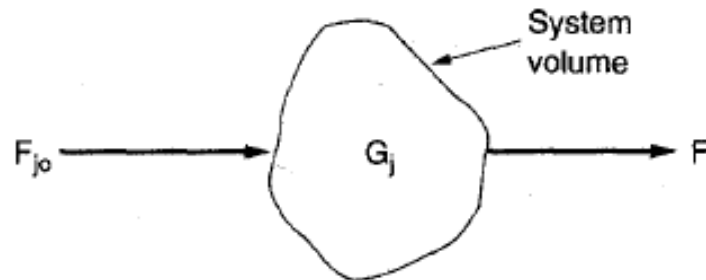


# **Chapter 2**

## **Kinetics of Homogeneous Reactions**



# The General Mole Balance Equation



$$\left[ \begin{array}{c} \text{rate of flow} \\ \text{of } j \text{ into} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] + \left[ \begin{array}{c} \text{rate of generation} \\ \text{of } j \text{ by chemical} \\ \text{reaction within} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] - \left[ \begin{array}{c} \text{rate of flow} \\ \text{of } j \text{ out of} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] = \left[ \begin{array}{c} \text{rate of} \\ \text{accumulation} \\ \text{of } j \text{ within} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right]$$

in + generation - out = accumulation

$$F_{j0} + G_j - F_j = \frac{dN_j}{dt}$$

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

$$G_j = \int^V r_j dV$$

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt}$$

# Rate expression

$$\frac{1}{V} \frac{dN_A}{dt} = r_A$$

$$\frac{dN_j}{dt} = r_j V$$

Constant-volume batch reactor

$$\frac{1}{V} \frac{dN_A}{dt} = \frac{d(N_A/V)}{dt} = \frac{dC_A}{dt} = r_A$$

$$F_j = C_j \cdot v$$

$$\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{volume}} \cdot \frac{\text{volume}}{\text{time}}$$

$$\frac{dF_A}{dV} = r_A$$

Constant-pressure batch reactor.

$$N_A = C_A V$$

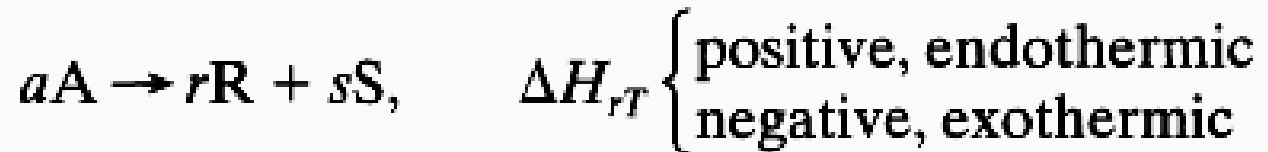
$$\frac{1}{V} \frac{dN_A}{dt} = \frac{1}{V} \frac{d(C_A V)}{dt} = \frac{dC_A}{dt} + \frac{C_A}{V} \frac{dV}{dt} = r_A$$

$$r_A = \frac{dC_A}{dt} + \frac{C_A}{V} \frac{dV}{dt}$$

# Thermodynamics

## Thermodynamics provides:

- ▶ heat liberated or absorbed for a given extent of reaction
- ▶ maximum possible conversion
- ▶ Equilibrium Constants from Thermodynamics  
standard free energy  $\Delta G^\circ$  for



$$\Delta G^\circ = rG_{\text{R}}^\circ + sG_{\text{S}}^\circ - aG_{\text{A}}^\circ = -\mathbf{RT} \ln K$$

$$-\mathbf{RT} \ln \frac{\left(\frac{f}{f^0}\right)_R \left(\frac{f}{f^0}\right)_S}{\left(\frac{f}{f^0}\right)_A} \quad \Delta n = r + s - a$$

$$K_f = \frac{f_R^r f_S^s}{f_A^a}, \quad K_p = \frac{p_R^r p_S^s}{p_A^a}, \quad K_y = \frac{y_R^r y_S^s}{y_A^a}, \quad K_C = \frac{C_R^r C_S^s}{C_A^a}$$

