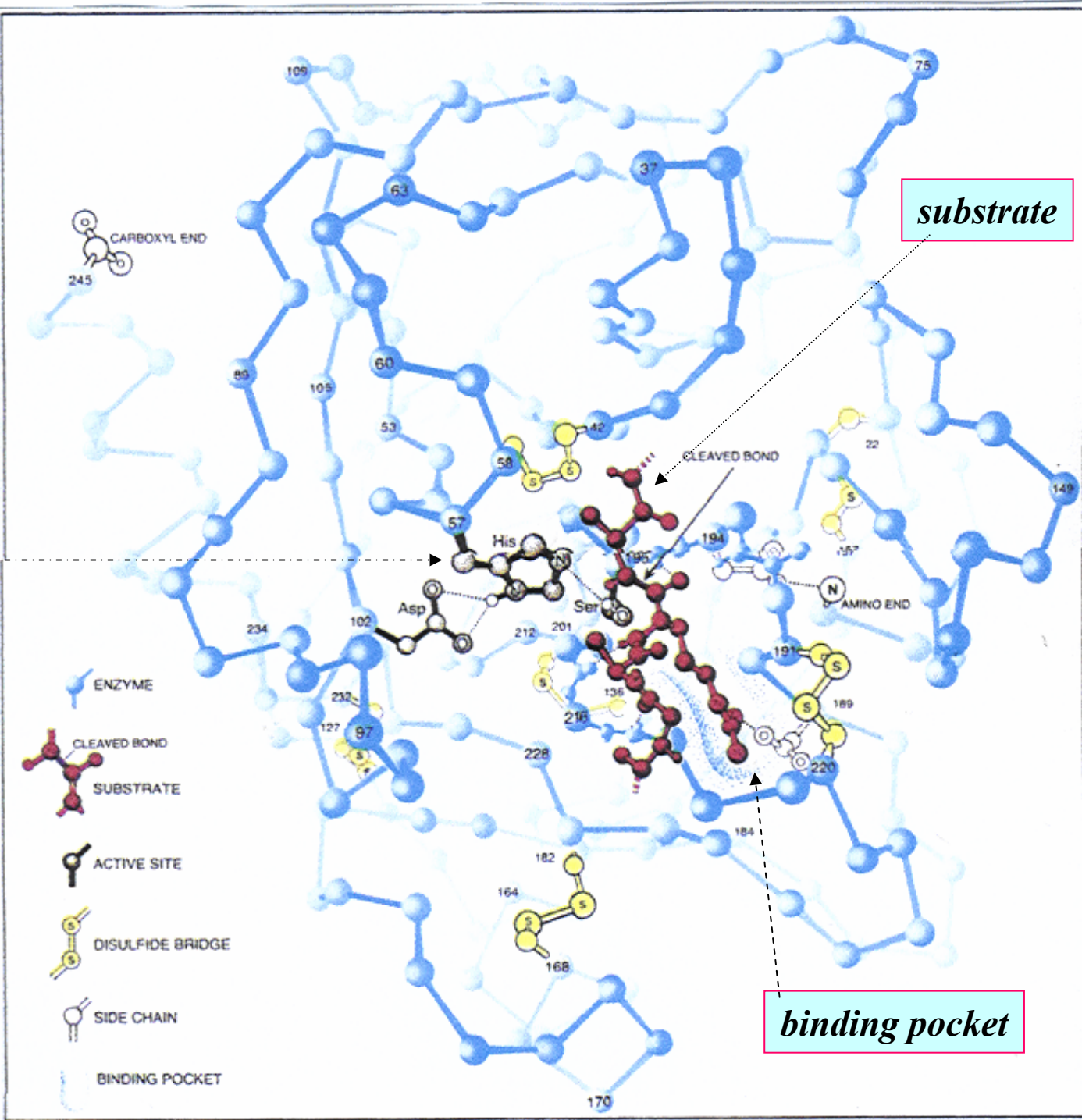
Space filling models of the two conformations of the enzyme hexokinase.  
 (a) the active site is not occupied. There is a cleft in the protein structure that allows the substrate molecule glucose to access the active site.  
 (b) the active site is occupied. The protein has closed around the substrate.



**Enzyme lock/key mechanism :  
 natural molecular recognition.**

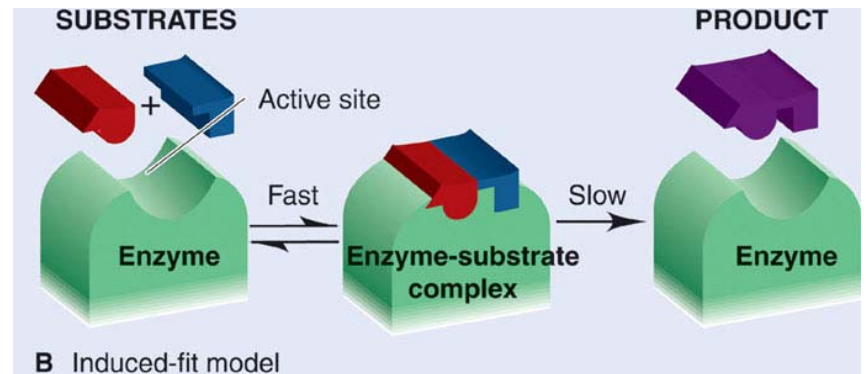
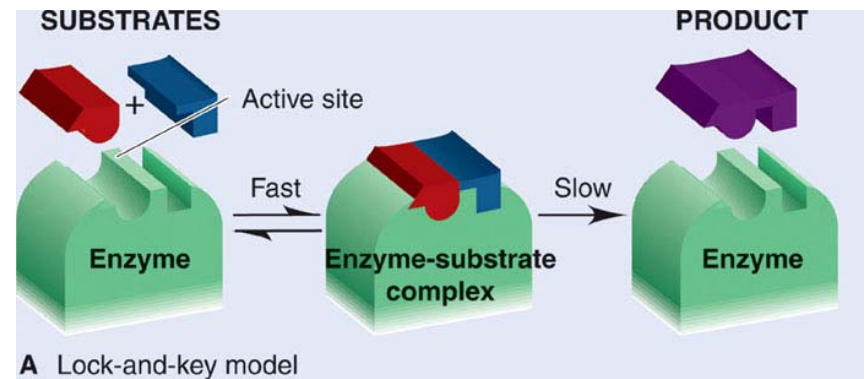
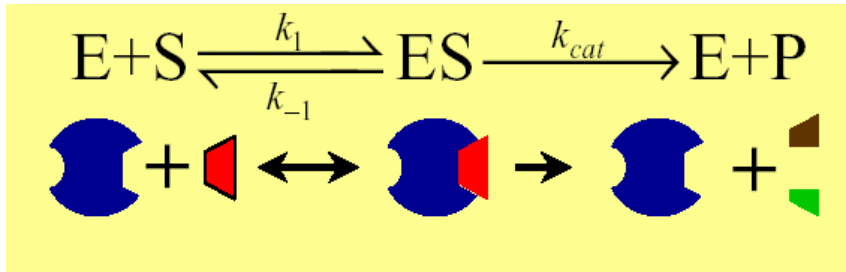
*Chymotrypsin :  
A digestive  
enzyme .*

*Natural  
molecular  
recognition in  
action.*



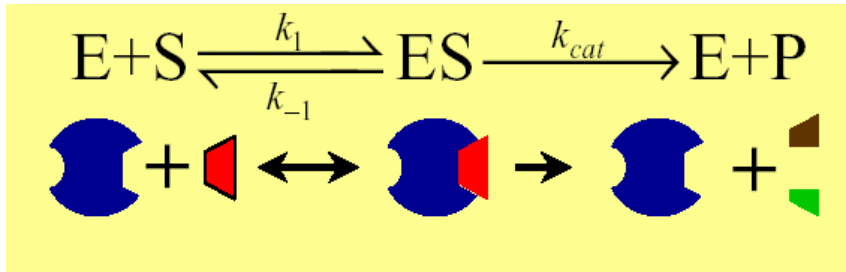


# Mechanism of enzyme action.





# Classification of enzymes.



*Oxidoreductases* Transfer electrons

*Transferases* Transfer functional groups

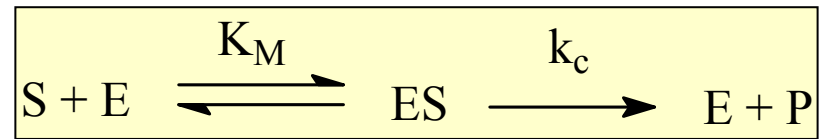
*Hydrolases* Transfer functional groups to water

*Lyases* Transfer groups to or from double bonds

*Isomerases* Transfer groups within molecules

*Ligases* Transfer by joining groups

# Michaelis-Menten kinetics.



substrate binding

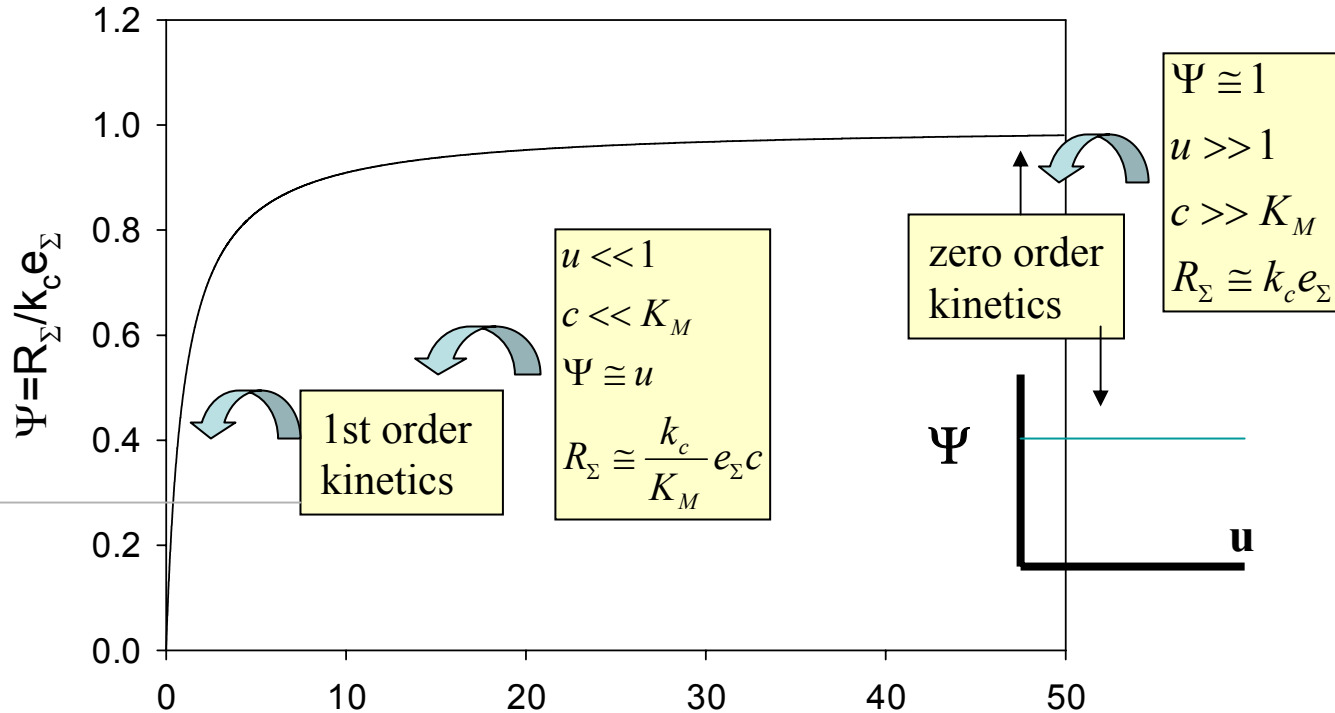
enzyme/substrate complex

ES complex decomposition to form products

Michaelis-Menten rate equation.

$$R_\Sigma = \frac{k_c e_\Sigma c}{K_M + c}$$

$$\Psi = \frac{R_\Sigma}{e_\Sigma k_c} = \frac{u}{1 + u}$$



$K_M$  = Michaelis constant (mol dm<sup>-3</sup>)  
 $k_c$  = catalytic rate constant (s<sup>-1</sup>)  
 $c$  = substrate concentration (mol dm<sup>-3</sup>)  
 $e_\Sigma$  = total enzyme concentration (mol dm<sup>-3</sup>).

$u = c/K_M$  This is an example of a complex rate equation, where the reaction rate varies with reactant concentration in a non linear way.

# Michaelis-Menten kinetics of enzyme reactions.

Experimental rate equation :

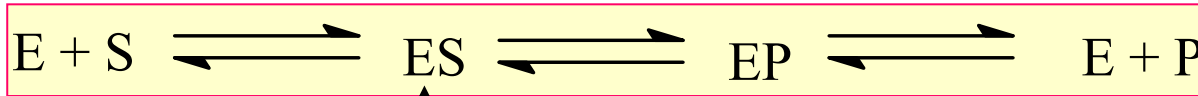
$$v = -\frac{ds}{dt} = \frac{as}{b+s}$$

substrate concentration

$a, b = \text{constants}$

Proposed mechanism should produce this rate law.

