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Thermodynamics **vs** Chemical Kinetics

Thermodynamics:

Does reaction take place?



Chemical Kinetics:

How fast a reaction takes place?



Chemical kinetics deals with the study of the rate of chemical reactions and the mechanism by which they occur.



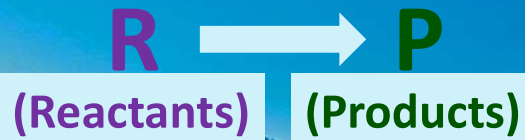
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“Chemical kinetics, also known as reaction kinetics, is the branch of physical chemistry that is concerned with understanding the rates of chemical reactions. It involves the experimental study of reaction rates in order to infer about the kinetic mechanisms for chemical conversion of reactants into products.”



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Rate of a Reaction

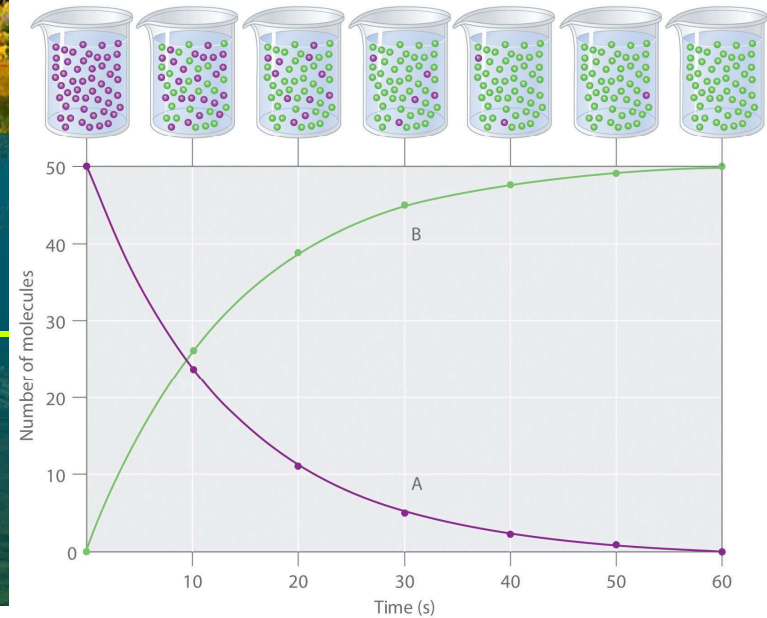


✓ Rate of a reaction is the rate at which the concentration of a reactant changes with time.

✓ It is the change in concentration of reactants or products per unit time.

Rate expression: Rate, $r = - d[R]/dt$
 $= + d[P]/dt$

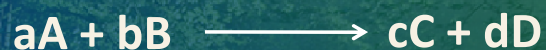
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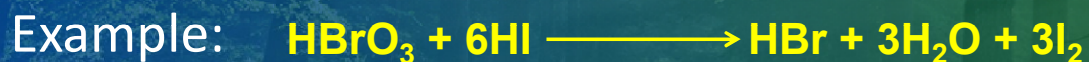


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Differential Rate Equation



$$\text{Rate of reaction, } r = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt}$$



$$\text{Rate of reaction, } r = -\frac{d[\text{HBrO}_3]}{dt} = -\frac{1}{6} \frac{d[\text{HI}]}{dt} = +\frac{d[\text{HBr}]}{dt} = +\frac{1}{3} \frac{d[\text{H}_2\text{O}]}{dt} = +\frac{1}{3} \frac{d[\text{I}_2]}{dt}$$

Units of rate of reaction: mol L⁻¹ time⁻¹

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Factors Affecting Rate of a Reaction

Concentration of reactants	→	As the concentration of reactants increases, number of collisions increases and thus rate increases.
Nature of reactants	→	Reactions between polar or ionic molecules are very fast. <i>Ex: Neutralization or double displacement reactions.</i> Reactions involving bond rearrangements or \bar{e} transfer are slow.
Effect of Catalyst	→	$2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$; Positive catalyst: Pt $2\text{Na}_2\text{S}_2\text{O}_3 + \text{O}_2 \longrightarrow 2\text{Na}_2\text{S}_2\text{O}_4$; slow in presence of $\text{C}_2\text{H}_5\text{OH}$
Surface area of reactants	→	In heterogeneous reactions, as the surface area of reactants increases, the rate of reaction increases.
Temperature	→	For most of the reactions, as the temperature increases the rate of reaction increases. Get doubled or tripled by 10°C raise.
Nature of light	→	$\text{H}_2 + \text{Cl}_2$ reaction takes place only in sunlight.



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Rate Law & Rate Constant

“Rate law is the mathematical expression that describes the relation between the rate of a chemical reaction and concentration of its reactants.”



$$\text{Rate Law: } r = k[A]^x[B]^y$$

where, k is the *rate constant* or *velocity constant*.
 x and y are experimentally determined ($x+y$ = Order of reaction).
 They are not stoichiometric coefficients.

