

Chemistry Lecture

B.Tech First Year

Chemical Kinetics

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| To analyze the kinetics of multistep reactions as well as theories of reaction rates | Outline |
|--|--|
| | Rate laws of multi-step reactions (steady state approximation) and numericals |
| | Introduction, Kinetics of simple parallel, opposing and consecutive reactions |
| | Theory of reaction: Collision theory, Arrhenius equation |
| | Calculation of activation energy, Lindemann's modification of collision theory |
| | Absolute reaction rate theory |
| | Catalysis: types, theories |
| | Kinetics of enzyme catalysis Michaeli's-Menten mechanism |

Introduction

We will now study:

- Kinetics: the study of how fast chemical reactions occur.

(in contrast to Thermodynamics: which determines if a reaction take place)

Our goal: is to understand chemical reactions at the molecular level.

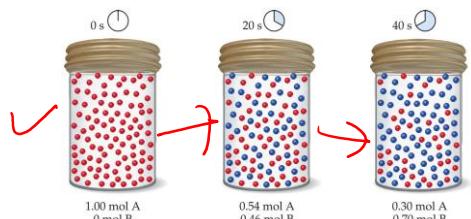
Speed of a reaction: is measured by the change in concentration with time.

Important factors which affect rates of reactions:

- reactant concentration
- temperature
- action of catalysts
- surface area
- pressure of gaseous reactants or products

Introduction

Reaction Rates



Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time t .

[A] = concentration of reactant A

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Introduction

- For the reaction $A \rightarrow B$ there are two ways of measuring **rate**:
 - the speed at which the reactants disappear
 - the speed at which the products appear
- Reactions are reversible, so as products accumulate they can begin to turn back into reactants.
- Early on the rate will depend on only the amount of reactants present. We want to measure the reactants as soon as they are mixed.
- The most useful (and general) way of measuring the rate of the reaction is in terms of change in concentration per unit time...

$$\text{Rate} = \Delta[A]/\Delta t \text{ limits to } d[A]/dt$$

Most Common Units... Rate = M/s

Where Molarity (M) = moles/Liter

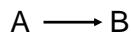
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Introduction

Thermodynamics – does a reaction take place?

Kinetics – how fast does a reaction proceed?

Reaction rate is the change in the concentration of a reactant or a product with time (M/s).



$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$\Delta[A] = \text{change in concentration of A over time period } \Delta t$

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B] = \text{change in concentration of B over time period } \Delta t$

Because [A] decreases with time, **$\Delta[A]$ is negative.**

Introduction

Factors that Affect the Reaction Rate Constant

- Temperature:** At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy
 - Collision Theory:** When two chemicals react, their molecules have to collide with each other with sufficient energy for the reaction to take place.
 - Kinetic Theory:** Increasing temperature means the molecules move faster.
- Concentrations of reactants**
 - As the concentration of reactants increases, so does the likelihood that reactant molecules will collide.
- Catalysts**
 - Speed up reactions by lowering activation energy
- Surface area of a solid reactant**
 - Bread and Butter theory: more area for reactants to be in contact
- Pressure of gaseous reactants or products**
 - Increased number of collisions

Introduction

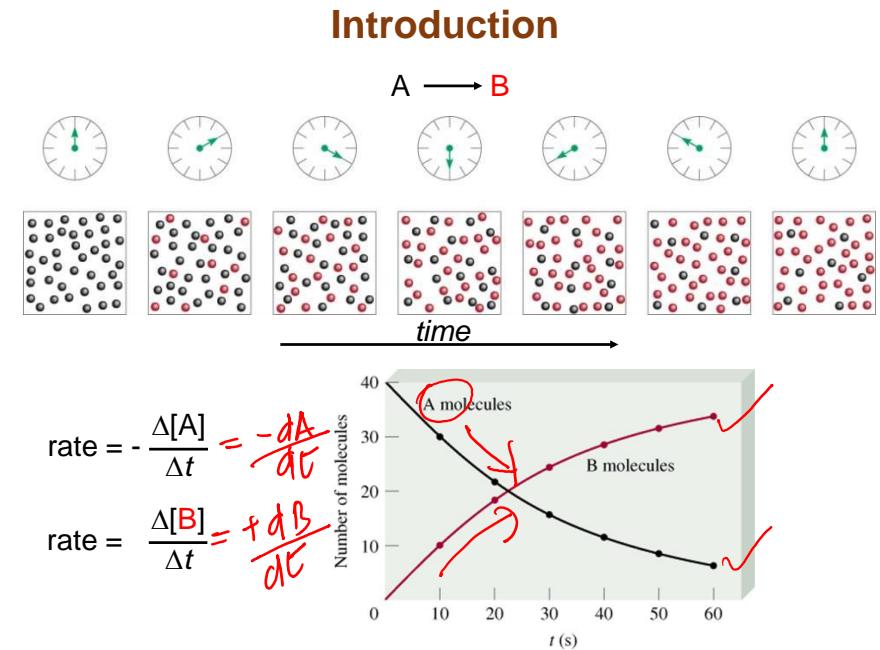
Concentration and Rate

Each reaction has its own equation that gives its rate as a function of reactant concentrations.

This is called its **Rate Law**

To determine the rate law we measure the rate at different starting concentrations.

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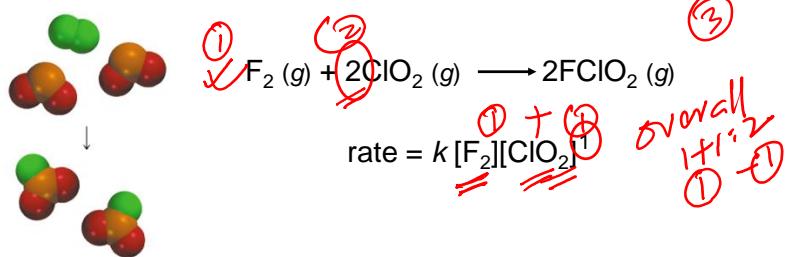


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Introduction

Rate Laws

- Rate laws are **always** determined experimentally.
- Reaction order is **always** defined in terms of reactant (not product) concentrations.
- The order of a reactant is **not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.



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Introduction

Rate Law

- In general, rates of reactions increase as concentrations increase since there are more collisions occurring between reactants.
- The overall concentration dependence of reaction rate is given in a **rate law** or rate expression.
- Here's what a general rate law for a reaction will look like...

$\text{Rate} = \cancel{k} \cancel{\text{Rate const}} [\text{A}]^m [\text{B}]^n$

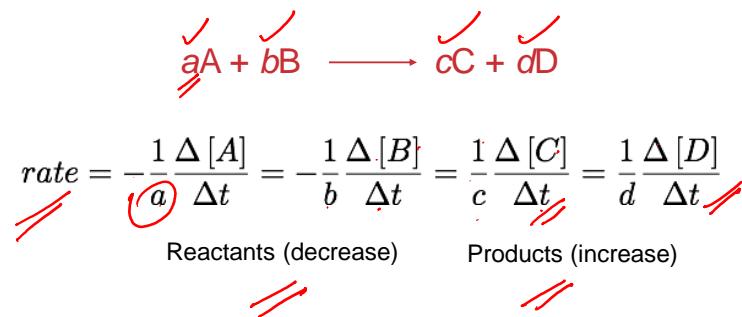
- [A] & [B] represent the reactants.
- The exponents *m* and *n* are called "**reaction orders**".
- The proportionality constant *k* is called the **rate constant**.
- The **overall reaction order** is the sum of the reaction orders:

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Introduction

Reaction Rates and Stoichiometry

- To generalize, for the reaction



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Introduction

The **rate law** expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.



$$\text{Rate} = k [A]^m [B]^n$$



reaction is ***m*th order** in A

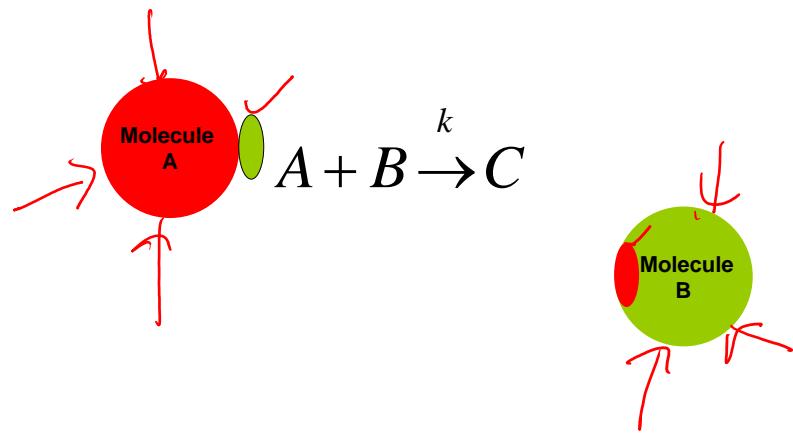
reaction is ***n*th order** in B

reaction is **(*m+n*)th order overall**

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Introduction

Example chemical reaction that models collisions of molecules A & B to form C



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Introduction

Zero-Order Reactions

$$\text{rate} = -\frac{\Delta[A]_t}{\Delta t}$$

$$\text{rate} = k [A]_0 = k$$

$$[A]_t - [A]_0 = kt$$

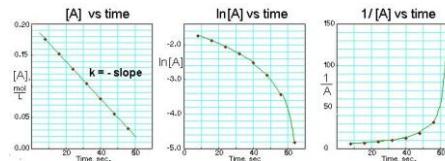
$[A]_t$ is the concentration of A at any time t

$[A]_0$ is the concentration of A at time $t=0$

Half life for zero order

$$t_{1/2} = t \text{ when } [A]_t = [A]_0/2$$

$$t_{1/2} = \frac{[A]_0}{2k}$$



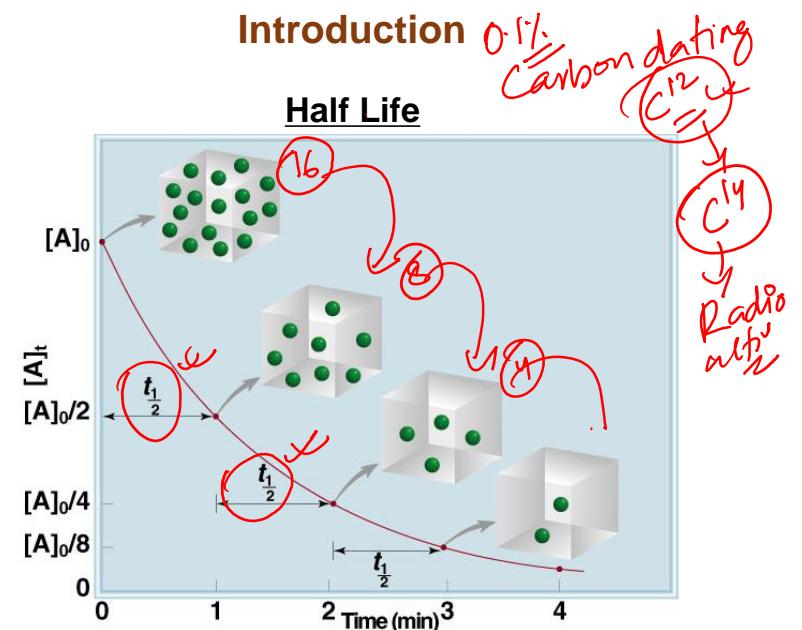
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Introduction

Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

| Order | Rate Law | Concentration-Time Equation | Half-Life |
|-------|------------------------|--|--------------------------------------|
| 0 | $\text{rate} = k$ | $[A] - [A]_0 = - kt$ | $t_{\frac{1}{2}} = \frac{[A]_0}{2k}$ |
| 1 | $\text{rate} = k[A]$ | $\ln[A] - \ln[A]_0 = - kt$ | $t_{\frac{1}{2}} = \frac{\ln 2}{k}$ |
| 2 | $\text{rate} = k[A]^2$ | $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$ | $t_{\frac{1}{2}} = \frac{1}{k[A]_0}$ |

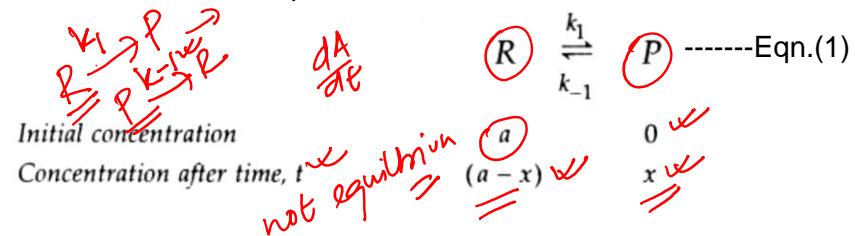
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Reversible Reactions

Let us consider a simple first order reversible reaction

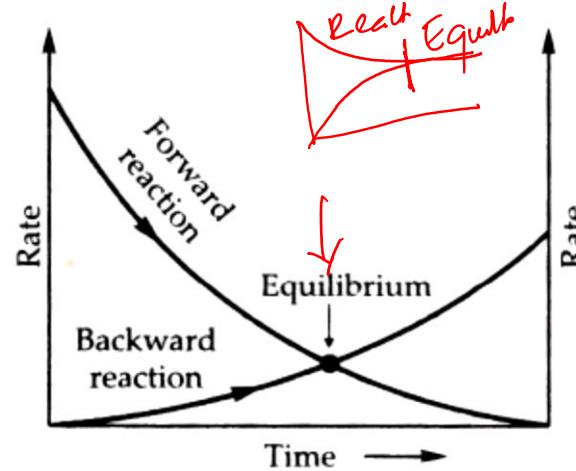


where R is reactant, P is product, k_1 is first order rate constant for forward reaction and k_{-1} is first order rate constant for backward reaction.

$$\text{Now, the rate of forward reaction} = k_1 (a-x) \quad \text{Eqn (2)}$$

$$\text{the rate of backward reaction} = k_{-1} x \quad \text{Eqn (3)}$$

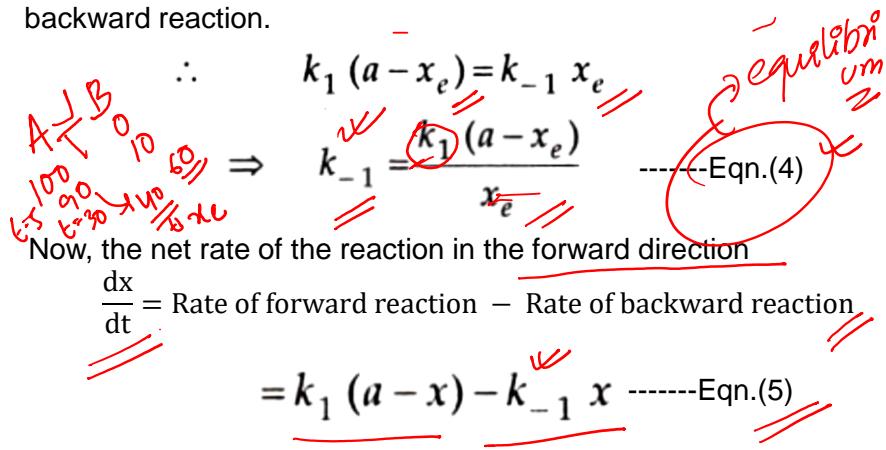
Reversible Reactions



As more and more products are formed, the rate of the backward reaction increases and eventually it becomes equal to the rate of forward direction ; **the overall rate is then zero.**

Reversible Reactions

Thus, at equilibrium; $x = \underline{x_e}$ = concentration of product (P) at equilibrium. And the rate of forward reaction = the rate of backward reaction.



Reversible Reactions

Substituting the value of k_{-1} from equation (4) into equation (5), we get:

$$\frac{dx}{dt} = k_1 (a - x) - \frac{k_1 (a - x_e)}{x_e} \times x \quad \text{--- Eqn.(5)}$$

$$\Rightarrow \frac{dx}{dt} = \frac{k_1 a x_e - k_1 x x_e - k_1 a x + k_1 x x_e}{x_e} \quad \text{--- Eqn.(5)}$$

$$\Rightarrow \frac{dx}{dt} = \frac{k_1 a (x_e - x)}{x_e} \quad \text{--- Eqn.(6)}$$

Reversible Reactions

Imposing boundary conditions we have

$$\begin{aligned} \text{at } t=0 &\Rightarrow x=0 \\ \text{at } t=t &\Rightarrow x=x_e, \text{ we get } x=0 \quad \text{--- Eqn.(7)} \\ \int_0^x \frac{dx}{x_e - x} &= \frac{k_1 a}{x_e} \int_0^t dt \end{aligned}$$

$$\begin{aligned} \Rightarrow -[\ln(x_e - x)]_0^x &= \frac{k_1 a}{x_e} [t]_0^t \\ \Rightarrow -[\ln(x_e - x) - \ln(x_e)] &= \frac{k_1 a}{x_e} (t - 0) \end{aligned}$$

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Reversible Reactions

$$\Rightarrow \ln\left(\frac{x_e}{x_e - x}\right) = \frac{k_1 at}{x_e} \quad \text{--- Eqn.(7)}$$

$$\Rightarrow k_1 = \frac{x_e}{a t} \ln\left(\frac{x_e}{x_e - x}\right) \quad \text{--- Eqn.(8)}$$

Substituting this value of k_1 from equation (8) into equation (4), we get k_{-1} ,

$$k_{-1} = \frac{k_1(a-x_e)}{x_e} = \frac{x_e / at \left[\ln\left(\frac{x_e}{x_e - x}\right) \right] \times (a-x_e)}{x_e}$$

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Reversible Reactions

$$\Rightarrow k_{-1} = \frac{(a-x_e) \ln\left(\frac{x_e}{x_e-x}\right)}{at} \quad \text{-----Eqn.(9)}$$

From equations (8) and (9), we have

$$\begin{aligned} \cancel{k_1 + k_{-1}} &= \frac{x_e}{at} \ln\left(\frac{x_e}{x_e-x}\right) + \frac{(a-x_e)}{at} \ln\left(\frac{x_e}{x_e-x}\right) \\ \Rightarrow \cancel{k_1 + k_{-1}} &= \frac{1}{t} \ln\left(\frac{x_e}{x_e-x}\right) \quad \text{-----Eqn.(10)} \\ &\hookrightarrow (k = 1/t \ln \frac{s}{a-n}) \end{aligned}$$

Reversible Reactions

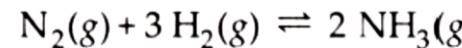
Comparing the equation (10) with first order reaction,

$$k = \frac{1}{t} \ln \frac{[R]_0}{[R]_t}$$

A reversible first order reaction may be treated as simple first order reaction provided the initial concentration is replaced by equilibrium concentration and rate constant k is replaced by ($k_1 + k_{-1}$) .

Examples of Reversible Reactions *(Habour's process)*

Conversion of nitrogen and hydrogen into ammonia



Consecutive Reactions

The reactions which proceed from reactants (R) to products (P) in two or more steps, one after the other through **one or more intermediate steps**, involving intermediate (I) are called consecutive reactions.

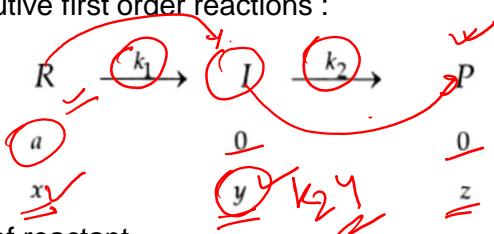


Consider a simple consecutive first order reactions :

$$a = x + y + z$$

Initial concentration

Concentration at time, t



The rate of consumption of reactant

$$R = \frac{-dx}{dt} = k_1 x \quad \text{-----Eqn.(1)}$$

Consecutive Reactions

Separating the variables of equation (1) and integrating between the limits

at $t=0, x=a$ and at $t=t, x=x$, we get

$$\int_a^x \frac{dx}{x} = -k \int_0^t dt$$

$$\Rightarrow \ln \frac{x}{a} = -k_1 t$$

$$\Rightarrow x = a e^{-k_1 t}$$

-----Eqn.(2)

Reactant R decreases exponentially with time

Consecutive Reactions

The rate of formation of Intermediate

$$\textcircled{1} \quad I = \frac{dy}{dt} = k_1 x - k_2 y \quad \text{Eqn.(3)}$$

Substituting the value of x from equation (2) in equation (3), we get

$$\frac{dy}{dt} = k_1 a e^{-k_1 t} - k_2 y \quad \text{Eqn.(4)}$$

Equation (4) is a linear first order differential equation whose solution is

$$\textcircled{2} \quad y = \frac{k_1 a}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}] \quad \text{Eqn.(5)}$$

Consecutive Reactions

As per the condition of conservation of mass we have

$$a = x + y + z$$

The concentration of product P (=z) may be calculated as

$$\textcircled{3} \quad z = a - x - y$$

Substituting the values of x and y from equations (2) and (5), we get

$$\textcircled{4} \quad z = a - a e^{-k_1 t} - \frac{a k_1}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}] \quad \checkmark$$

Consecutive Reactions

$$\begin{aligned}
 &= a [1 - e^{-k_1 t} - \frac{k_1}{(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t})] \\
 &= a \left[\frac{(k_2 - k_1) - k_2 e^{-k_1 t} + k_1 e^{-k_1 t} - k_1 e^{-k_1 t} + k_1 e^{-k_2 t}}{(k_2 - k_1)} \right] \\
 z &= \frac{a}{(k_2 - k_1)} [(k_2 - k_2 e^{-k_1 t}) - (k_1 - k_1 e^{-k_2 t})] \quad \text{Eqn.(6)}
 \end{aligned}$$



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Consecutive Reactions

Formation of P

Case I. When $k_1 \gg k_2$

Then $e^{-k_1 t} \ll e^{-k_2 t}$
hence $e^{-k_1 t}$ can be neglected in equation (6),

$$z \approx \frac{a}{k_2 - k_1} [(k_2 - k_1) + k_1 e^{-k_2 t}]$$

As $k_1 \gg k_2 \quad \therefore k_2 - k_1 \approx -k_1$

$$z = \frac{a}{-k_1} (-k_1 + k_1 e^{-k_2 t}) \quad \checkmark$$

$$z = a (1 - e^{-k_2 t}) \quad \text{Eqn.(7)}$$

The formation of product P therefore involves only k_2 , which therefore is the rate determining step.