Fugacity and pressure are identical

$$f^0 = p^0 = 1 \text{ atm.}$$

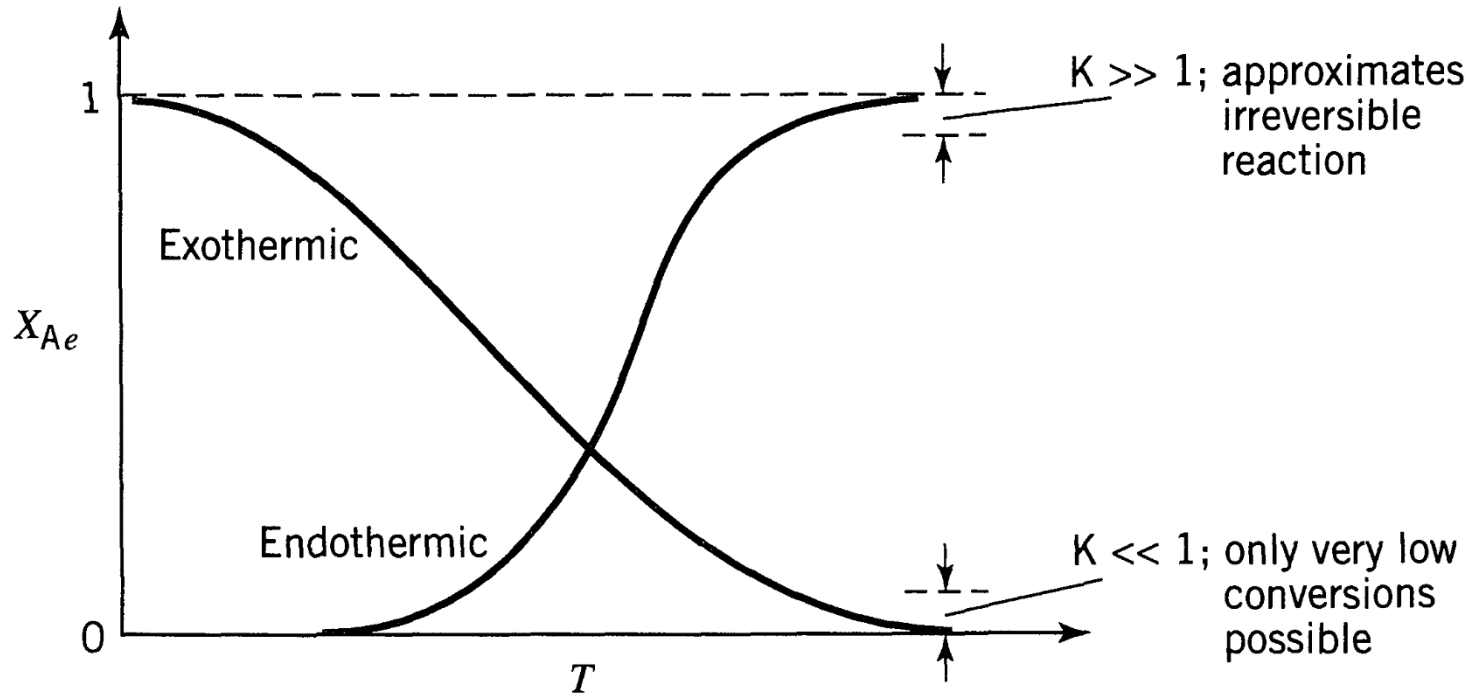
**Equilibrium Conversion.**

$$\frac{d(\ln K)}{dT} = \frac{\Delta H_r}{\mathbf{RT}^2}$$

K provides maximum attainable conversion


$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_r}{\mathbf{R}} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

# Effect of temperature on equilibrium conversion as predicted by thermodynamics (pressure fixed.)



# Equilibriums define in three ways

- ▶ **Thermodynamic view:** System is in equilibrium with its surroundings of given temperature and pressure.  
If  $\Delta G^\circ < 0$ , lowest possible value
- ▶ **Statistical mechanism:** System consist of the greatest no. of equally likely molecular configuration which are macroscopically indistinguishable.
- ▶ **Chemical Kinetics view:** Rate of change of all the forward reaction and reverse reaction are equal

- ▶ **Chemical Kinetics:** Study of the rate and mechanism by which one chemical species converted to another
  - ▶ **Rate:** reactant consumed per unit time
  - ▶ **Mechanism:** sequence of individual chemical event. Whose overall result produce the observed reaction.
  - ▶ Postulate theories are available
- 



# The Rate Equation

- ▶ single-phase reaction  $aA + bB = rR + sS$

rate of disappearance of A

$$-r_A = \frac{1}{V} \frac{dN_A}{dt} = \frac{\text{(amount of A disappearing)}}{\text{(volume) (time)}}, \left[ \frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right]$$