“Rate constant is defined as the rate of the reaction when the molar concentration of each reactant is unity. It is also known as Specific reaction rate.”

$$r = k[1]^x[1]^y \longrightarrow r = k$$



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Complex Reactions

Those reactions which occur in two or more steps are known as complex reactions.
Each step of it is known as elementary reaction.

Example: Reduction of Bromic acid. $\text{HBrO}_3 + 6\text{HI} \longrightarrow \text{HBr} + 3\text{H}_2\text{O} + 3\text{I}_2$

Mechanism:



The rate of overall reaction will be equal to the rate of the slowest reaction, i.e., **rate determining step**.

Thus, molecularity = 2 and order = 2



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Order **vs** Molecularity

Order of a reaction	Molecularity
<i>It is "the sum of the powers to which the concentration or pressure of the reactants are raised in the rate law expression".</i>	It is "the number of ions or molecules or atoms that take part in the rate-determining step" (i.e., forming the activated complex).
It can either be a whole number or a fraction.	It is always a whole number.
It is an experimental quantity. Nothing to do with stoichiometry.	It is determined by looking at the reaction mechanism. A theoretical concept.
It is assigned for overall reaction.	It is assigned for each elementary step of the mechanism.
Its value can be negative.	It can never have a negative value.
It depends on pressure, temperature and concentration.	It does not depend on pressure, temperature and concentration.
It gives the information about the slowest step and hence explain the mechanism of a reaction.	It does not give details about the mechanism of a reaction.



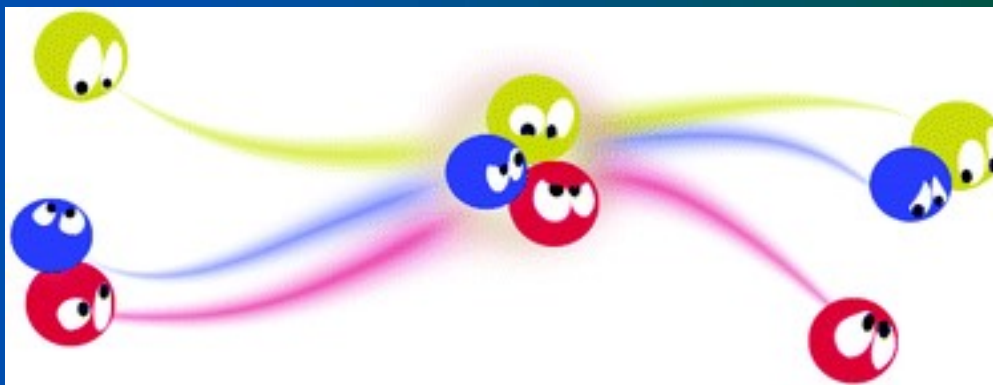
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Reactions of Higher Order are Rare

Reactions of third and higher order are very rare and most of the reactions are of first and second order.

Example: $2A + 3B \longrightarrow P$ Molecularity $\neq 5$; Order $\neq 5$

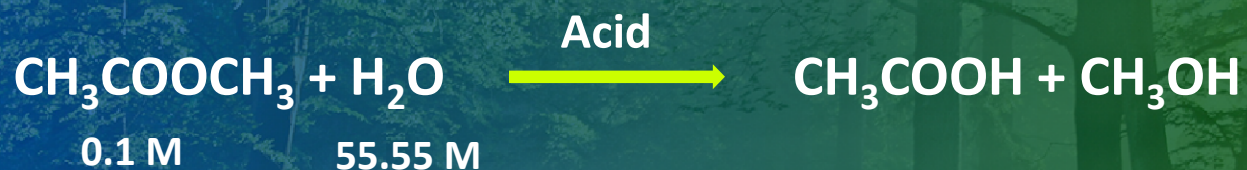
Reason: The chances for even 3 molecules to collide simultaneously are not high.





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Pseudo-Molecular Reactions



Expected order: Second order (Acc. to law of mass action)

Observed: First order reaction

How? : First order *w.r.t.* the ester and independent of water.

Reason: Water is present in such extent that it's concentration remain practically constant.