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Consecutive Reactions

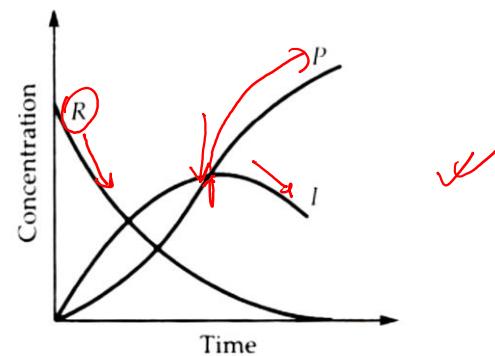
~~Case II. When $k_1 \ll k_2$, then $e^{-k_1 t} \gg e^{-k_2 t}$~~

~~Then equation (18) reduces to~~

$$z \approx a(1 - e^{-k_1 t}) \quad \text{-----Eqn.(8)}$$

The concentrations of x, y and z are plotted as functions of time in the consequent figure

Consecutive Reactions



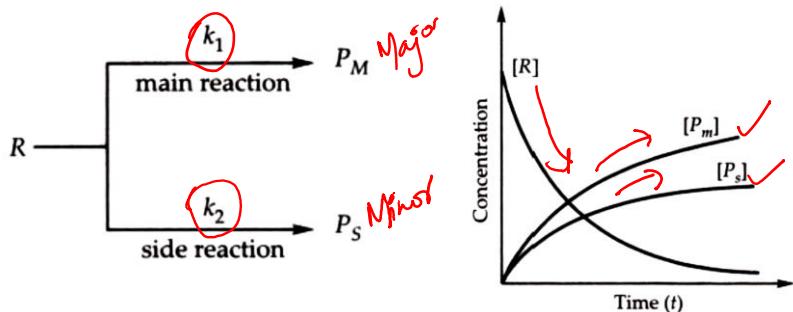
From the figure , it can be concluded that the concentration of reactant (R) decreases exponentially with time, while equations (7) or (8) suggest the concentration of product (P) increases gradually to the value of a when all reactant has changed into product. **The concentration of the intermediate (I) rises to a maximum value and then falls asymptotically to zero.**

Parallel Reactions ✓

Reactions in which the reactants react in more than one way yielding different sets of products are known as parallel reactions. Parallel reactions basically consist of two reactions :

- (i) **Major (or main) reaction** : which produces maximum amount of the products $[P_M]$.
- (ii) **Parallel (or side) reaction** : which produces side product $[P_S]$.

Let us consider a general parallel reaction



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Parallel Reactions

The rate of formation of major product ✓ - $\frac{d[P_M]}{dt}$

$$(P_M) = \frac{d[P_M]}{dt} = k_1 [R] \quad \text{-----Eqn.(1)}$$

The rate of formation of side product

$$(P_S) = \frac{d[P_S]}{dt} = k_2 [R] \quad \text{-----Eqn.(2)}$$

The overall rate of disappearance of reactant (R)

$$\begin{aligned} &= \frac{-d[R]}{dt} = \frac{d[P_M]}{dt} + \frac{d[P_S]}{dt} \\ &= (k_1 + k_2)[R] \quad \text{-----Eqn.(3)} \end{aligned}$$

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Parallel Reactions

The ratio of the two rates

$$\frac{d[P_M]/dt}{d[P_S]/dt} = \frac{k_1}{k_2} \quad \text{----- Eqn.(4)}$$

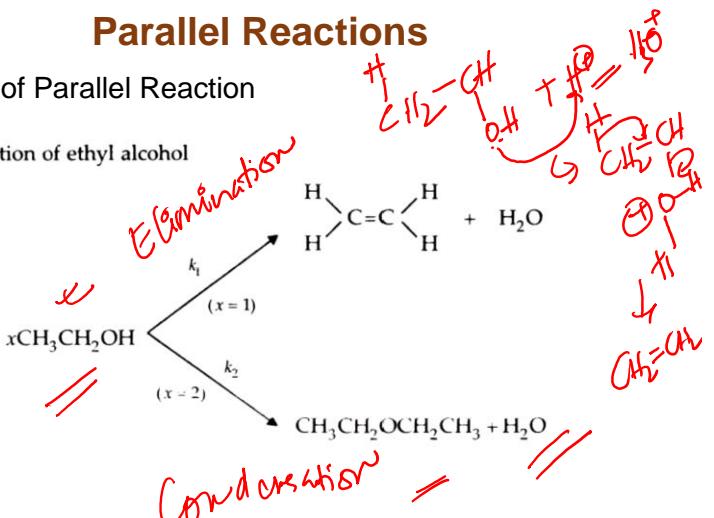
From equation (3),

$$\begin{aligned} -\int_{R_0}^{R_t} \frac{d[R]}{[R]} &= (k_1 + k_2) \int_0^t dt \\ \Rightarrow \ln(R_0/R_t) &= (k_1 + k_2)t \quad \text{1st order} \\ \Rightarrow (k_1 + k_2) &= \frac{1}{t} \ln\left(\frac{R_0}{R_t}\right) \quad \text{----- Eqn.(5)} \end{aligned}$$

Parallel Reactions

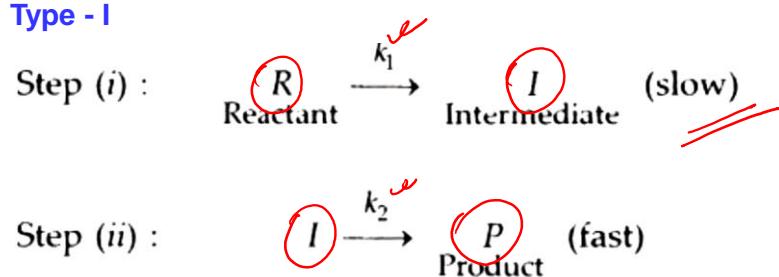
Examples of Parallel Reaction

(i) Dehydration of ethyl alcohol



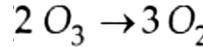
Complex Reactions

Type - I



First step is slow, rate determining step which is followed by rapid subsequent step in which product is formed.

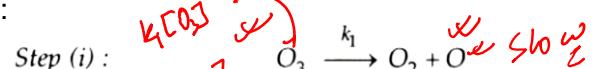
Decomposition of ozone



Complex Reactions

Type - I

Decomposition of ozone may have the following proposed mechanism :



From the proposed mechanism, the rates of decomposition of O_3 can be given as

$$\dot{r}_1 = -\frac{d}{dt} [\text{O}_3] = k_1 [\text{O}_3] \quad \text{Eqn.(1)}$$

$$\dot{r}_2 = -\frac{d}{dt} [\text{O}_3] = k_2 [\text{O}_3][\text{O}] \quad \text{Eqn.(2)}$$

Complex Reactions

Type - I

Thus, the total rate of decomposition of ozone is given by

$$\text{O}_3 = r = r_1 + r_2 \quad \cancel{\checkmark}$$

$$-\frac{d}{dt} [\text{O}_3] = k_1 [\text{O}_3] + k_2 [\text{O}_3][\text{O}] \quad \cancel{\checkmark}$$

$$= [\text{O}_3] \{k_1 + k_2 [\text{O}]\} \quad \text{Eqn.(3)}$$

In the above expression, we require the concentration of intermediate, atomic oxygen i.e., $[\text{O}]$. Therefore, applying steady-state approximation to it.

Rate of formation of atomic oxygen = Rate of consumption of atomic oxygen



Complex Reactions

Type - I

$$\Rightarrow k_1 \cancel{[\text{O}_3]} = k_2 \cancel{[\text{O}_3]} [\text{O}]$$

$$\cancel{[\text{O}]} = \frac{k_1}{k_2} \quad \text{Eqn.(4)} \quad \cancel{\checkmark}$$

Substituting $[\text{O}]$ from equation (4) in equation (3), we get

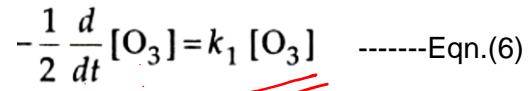
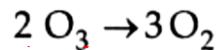
$$-\frac{d}{dt} [\text{O}_3] = [\text{O}_3] \left\{ k_1 + k_2 \times \frac{k_1}{k_2} \right\} = [\text{O}_3] \cancel{2 k_1}$$

$$\Rightarrow -\frac{1}{2} \frac{d}{dt} [\text{O}_3] = k_1 [\text{O}_3] \quad \text{Eqn.(5)}$$

Complex Reactions

Type - I

Now, in the overall reaction:

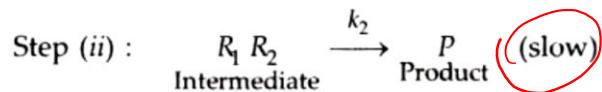
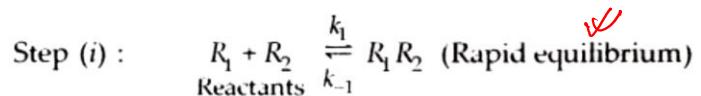


From equations (5) and (6), we can conclude that the rate of decomposition of ozone

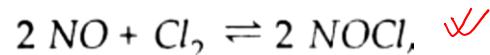
$$= k_1 [\text{O}_3]$$

Complex Reactions

Type - II



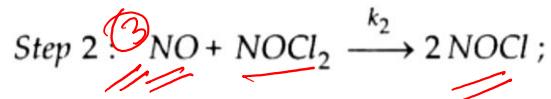
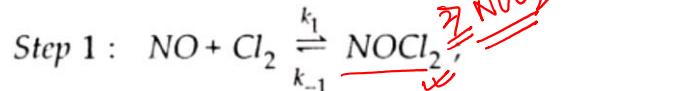
Intermediate is formed in the first fast equilibrium step which subsequently slowly reacts in the second rate determining step.