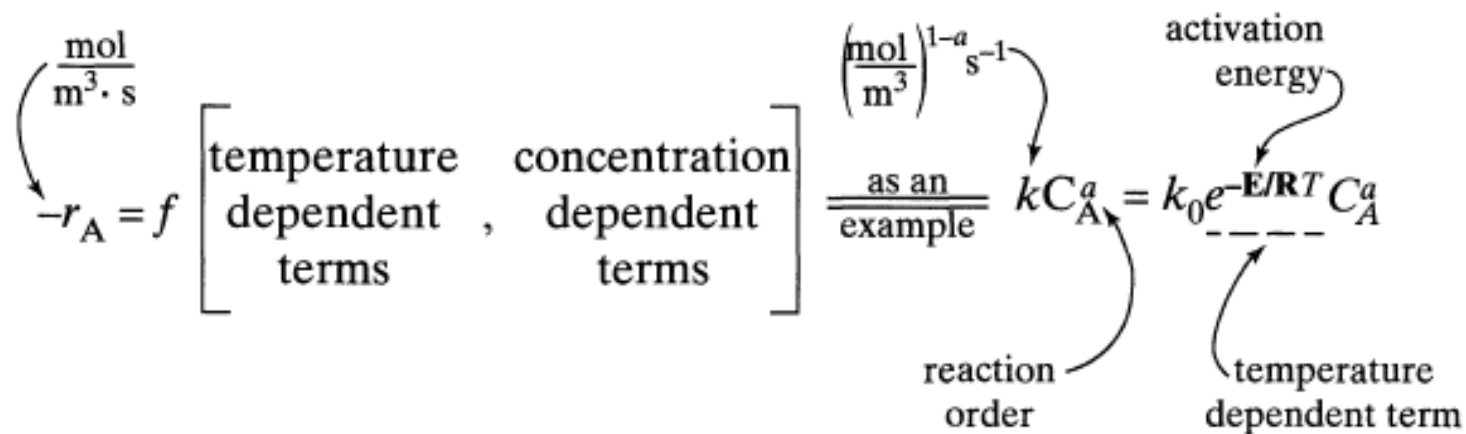
note that this is an intensive measure

the minus sign means disappearance

- ▶ rates of reaction of all materials are related by

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$$

# Rate of reaction is influenced by the composition and the energy of the material



## CONCENTRATION-DEPENDENT TERM:

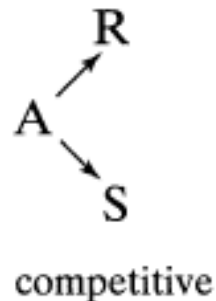
- hold the temperature of the system constant
- Based on the form and number of kinetic equations used to describe the progress of reaction

# Single and Multiple Reactions

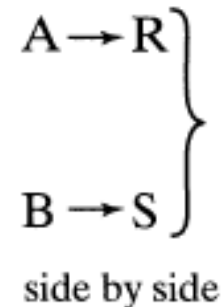
- ▶ **Single reaction:** Single rate equation are chosen to represent the progress
- ▶ **Multiple reactions:** more than one kinetic expression is needed



- ▶ **Series reactions:**
- ▶ **Parallel reactions:** Reactions of two type



and



- ▶ More complicated scheme:



- ▶ Reaction proceeds in parallel with respect to B
- ▶ Series with respect to A, R, and S.

# Elementary and Non-elementary Reactions

## Elementary reactions:

- ▶ Stoichiometric equation  $A + B \rightarrow R$
- ▶ Rate of disappearance of A is given by

$$-r_A = kC_A C_B$$

## Non-elementary reactions:

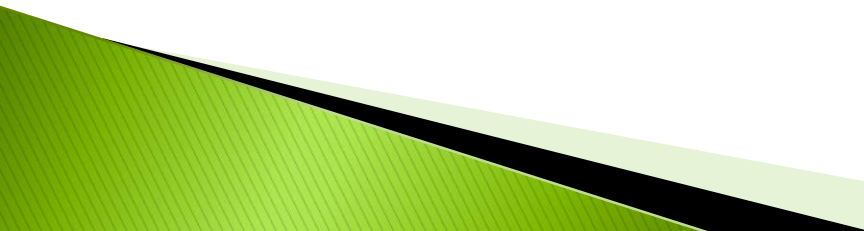
rate expression:  $H_2 + Br_2 \rightarrow 2HBr$

$$r_{HBr} = \frac{k_1[H_2][Br_2]^{1/2}}{k_2 + [HBr]/[Br_2]}$$

- ▶ Overall effect of a sequence of elementary reactions

reason for observing only a single reaction rather than two or more elementary reactions is that the amount of intermediates formed is negligibly small.