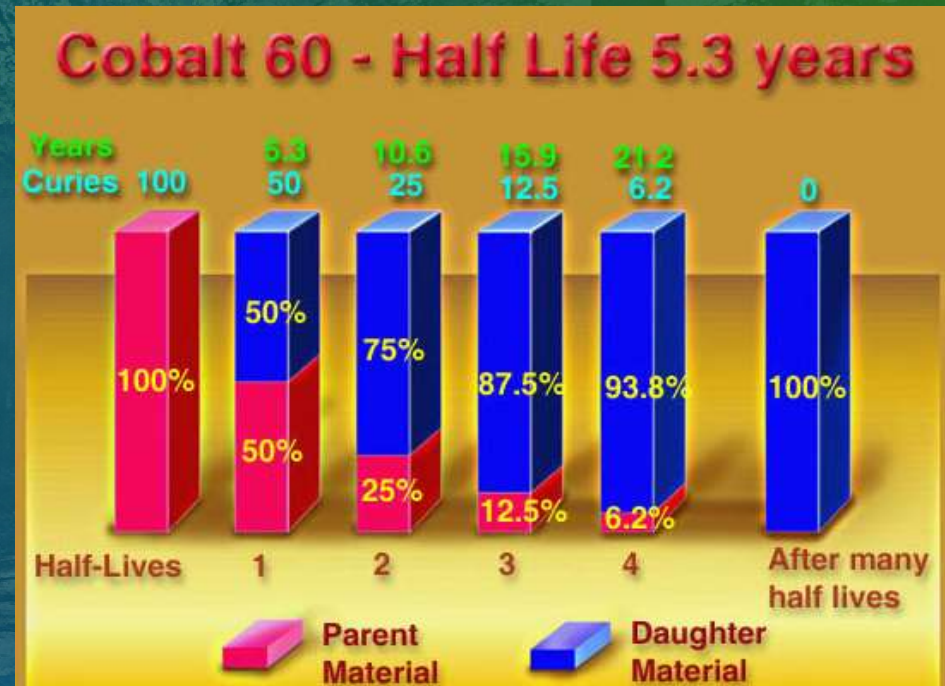


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Half Life Period

“Half life of a reaction is the time taken for the reactant concentration to reach half of its initial value.”

It is denoted by the symbol ' $t_{1/2}$ ' and is usually expressed in seconds.





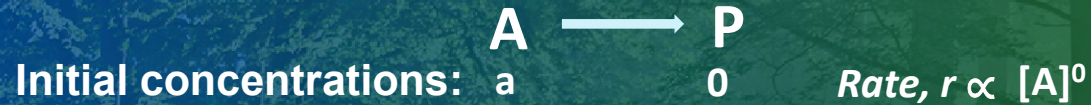
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Zero Order Reactions

“Reactions in which the reaction rate is not affected by the changes in concentrations of one or more reactants”.



Rate Constant of Zero Order Reaction:



Rate of reaction at any time 't', $r = \frac{dx}{dt} = k[A]^0$

where, $x =$ Initial concentration of A (a or $[A_0]$)
 - Concentration of A at any time t
 $= [A_0] - [A_t]$
 $=$ Change in concentration of A
 $=$ concentration of A decomposed after time t

$$\longrightarrow dx = k dt$$

Integrate on both sides: $\int dx = k \int dt$

$$\longrightarrow x = kt + I \quad \text{where, } I = \text{Integration constant}$$

Initially (time $t = 0$), $x = 0 \longrightarrow I = 0$

$$\therefore x = kt \quad \text{or} \quad [A_0] - [A_t] = kt$$

$$\text{Rate, } r = -\frac{d[A]}{dt} = k[A]^0$$

$$\longrightarrow -d[A] = k dt$$

Integrate on both sides: $-\int_{[A_0]}^{[A_t]} d[A] = k \int_0^t dt$

$$-([A_t] - [A_0]) = k(t-0)$$

$$kt = [A_0] - [A_t]$$

$$\longrightarrow k = 1/t ([A_0] - [A_t])$$

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Characteristics of Zero Order Reaction

(i) Units of rate constant, $k = \text{mol L}^{-1} \text{time}^{-1}$

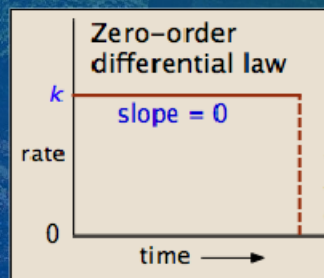
(ii) Half-life time: $[A_0] - [A_t] = kt$

At time, $t = t_{1/2}$; $[A] = [A_0]/2 \rightarrow [A_0] - [A_0]/2 = kt_{1/2}$

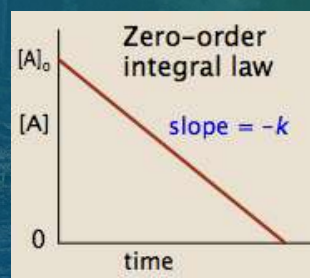
$\rightarrow t_{1/2} = [A_0]/2k$ or $t_{1/2} = a/2k$

Half-life time of Zero order reaction is directly proportional to the initial concentration.

(iii) Graphs:



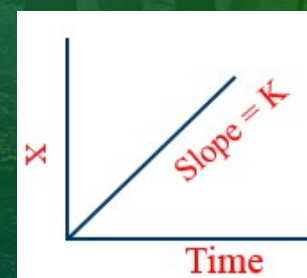
$$r = k$$



$$[A_0] - [A] = kt$$

$$[A] = -kt + [A_0]$$

$$y = -mx + c$$



$$x = kt$$



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Examples of Zero Order Reaction

- Photochemical reaction of H_2 and Cl_2 over water surface (saturated with HCl).
- Heterogeneous reactions like thermal decomposition of HI on gold surface.
- Enzyme Reactions, etc.



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First Order Reactions

"The reaction rate is determined by the change of only one concentration term of reactants".