Complex Reactions

Type - II

Mechanism of the reaction is



As the product NOCl is being formed in second step, so we can consider the rate of formation of product as the overall rate of the reaction.

$$\frac{1}{2} \frac{d[\text{NOCl}]}{dt} = k_2 [\text{NO}] [\text{NOCl}_2] \quad \text{----- Eqn.(1)}$$

Complex Reactions

Type - II

For the calculation of concentration of intermediate, $[\text{NOCl}_2]$, we can apply the steady state approximation.

Rate of formation of Intermediate, NOCl_2 = Rate of consumption of intermediate, NOCl_2

$$\Rightarrow k_1 [\text{NO}] [\text{Cl}_2] = k_{-1} [\text{NOCl}_2] + k_2 [\text{NO}] [\text{NOCl}_2]$$

$$\Rightarrow k_1 [\text{NO}] [\text{Cl}_2] = [\text{NOCl}_2] (k_{-1} + k_2 [\text{NO}])$$

$$\Rightarrow [\text{NOCl}_2] = \frac{k_1 [\text{NO}] [\text{Cl}_2]}{k_{-1} + k_2 [\text{NO}]} \quad \text{----- Eqn.(2)}$$

Complex Reactions

Type - II

Substituting the value of $[NOCl_2]$ from equation (2) into equation (1), we get

$$= \frac{1}{2} \frac{d}{dt} [NOCl] = k_2 [NO] \times \frac{k_1 [NO] [Cl_2]}{\{k_{-1} + k_2 [NO]\}}$$

$$= \frac{k_1 k_2 [NO]^2 [Cl_2]}{\{k_{-1} + k_2 [NO]\}} \quad \text{-----Eqn.(3)}$$

Complex Reactions

Type - II

Assuming $k_2 [NO] \ll k_{-1}$ and neglecting the former, we get

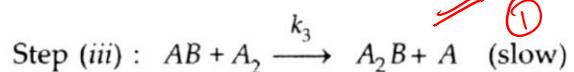
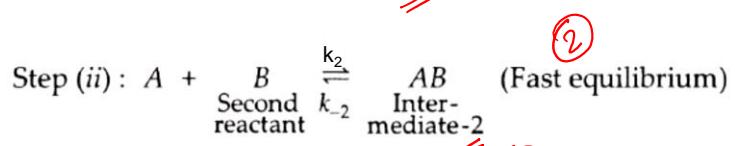
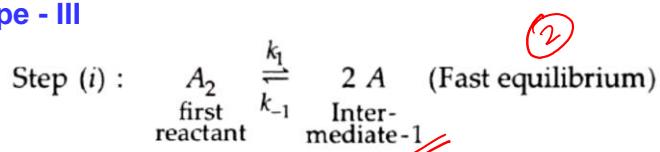
The overall rate of the reaction

$$= \frac{k_1 k_2 [NO]^2 [Cl_2]}{k_{-1}} = k [NO]^2 [Cl_2]$$

where $k = k_1 k_2 / k_{-1}$

Complex Reactions

Type - III

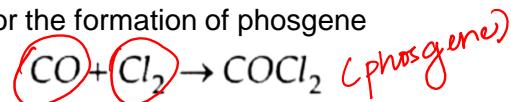


Such reactions involve more than two elementary steps with atleast one slow step

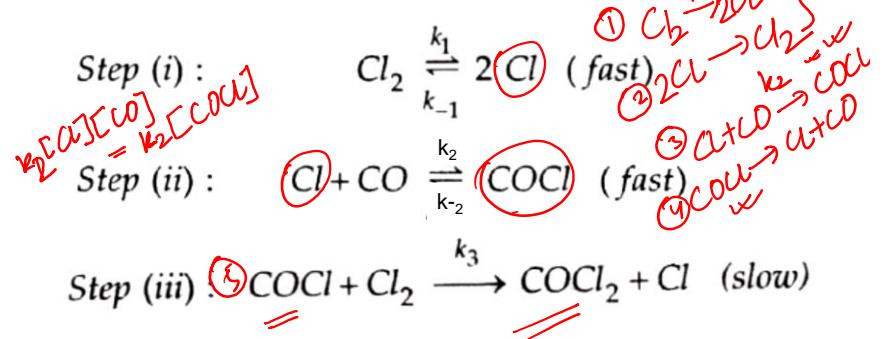
Complex Reactions

Type - III

The reaction for the formation of phosgene



For this reaction, the following mechanism has been proposed :



Complex Reactions

Type - III

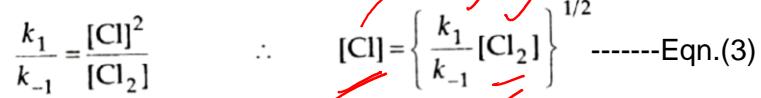
From step (iii), the rate of formation of phosgene is



From step (ii) $R_f \text{COCl} = R_d \text{COCl}$



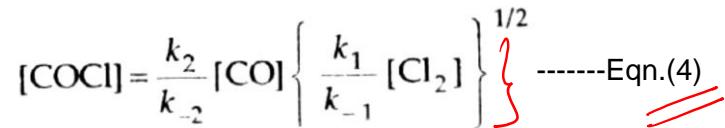
From step (i)



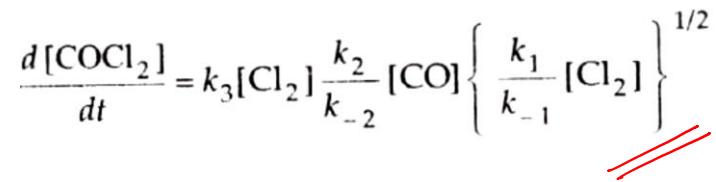
Complex Reactions

Type - III

Substituting the value of $[\text{Cl}]$ from equation (3) in equation (2), we get

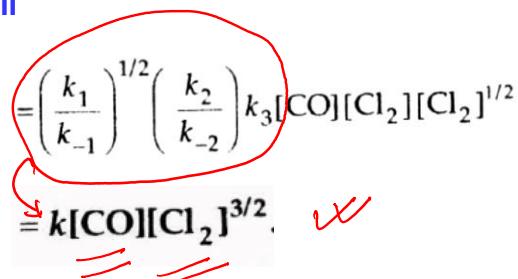


Substituting this value of $[\text{COCl}]$ from equation (4) in equation (1), we get



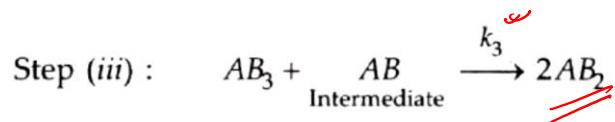
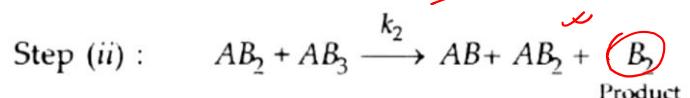
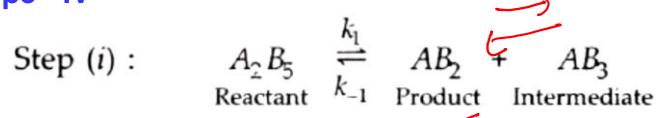
Complex Reactions

Type - III



Complex Reactions

Type - IV

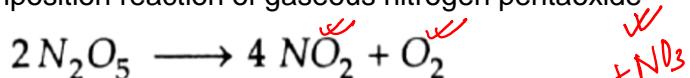


Complex reactions with more than one step having comparable rate constants (i.e., it is not known whether the steps are slow or fast).

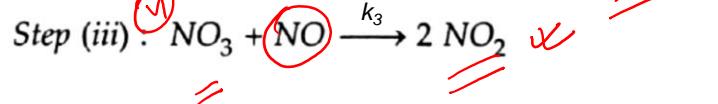
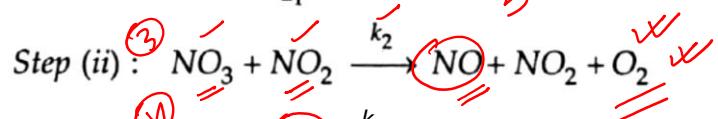
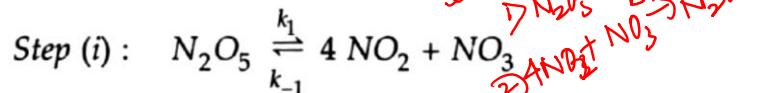
Complex Reactions

Type - IV

The decomposition reaction of gaseous nitrogen pentaoxide



The following mechanism has been proposed



Complex Reactions

Type - IV

From step (ii) we have

$$\frac{d}{dt} [O_2] = k_2 [NO_3][NO_2] \quad \text{Eqn.(1)}$$

Applying the steady-state approximation principles to intermediates NO and NO₃ we get

$$\begin{aligned} k_2 [NO_3][NO_2] &= k_3 [NO_3][NO] \\ \therefore [NO] &= \frac{k_2}{k_3} [NO_2] \end{aligned} \quad \text{Eqn.(2)}$$

$$\begin{aligned} k_1 [N_2O_5] &= \underline{k_{-1} [NO_2][NO_3]} + \underline{k_2 [NO_3][NO_2]} + \underline{k_3 [NO_3][NO]} \\ &= [NO_3] \{k_{-1} [NO_2] + k_2 [NO_2] + k_3 [NO]\} \end{aligned}$$

Complex Reactions

Type - IV

$$\therefore [\text{NO}_3] = \frac{k_1 [\text{N}_2\text{O}_5]}{k_{-1} [\text{NO}_2] + k_2 [\text{NO}_2] + k_3 [\text{NO}]} \quad \text{Eqn.(3)}$$

Substituting [NO] from equation (2) in equation (3), we get

$$\begin{aligned} [\text{NO}_3] &= \frac{k_1 [\text{N}_2\text{O}_5]}{k_{-1} [\text{NO}_2] + k_2 [\text{NO}_2] + k_3 \times \frac{k_2}{k_3} [\text{NO}_2]} \\ &= \frac{k_1 [\text{N}_2\text{O}_5]}{[\text{NO}_2] \{k_{-1} + 2k_2\}} \quad \text{Eqn.(4)} \end{aligned}$$

Substituting $[\text{NO}_3]$ from equation (4) in equation (1), we get

Complex Reactions

Type - IV

$$\begin{aligned} \frac{d}{dt} [\text{O}_2] &= k_2 [\text{NO}_2] \times \frac{k_1 [\text{N}_2\text{O}_5]}{[\text{NO}_2] \{k_{-1} + 2k_2\}} \\ &= \frac{k_1 k_2}{(k_{-1} + 2k_2)} [\text{N}_2\text{O}_5] \end{aligned}$$

The Collision Theory of Chemical Reactions

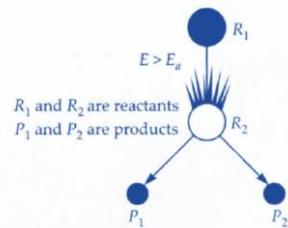
This theory is satisfactory for gaseous reactions. The essential requirements for reactions according to collision theory are :

1. Collisions between the reactant molecules.
2. Activation of molecules.
3. Proper orientation at the time of collision.