## Postulate:

- ▶ That the rate-controlling mechanism involves the collision or interaction of a single molecule of A with a single molecule of B
  - ▶ Number of collisions of molecules A with B is proportional to the rate of reaction.
  - ▶ At a given temperature the number of collisions is proportional to the concentration of reactants in the mixture.
- 

# Molecularity and Order of Reaction

## Molecularity:

- ▶ number of molecules involved in the reaction
- ▶ have the values of one, two, or occasionally three;
- ▶ must be an integer because it **refers to the mechanism**

Note: that the molecularity refers **only to an elementary reactions**

$$-r_A = kC_A^a C_B^b \dots C_D^d$$
$$a + b + \dots + d = n$$

## Order of the reaction:

- ▶ where a, b, . . . , d are not necessarily related to the **stoichiometric coefficients**.
- ▶ can have a fractional value

a<sup>th</sup> order with respect to A

b<sup>th</sup> order with respect to B

n<sup>th</sup> order overall

# Difference between Molecularity and Order of reaction

Molecularity	Order of reaction
It is defined as number of molecules or atoms or ions participating <b>in rate determining</b> step.	Order is defined as sum of powers of concentration terms in a rate equation.
It is a theoretical quantity, which can be determined through <b>reaction mechanism</b> .	Order of reaction can be determined <b>experimentally</b> .
It is always <b>whole number</b> or integer. It can never be fraction or zero.	Order of reaction is zero, fraction , integer & whole number.



# Rate Constant, k

$$r_A = \frac{dC_A}{dt}$$

$$r_A = k C_A^n$$

▶  $\frac{\text{mol}}{\text{lit.time}} = k \left( \frac{\text{mol}}{\text{lit}} \right)^n;$

$$\frac{1}{\text{time}} = \left( \frac{\text{mol}}{\text{lit}} \right)^{n-1}$$

- ▶ Dimensions of the rate constant k for the

nth-order reaction

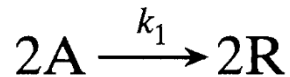
$$(\text{time})^{-1}(\text{concentration})^{1-n}$$

first-order reaction

$$(\text{time})^{-1}$$

# Representation of an Elementary Reaction

- Elementary reactions are often represented by an equation showing both the molecularity and the rate constant
- Biomolecular irreversible reaction with second-order rate constant  $k_1$



$$-r_A = r_R = k_1 C_A^2$$

- Rate is measured



$$-r_B = k_B C_B C_D^2$$

$$-r_D = k_D C_B C_D^2$$

$$r_T = k_T C_B C_D^2$$

- from the stoichiometry

$$-r_B = -\frac{1}{2} r_D = \frac{1}{3} r_T$$

$$k_B = \frac{1}{2} k_D = \frac{1}{3} k_T$$

# Representation of a Non-elementary Reaction

- ▶ Stoichiometry does not match its kinetics

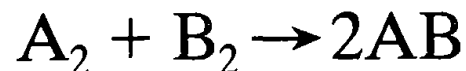


Rate: 
$$r_{\text{NH}_3} = k_1 \frac{[\text{N}_2][\text{H}_2]^{3/2}}{[\text{NH}_3]^2} - k_2 \frac{[\text{NH}_3]}{[\text{H}_2]^{3/2}}$$

- ▶ try to develop a multistep reaction model to explain the kinetics

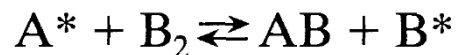
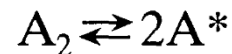
# Kinetic Models for Non-elementary Reactions

- ▶ Kinetics of the reaction (non-elementary):



- ▶ Cannot measure or observe the intermediates formed because they are only present in very minute quantities

- ▶ May postulate a series of elementary steps to explain the kinetics



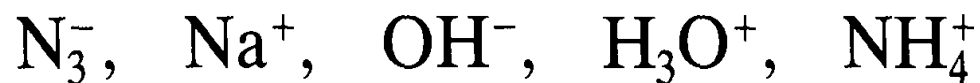
- ▶ we may postulate different types of intermediates

# Types of intermediates

- ▶ Free Radicals



- ▶ Ions and Polar Substances



- ▶ Molecules

- A, B, R S

- ▶ Transition Complexes

**Based on these four kinds of intermediates Postulated reaction schemes can be of two types.**

- a. Non-chain Reactions
- b. Chain Reactions

# Free radicals, chain reaction mechanism

unstable and highly reactive



- ▶ The reaction



- ▶ Experimental rate

$$r_{\text{HBr}} = \frac{k_1[\text{H}_2][\text{Br}_2]^{1/2}}{k_2 + [\text{HBr}]/[\text{Br}_2]}$$