Initial concentrations: a 0 0

After a time interval 't': $a - x$ x x where,

a = Initial concⁿ of A

x = concⁿ of A decomposed after time t

$a - x$ = concⁿ of A left behind.

$$\text{Rate of reaction, } r = \frac{dx}{dt} = k[A]$$

$$dx = k[A] dt$$

$$dx = k(a-x) dt$$

$$\rightarrow \frac{dx}{(a-x)} = k dt$$

Integrate on both sides:

$$\int \frac{dx}{(a-x)} = k \int dt$$



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$$\rightarrow -\ln(a-x) = kt + I \quad \text{where, } I = \text{Integration constant}$$

Initially (time $t = 0$), $x = 0$ $\rightarrow -\ln a = I$

$$\therefore -\ln(a-x) = kt - \ln a$$

$$\rightarrow k = \frac{1}{t} \ln \frac{a}{(a-x)}$$

or $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$

or $k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$



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Characteristics of First Order Reaction

(i) Units of rate constant, $k = \text{Time}^{-1}$ $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$

(ii) The value of rate constant is independent of units of conc^n chosen (ex: molar, normal, moles, mole fraction, etc).

(iii) Half-life time:

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

At time $t = t_{1/2}$:

$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{(a-(a/2))}$$

$$\rightarrow k = \frac{2.303}{t_{1/2}} \log \frac{a}{(a/2)}$$

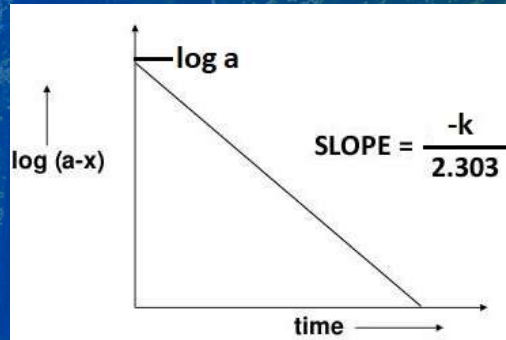
$$t_{1/2} = \frac{2.303}{k} \log 2$$

$$\therefore t_{1/2} = \frac{0.693}{k}$$

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Half life time is independent of initial conc^n .

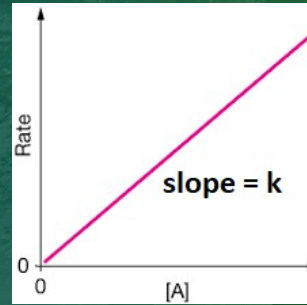
(iv) Graphs:



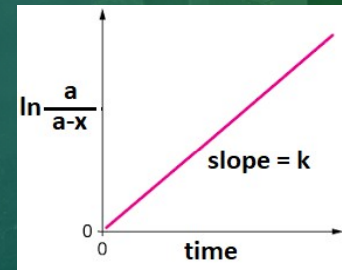
$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

$$\Rightarrow \frac{kt}{2.303} = \log a - \log(a-x)$$

$$\Rightarrow \log(a-x) = -\frac{kt}{2.303} + \log a$$

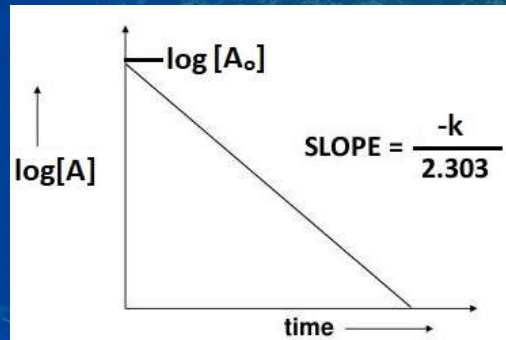


$$r = k[A]$$



$$k = \frac{1}{t} \ln \frac{a}{(a-x)}$$

$$\Rightarrow \ln \frac{a}{(a-x)} = kt$$



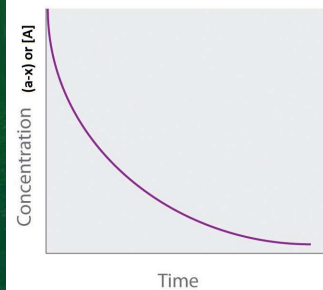
$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$\Rightarrow \frac{kt}{2.303} = \log[A_0] - \log[A]$$

$$\Rightarrow \log[A] = -\frac{kt}{2.303} + \log[A_0]$$

$$\frac{[A_0]}{[A]} = e^{\left[\frac{kt}{2.303}\right]}$$

$$[A] = [A_0] e^{\left[\frac{-kt}{2.303}\right]}$$

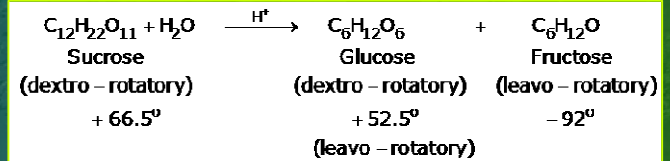




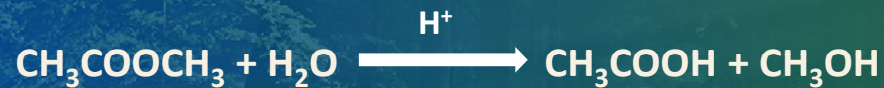
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Examples of First Order Reaction

- Inversion of cane sugar.