Mechanism :



enzyme

substrate

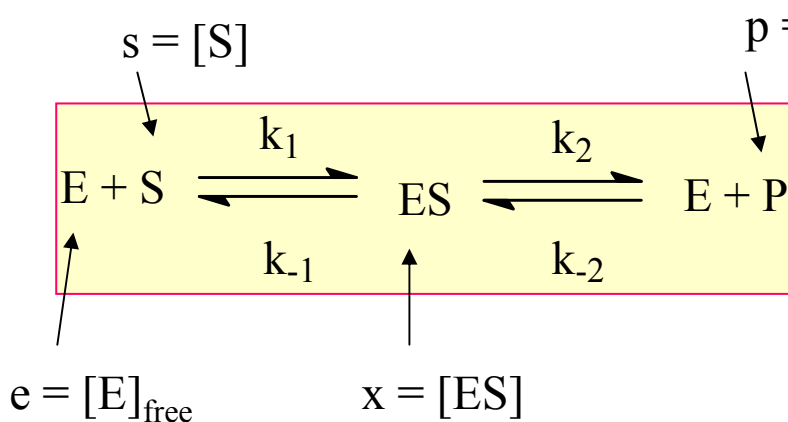
enzyme/substrate complex

enzyme/product complex

product

Rate equations

We analyse a simpler scheme which includes all the essentials.



$$\begin{aligned} -\frac{ds}{dt} &= k_1 e s - k_{-1} x \\ -\frac{dx}{dt} &= (k_2 + k_{-1}) x - k_1 e s - k_{-2} e p \\ \frac{dp}{dt} &= k_2 x - k_{-2} e p \end{aligned}$$

What forms does the enzyme take?

- free enzyme  $E$
- bound enzyme  $ES$

$$e_{\Sigma} = x + e$$

total initial  
enzyme concentration

Usually  $e_{\Sigma} \ll s$ . Subsequent to mixing one has an initial period during which  $x = [ES]$  builds up. We then assume that the equilibrium concentration of  $ES$  is rapidly attained and reaches a constant low value during the course of the reaction.

This requirement satisfies the QSSA.

QSSA

$$\frac{dx}{dt} = \{k_1 s + k_{-1} + k_2 + k_{-2} p\} x_{SS} - k_1 s e_{\Sigma} - k_{-2} p e_{\Sigma} \cong 0$$

$$x_{SS} = \frac{(k_1 s + k_{-2} p) e_{\Sigma}}{k_1 s + k_{-2} p + k_{-1} + k_2}$$

$$R_{\Sigma} = -\frac{ds}{dt} = \frac{\{k_1 k_2 s - k_{-1} k_{-2} p\} e_{\Sigma}}{k_1 s + k_{-2} p + k_{-1} + k_2}$$

Let's assume that measurement of the reaction rate occurs during a time period when only a small percentage (1-3%) of substrate is transformed to product.

$$p \cong 0$$

$$s \cong s_0$$

initial substrate  
concentration

$$R_{\Sigma} \cong R_{\Sigma,0} \cong \frac{k_1 k_2 e_{\Sigma} s_0}{k_{-1} + k_2 + k_1 s_0} = \frac{k_2 e_{\Sigma} s_0}{\frac{k_{-1} + k_2}{k_1} + s_0}$$

This has the same form as the empirical rate equation observed experimentally.

*Michaelis constant*

*initial rate*

$$K_M = \frac{k_{-1} + k_2}{k_1}$$

$$k_C = k_2$$

$s^{-1}$

*catalytic rate constant*

$$R_{\Sigma,0} = \frac{k_C e_{\Sigma} s_0}{K_M + s_0}$$

*Michaelis-Menten (MM) equation for steady state enzyme kinetics.*

*Fundamental kinetic parameters :  $K_M$  and  $k_C$ .*

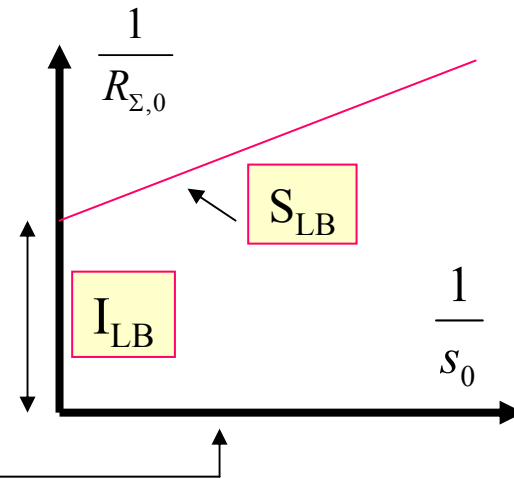
*$K_M$  : enzyme/substrate binding  
 $k_C$  : decomposition of enzyme/substrate complex.*

*How can we evaluate  $K_M$  and  $k_C$ ?*

- Non linear least squares fitting to MM equation.
- Suitable linearization of MM equation.

$$\frac{1}{R_{\Sigma,0}} = \frac{K_M}{k_C e_{\Sigma}} \frac{1}{s_0} + \frac{1}{k_C e_{\Sigma}}$$

*Lineweaver-Burk Plot.*



$$S_{LB} = \frac{K_M}{k_C e_{\Sigma}}$$

$$I_{LB} = \frac{1}{k_C e_{\Sigma}}$$

# How do we interpret the MM equation?

$$R_{\Sigma,0} = \frac{dp}{dt} = k_{\Sigma} e_{\Sigma} = \frac{k_C e_{\Sigma} s_0}{K_M + s_0}$$

$$k_{\Sigma} = \frac{k_C s_0}{K_M + s_0}$$



$$\frac{1}{k_{\Sigma}} = \frac{K_M}{k_C s_0} + \frac{1}{k_C}$$

*composite rate constant*

*unsaturated enzyme kinetics*

*saturated enzyme kinetics*

We consider two limiting behaviours.

- $s_0 \ll K_M$  *unsaturated enzyme kinetics ; not all active sites bound with substrate*
- $s_0 \gg K_M$  *saturated enzyme kinetics ; all active sites bound with substrate.*

**Case US**

$$\frac{s_0}{K_M} \ll 1$$

$$\frac{K_M}{k_C s_0} \gg \frac{1}{k_C}$$

$$\frac{1}{k_{\Sigma}} \cong \frac{K_M}{k_C s_0}$$

$$k_{\Sigma} \cong \frac{k_C}{K_M} s_0$$



$$k_U = \frac{k_C}{K_M} = \frac{k_1 k_2}{k_{-1} + k_2} = \frac{(k_1/k_{-1})k_2}{1 + \frac{k_2}{k_{-1}}} = \frac{K_1 k_2}{1 + \theta}$$

*equilibrium constant for ES formation*

$$K_1 = \frac{k_1}{k_{-1}}$$

$$\theta = \frac{k_2}{k_{-1}}$$

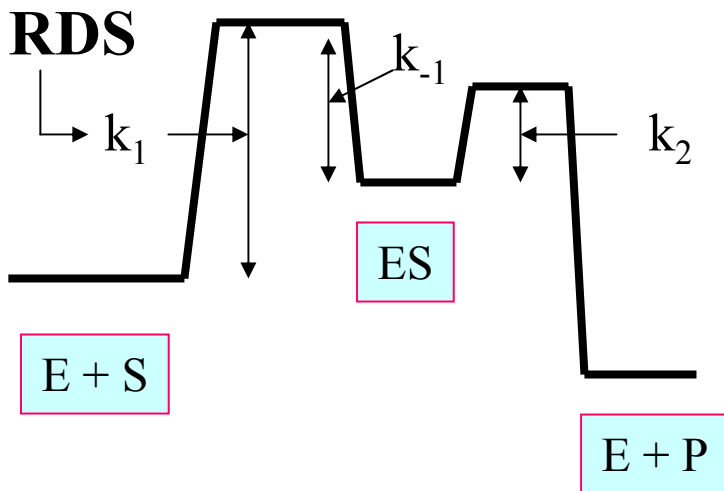
*We consider two sub cases depending on the value of  $\theta$ .*

$\theta \gg 1$  scenario.

$$1 + \theta \cong \theta = \frac{k_2}{k_{-1}}$$

$$k_U \cong K_1 k_2 \left( \frac{k_{-1}}{k_2} \right) = k_{-1} K_1 = k_1$$

When  $k_2 \gg k_{-1}$ , ES complex decomposition to form products is faster than ES decomposition back to reactants. The rds will involve the rate of combination of E and S to form the ES complex. The ES complex will be short lived since it does not accumulate to form products.

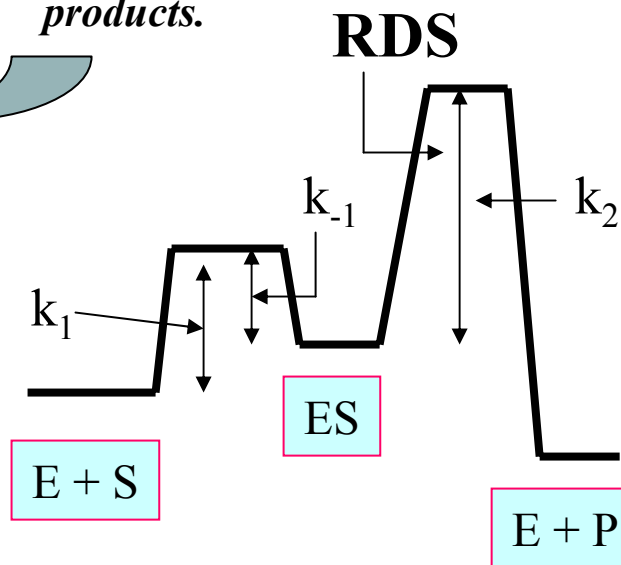


$\theta \ll 1$  scenario.

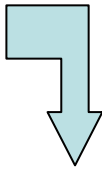
$$1 + \theta \cong 1$$

$$k_U \cong K_1 k_2$$

Have a fast pre-equilibrium followed by a slow rate determining decomposition of the ES complex to form products.



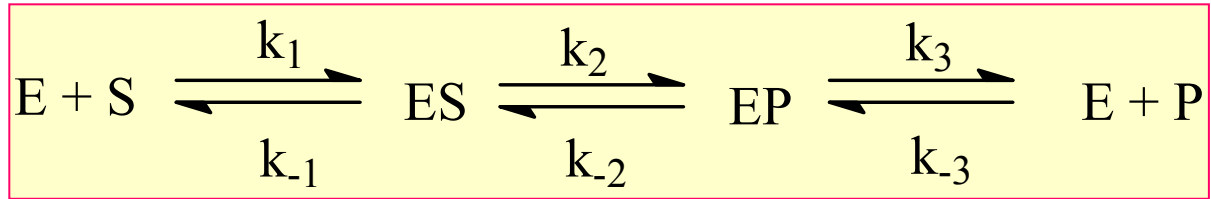
# Case S



$$\begin{aligned}
 s_0 &\gg K_M \\
 \frac{s_0}{K_M} &\gg 1 \\
 \frac{K_M}{k_C s_0} &\ll \frac{1}{k_C} \\
 \frac{1}{k_\Sigma} &\cong \frac{1}{k_C} \\
 k_\Sigma &\cong k_C = k_2
 \end{aligned}$$

*Saturated enzyme kinetics : all active sites in enzyme bound with substrate.  
Have slow rate determining breakdown of ES complex to form products.*

*The detailed form of  $K_M$  and  $k_C$  in terms of fundamental rate constants will depend on the nature of the mechanism.*



*LB inverse plot will always pertain.*

$$\frac{e_\Sigma}{R_{\Sigma,0}} = \frac{K_M}{k_C} \frac{1}{s_0} + \frac{1}{k_C}$$

*Pre equilibrium*

# Case US

$$\frac{K_M}{k_C} = \frac{1}{k_1} + \frac{1}{K_1 k_2} + \frac{1}{K_1 K_2 k_3}$$

*ES complex formation rds*

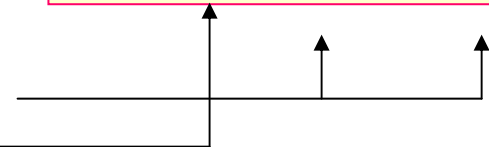
*Slow rate determining ES->EP transformation*