- ▶ Introduces and involves the intermediates  $\text{H}\cdot$  and  $\text{Br}\cdot$



Initiation and termination



Propagation



Propagation

# Molecular intermediates, non-chain mechanism

Enzyme-catalyzed fermentation reactions:

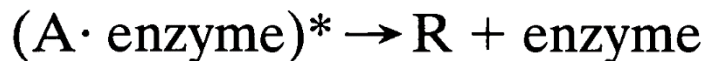
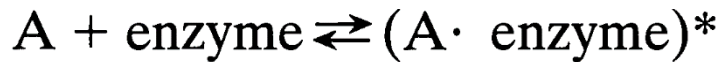


Experimental rate

$$r_R = \frac{k[A][E_0]}{[M] + [A]}$$

↖ constant

- ▶ Intermediate: concentration of intermediate not negligible



Proposed by  
**Michaelis and Menten**

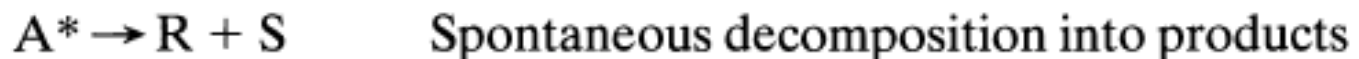
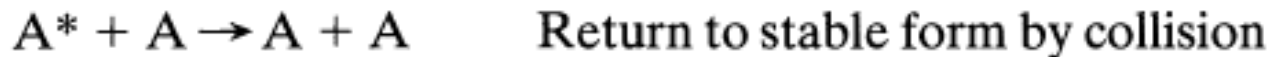
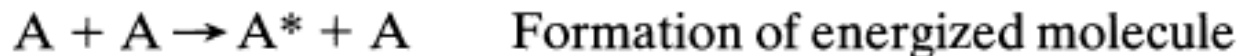
$(A \cdot \text{enzyme})^*$  as intermediate

# Transition complex, non-chain mechanism

- Numerous collisions between reactant molecules result in a wide distribution of energies among the individual molecules
- Result in strained bonds, unstable forms of molecules, or unstable association of molecules
- Decompose to give products, or by further collisions return to molecules in the normal state




- Energized and unstable form for the reactant,  $A^*$





# Testing Kinetic Models

- ▶ Search for the correct mechanism
  - ▶ Reaction may proceed by more than one mechanism
  - ▶ More than one mechanism can be consistent with kinetic data
  - ▶ Requires an extensive knowledge of the chemistry
  - ▶ Test the correspondence between experiment and a proposed mechanism
  - ▶ Hypothesize the existence of either of two types of intermediates
- 

# Testing Kinetic Models

## ▶ Type 1.

Intermediate X usually present at such small concentration that its rate of change in the mixture can be taken to be zero

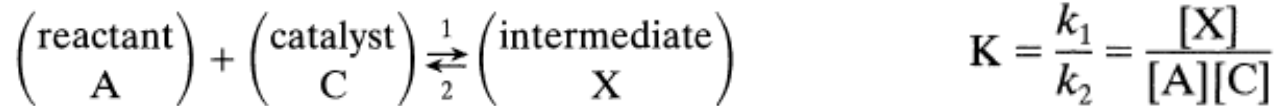
$$[X] \text{ is small and } \frac{d[X]}{dt} \cong 0$$

Steady-state approximation

## ▶ Type 2.

Where a homogeneous catalyst of initial concentration  $C_0$  is present in two forms, either as free catalyst C or combined in an appreciable extent to form intermediate X,

$$[C_0] = [C] + [X] \qquad \frac{dX}{dt} = 0$$



▶ Trial-and-error procedure involved in searching for a mechanism

# SEARCH FOR THE REACTION MECHANISM

- ▶ Irreversible reaction:



- ▶ Rate of formation of product

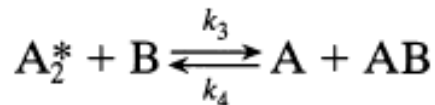
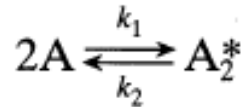
$$r_{AB} = kC_B^2 \dots \text{independent of } C_A$$

- ▶ Chemistry of the reaction suggests that the intermediate consists of an association of reactant molecules and that a chain reaction does not occur
- ▶ If this were an elementary reaction,  $r_{AB} = kC_A C_B = k[A][B]$
- ▶ Start with simple two-step models, and if these are unsuccessful we will try more complicated three-, four-, or five-step models