- Acid hydrolysis of methyl acetate.



- Decomposition of N_2O .

- Radioactive decompositions.



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Second Order Reactions

"The reaction rate is determined by the variation of two concentration terms of reactants".

(a) Concentration of both reactants is equal



$$\text{Rate of reaction, } r = \frac{dx}{dt} = k[A]^2$$

(b) Concentration of both reactants is not equal



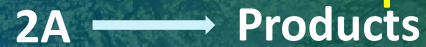
$$\text{Rate of reaction, } r = \frac{dx}{dt} = k[A][B]$$





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(a) Concentration of both reactants is equal:



$$\text{Rate of reaction, } r = \frac{dx}{dt} = k[A]^2$$

$$r = \frac{dx}{dt} = k(a-x)^2 \quad \Rightarrow \quad \frac{dx}{(a-x)^2} = k dt$$

Integrate on both sides:

$$\int \frac{dx}{(a-x)^2} = k \int dt \quad \Rightarrow \quad \frac{-1}{(a-x)} (-1) = kt + I$$

where, $I = \text{Integration constant}$

$$\Rightarrow \frac{1}{(a-x)} = kt + I$$

$$\text{Initially (time } t = 0), x = 0 \quad \Rightarrow \quad I = 1/a \quad \Rightarrow \quad \frac{1}{(a-x)} = kt + \frac{1}{a}$$

$$\therefore k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right] \quad (22)$$

$$\text{or } k = \frac{1}{t} \left[\frac{x}{a(a-x)} \right]$$

(b) Concentration of both reactants is not equal:

$$\text{Rate of reaction, } r = \frac{dx}{dt} = k[A][B]$$

$$\frac{dx}{dt} = k(a-x)(b-x) \quad \longrightarrow \quad \frac{dx}{(a-x)(b-x)} = k dt$$

$$\text{Split into partial fractions: } \frac{1}{(a-b)} \left[\frac{dx}{(b-x)} - \frac{dx}{(a-x)} \right] = k dt$$

$$\text{Upon integration: } \frac{1}{(a-b)} \left[\int \frac{dx}{(b-x)} - \int \frac{dx}{(a-x)} \right] = k \int dt$$

$$\frac{1}{(a-b)} \left[-\ln(b-x) + \ln(a-x) \right] = kt + I$$

$$\text{Initially (time } t = 0), x = 0 \quad \longrightarrow \quad I = \frac{1}{(a-b)} \ln a/b \quad (23)$$

$$\frac{1}{(a-x)(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)}$$

$$A(b-x) + B(a-x) = 1$$

$$\text{For } x=a, \quad A(b-a) = 1$$

$$A = \frac{1}{(b-a)} = -\frac{1}{(a-b)}$$

$$\text{For } x=b, \quad B(a-b) = 1$$

$$B = \frac{1}{(a-b)}$$



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$$\frac{1}{(a-b)} \left[-\ln(b-x) + \ln(a-x) \right] = kt + \frac{1}{(a-b)} \ln a/b$$

$$\rightarrow \frac{1}{(a-b)} \left[\ln \frac{(a-x)}{(b-x)} - \ln a/b \right] = kt$$

$$\therefore k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

$$\rightarrow k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

Characteristics of Second Order Reaction

(i) Units of rate constant, $k = L \text{ mole}^{-1} \text{ Time}^{-1}$ $\therefore k = \frac{1}{t} \left[\frac{x}{a(a-x)} \right]$

(ii) The numeral value of rate constant will change with the change in units in which conc^n is expressed. $\therefore k = \frac{1}{t} \left[\frac{x}{a(a-x)} \right]$

(iii) Half-life time:

$$k = \frac{1}{t} \left[\frac{x}{a(a-x)} \right]$$

At time $t = t_{1/2} : x = a/2 \rightarrow k = \frac{1}{t_{1/2}} \left[\frac{a/2}{a(a-a/2)} \right]$

$$\rightarrow k = \frac{1}{t_{1/2}} \left[\frac{a/2}{a(a/2)} \right]$$

$$\therefore t_{1/2} = \frac{1}{ak}$$

Half life time is inversely proportional to the initial conc^n .