*Slow rate determining EP complex decomposition.*

# Case S

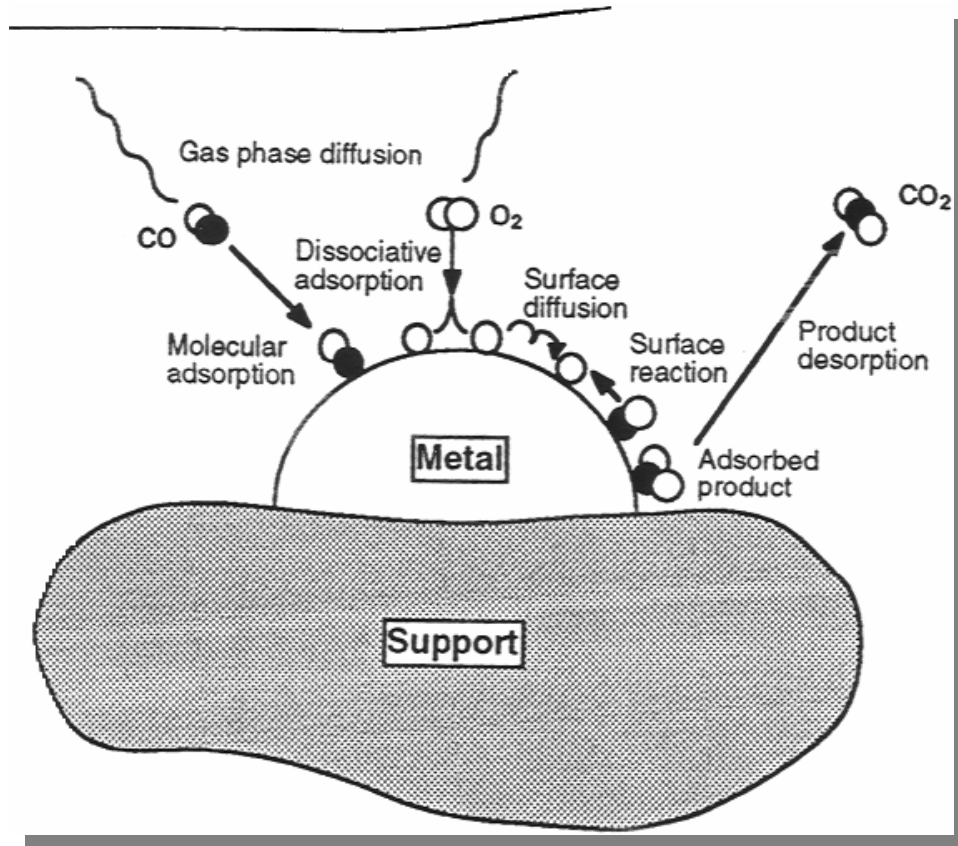
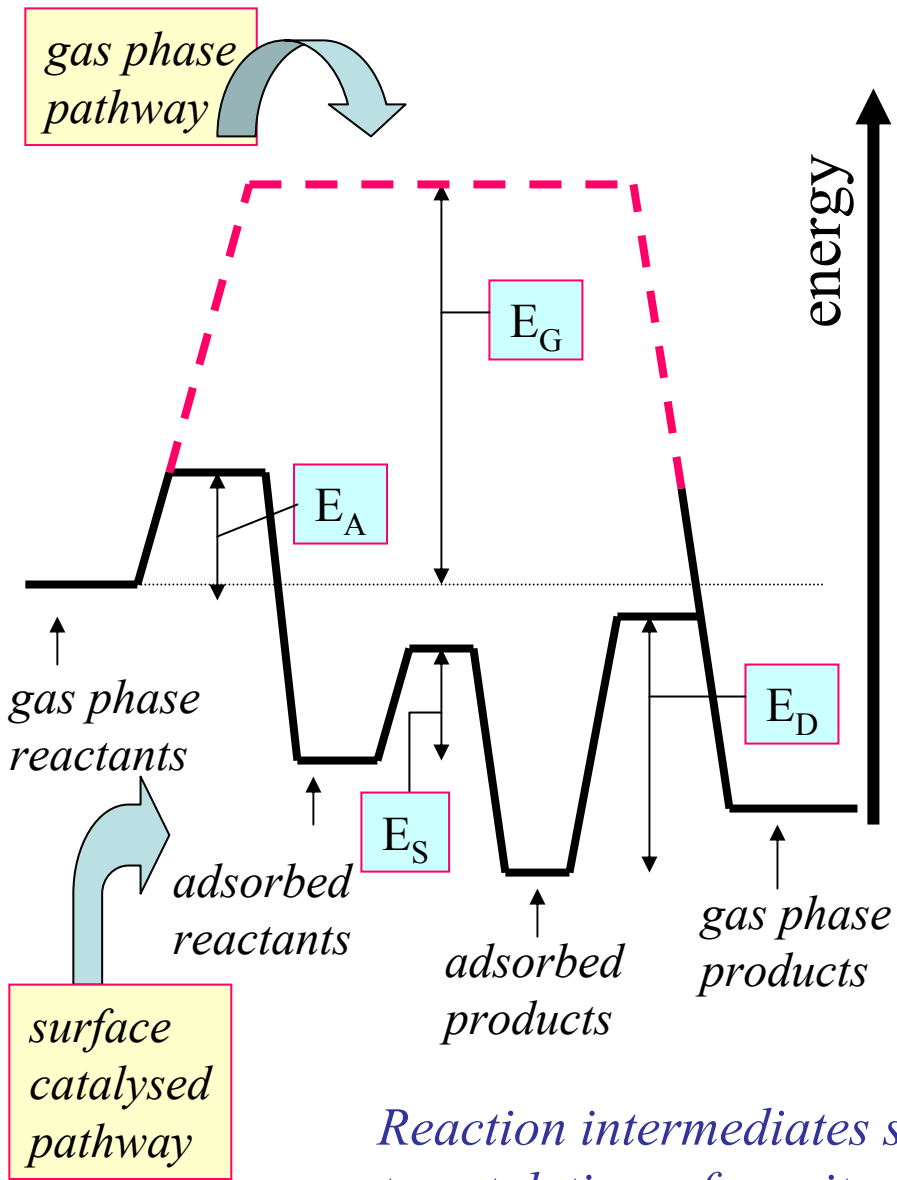
*Pre equilibrium*

$$\frac{1}{k_C} = \frac{1}{k_2} + \frac{1}{k_3} + \frac{1}{K_2 k_3}$$





# Catalysis at solid surfaces.



$E_j$  = activation energy for step  $j$ .

- G : gas phase reaction
- A : adsorption
- S : surface reaction
- D : desorption

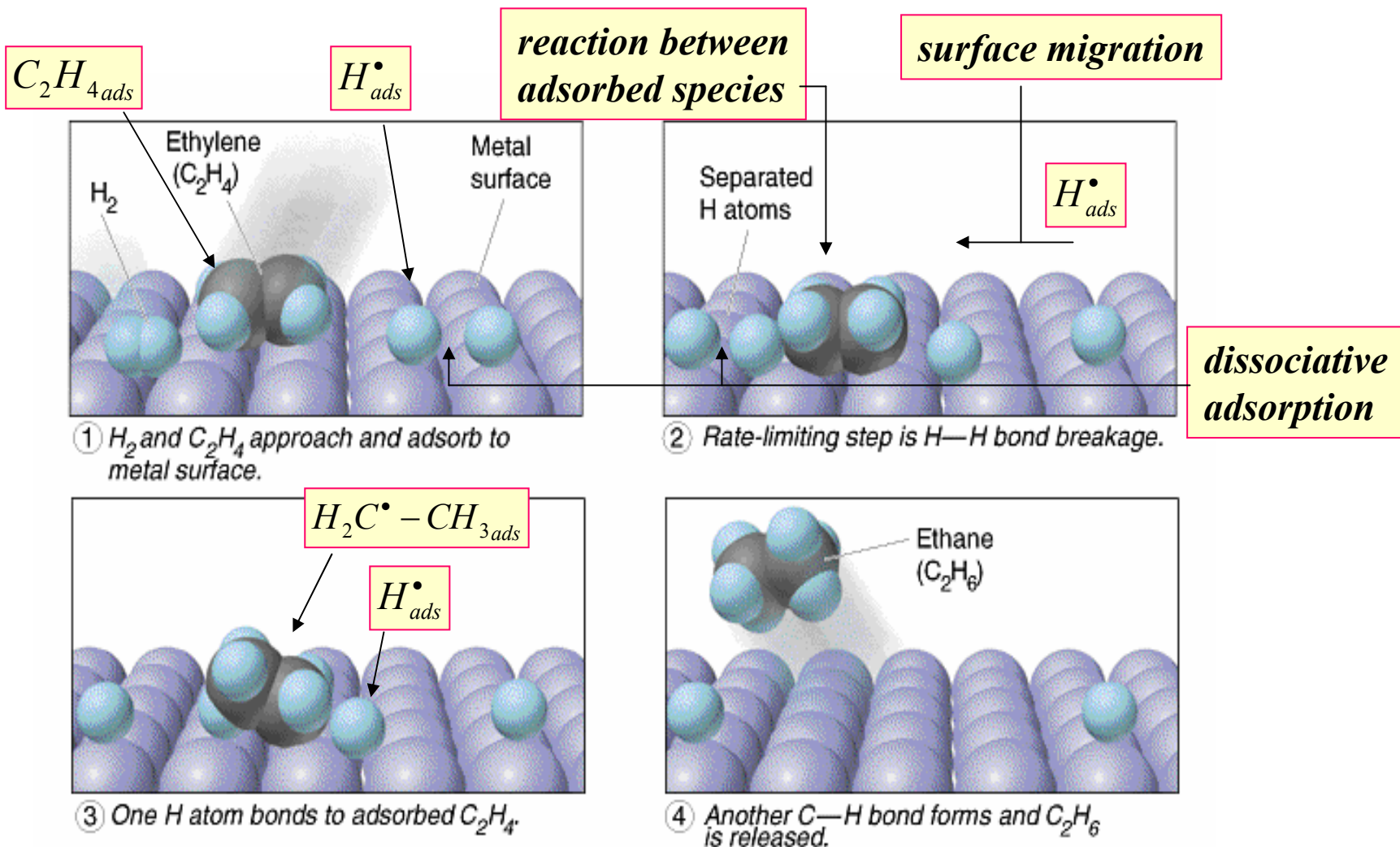
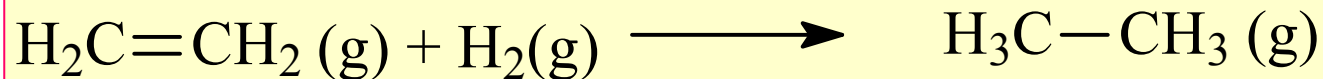
*Reaction intermediates stabilized via bonding to catalytic surface sites.*

# Processes Based on Catalysis

**Table 16.7 Some Modern Processes Based on Catalysis**

<b>Reactants</b>	<b>Catalyst</b>	<b>Product</b>	<b>Use</b>
<b>Homogeneous</b>			
Propylene, oxidizer	Mo(VI) complexes	Propylene oxide	Polyurethane foams; polyesters
Methanol, CO	$[\text{Rh}(\text{CO})_2\text{I}_2]^-$	Acetic acid	Poly (vinyl acetate) coatings; poly(vinyl alcohol)
Butadiene, HCN	Ni/P compounds	Adiponitrile	Nylons (fibers, plastics)
$\alpha$ -Olefins, CO, H <sub>2</sub>	Rh/P compounds	Aldehydes	Plasticizers, lubricants
<b>Heterogeneous</b>			
Ethylene, O <sub>2</sub>	Silver, cesium chloride on alumina	Ethylene oxide	Polyesters, ethylene glycol, lubricants
Propylene, NH <sub>3</sub> , O <sub>2</sub>	Bismuth molybdates	Acrylonitrile	Plastics, fibers, resins
Ethylene	Organochromium and titanium halides on silica	High-density polyethylene	Molded products

# The Metal-Catalyzed Hydrogenation of Ethylene



# Adsorption at gas/solid interface.

**Adsorption.** Term used to describe the process whereby a molecule (the **adsorbate**) forms a bond to a solid surface (an **adsorbent**).

Fractional surface coverage  $\theta$

$$\theta = \frac{N_s}{N_\Sigma}$$

← number of sites occupied by adsorbate

← total number of adsorption sites

When  $\theta = 1$ ,  $N_s = N_\Sigma$  and an adsorbed monolayer is formed.

The fractional coverage  $\theta$  depends on pressure of adsorbing gas phase species.

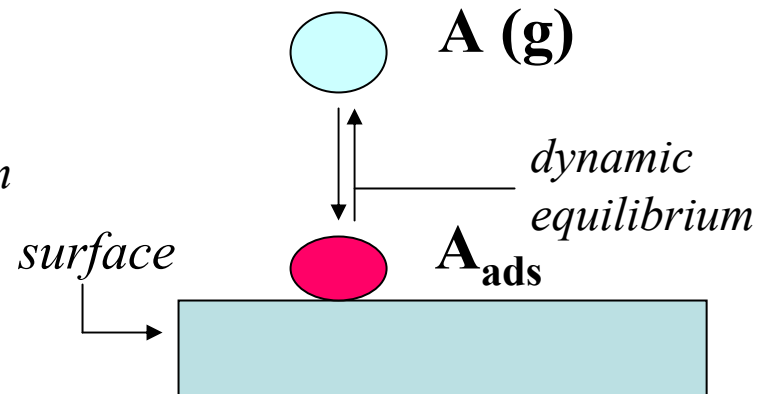
This  $\theta = \theta(p)$  relationship is called an adsorption isotherm.

## Langmuir Adsorption Isotherm.

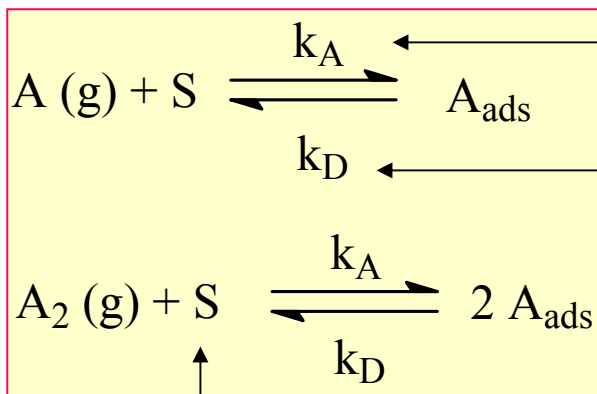
Simple approach to quantitatively describe an adsorption process at the gas/solid interface.