Consider a reaction between two reactants R_1 and R_2

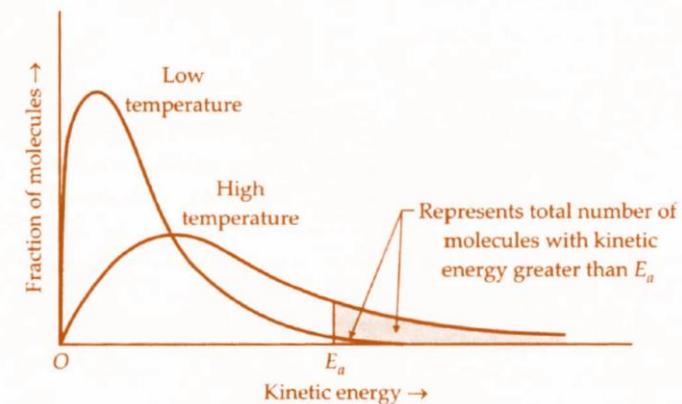
$$\text{Rate of collisions} = \text{Constant} \times [R_1][R_2]$$

It is assumed in collision theory that a collision is successful only if the molecules collide with at least the activation energy of the reaction



The Collision Theory of Chemical Reactions

Therefore the activation energy is the minimum energy required for reaction. The fraction of collisions with at least the energy E_a is given by the Maxwell distribution of speeds



The Collision Theory of Chemical Reactions

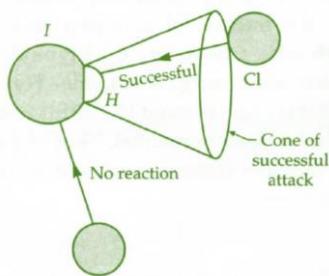
Interpretation of the graph:

At low temperature only a very tiny fraction of molecules have enough energy to react. At higher temperature, a much larger fraction of molecules can react.

Consider the reaction

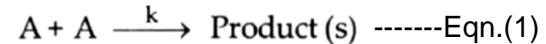


The Cl atom reacts with the HI molecule only if its line of approach is inside a cone of half-angle 30° surrounding the hydrogen atom



The Collision Theory of Chemical Reactions

Let us now find rate expression for a bimolecular gaseous reaction



According to collision theory

$$\frac{-(d[A])}{dt} = Z_{11} \theta p \quad \text{Eqn.(2)}$$

where:

Z_{11} is the number of collisions between the reacting molecules per second per dm^3

θ is the fraction of the total number of molecules which are activated, and

p is referred to as the probability or stearic factor and is related to the geometry of the molecule.

The Collision Theory of Chemical Reactions

From the kinetic theory of gases

$$Z_{11} = \frac{1}{2} \sqrt{2} \pi \sigma^2 (n')^2 v_{avg} \quad \text{Eqn.(3)}$$

$$\theta = \frac{n^*}{n'} = e^{-E_a/RT} \quad \text{Eqn.(4)}$$

$$\text{rate} = k_2 = p Z_{11} \exp\left(-\frac{E_a}{RT}\right) \quad \text{Eqn.(4a)}$$

σ is the collision diameter,

v_{avg} is the average velocity of the molecules in dm per second,

n^* is the number of molecules per dm^3 having $E > E_a$,

E_a is the activation energy,

n' is the total number of molecules per dm^3

The Collision Theory of Chemical Reactions

$$v_{avg} = \sqrt{\frac{8 RT}{\pi M}} \quad \text{Eqn.(5)}$$

Therefore from Eqn. 3, 4 and 5 we have

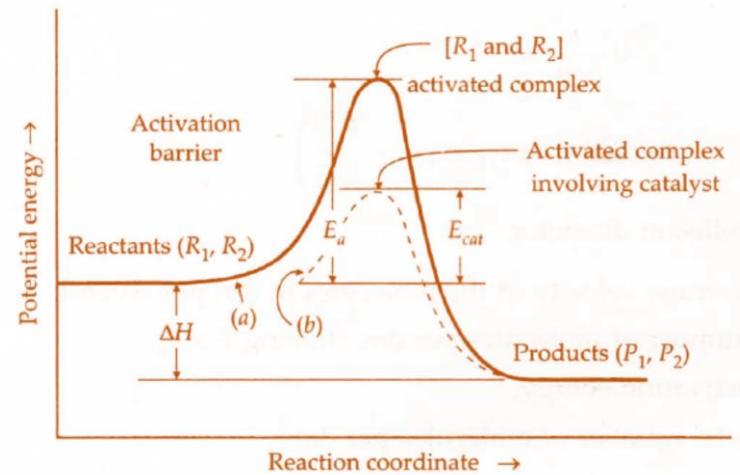
$$Z_{11} = \frac{1}{2} \sqrt{2} \pi \sigma^2 (n')^2 \sqrt{\frac{8 RT}{\pi M}}$$

$$Z_{11} = 2 \sigma^2 (n')^2 \sqrt{\frac{\pi RT}{M}} \quad \text{Eqn.(6)}$$

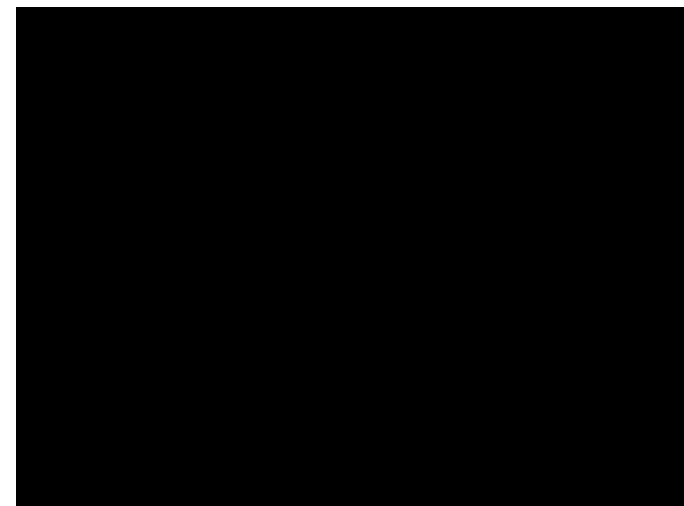
Limitations

- (i) This theory is applicable to gaseous molecules,
- (ii) It is difficult to calculate p , the stearic factor from molecular geometry for complex molecules.

Transition State Theory of Reaction Rates



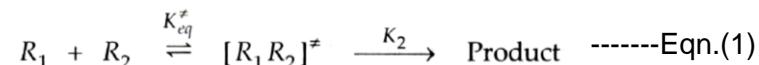
Transition State Theory of Reaction Rates



Source: <https://www.youtube.com/watch?v=VblaK6PLrRM>

Transition State Theory of Reaction Rates

All the reactions proceed through an activated or transition state which has energy higher than the reactants or products. It is assumed that an equilibrium is established between the reactants and the activated complex.



The rate of such a reaction depends on :

- (i) concentration of the activated complex molecule
- (ii) the rate at which it decomposes.

$$\text{Rate} = \left(\frac{\text{Concentration of the activated complex molecule}}{} \right) \times \left(\frac{\text{Frequency of decomposition of the activated complex}}{} \right)$$

As the activated complex is in equilibrium with the reactants

$$K_{eq}^{\neq} = \frac{[R_1 R_2]^{\neq}}{[R_1][R_2]}$$

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Transition State Theory of Reaction Rates

$$\Rightarrow [R_1 R_2]^{\neq} = K_{eq}^{\neq} [R_1][R_2] \quad \text{Eqn.(2)}$$

As the activated complex **[R1 R2][#] is unstable so at a particular vibration it decomposes to form products.** The rate of decomposition of the complex is dependent (proportional) to the frequency of vibration.

$$\begin{aligned} -\frac{d}{dt} [R_1] &= -\frac{d}{dt} [R_2] = k_2 [R_1][R_2] \\ &= [R_1 R_2]^{\neq} v = K_{eq}^{\neq} [R_1][R_2](v) \end{aligned} \quad \text{Eqn.(3)}$$

According to Planck's expression

$$E = h v \quad \text{Eqn.(4)}$$

The average energy of such a vibrational degree of freedom is given by kT , where k is Boltzmann's constant. Therefore we have

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Transition State Theory of Reaction Rates

$$v = \frac{E}{h} = \frac{kT}{h} = \frac{RT}{Nh} \quad \text{Eqn.(5)}$$

Substituting this value of v in equation (3), we get

$$\begin{aligned} k_2 [R_1][R_2] &= K_{eq}^{\neq} [R_1][R_2] v \\ \Rightarrow k_2 [R_1][R_2] &= K_{eq}^{\neq} [R_1][R_2] \frac{RT}{Nh} \\ \Rightarrow k_2 &= K_{eq}^{\neq} \frac{RT}{Nh} \quad \text{Eqn.(6)} \end{aligned}$$

Transition State Theory of Reaction Rates

Free energy of activation, ΔG^{\neq} is given by

$$\begin{aligned} \Delta G^{\neq} &= -RT \ln K_{eq}^{\neq} \Rightarrow \ln K_{eq}^{\neq} = \frac{-\Delta G^{\neq}}{RT} \\ \Rightarrow \ln k_{eq}^{\neq} &= \frac{-(\Delta H^{\neq} - T\Delta S^{\neq})}{RT} \\ \Rightarrow k_{eq}^{\neq} &= \exp\left(\frac{-\Delta H^{\neq}}{RT}\right) \exp\left(\frac{\Delta S^{\neq}}{R}\right) \quad \text{Eqn.(7)} \end{aligned}$$