(iv) When one of the reactants is present in large excess: **Second order becomes first order.**

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

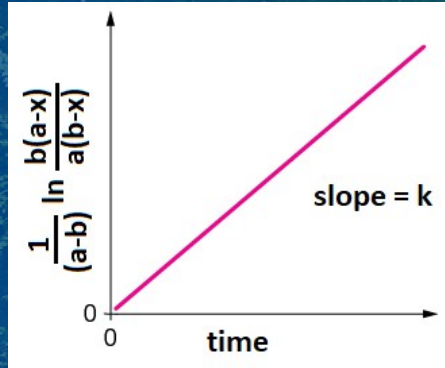
If $a \gg b$, then b and x can be neglected.

$$\rightarrow k = \frac{2.303}{t(a)} \log \frac{b(a)}{a(b-x)}$$

$$\rightarrow k = \frac{2.303}{at} \log \frac{b}{(b-x)} \quad \rightarrow ka = \frac{2.303}{t} \log \frac{b}{(b-x)}$$

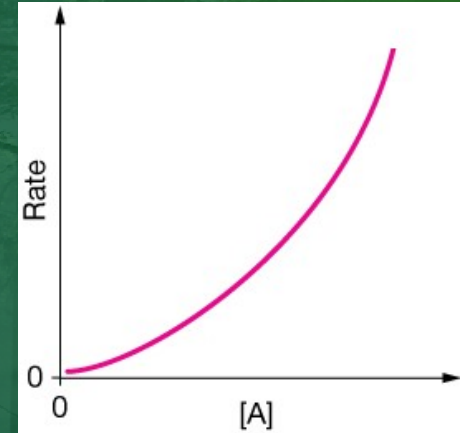
$$\rightarrow k' = \frac{2.303}{t} \log \frac{b}{(b-x)}$$

(v) Graphs:

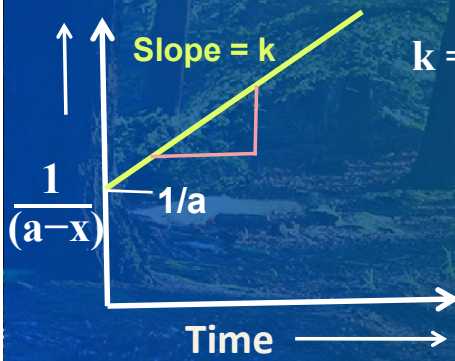


$$k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

$$\frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)} = kt$$



$$r = \frac{dx}{dt} = k[A]^2$$

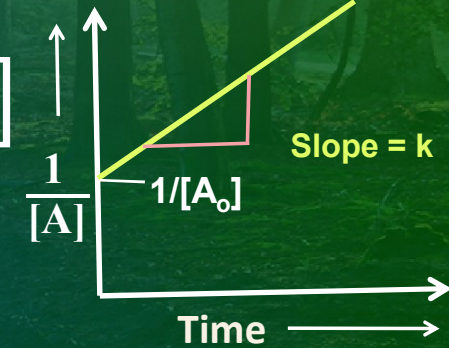


$$k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right]$$

$$\frac{1}{(a-x)} = kt + \frac{1}{a}$$

$$k = \frac{1}{t} \left[\frac{1}{[A]} - \frac{1}{[A_0]} \right]$$

$$\frac{1}{[A]} = kt + \frac{1}{[A_0]}$$



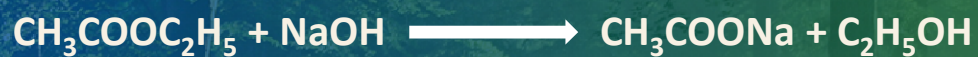
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Examples of Second Order Reaction

- Saponification of esters.



- Reaction between persulphate and Iodide ions (ionic reactions).





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Units of Rate constant

$$k = \frac{\text{concentration}}{\text{time}} \times \frac{1}{\text{concentration}^n}$$

$$k = \frac{\text{mol dm}^{-3}}{\text{sec}} \times \frac{1}{(\text{mol dm}^{-3})^n}$$

n=0

$$k = \frac{\text{mol dm}^{-3}}{\text{sec}} \times \frac{1}{(\text{mol dm}^{-3})^0}$$

$$= \text{mol dm}^{-3} \text{sec}^{-1}$$

n=1

$$k = \frac{\cancel{\text{mol dm}^{-3}}}{\text{sec}} \times \frac{1}{(\cancel{\text{mol dm}^{-3}})^1}$$

$$= \text{sec}^{-1}$$

n=2

$$k = \frac{\cancel{\text{mol dm}^{-3}}}{\text{sec}} \times \frac{1}{(\cancel{\text{mol dm}^{-3}})^2}$$

$$= \frac{1}{\text{mol dm}^{-3} \text{sec}}$$

$$= \text{mol}^{-1} \text{dm}^3 \text{sec}^{-1}$$

Reaction	order	Units of rate constant
Zero order reaction	0	$\text{mol dm}^{-3} \text{sec}^{-1}$
First order reaction	1	sec^{-1}
Second order reaction	2	$\text{mol}^{-1} \text{dm}^3 \text{sec}^{-1}$

Third Order Reactions

"The reaction rate is determined by the variation of three concentration terms of reactants".