Assumptions :

- solid surface is homogeneous and contains a number of equivalent sites, each of which is occupied by a single adsorbate molecule
- a dynamic equilibrium exists between gas phase reactant and adsorbed species
- no interactions between adsorbed species
- adsorbed species localised,  $\Delta H_{ads}$  is independent of coverage  $\theta$



associative adsorption



adsorption rate constant

desorption rate constant

surface adsorption site

K measures affinity of a particular molecule for an adsorption site.

$$K = \frac{k_A}{k_D}$$

dissociative adsorption

At equilibrium :  $R_A = R_D$

$$k_A p(1 - \theta) = k_D \theta$$

Rate of adsorption :

$$R_A = k_A p(1 - \theta)$$

pressure  
fractional coverage of vacant sites

$$\theta = \frac{Kp}{1 + Kp}$$

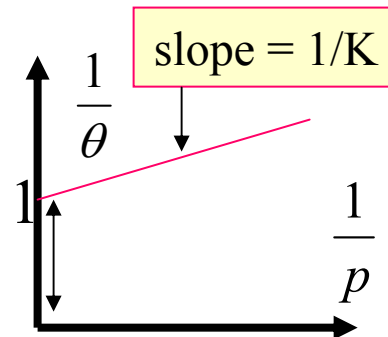
Langmuir adsorption isotherm :  
associative adsorption.

Rate of desorption :

$$R_D = k_D \theta$$

← fractional surface coverage

$$\frac{1}{\theta} = 1 + \frac{1}{Kp}$$



A similar analysis can be done for **dissociative** adsorption.

Adsorption  
rate

$$R_A = k_A p (1 - \theta)^2$$

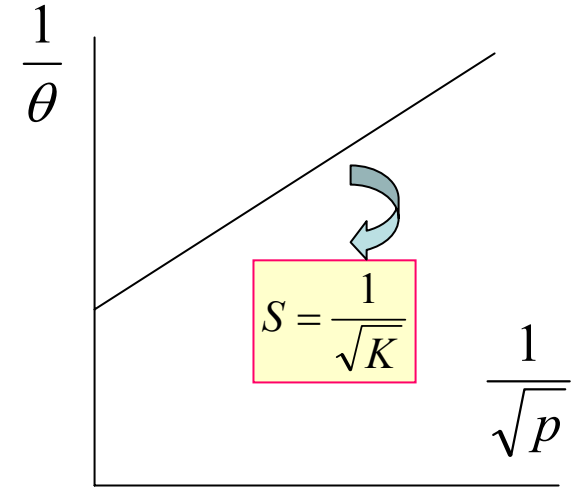
Desorption  
rate

$$R_D = k_D \theta^2$$

At equilibrium :

$$R_A = R_D$$

$$k_A p (1 - \theta)^2 = k_D \theta^2$$



Adsorption isotherm  
for dissociative  
adsorption.

$$\frac{\theta^2}{(1 - \theta)^2} = \frac{k_A}{k_D} p = Kp$$

$$\theta = \frac{\sqrt{Kp}}{1 + \sqrt{Kp}}$$

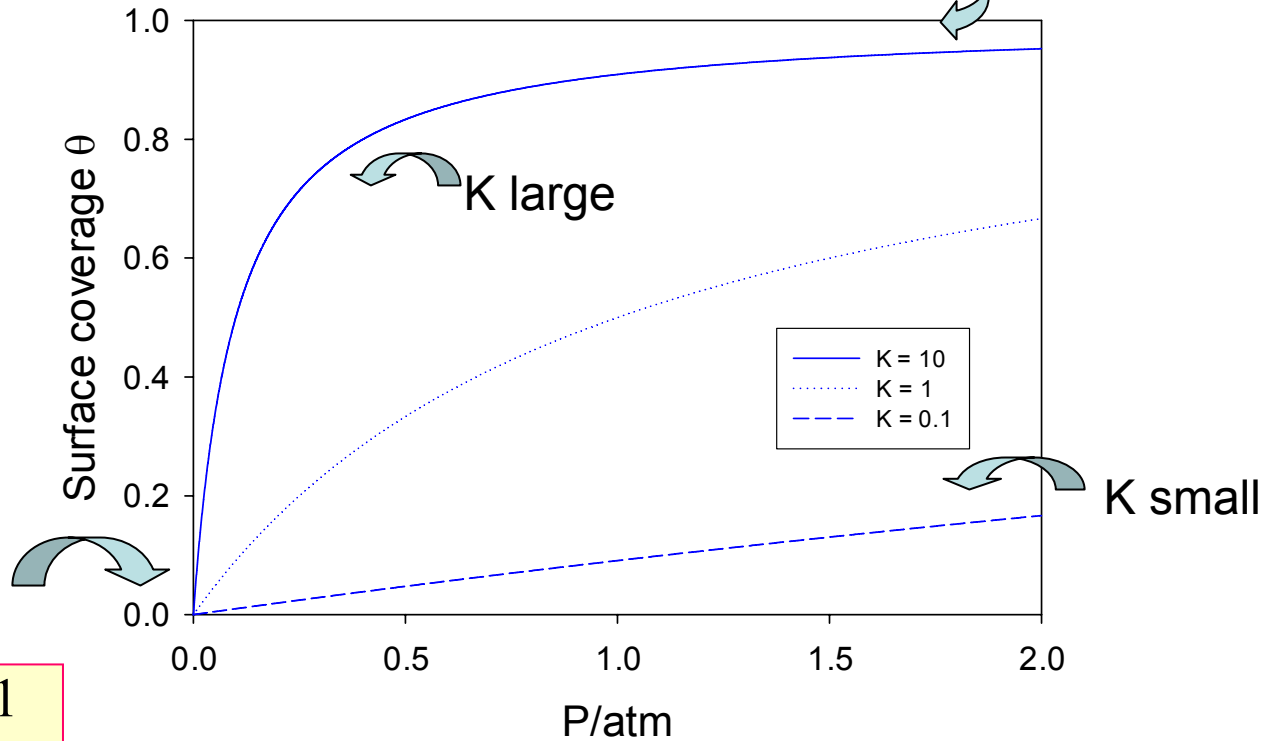
$$\frac{1}{\theta} = 1 + \frac{1}{\sqrt{Kp}}$$



# Langmuir Adsorption Isotherm.

high p  
limit :  
monolayer  
formed

$$Kp \gg 1$$
$$1 + Kp \cong Kp$$
$$\theta \rightarrow 1$$



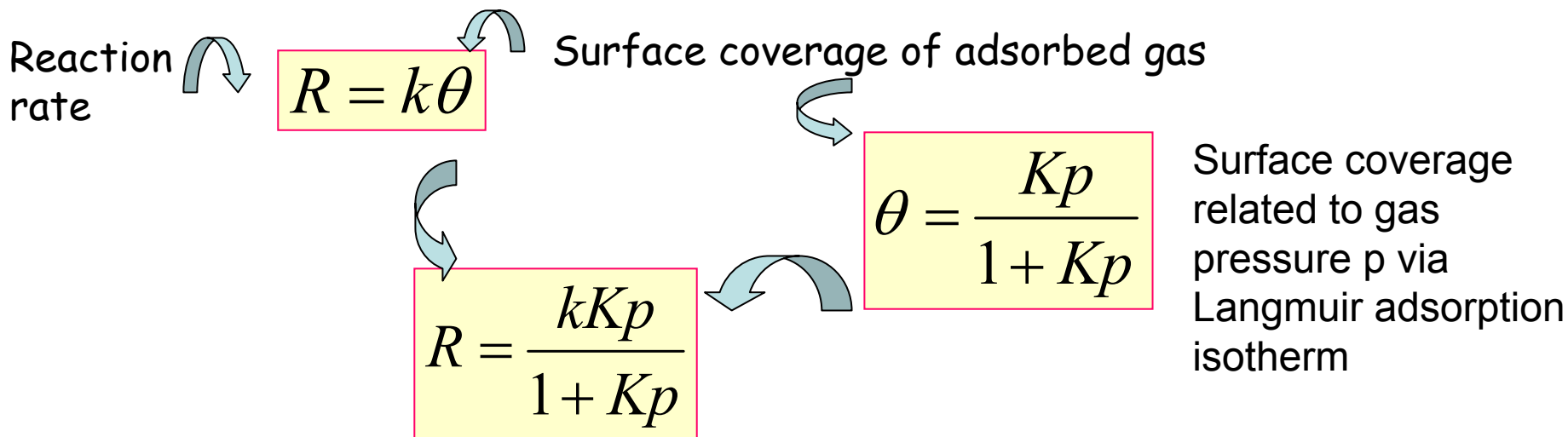
Low p limit :  
Henry Law

$$Kp \ll 1$$
$$1 + Kp \cong 1$$
$$\theta \cong Kp$$

$$\theta = \frac{Kp}{1 + Kp}$$

# Kinetics of surface reactions.

Assume that gaseous reactant decomposes when it is adsorbed.



We can consider two limits.

## High pressures.

$$Kp \gg 1$$

Rate independent of Gas pressure  $p$   
Zero order kinetics.

$$R \cong k$$

Adsorption rate very large when  $p$  is high.  
Decomposition step rds.

## Low pressures.

$$Kp \ll 1$$

Rate depends linearly on gas Pressure  $p$   
First order kinetics.  
Adsorption process is rate determining when  $p$  is low.  
Decomposition is fast.

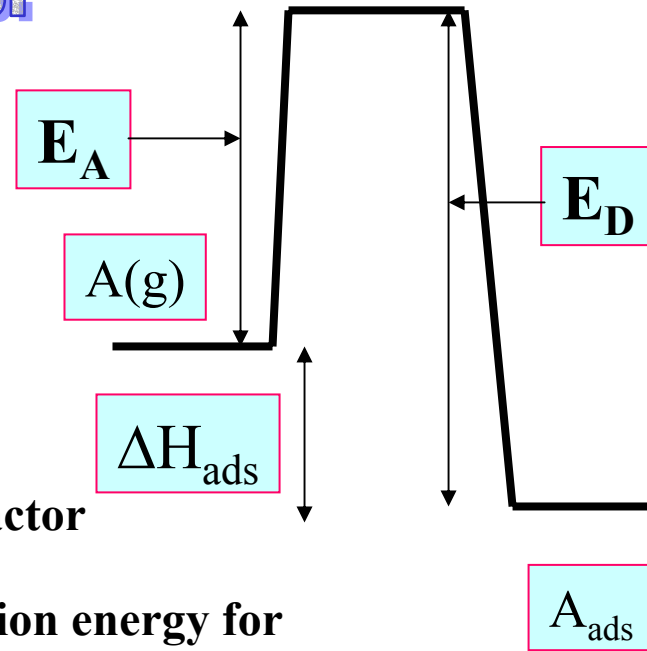
$$R \cong kKp$$



# Adsorption energetics.

Adsorption of a gas on a solid is an exothermic process :  $\Delta H_{ads}$  is negative.

Both adsorption and desorption processes follow the Arrhenius equation.



adsorption pre-exponential factor

$$k_A = A_A \exp\left[-\frac{E_A}{RT}\right]$$

activation energy for adsorption

$$k_D = A_D \exp\left[-\frac{E_D}{RT}\right]$$

activation energy for desorption

temperature (K)

desorption pre-exponential factor

$$K = \frac{k_A}{k_D} = \frac{A_A}{A_D} \exp\left[-\frac{\Delta H_{ads}}{RT}\right]$$

$$\Delta H_{ads} = E_A - E_D$$

$R = \text{gas constant} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

How is  $\Delta H_{ads}$  measured ? *entropy of adsorption*

$$\Delta G_{ads}^0 = -RT \ln K = \Delta H_{ads}^0 - T\Delta S_{ads}^0$$

*Gibbs energy of adsorption*

*enthalpy of adsorption*

$$\ln K = -\frac{\Delta H_{ads}^0}{RT} + \frac{\Delta S_{ads}^0}{R}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_\theta = \frac{\Delta H_{ads}^0}{RT^2}$$

*constant surface coverage*

*Langmuir adsorption assumed*

$$Kp = \frac{\theta}{1-\theta}$$

$$\ln K + \ln p = \ln \left\{ \frac{\theta}{1-\theta} \right\}$$

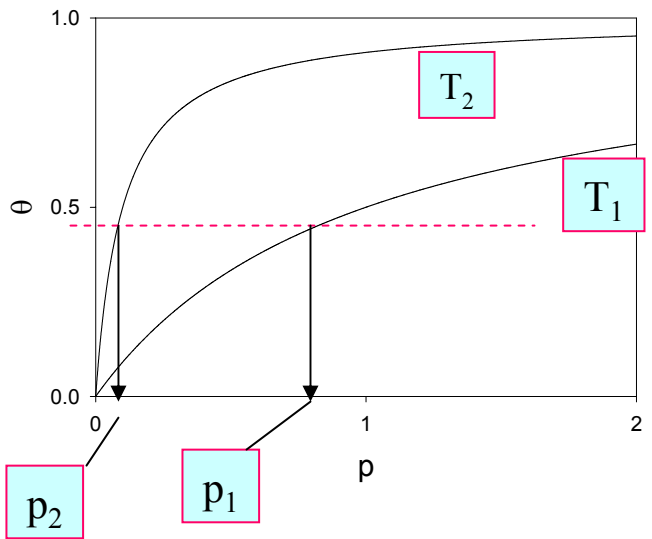
$$\left(\frac{\partial \ln K}{\partial T}\right)_\theta + \left(\frac{\partial \ln p}{\partial T}\right)_\theta = 0$$

$$\left(\frac{\partial \ln p}{\partial T}\right)_\theta = -\left(\frac{\partial \ln K}{\partial T}\right)_\theta$$

*constant surface coverage*

$$\left(\frac{\partial \ln p}{\partial T}\right)_\theta = -\frac{\Delta H_{ads}^0}{RT^2}$$

$$\left[ \ln \left( \frac{p_1}{p_2} \right) \right]_\theta = \frac{\Delta H_{ads}^0}{R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}$$



$p_1, p_2, T_1$  and  $T_2$  can be measured so  $\Delta H_{ads}$  can be determined.