# Trial – Error Method

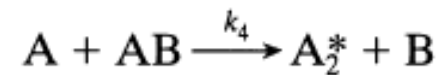
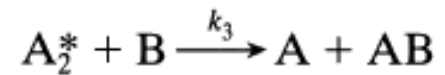
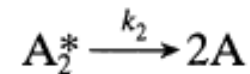
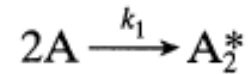
## Model 1

- ▶ Hypothesize a two-step reversible scheme
- ▶ intermediate substance  $A_2^*$
- ▶ Involves four elementary reactions



$$r_{AB} = k_3[A_2^*][B] - k_4[A][AB]$$

$$r_{A_2^*} = \frac{1}{2} k_1[A]^2 - k_2[A_2^*] - k_3[A_2^*][B] + k_4[A][AB]$$



# Two-step reversible scheme

- ▶ Concentration of  $A_2^*$  is always extremely small
- ▶ Rate of change is zero

$$r_{A_2^*} = 0$$

$$[A_2^*] = \frac{\frac{1}{2} k_1 [A]^2 + k_4 [A] [AB]}{k_2 + k_3 [B]}$$

- ▶ If  $k_2$ , is very small, this expression reduces

$$r_{AB} = \frac{\frac{1}{2} k_1 k_3 [A]^2 [B] - k_2 k_4 [A] [AB]}{k_2 + k_3 [B]}$$

$$r_{AB} = \frac{1}{2} k_1 [A]^2$$

# Two-step reversible scheme

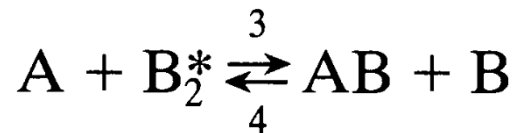
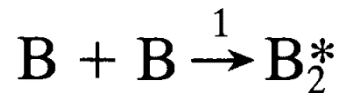
If  $k_4$  is very small

$$r_{AB} = \frac{(k_1 k_3 / 2k_2) [A]^2 [B]}{1 + (k_3 / k_2) [B]}$$

- ▶ Neither of these special forms matches the experimentally

**So another model needs to be tried**

- ▶ **Model 2.**



# SEARCH FOR A MECHANISM FOR THE ENZYME SUBSTRATE REACTION

▶ **Reactant:** *Substrate*

▶ **Enzyme:** Molecular weight (mw > 10 000) protein-like substance

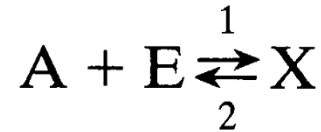


▶ **Many of these reactions exhibit the following behaviour:**

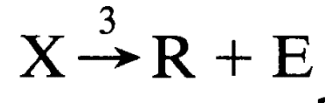
1. A rate proportional to the concentration of enzyme introduced into the mixture  $[E_0]$ .
2. At low reactant concentration the rate is proportional to the reactant concentration,  $[A]$
3. At high reactant concentration the rate levels off and becomes independent of reactant concentration.

# ENZYME SUBSTRATE REACTION

- ▶ **Michaelis and Menten**



- ▶ **Two assumptions**



$$[E_0] = [E] + [X]$$

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

- ▶ **First expression**

$$\frac{d[X]}{dt} = k_1[A][E] - k_2[X] - k_3[X] = 0$$

- ▶ **Second expression**

$$\frac{d[R]}{dt} = k_3[X]$$



# SEARCH FOR A MECHANISM

- ▶ Eliminating [E]

$$[X] = \frac{k_1[A][E_0]}{(k_2 + k_3) + k_1[A]}$$

- ▶ Substituting in second expression

$$\frac{d[R]}{dt} = \frac{k_1 k_3 [A][E_0]}{(k_2 + k_3) + k_1 [A]} = \frac{k_3 [A][E_0]}{[M] + [A]}$$

$[M] = \left(\frac{k_2 + k_3}{k_1}\right)$  is called  
the Michaelis constant

- ▶ Comparing with experiment, we see that this equation fits the three reported facts

$$\frac{-d[A]}{dt} = \frac{d[R]}{dt} \begin{cases} \propto [E_0] \\ \propto [A] \text{ when } [A] \ll [M] \\ \text{is independent of } [A] \text{ when } [A] \gg [M] \end{cases}$$

# TEMPERATURE-DEPENDENT TERM OF A RATE EQUATION

## Arrhenius' Law:

$$\begin{aligned}r_i &= f_1(\text{temperature}) \cdot f_2(\text{composition}) \\ &= k \cdot f_2(\text{composition})\end{aligned}$$

$$k = k_0 e^{-E/RT}$$

$k_0$  = Frequency or pre-exponential factor

E = Activation energy of the reaction.