Substituting this value of K_{eq}^{\neq} in equation (6), we get

$$k_2 = \frac{RT}{Nh} \left[\exp\left(\frac{-\Delta H^{\neq}}{RT}\right) \exp\left(\frac{\Delta S^{\neq}}{R}\right) \right] \quad \text{Eqn.(8)}$$

Transition State Theory of Reaction Rates

Now taking logarithm of equation (6), we get

$$\ln k_2 = \ln T + \ln K_{eq}^{\ddagger} + \ln \frac{R}{Nh}$$

Differentiating w.r.t. temperature, we obtain

$$\frac{d \ln k_2}{dT} = \frac{1}{T} + \frac{d \ln k_{eq}^{\ddagger}}{dT} \quad \text{Eqn.(9)}$$

As the variation of equilibrium constant with temperature is given by

$$\frac{d \ln k_{eq}^{\ddagger}}{dT} = \frac{\Delta E^{\ddagger}}{RT^2} \quad \text{Eqn.(10)}$$

Transition State Theory of Reaction Rates

From equations (9) and (10), we get

$$\frac{d \ln k_2}{dT} = \frac{1}{T} + \frac{\Delta E^{\ddagger}}{RT^2} = \frac{RT + \Delta E^{\ddagger}}{RT^2} \quad \text{Eqn.(11)}$$

Comparing equation (11) with $\frac{d \ln k_2}{dT} = \frac{E_a}{RT^2}$, we get

$$E_a = \Delta E^{\ddagger} + RT \quad \text{Eqn.(12)}$$

$$\text{But } \Delta H^{\ddagger} = \Delta E^{\ddagger} + P \Delta V^{\ddagger}$$

$$\Rightarrow \Delta E^{\ddagger} = \Delta H^{\ddagger} - P \Delta V^{\ddagger}$$

Transition State Theory of Reaction Rates

For ideal gases

$$P\Delta V^\ddagger = \Delta n^\ddagger RT$$

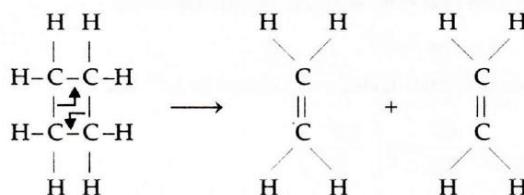
$$\Delta E^\ddagger = \Delta H^\ddagger - \Delta n^\ddagger RT \quad \text{Eqn.(13)}$$

Substituting the value of ΔE^\ddagger from equation (13) in equation (12), we get

$$E_a = \Delta H^\ddagger - \Delta n^\ddagger RT + RT \quad \text{Eqn.(14)}$$

Lindemann Unimolecular Reactions

An elementary reaction is unimolecular if the rearrangement of a single molecule or ion produces one or more molecules of product.

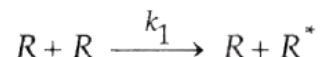


In unimolecular reactions, only one reactant molecule takes part in the reaction like

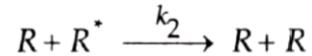
$$R \rightarrow \text{Products} \quad \text{Eqn.(1)}$$

According to this theory, the reactant molecules (R) are first activated by collisions with other reactant molecules.

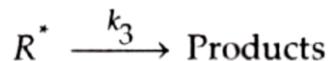
Lindemann Unimolecular Reactions



The activated reactant molecule do not decompose immediately but it remains in the activated state for a finite time. **There is a time lag before decomposition of the activated reactant molecules.** During this time lag, the activated molecules may get deactivated to ordinary molecules in second biomolecular collisions.



If in the time lag, **activated reactant molecules are not deactivated, they will undergo a decomposition reaction leading to the formation of products.**



Lindemann Unimolecular Reactions

In this mechanism, according to Lindemann, the activated reactant molecules are produced as reactive intermediate. So, we can apply steady-state-approximation to find out the concentration of this short-lived species.

$$\text{Rate of formation of } R^* = \text{Rate of decomposition of } R^*$$

$$k_1 [R]^2 = k_2 [R][R^*] + k_3 [R^*]$$

$$\Rightarrow [R^*] = \frac{k_1 [R]^2}{k_2 [R] + k_3}$$

Lindemann Unimolecular Reactions

As the products are being formed in the last step.

$$\text{rate of reaction} = k_3 [R^+] = \frac{k_3 k_1 [R]^2}{k_2 [R] + k_3}$$

Case I. When $k_2 [R] \gg k_3$,

$$\text{rate of reaction} = \frac{k_1 k_3}{k_2} [R]$$

first order rate equation.

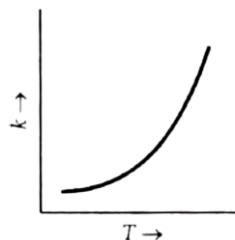
Case II. When $k_2 [R] \ll k_3$,

$$\text{rate of reaction} = k_1 [R]^2$$

second order rate equation.

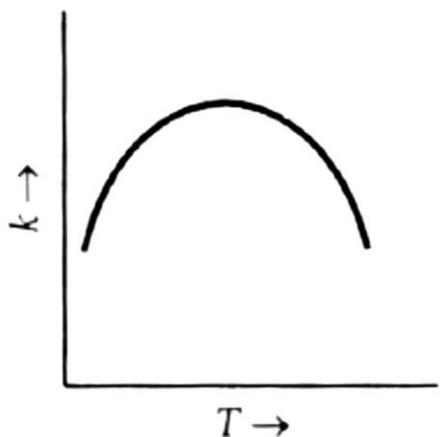
Effect of Temperature on Reaction Rates

Temperature dependence of reaction rates can be studied by plotting a graph between rate constant (k) and temperature (T) for different reactions as shown below



This curve is applicable for most of the reactions and indicates that rate increases with increase in temperature. This is easy to understand because number of effective collisions between the reactant molecules increases with increase in temperature. Thus, rate increases.

Effect of Temperature on Reaction Rates



This curve is applicable for enzyme catalyzed reactions because enzymes show maximum efficiency at some optimum temperature, beyond which they undergo denaturation.

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Effect of Temperature on Reaction Rates

The ratio of the rate constants of a reaction at two temperatures differing by 10° C is known as temperature coefficient of the reaction.

A more correct dependence of k on temperature is given by **Arrhenius equation**

$$k = A e^{-E_a/RT} \quad \text{Eqn.(1)}$$

k = Rate constant, T = Temperature

A = Arrhenius constant or pre-exponential factor

R = Gas constant and E_a = Activation energy of the reaction.

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Effect of Temperature on Reaction Rates

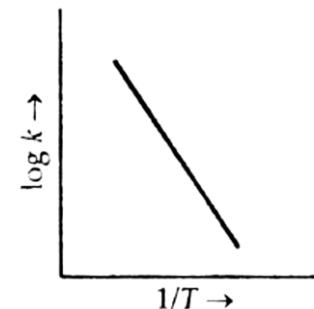
In equation (1), $e^{-E_a/RT}$ represents the fraction of molecules having energies equal to or greater than the energy of activation.

Taking logarithm of equation (1),

$$\ln(k) = \ln(A e^{-E_a/RT}) \\ \Rightarrow \ln k = \ln A - \frac{E_a}{RT} \quad \text{Eqn.(2)}$$

$$\Rightarrow \log k = \log A + \frac{-E_a}{2.303 R} \times \frac{1}{T}$$

Effect of Temperature on Reaction Rates



Thus, a plot of $\log k$ versus $1/T$ should be a straight line (above figure) with **slope equal to $- E_a / 2.303 R$** and **intercept equal to $\log A$** so from the slope of this plot the activation energy can be evaluated.

Effect of Temperature on Reaction Rates

Let k_1 = rate constant of a reaction at temperature T_1 and
 k_2 = rate constant of same reaction at temperature T_2 .

From equation (2), we get

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \text{Eqn.(3)}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad \text{Eqn.(4)}$$

From equations (4) and (5),

$$\ln k_2 - \ln k_1 = -\frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

Effect of Temperature on Reaction Rates

$$\log(k_2/k_1) = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \text{Eqn.(5)}$$

Effect of Temperature on Reaction Rates

A first order reaction has rate constant of 4500 s^{-1} at 1°C and an activation energy of 58000 J.mol^{-1} . At what temperature would rate constant be $10,000 \text{ s}^{-1}$?

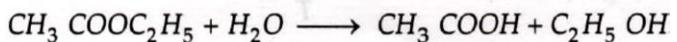
$$\text{As } \log(k_2/k_1) = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log\left(\frac{10,000}{4500}\right) = \frac{58000}{2.303 \times 8.314} \left(\frac{1}{274} - \frac{1}{T_2} \right)$$

$$\frac{1}{T_2} = \frac{1}{274} - 1.145 \times 10^{-4} \quad \Rightarrow \quad T_2 = 282.87 \text{ K}$$

Effect of Temperature on Reaction Rates

For the reaction



The following data was obtained :

The rate constant at 500°C was $5 \times 10^3 \text{ s}^{-1}$, find rate constant at 600°C . Given $E_a = 50,000 \text{ J mol}^{-1}$

Solution

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] = \frac{50,000}{2.303 \times 8.314} \left[\frac{873 - 773}{873 \times 773} \right] = 0.387$$

$$k_2 = k_1 \text{ antilog}(0.387) = 5 \times 10^3 \times 2.44 = 1.22 \times 10^4 \text{ s}^{-1}$$

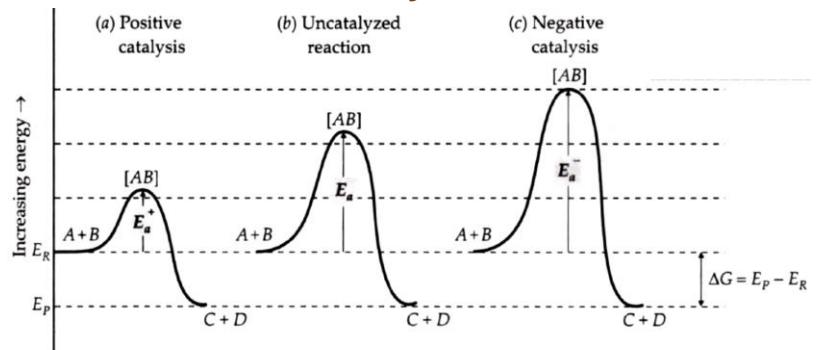
$$k_2 = 1.22 \times 10^4 \text{ s}^{-1}$$

Catalysis

Catalyst is defined as a substance, a small amount of which alters (**increases or decreases**) the velocity of a chemical reaction by its mere presence, without itself undergoing any change in mass and composition at the end of the reaction.