# Chemical Kinetics.

Lectures 5-6.

Microscopic theory of chemical  
reaction kinetics.

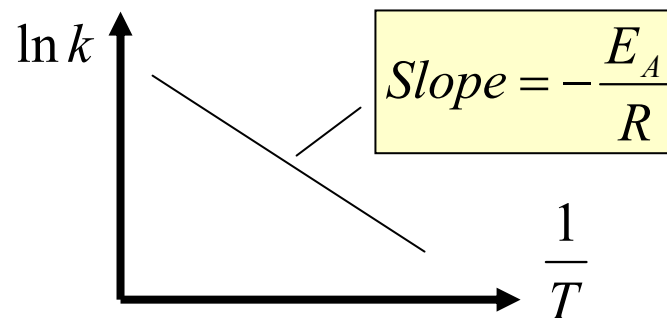
# Temperature effects in chemical kinetics.

- Chemical reactions are activated processes : they require an energy input in order to occur.
- Many chemical reactions are activated via thermal means.
- The relationship between rate constant  $k$  and temperature  $T$  is given by the empirical **Arrhenius equation**.
- The activation energy  $E_A$  is determined from experiment, by measuring the rate constant  $k$  at a number of different temperatures. The Arrhenius equation is used to construct an Arrhenius plot of  $\ln k$  versus  $1/T$ . The activation energy is determined from the slope of this plot.

$$E_A = -R \left( \frac{d \ln k}{d(1/T)} \right) = RT^2 \left( \frac{d \ln k}{dT} \right)$$

$$k = A \exp \left[ -\frac{E_A}{RT} \right]$$

Pre-exponential factor



# Microscopic theories of chemical reaction kinetics.

- A basic aim is to calculate the rate constant for a chemical reaction from first principles using fundamental physics.
- Any microscopic level theory of chemical reaction kinetics must result in the derivation of an expression for the rate constant that is consistent with the empirical Arrhenius equation.
- A microscopic model should furthermore provide a reasonable interpretation of the pre-exponential factor  $A$  and the activation energy  $E_A$  in the Arrhenius equation.
- We will examine two microscopic models for chemical reactions :
  - The collision theory.
  - The activated complex theory.
- The main emphasis will be on **gas phase bimolecular reactions** since reactions in the gas phase are the most simple reaction types.

# References for Microscopic Theory of Reaction Rates.

- **Collision Theory.**

- Atkins, de Paula, Physical Chemistry 7<sup>th</sup> edition, Chapter 27, Section. 27.1, pp.944-951.

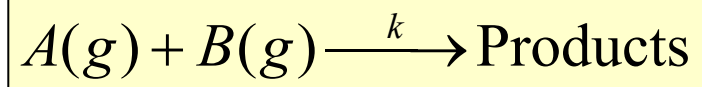
- **Activated Complex Theory.**

- Atkins, de Paula, Physical Chemistry 7<sup>th</sup> edition, Chapter 27, Section.27.4-27.5, pp. 956-961.

# Collision theory of bimolecular gas phase reactions.

- We focus attention on gas phase reactions and assume that chemical reactivity is due to collisions between molecules.
- The theoretical approach is based on the kinetic theory of gases.
- Molecules are assumed to be hard structureless spheres. Hence the model neglects the discrete chemical structure of an individual molecule. This assumption is unrealistic.
- We also assume that no interaction between molecules until contact.
- Molecular spheres maintain size and shape on collision. Hence the centres cannot come closer than a distance  $\delta$  given by the sum of the molecular radii.
- The reaction rate will depend on two factors :
  - *the number of collisions per unit time (the collision frequency)*
  - *the fraction of collisions having an energy greater than a certain threshold energy  $E^*$ .*

# Simple collision theory : quantitative aspects.



↑  
Hard sphere reactants

→ Molecular structure and details of internal motion such as vibrations and rotations ignored.

Two basic requirements dictate a collision event.

- One must have an A,B encounter over a sufficiently short distance to allow reaction to occur.
- Colliding molecules must have sufficient energy of the correct type to overcome the energy barrier for reaction. A threshold energy  $E^*$  is required.

Two basic quantities are evaluated using the Kinetic Theory of gases : the collision frequency and the fraction of collisions that activate molecules for reaction.

To evaluate the collision frequency we need a mathematical way to define whether or not a collision occurs.



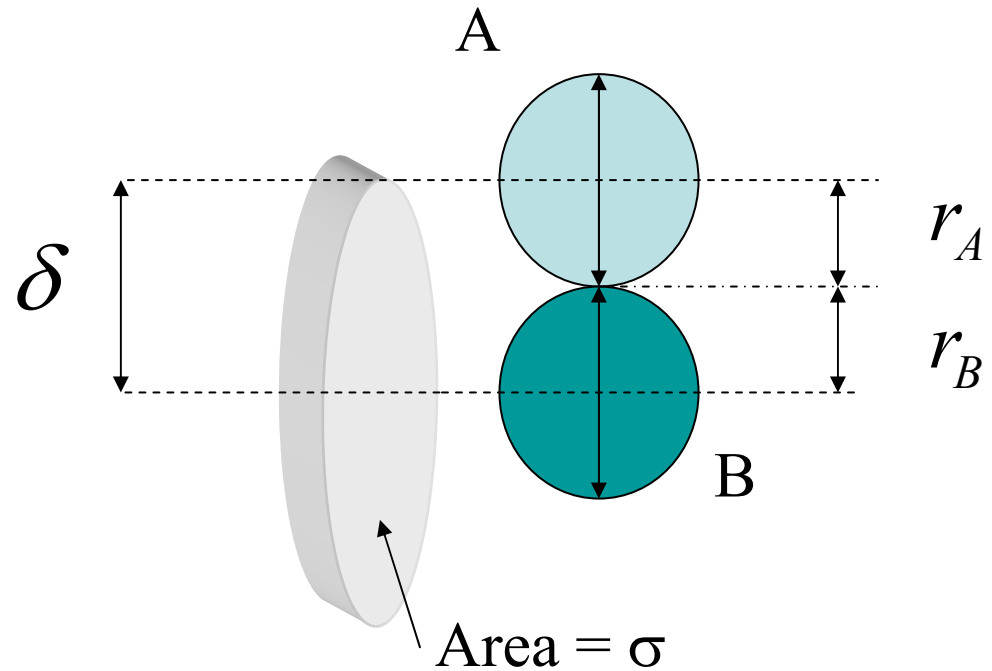
# Collision cross section and collision diameter.

The collision cross section  $\sigma$  defines when a collision occurs.

$$\sigma = \pi\delta^2 = \pi(r_A + r_B)^2$$

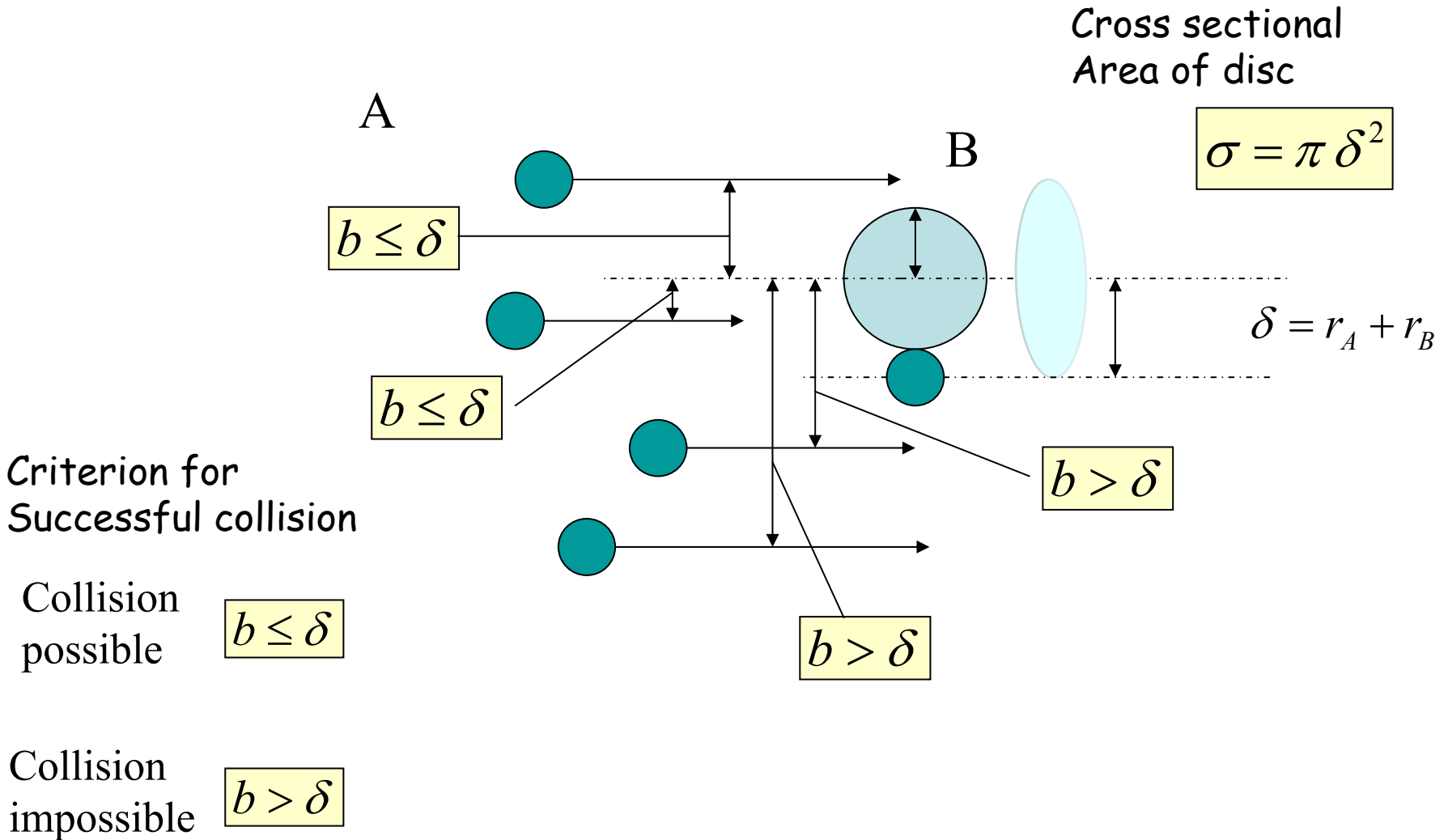
Effective collision diameter

$$\delta = r_A + r_B$$



The **collision cross section** for two molecules can be regarded to be the area within which the center of the projectile molecule A must enter around the target molecule B in order for a collision to occur.

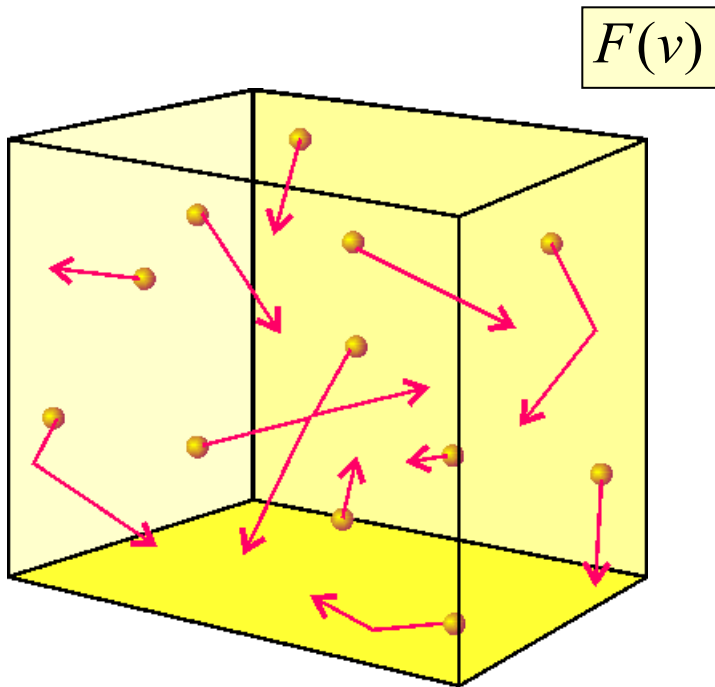
# Hit or miss: the impact parameter $b$ .