At two different temperatures

$$\ln \frac{r_2}{r_1} = \ln \frac{k_2}{k_1} = \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

E stays constant

# Comparison of Theories with Arrhenius' Law

- **Collision and transition state theories** for the temperature dependency of the rate constant

$$k = k_0' T^m e^{-E/RT}, \quad 0 \leq m \leq 1$$

- More complicated versions  $m$  can be as great as **3** or **4**
- Temperature dependency for **Collision theories**

$$K = k_0 T^{1/2} e^{-E/RT}$$

- Temperature dependency for **transition theories**

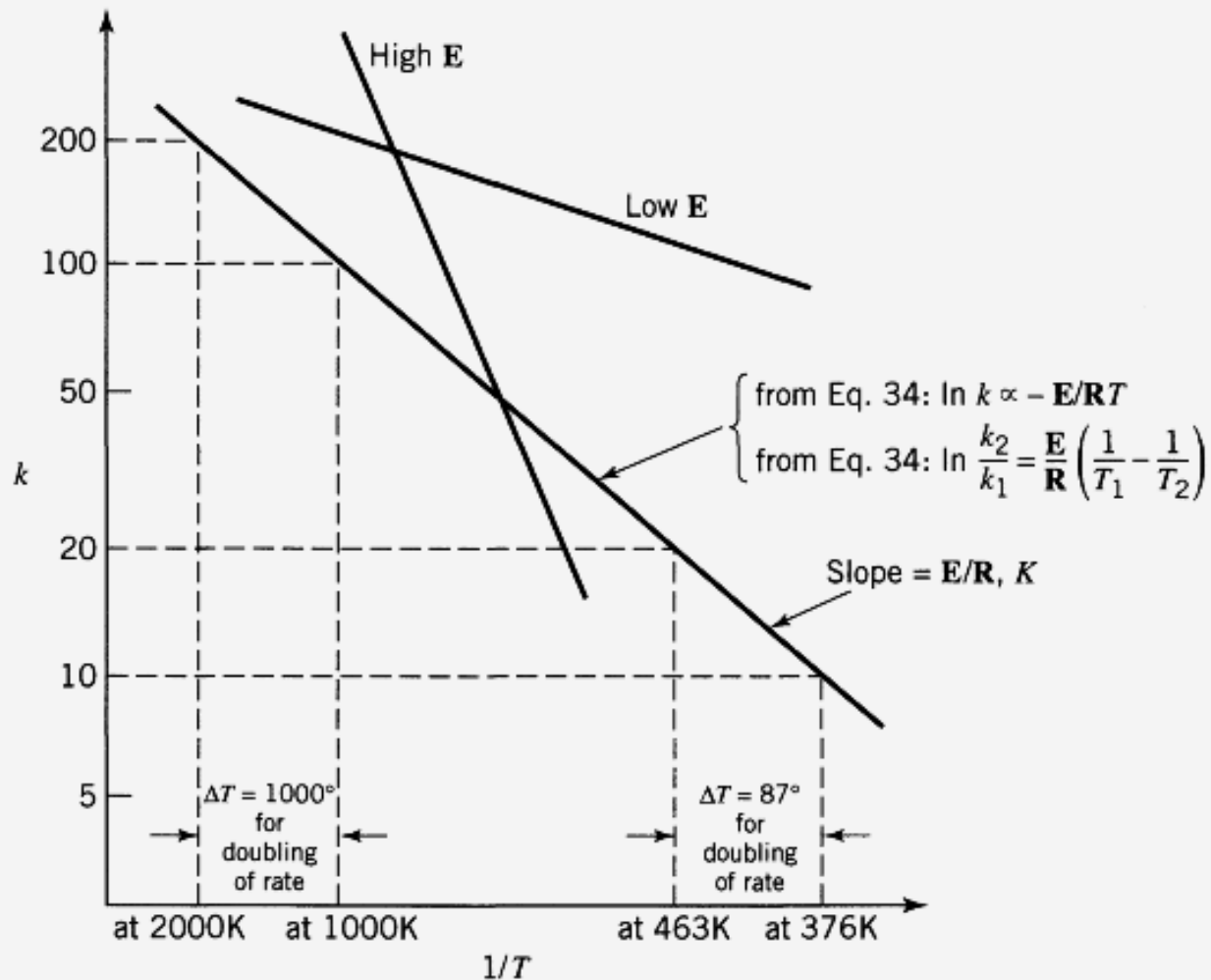
$$K = k_0 T e^{-E/RT}$$

# Comparison of Theories with Arrhenius' Law


- ▶ Exponential term is so much more temperature-sensitive than the pre-exponential term
- ▶ **Arrhenius' law** is a good approximation to the temperature dependency of both collision and transition-state theories