$$\text{Rate of reaction, } r = \frac{dx}{dt} = k(a-x)(b-x)(c-x)$$

Case (i): When $a = b = c$

$$\frac{dx}{dt} = k(a-x)^3 \quad \rightarrow \quad \frac{dx}{(a-x)^3} = k dt$$

Integrate on both sides:

$$\int \frac{dx}{(a-x)^3} = k \int dt \quad \rightarrow \quad \frac{-1}{2(a-x)^2} (-1) = kt + I$$

$$\int y^n dy = \frac{y^{n+1}}{n+1}$$

where, $I = \text{Integration constant}$

$$\rightarrow \frac{1}{2(a-x)^2} = kt + I$$

Initially (time, $t = 0$), $x = 0 \quad \rightarrow \quad I = 1/2a^2$

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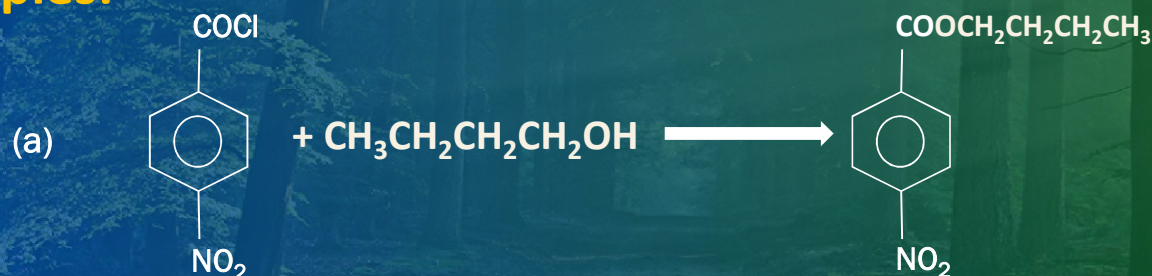
$$k = \frac{1}{2t} \left[\frac{x(2a-x)}{a^2(a-x)^2} \right]$$

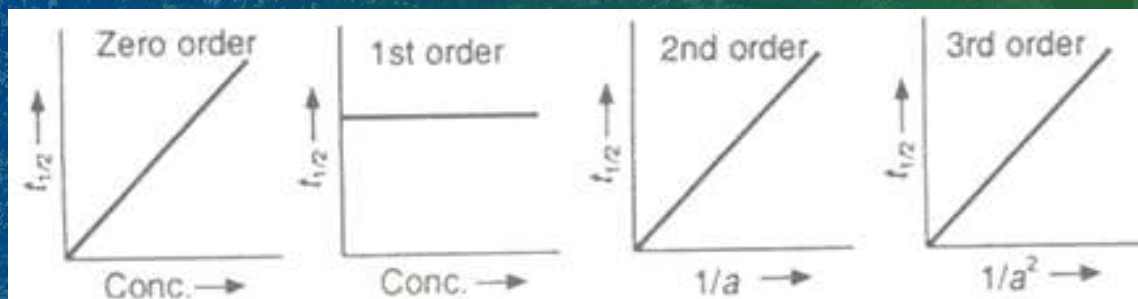
Characteristics of Third Order Reaction

(i) Units of rate constant, $k = L^2 \text{ mole}^{-2} \text{ Time}^{-1}$

(ii) Half-life time: $t_{1/2} = \frac{3}{2ka^2}$ For order 'n', $t_{1/2} = \frac{2^{(n-1)} - 1}{(n-1) k a^{(n-1)}}$

Examples:





	Zero-Order	First-Order	Second-Order	<i>n</i> th-Order
Rate Law	$-\frac{d[A]}{dt} = k$	$-\frac{d[A]}{dt} = k[A]$	$-\frac{d[A]}{dt} = k[A]^2$	$-\frac{d[A]}{dt} = k[A]^n$
Integrated Rate Law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$\frac{1}{[A]^{n-1}} = \frac{1}{[A]_0^{n-1}} + (n-1)kt$ [Except first order]
Units of Rate Constant (<i>k</i>)	$\frac{M}{s}$	$\frac{1}{s}$	$\frac{1}{M \cdot s}$	$\frac{1}{M^{n-1} \cdot s}$
Linear Plot to determine <i>k</i>	$[A]$ vs. t	$\ln([A])$ vs. t	$\frac{1}{[A]}$ vs. t	$\frac{1}{[A]^{n-1}}$ vs. t [Except first order]
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln(2)}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$	$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$ [Except first order]

Determination of Order of Reaction

- (i) Integration method
- (ii) Half-life method *or* Fractional change method
- (iii) Isolation method
- (iv) van't Hoff's differential method
- (v) Graphical method
- (vi) Method of ratio variation

(i) Integration method

- The initial concentrations of all the reactants are determined.
- The concentration of reacting substance is then determined at different intervals of time.
- These values are substituted in various order rate expressions and the equation which gives the most constant value of rate constant for a series of intervals of times gives the order of reaction.