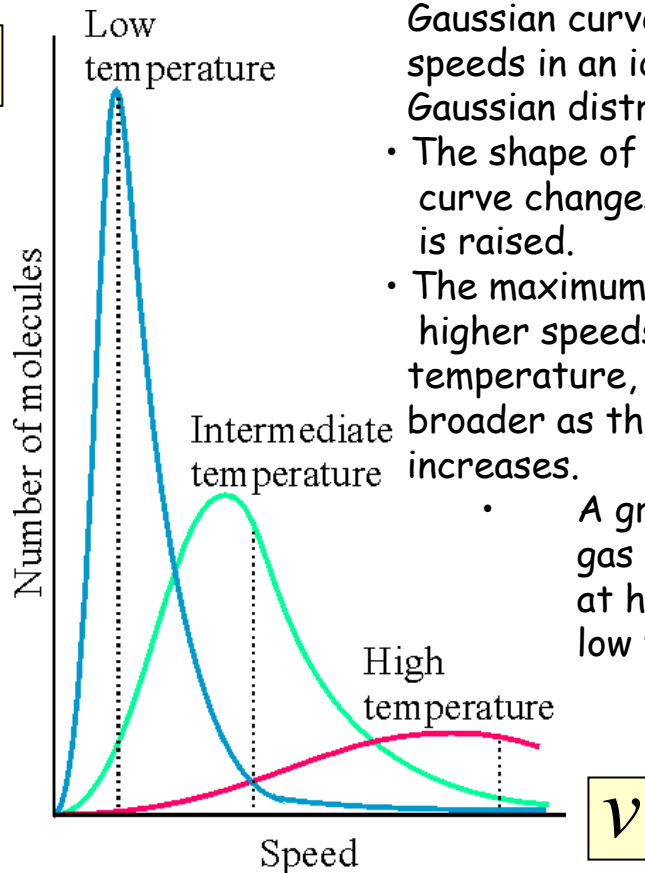
# Maxwell-Boltzmann velocity

## Distribution function

$$F(v) = 4\pi v^2 \left\{ \frac{m}{2\pi k_B T} \right\}^{3/2}$$



Gas molecules exhibit a spread or distribution of speeds.



- The velocity distribution curve has a very characteristic shape.
- A small fraction of molecules move with very low speeds, a small fraction move with very high speeds, and the vast majority of molecules move at intermediate speeds.
- The bell shaped curve is called a Gaussian curve and the molecular speeds in an ideal gas sample are Gaussian distributed.
- The shape of the Gaussian distribution curve changes as the temperature is raised.
- The maximum of the curve shifts to higher speeds with increasing temperature, and the curve becomes broader as the temperature increases.
  - A greater proportion of the gas molecules have high speeds at high temperature than at low temperature.

The collision frequency is computed via the kinetic Theory of gases.

We define a collision number (units:  $\text{m}^{-3}\text{s}^{-1}$ )  $Z_{AB}$ .

$$Z_{AB} = \pi \delta^2 n_A n_B \langle v_r \rangle$$

Mean relative velocity  
Units:  $\text{m}^2\text{s}^{-1}$

$n_j$  = number density of molecule j (units :  $\text{m}^{-3}$ )

$$\delta = r_A + r_B$$

Mean relative velocity evaluated via kinetic theory.

Average velocity of a gas molecule

$$\langle v \rangle = \int_0^\infty v F(v) dv$$

$$F(v) = 4\pi v^2 \left\{ \frac{m}{2\pi k_B T} \right\}^{3/2} \exp\left[ -\frac{mv^2}{2k_B T} \right]$$

Maxwell-Boltzmann velocity Distribution function

MB distribution of velocities enables us to statistically estimate the spread of molecular velocities in a gas

Some maths !

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$$

Mass of molecule

We now relate the average velocity to the mean relative velocity.

If A and B are **different molecules** then

$$\langle v_r \rangle = \sqrt{\langle v_A \rangle^2 + \langle v_B \rangle^2}$$

$$\langle v_j \rangle = \sqrt{\frac{8k_B T}{\pi m_j}}$$

$$\langle v_r \rangle = \sqrt{\frac{8k_B T}{\pi \mu}}$$

Reduced mass

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

Hence the collision number between unlike molecules can be evaluated.

$$Z_{AB} = \pi \delta^2 n_A n_B \langle v_r \rangle$$

$$Z_{AB} = n_A n_B \sigma \left\{ \frac{8k_B T}{\pi \mu} \right\}^{1/2}$$

$$= Z n_A n_B$$

Collision frequency factor

For **collisions between like molecules**

$$\langle v_r \rangle = \sqrt{2} \langle v \rangle$$

The number of collisions per unit time between a single A molecule and other A molecules

$$Z_A = n_A \sigma \sqrt{2} \left\{ \frac{8k_B T}{\pi m_A} \right\}^{1/2}$$

Total number of collisions between like molecules

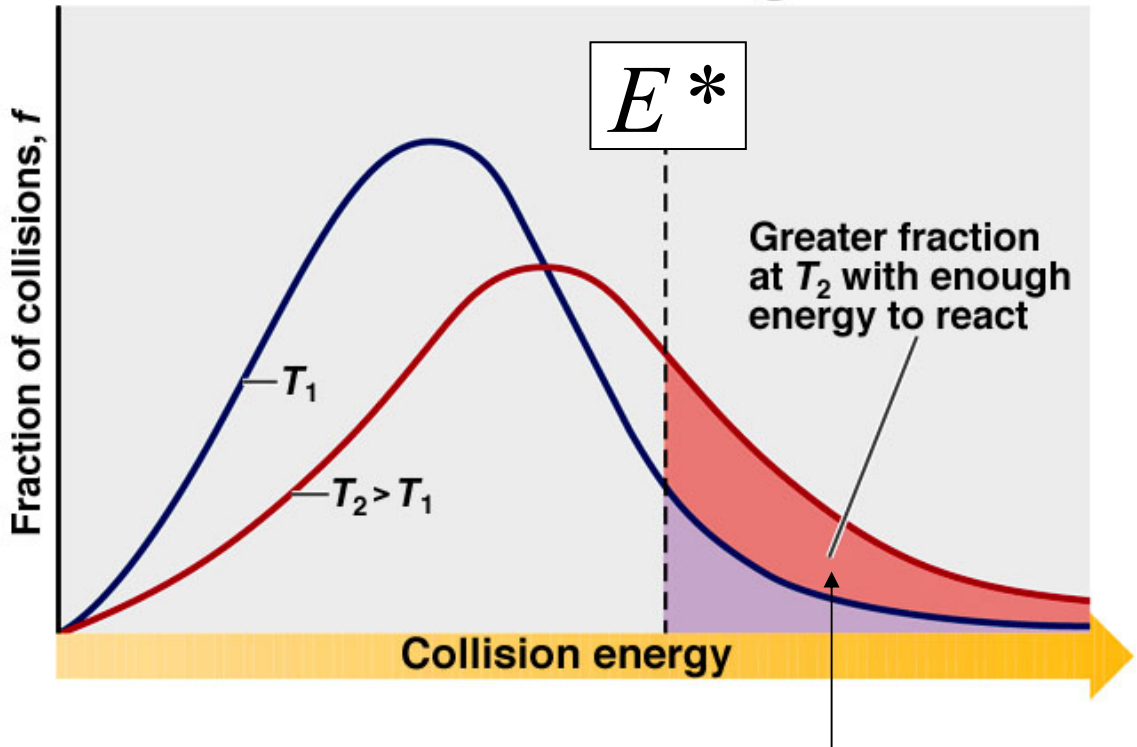
$$Z_{AA} = \frac{Z_A n_A}{2} = \frac{\sqrt{2}}{2} n_A^2 \sigma \left\{ \frac{8k_B T}{\pi m_A} \right\}^{1/2}$$

We divide by 2 to ensure that each A,A encounter is not counted twice.

# Temperature and the Distribution of Collision Energies

Molecular collision is effective only if translational energy of reactants is greater than some threshold value.

Fraction of molecules with kinetic energy greater than some minimum threshold value  $\varepsilon^*$



$$F(\varepsilon > \varepsilon^*) = \exp\left[-\frac{\varepsilon^*}{k_B T}\right]$$

# Activation Energy

**Table 16.5** The Effect of  $E_a$  and  $T$  on the Fraction ( $f$ ) of Collisions with Sufficient Energy to Allow Reaction

$E_a$ (kJ/mol)	$f$ (at $T = 298$ K)
50	$1.70 \times 10^{-9}$
75	$7.03 \times 10^{-14}$
100	$2.90 \times 10^{-18}$
$T$	$f$ (at $E_a = 50$ kJ/mol)
25°C (298 K)	$1.70 \times 10^{-9}$
35°C (308 K)	$3.29 \times 10^{-9}$
45°C (318 K)	$6.12 \times 10^{-9}$

- The simple collision theory expression for the reaction rate  $R$  between unlike molecules

$$R = -\frac{dn_A}{dt} = Zn_A n_B \exp\left[-\frac{\varepsilon^*}{k_B T}\right]$$

$$Z = \sigma \left\{ \frac{8k_B T}{\pi \mu} \right\}^{1/2}$$

- The more usual rate expression for a bimolecular reaction between A and B is
- We introduce molar variables

$$R = -\frac{da}{dt} = kab$$

- Hence the SCT rate expression becomes

$$R = -\frac{da}{dt} = ZN_A ab \exp\left[-\frac{E^*}{RT}\right]$$

$$\begin{aligned} E^* &= N_A \varepsilon^* \\ a &= \frac{n_A}{N_A} \quad b = \frac{n_B}{N_A} \\ \frac{dn_A}{dt} &= N_A \frac{da}{dt} \end{aligned}$$

Avogadro constant

- The bimolecular rate constant for collisions between unlike molecules is given by

$$\begin{aligned} k &= 2N_A \sigma \left\{ \frac{k_B T}{\pi m} \right\}^{1/2} \exp\left[-\frac{E^*}{RT}\right] \\ &\downarrow \\ &= z_{AA} \exp\left[-\frac{E^*}{RT}\right] \end{aligned}$$

Collision Frequency factor

$$\begin{aligned} k &= N_A \sigma \left\{ \frac{8k_B T}{\pi \mu} \right\}^{1/2} \exp\left[-\frac{E^*}{RT}\right] \\ &\Rightarrow z_{AB} \exp\left[-\frac{E^*}{RT}\right] \end{aligned}$$

Both of these expressions are similar to the Arrhenius equation.

- Similarly for bimolecular collisions between like molecules



We compare the results of SCT with the empirical Arrhenius eqn. In order to obtain an interpretation of the activation energy and Pre-exponential factor.

$$k = 2N_A\sigma \left\{ \frac{k_B T}{\pi m} \right\}^{1/2} \exp\left[-\frac{E^*}{RT}\right]$$

$$= z_{AA} \exp\left[-\frac{E^*}{RT}\right]$$

**A,A encounters**

- SCT predicts that the pre-exponential factor should depend on temperature.

$$A_{obs} = z_{AA} = A''\sqrt{T}A$$

$$A'' = 2N_A\sigma \sqrt{\frac{8k_B}{\pi m}}$$

$$k = A_{obs} \exp\left[-\frac{E_A}{RT}\right]$$



**Arrhenius**

$$\frac{d \ln k}{dT} = \frac{E_A}{RT^2}$$

**A,B encounters**

$$k = N_A\sigma \left\{ \frac{8k_B T}{\pi \mu} \right\}^{1/2} \exp\left[-\frac{E^*}{RT}\right]$$

$$= z_{AB} \exp\left[-\frac{E^*}{RT}\right]$$



**SCT**

$$\frac{d \ln k}{dT} = \frac{E^* + RT/2}{RT^2}$$

- The threshold energy and the activation energy can also be compared.
- Activation energy exhibits a weak T dependence.

$$E_A = E^* + \frac{RT}{2}$$

$$E_A \cong E^*$$

**Pre-exponential factor**

# SCT : a summary.

- The major problem with SCT is that the threshold energy  $E^*$  is very difficult to evaluate from first principles.
- The predictions of the collision theory can be critically evaluated by comparing the experimental pre-exponential factor with that computed using SCT.
- We define the **steric factor**  $P$  as the ratio between the experimental and calculated  $A$  factors.

$$P = A_{\text{exp}} / A_{\text{calc}}$$
- We can incorporate  $P$  into the SCT expression for the rate constant.

$$k = Pz_{AB} \exp\left[-\frac{E^*}{RT}\right]$$
$$k = Pz_{AA} \exp\left[-\frac{E^*}{RT}\right]$$
- For many gas phase reactions  $P$  is considerably less than unity.
- Typically SCT will predict that  $A_{\text{calc}}$  will be in the region  $10^{10}$ - $10^{11}$   $\text{Lmol}^{-1}\text{s}^{-1}$  regardless of the chemical nature of the reactants and products.
- What has gone wrong? The SCT assumption of hard sphere collision neglects the important fact that **molecules possess an internal structure**. It also neglects the fact that the relative orientation of the colliding molecules will be important in determining whether a collision will lead to reaction.
- We need a better theory that takes molecular structure into account. The **activated complex theory** does just that .