$$k = k_0 e^{-\mathbf{E}/RT}$$

# Activation Energy and Temperature Dependency



# Arrhenius' law

- ▶ Plot of  $\ln k$  vs  $1/T$  gives a straight line
  - ▶ Large slope for large  $E$  and small slope for small  $E$
  - ▶ Reactions with high activation energies are very temperature-sensitive
  - ▶ low activation energies are relatively temperature-insensitive
  - ▶ Frequency factor  $k_0$ , does not affect the temperature sensitivity
- 

# Shift in controlling mechanism of reaction

## Multiple reactions

Change in the observed activation energy with temperature indicates a shift in the controlling mechanism of reaction

Parallel reactions

Series reactions

► Increase in temperature

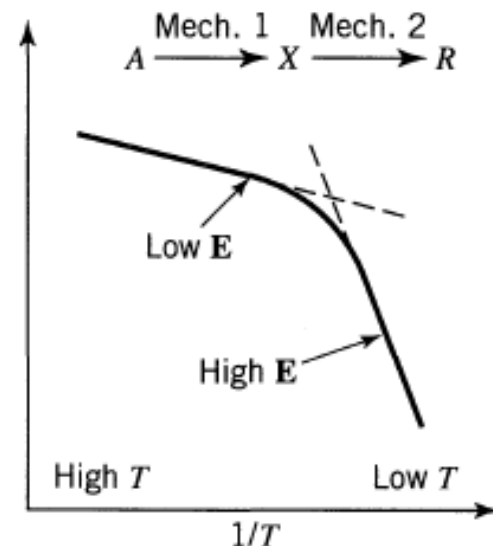
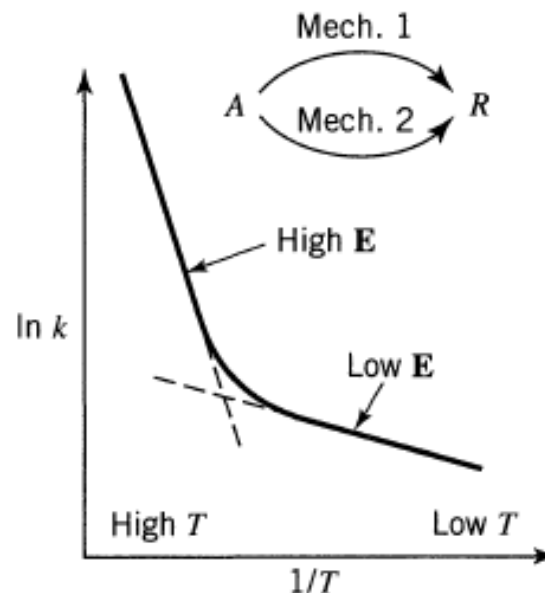
$E_{\text{obs}}$  rises

$E_{\text{obs}}$  falls

► Decrease in temperature

$E_{\text{obs}}$  falls

$E_{\text{obs}}$  rises



# SEARCH FOR THE ACTIVATION ENERGY OF A PASTEURIZATION PROCESS

**Example :** Milk is pasteurized if it is heated to 63°C for 30 min, but if it is heated to 74°C it only needs 15 s for the same result. Find the activation energy of this sterilization process.

**Solution :**

Arrhenius temperature dependency for the process

$$\ln \frac{r_2}{r_1} = \ln \frac{t_1}{t_2} = \frac{\mathbf{E}}{\mathbf{R}} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

**Given**

**Substituting values**

$$t_1 = 30 \text{ min} \quad \text{at a} \quad T_1 = 336 \text{ K}$$

$$t_2 = 15 \text{ sec} \quad \text{at a} \quad T_2 = 347 \text{ K}$$

$$\ln \frac{30}{0.25} = \frac{\mathbf{E}}{8.314} \left( \frac{1}{336} - \frac{1}{347} \right)$$

from which the activation energy

$$\mathbf{E} = 422\,000 \text{ J/mol}$$