- Catalyst **provides an alternative path** of lower or higher activation energy in positive and negative catalysis respectively.
- There is **no difference in free energy (ΔG)** between uncatalyzed and catalyzed reactions.
- **Activation energy (E_a) determines kinetic feasibility** of reaction.
- **Free energy change (ΔG) determines thermodynamic feasibility** of reaction.

Catalysis



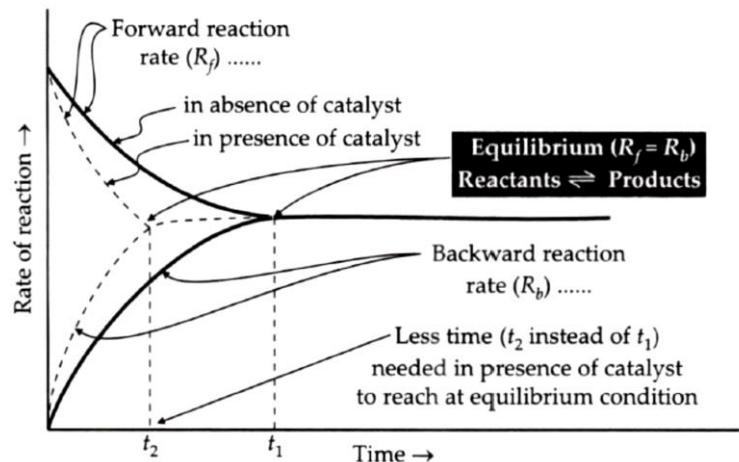
Hydrogenation of vegetable oil (during manufacture of vegetable ghee) by Nickel (150 -300° C).

Progress of reaction →

Alcohol retards the oxidation of chloroform to poisonous phosgene.

Catalysis

The catalyst does not alter the position of equilibrium in a reversible reaction.

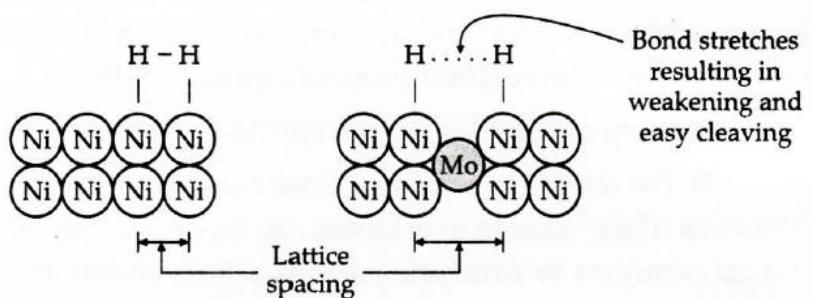


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Catalysis

Catalytic Promoters

A catalytic promoter or activator may be defined as a substance which promotes the activity of the catalyst to which it is added (in small amounts) and this process is known as activation

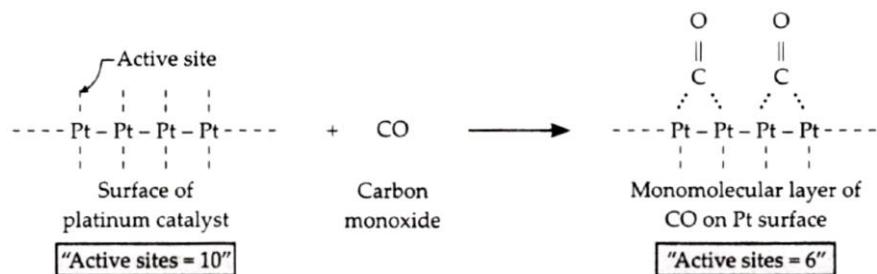


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Catalysis

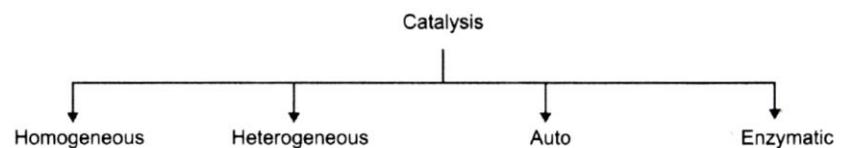
Catalytic Poisons

Catalytic Poisons (anti catalyst) are substances that decrease or inhibit the activity of catalysts.



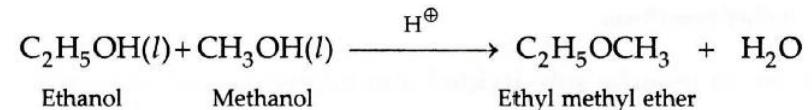
Catalysis

The catalysis can be broadly sub-divided into following four categories :



Homogeneous Catalysis

In Homogeneous catalysis, the catalyst and the reactants are in same phase.

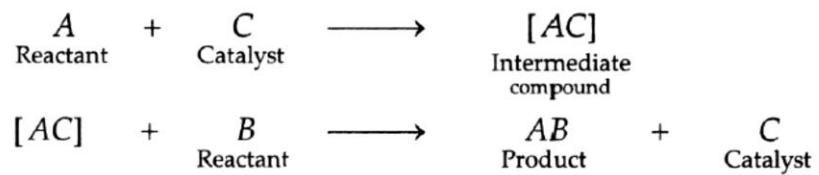


Catalysis

Intermediate Compound Formation Theory for Homogenous Catalysis

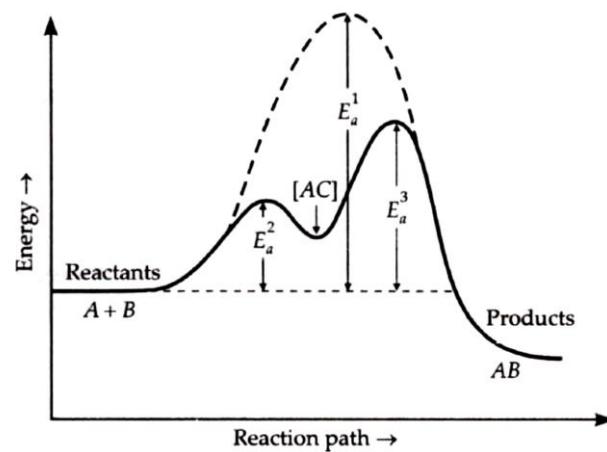


This reaction in the presence of a catalyst C, may occurs as:



where A and B are reactants, [AC] is an intermediate and AB is product.

Catalysis

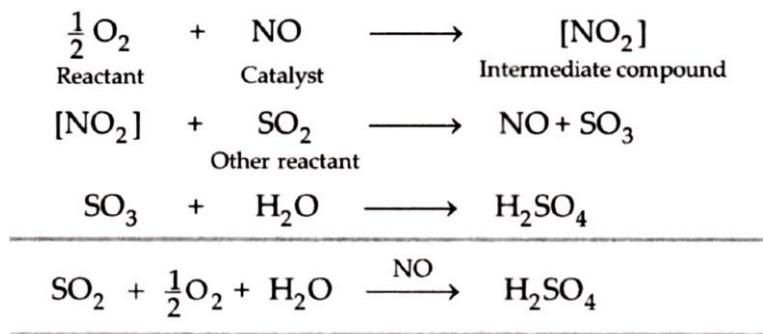


The formation of intermediate, $[AC]$ provides an alternative reaction path with lower activation energy, compared to activation energy in absence of catalyst.

Catalysis

Example

Catalytic action of NO in the manufacture of H_2SO_4 by chamber process (Lead chamber)



Catalysis

Limitations of Intermediate Compound Formation Theory

This theory fails to explain :

- (i) the action of promoters and catalytic poisons,
- (ii) the function of catalyst in heterogeneous reactions, where intermediate compound formation is not possible.

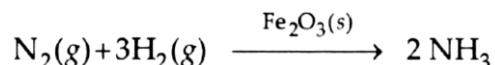
Catalysis

Heterogeneous Catalysis

In Heterogeneous catalysis, the catalyst and the reactants are in different phases.

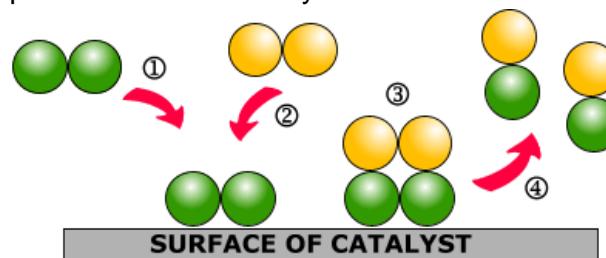
Reacting system remains heterogeneous throughout and reactions proceed at an interface between two discrete phases.

Haber's process :



Catalysis

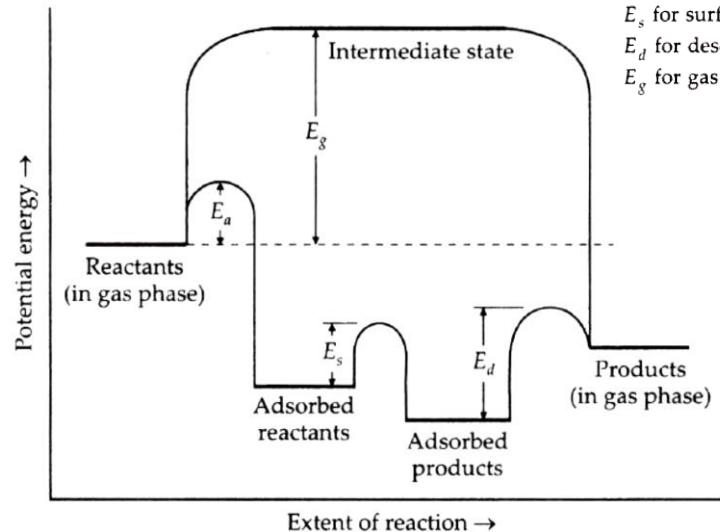
Adsorption or Contact Theory Mechanism



- ① One of the reactants approaches the catalyst's surface and settles onto an active site - **ADSORPTION**
- ② Another reactant approaches the catalyst
- ③ Re-arrangement of electrons takes place - **REACTION**
- ④ The products are released from the surface - **DESORPTION**