# Summary of SCT.

## A, B encounters

$$k = N_A \sigma \left\{ \frac{8k_B T}{\pi \mu} \right\}^{1/2} \exp \left[ -\frac{E^*}{RT} \right]$$
$$= z_{AB} \exp \left[ -\frac{E^*}{RT} \right]$$

## A, A encounters

$$k = 2N_A \sigma \left\{ \frac{k_B T}{\pi m} \right\}^{1/2} \exp \left[ -\frac{E^*}{RT} \right]$$
$$= z_{AA} \exp \left[ -\frac{E^*}{RT} \right]$$

Transport property

Energy criterion

$$k = P z_{AB} \exp \left[ -\frac{E^*}{RT} \right]$$
$$k = P z_{AA} \exp \left[ -\frac{E^*}{RT} \right]$$

Steric factor  
(Orientation requirement)

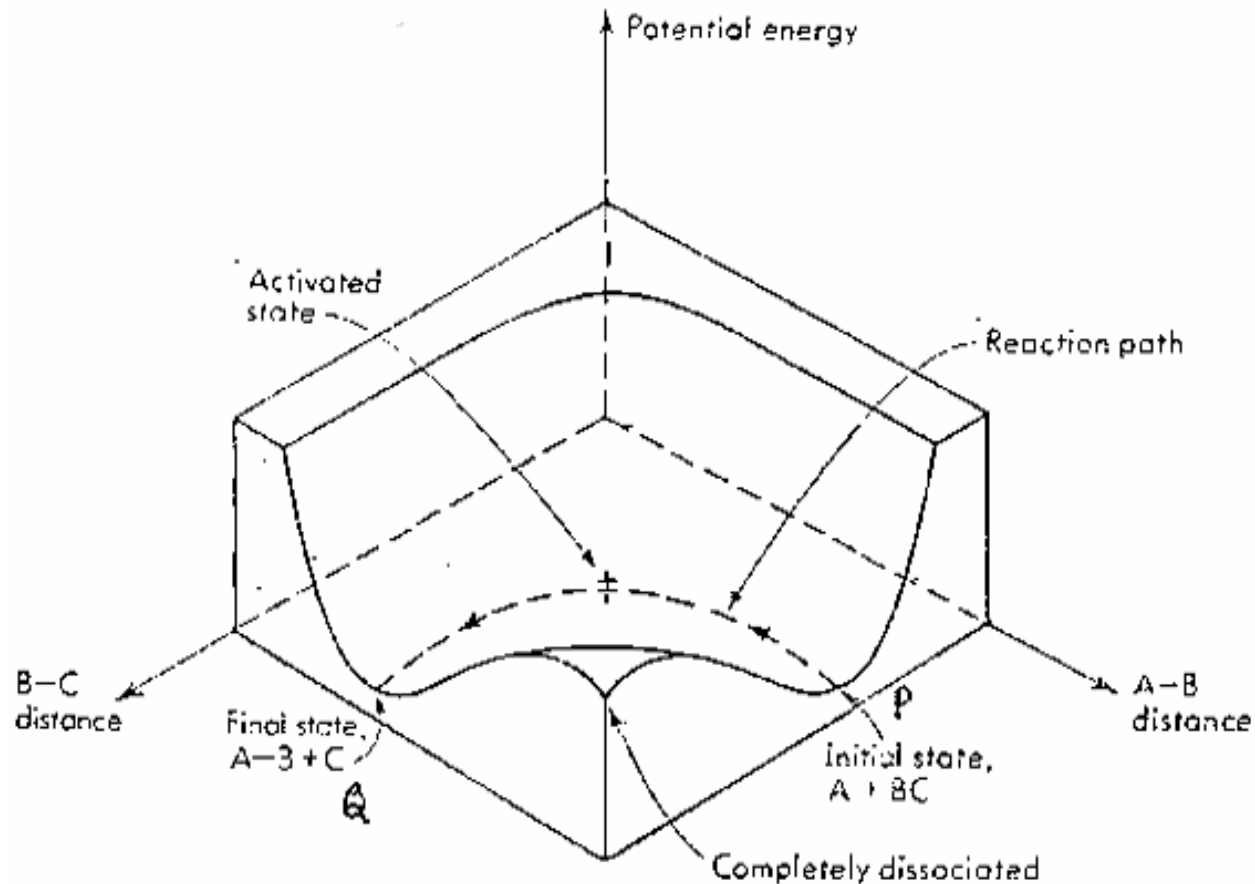
Weaknesses:

- No way to compute P from molecular parameters
  - No way to compute E\* from first principles.
- Theory not quantitative or predictive.

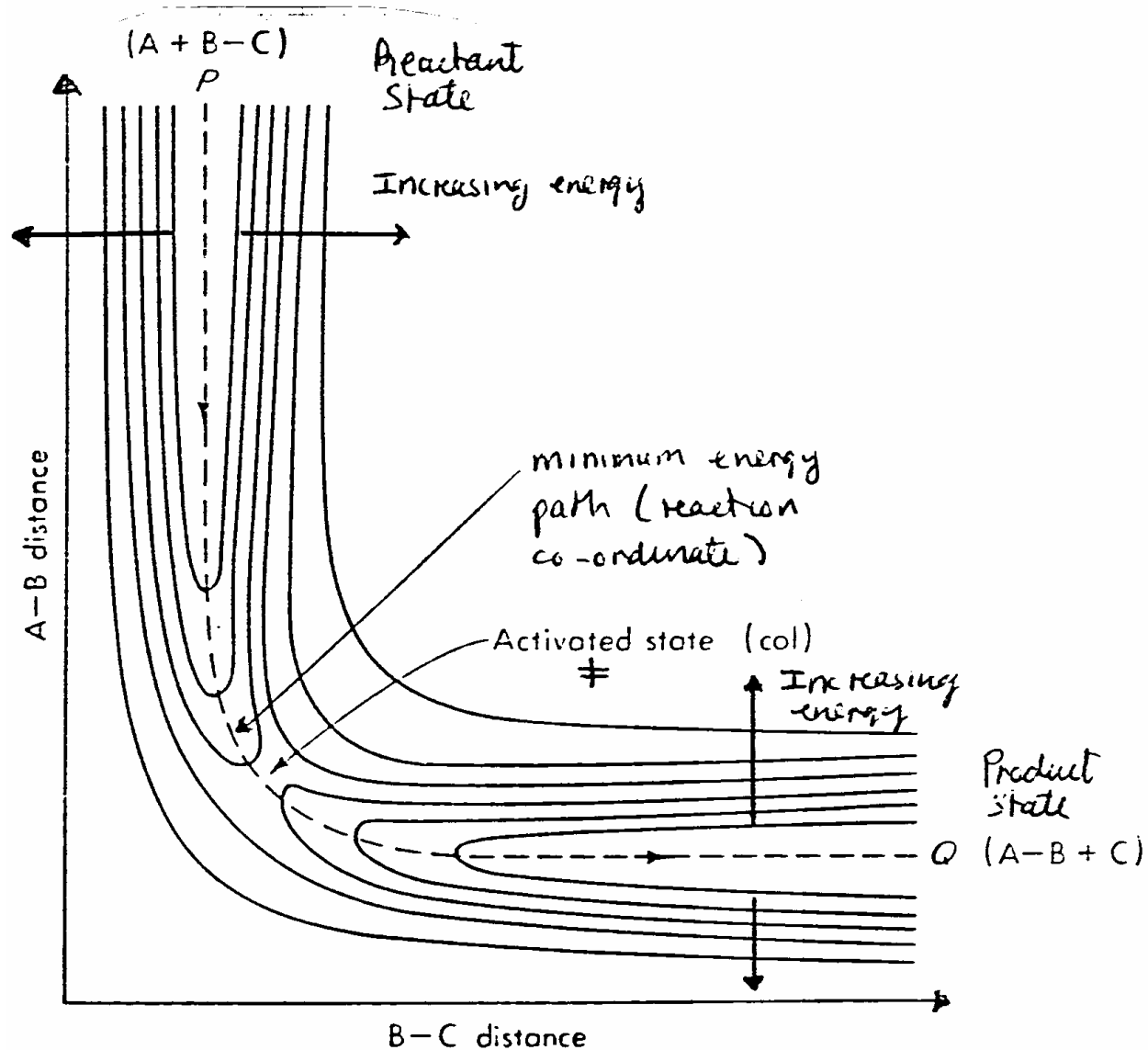
Strengths:

- Qualitatively consistent with observation (Arrhenius equation).
- Provides plausible connection between microscopic molecular properties and macroscopic reaction rates.
- Provides useful guide to upper limits for rate constant k.

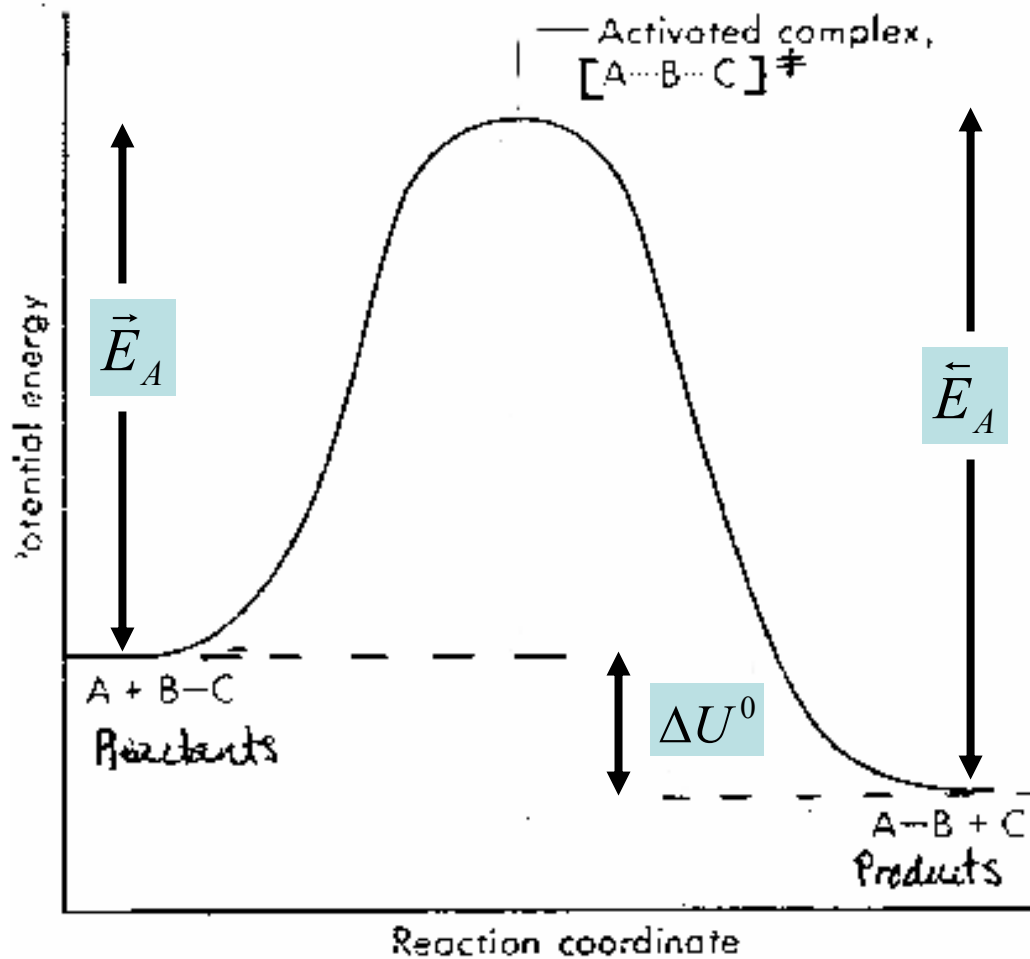
# Potential Energy Surface for a chemical reaction.



# Contour diagram illustrating reaction coordinate.



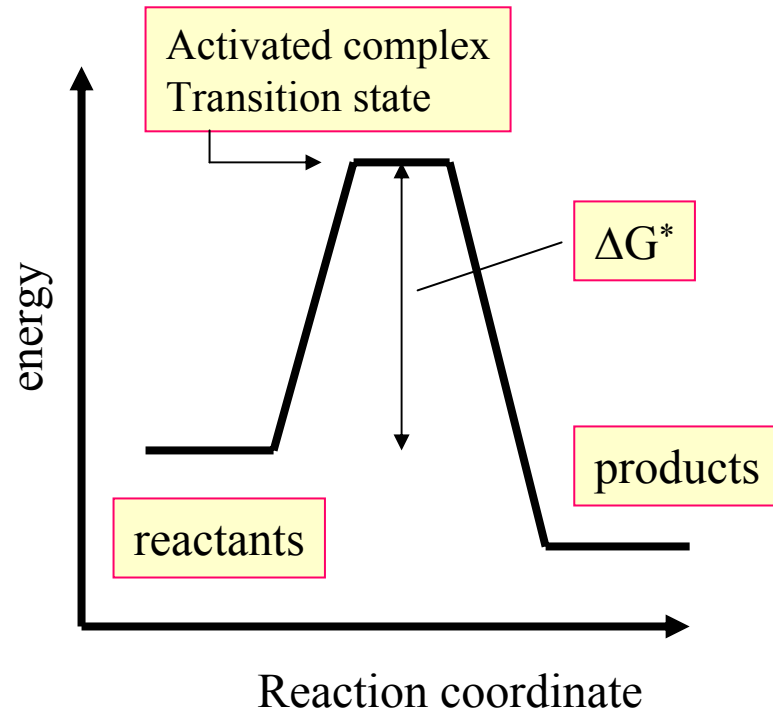
# Potential energy/reaction coordinate diagram.