Catalysis

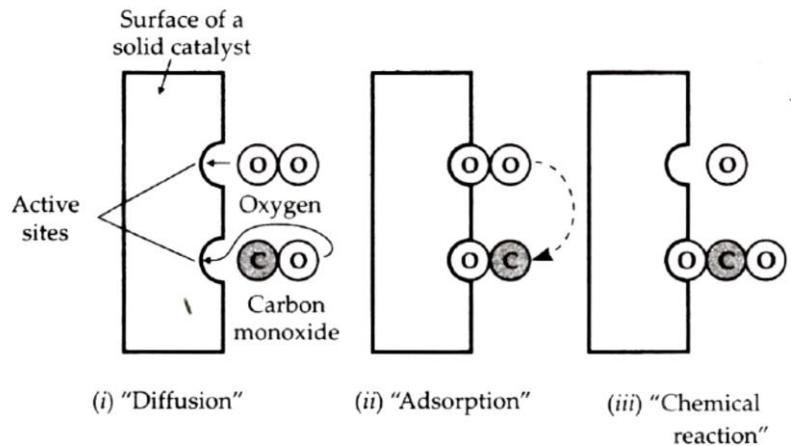
Adsorption or Contact Theory Mechanism



Activation energies :
 E_a for adsorption ;
 E_s for surface reaction ;
 E_d for desorption ; and
 E_g for gas phase reaction

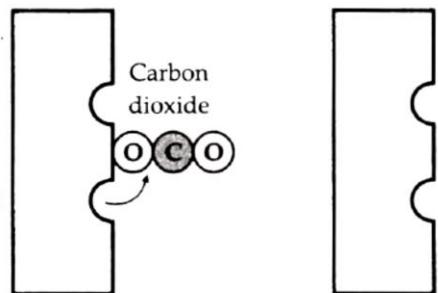
Catalysis

The Langmuir-Hinshelwood Mechanism



Catalysis

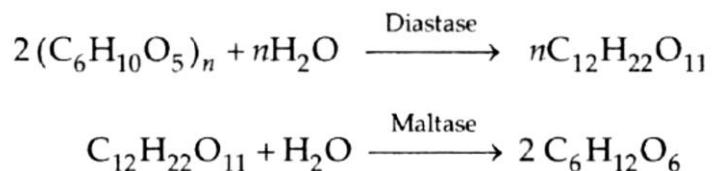
The Langmuir-Hinshelwood Mechanism



(iv) "Desorption" (v) Product diffusion and catalyst regeneration

Enzyme Catalysis

Enzymes are proteins with high relative molar mass of the order of 10,000 or even more and are derived from living organisms and they catalyse the biochemical reactions.



Enzyme Catalysis

Lock and key model

An enzyme is ordinarily a very large protein molecule that contains one or more active sites, where the reactions with the substrate take place.

The rest of the molecule maintains the three-dimensional integrity of the network.

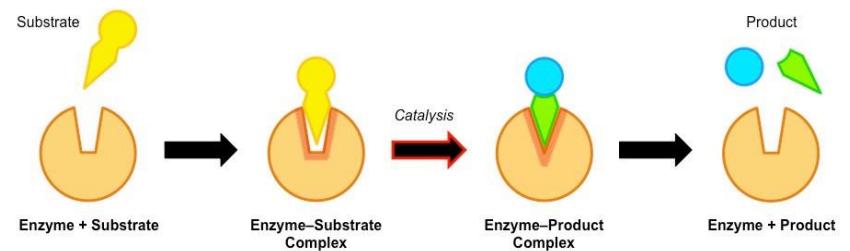
According to Fischer's hypothesis, the active site has a rigid structure, similar to a lock.

A substrate molecule has the complementary structure that causes it to fit and function like a key.

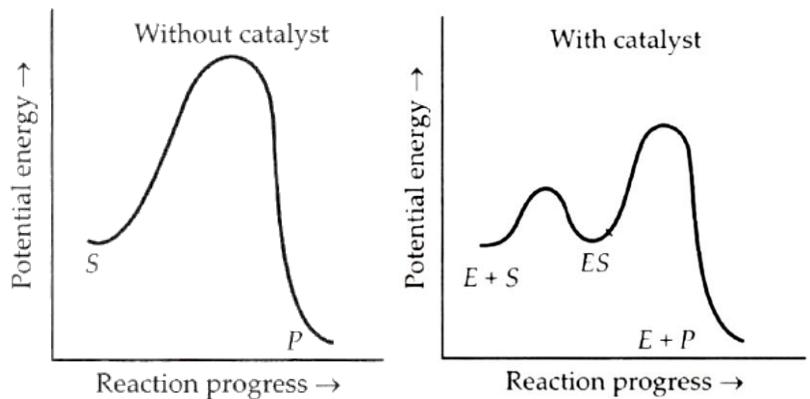
Geometry of an active site only fit one type of substrate in most cases. That's why enzymes are highly specific in action.

Enzyme Catalysis

Lock and key model



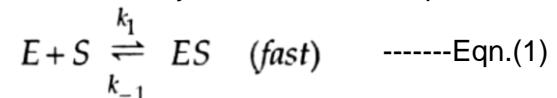
Enzyme Catalysis



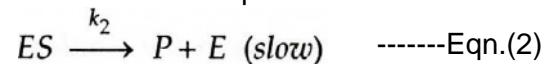
Enzyme Catalysis

In 1913, biochemists L Michaelis and Mary Menten proposed a mechanism for the kinetics of enzyme-catalyzed reactions which envisages the following steps :

Step 1. Formation of the enzyme-substrate complex :



Step 2. Decomposition of the complex:



where

E is the (free) enzyme ;

S is the substrate (i.e., the reactant) ;

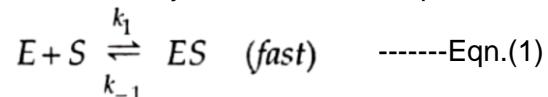
ES is the enzyme-substrate complex and

P is the product.

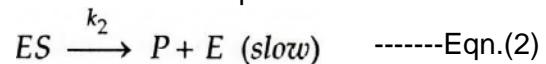
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S is the substrate (i.e., the reactant) ;

ES is the enzyme-substrate complex and

P is the product.

Enzyme Catalysis

According to the slow rate-determining step, the rate of the reaction is given by

$$r = -\frac{d}{dt}[S] = +\frac{d}{dt}[P] = k_2[ES] \quad \text{Eqn.(3)}$$

Using steady state approximation for ES, we have

Rate of formation of ES = Rate of consumption of ES

$$k_1[E][S] = k_{-1}[ES] + k_2[ES] \quad \text{Eqn.(4)}$$

$$\frac{d}{dt}[ES] = k_1[S][E] - k_{-1}[ES] - k_2[ES] = 0 \quad \text{Eqn.(5)}$$

Enzyme Catalysis

The equilibrium between the free and bound enzyme is given by the enzyme conservation equation,

$$[E]_o = [E] + [ES] \quad \text{Eqn.(6)}$$

$[E]_o$ is total enzyme concentration (which can be measured) ;
 $[E]$ is the free enzyme concentration and
 $[ES]$ is the bound (or reacted) enzyme concentration

$$[E] = [E]_o - [ES] \quad \text{Eqn.(7)}$$

Substituting for $[E]$ in Eqn. (5)

$$\frac{d}{dt} [ES] = k_1 [S] \{ [E]_o - [ES] \} - k_{-1} [ES] - k_2 [ES] = 0$$

Enzyme Catalysis

$$\Rightarrow k_1 [S][E]_o = \{k_1[S] + k_{-1} + k_2\} [ES]$$

$$\Rightarrow [ES] = \frac{k_1 [S][E]_o}{k_1 [S] + k_{-1} + k_2} \quad \text{Eqn.(8)}$$

Substituting for $[ES]$ in Eq. (4),

$$r = \frac{k_1 k_2 [S][E]_o}{k_1 [S] + k_{-1} + k_2} \quad \text{Eqn.(9)}$$

Dividing the numerator and the denominator by k_1

$$r = \frac{k_2 [E]_o [S]}{(k_{-1} + k_2)/k_1 + [S]} = \frac{k_2 [E]_o [S]}{k_m + [S]} \quad \text{Eqn.(10)}$$

Enzyme Catalysis

$k_m \left(= \frac{k_{-1} + k_2}{k_1} \right)$ is called the *Michaelis constant*.

Equation 10 is known as Michaelis-Menten equation

When all the enzyme has reacted with the substrate at high concentration, the reaction will be going at maximum rate.

No free enzyme will remain so that

$$\begin{aligned}[E]_o &= [ES] \\ r &= k_2 [ES] \\ r_{\max} &= V_{\max} = k_2 [E]_o \end{aligned} \quad \text{Eqn.(11)}$$

where V_{\max} is the maximum rate and k_2 is called the turnover number of the enzyme

Enzyme Catalysis

The Michaelis-Menten eqn. can now be written as

$$r = \frac{V_{\max} [S]}{k_m + [S]} \quad \text{Eqn.(12)}$$

Case I. $k_m > > [S]$ so that $[S]$ can be neglected in the denominator of eqn. 12, giving

$$r = \frac{V_{\max} [S]}{k_m} = k' [S] \quad (\text{First-order reaction}) \quad \text{Eqn.(13)}$$

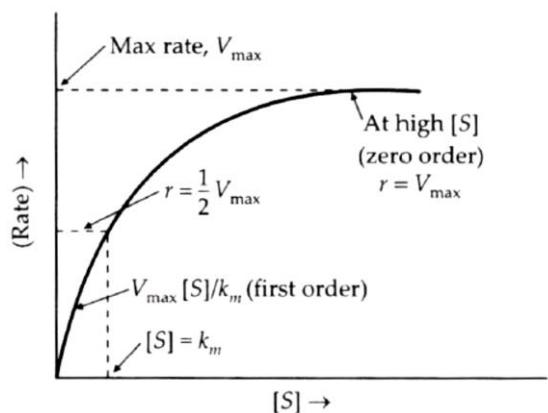
Case II. $k_m < < [S]$, so that k_m can be neglected in the denominator of eqn. 12, giving,

$$r = \frac{V_{\max} [S]}{[S]} = V_{\max} = \text{constant} \quad (\text{Zero-order reaction}) \quad \text{Eqn.(14)}$$

Enzyme Catalysis

Case III. If $k_m = [S]$

$$r = \frac{V_{\max} [S]}{k_m + [S]} = \frac{V_{\max} [S]}{2[S]} = \frac{1}{2} V_{\max} \quad \text{Eqn.(15)}$$



Enzyme Catalysis

Rearranging Michaelis-Menten equation (12)

$$\begin{aligned} r &= \frac{V_{\max} [S]}{k_m + [S]} \\ \Rightarrow \quad \frac{1}{r} &= \frac{k_m + [S]}{V_{\max} [S]} = \frac{k_m}{V_{\max}} \times \frac{1}{[S]} + \frac{1}{V_{\max}} \quad \text{Eqn.(16)} \end{aligned}$$