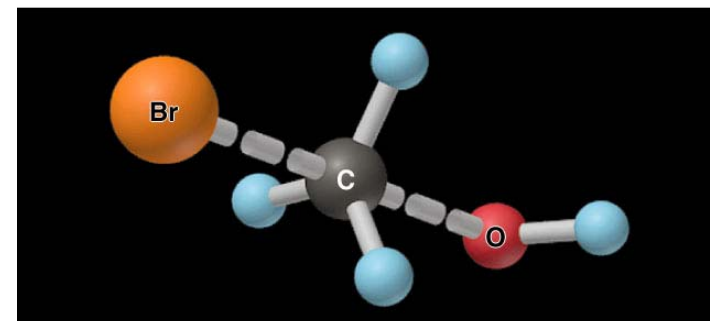
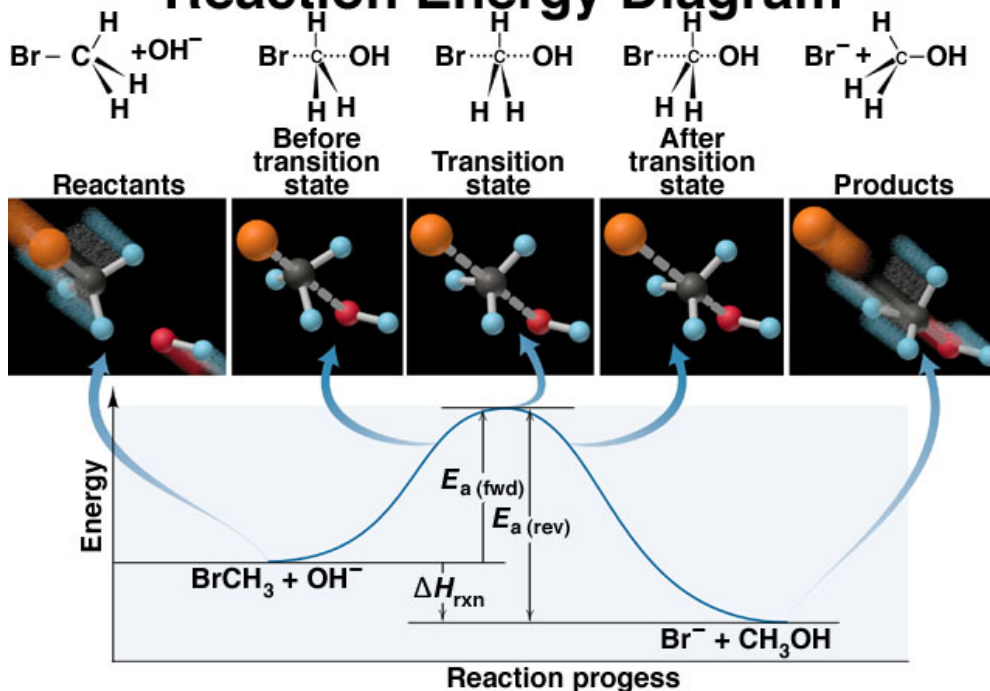
# Activated Complex Theory (ACT) of chemical reaction kinetics.

Progress of a chemical reaction can be expressed in terms of a plot of energy versus reaction co-ordinate.

The reaction coordinate may be described in terms of changes in particular bond lengths since these will vary as the reaction progresses.



## Reaction Energy Diagram



*Activated Complex  
or Transition State*

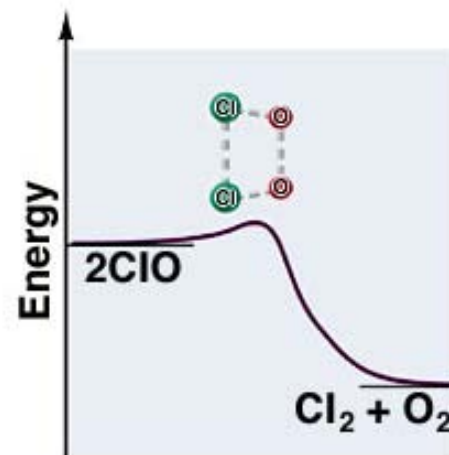
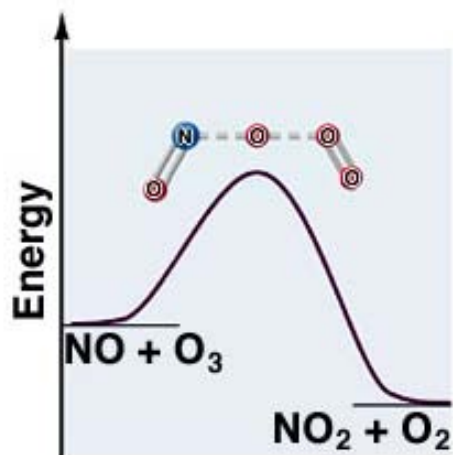
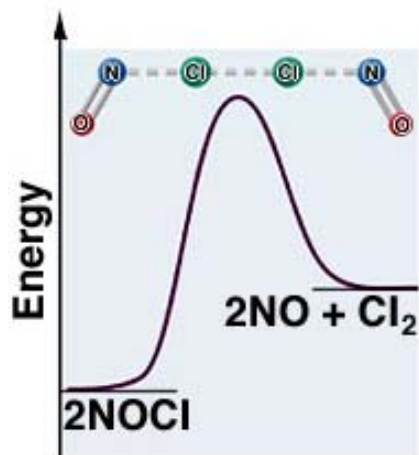
# Activated Complexes.

The *transition state* or *activated complex* is a high energy species of fleeting (ca fs lifetime,  $1\text{ fs} = 10^{-15}\text{ s}$ ) existence. Its structure has features both of the reactants and the products.

1999 Nobel Prize in Chemistry awarded to **Ahmed Zewail** from Caltech for his studies of transition states of chemical reactions by femtosecond spectroscopy using laser technology.

Experimental study of very short timescales is called *femtochemistry*.

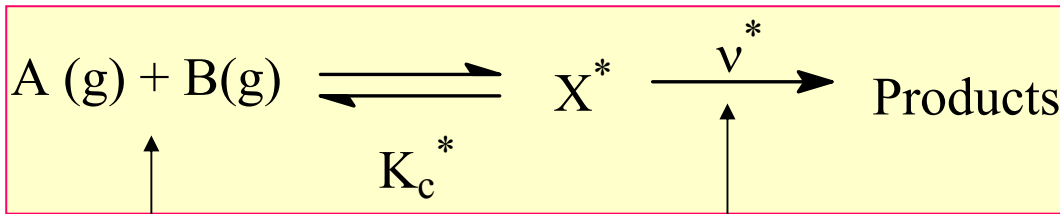
*Transition states can have different geometries.*





# Quantitative ACT.

Basic assumption : activated complex  $X^*$  is treated as a thermodynamic quantity in thermodynamic equilibrium with the reactants.



Bimolecular reaction

frequency of decomposition of activated complex

Equilibrium constant for reactant/transition state transformation.

Reaction rate  $R$  depends on the frequency of decomposition and concentration of activated complexes.

$$K_c^* = \frac{x^*}{ab}$$

$$R = \nu^* x^*$$

bimolecular reaction

$$R = \nu^* K_c^* ab$$

$$R = kab$$

$$x^* = K_c^* ab$$

rate constant

$$k = \nu^* K_c^*$$

Reaction molecularity  $m$  : number of molecules which come together to form the activated complex.

$m = 1$  : unimolecular reaction

$m = 2$  : bimolecular reaction .

This fundamental expression must now be evaluated.

For an ideal gas or for reactions in solution :

$$K_C^* = K^* (c^0)^{\Delta n^*}$$

thermodynamic  
equilibrium constant

1 molL<sup>-1</sup>

Change in # moles  
for reactant /TS  
transformation

$$\Delta n^* = 1 - 2 = -1$$

$$K_C^* = \frac{K^*}{c^0}$$

k has units Lmol<sup>-1</sup>s<sup>-1</sup>

We *assume* that the TS  
decomposes with a  
frequency given by:

$$\nu^* = \frac{k_B T}{h}$$

$$k = \nu^* K_C^* = \nu^* \left( \frac{K^*}{c^0} \right)$$

Not all transition states go and form  
products.

$$k = \kappa \nu^* K_C^* = \kappa \nu^* \left( \frac{K^*}{c^0} \right)$$

$$= \kappa \left\{ \frac{k_B T}{h c^0} \right\} K^*$$

$\kappa$  = transmission coefficient  
 $0 < \kappa < 1$

h = Planck's constant = 6.63x10<sup>-34</sup>J s  
k<sub>B</sub> = Boltzmann constant = 1.38x10<sup>-23</sup> JK<sup>-1</sup>

For T = 298 K

$$\nu^* \cong 6 \times 10^{12} \text{ s}^{-1}$$

This is of the correct  
order of magnitude for  
a molecular vibration  
frequency.

We relate  $K^*$  to the Gibbs energy of activation  $\Delta G^*$

$$\Delta G^{0*} = -RT \ln K^*$$

$$k = \kappa \left\{ \frac{k_B T}{hc^0} \right\} \exp \left[ -\frac{\Delta G^{0*}}{RT} \right]$$

$$K^* = \exp \left[ -\frac{\Delta G^{0*}}{RT} \right]$$

**Eyring equation** : fundamental ACT result.

$$\Delta G^{0*} = \Delta H^{0*} - T\Delta S^{0*}$$

$$k = \kappa \left\{ \frac{k_B T}{hc^0} \right\} \exp \left[ \frac{\Delta S^{0*}}{R} \right] \exp \left[ -\frac{\Delta H^{0*}}{RT} \right]$$

enthalpy of  
activation

entropy of  
activation

$$k = A \exp \left[ -\frac{E_A}{RT} \right]$$

We obtain a useful  
interpretation for  
activation energy and  
pre-exponential factor.

# Relating Arrhenius parameters and ACT results.

$$E_A = RT^2 \left( \frac{d \ln k}{dT} \right)$$

*internal energy of activation*

$$E_A = \Delta U^{0*} + RT$$

$$\Delta H^{0*} = \Delta U^{0*} + P\Delta V^{0*}$$

*condensed phases*

$$\Delta V^{0*} \cong 0$$

$$P\Delta V^{0*} = \Delta n^* RT = (1-m)RT = -RT$$

*ideal gases*

*volume of activation*

*m = 2 bimolecular reaction*

*reaction molecularity*

$$k = \kappa \left\{ \frac{k_B T}{hc^0} \right\} \exp \left[ \frac{\Delta S^{0*}}{R} \right] \exp \left[ -\frac{\Delta H^{0*}}{RT} \right]$$

*pre-exponential factor A*

$$k = \kappa \left( \frac{k_B T}{hc^0} \right) \exp \left[ 2 + \frac{\Delta S^{0*}}{R} \right] \exp \left[ -\frac{E_A}{RT} \right]$$

*bimolecular gas phase reaction*

$$\Delta H^{0*} = E_A - mRT$$

*m = 1, condensed phases, unimolecular gas phase reactions*  
*m = 2, bimolecular gas phase reactions*

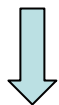
# ACT interpretation of the Arrhenius equation.

$$k_m = \kappa \left( \frac{k_B T}{h(c^0)^{m-1}} \right) \exp \left[ m + \frac{\Delta S^{0*}}{R} \right] \exp \left[ -\frac{E_A}{RT} \right]$$

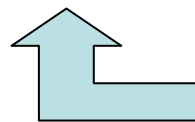
$m = \text{molecularity}$

$$A = \kappa \left( \frac{k_B T}{h(c^0)^{m-1}} \right) \exp \left[ m + \frac{\Delta S^{0*}}{R} \right]$$

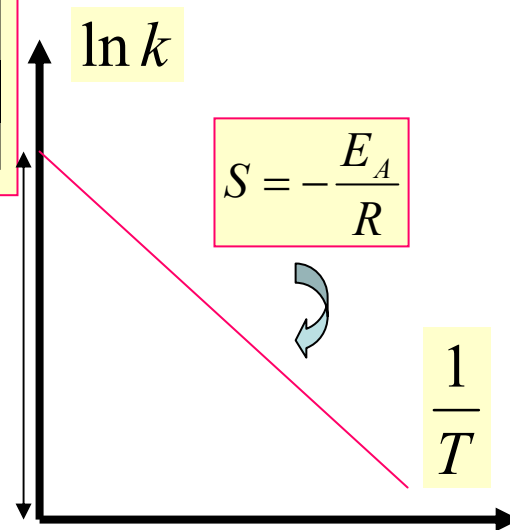
$\Delta S^{0*}$  explained in terms of changes in translational, rotational and vibrational degrees of freedom on going from reactants to TS.



pre-exponential factor related to entropy of activation (difference in entropy between reactants and activated complex)



$\ln A$



$$A = PZ = \kappa \left( \frac{k_B T}{h(c^0)^{m-1}} \right) \exp \left[ m + \frac{\Delta S^{0*}}{R} \right]$$

collision theory

steric factor

$P \cong 1$   $\Delta S^{0*} \cong 0$

$P < 1$   $\Delta S^{0*}$  negative

$P > 1$   $\Delta S^{0*}$  positive

TS more ordered than reactants

TS less ordered than reactants