Zero order Reaction: $x = kt$

Second order Reaction: $k = \frac{1}{t} \left[\frac{x}{a(a-x)} \right]$

First order Reaction: $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$

Third order Reaction: $k = \frac{1}{2t} \left[\frac{x(2a-x)}{a^2(a-x)^2} \right]$

(ii) Half-life method or Fractional change method

Provided all the reactants are present in same concentrations, $t_{1/2}$ of n^{th} order is given by

$$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1) a^{n-1}} \rightarrow t_{1/2} \propto \frac{1}{a^{n-1}}$$

If two experiments are carried out at different initial concentrations, then:

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

$$\rightarrow \log \frac{(t_{1/2})_1}{(t_{1/2})_2} = (n-1) \log \left(\frac{a_2}{a_1}\right)$$

$$\therefore n = 1 + \frac{\log [(t_{1/2})_1 / (t_{1/2})_2]}{\log(a_2/a_1)}$$

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In case of gaseous reactions:

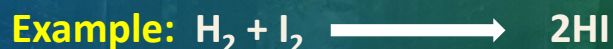
$$n = 1 + \frac{\log [(t_{1/2})_1 / (t_{1/2})_2]}{\log(p_2/p_1)}$$

(iii) Isolation method (By Ostwald in 1902)

In this method the concentration of all the reactants except one is taken in excess and the order of reaction is then determined by any method *w.r.t.* that reactant which is not taken in excess.

Then is another separate experiment the concentration of any other reactant is not taken in excess, keeping the concentration of all other reactants in excess. The order of reaction is again determined.

The reactant which is not taken in excess is said to be isolated from other reactants which are taken in excess.



It is pseudo first order *w.r.t.* H_2 when I_2 is large and pseudo first order *w.r.t.* I_2 when H_2 is in large excess.

Advantage: The mode of action of each component can be determined separately and disturbing effects can be traced to the origin.

(iv) van't Hoff's Differential method

The rate of n^{th} order reaction is given by: $r = k[A]^n$

$$\rightarrow \ln r = \ln k + n \ln[A]$$

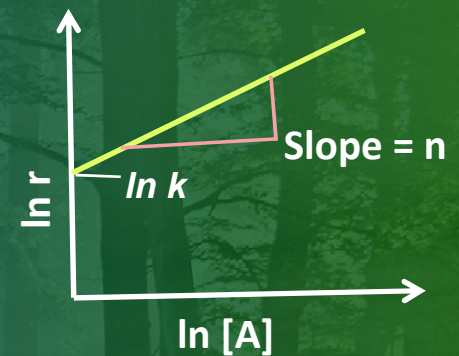
$$\rightarrow \text{Slope} = n$$

If r_1 and r_2 are the initial rates at two different initial concentrations c_1 and c_2 respectively, then

$$\frac{r_1}{r_2} = \frac{-dc_1/dt}{-dc_2/dt} = \frac{kc_1^n}{kc_2^n}$$

$$\rightarrow \frac{r_1}{r_2} = \left(\frac{c_1}{c_2}\right)^n$$

$$\therefore n = \frac{\ln(r_1/r_2)}{\ln(c_1/c_2)}$$



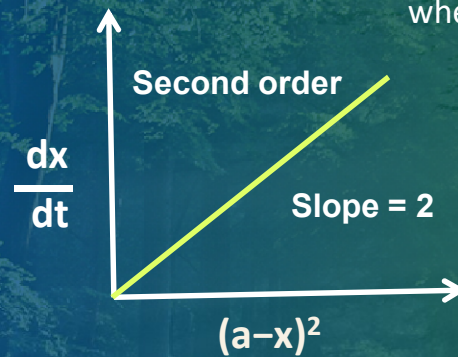
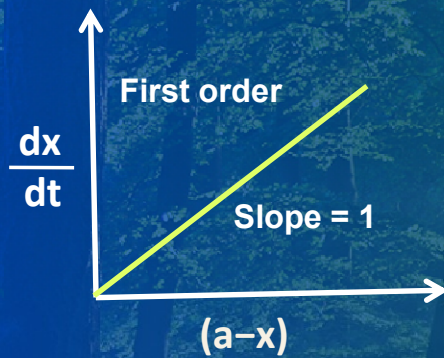
(v) Graphical method

The rate of n^{th} order reaction is given by: $\frac{dx}{dt} = k(a-x)^n$

where, a = Initial concentration

x = concentration of reactant decomposed after time t

If a straight line is obtained by plotting dx/dt and $(a-x)^n$, then order = n

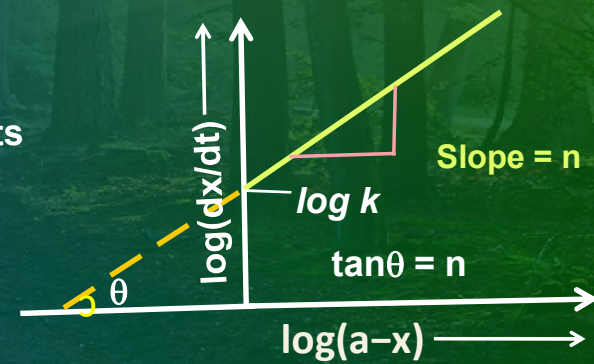
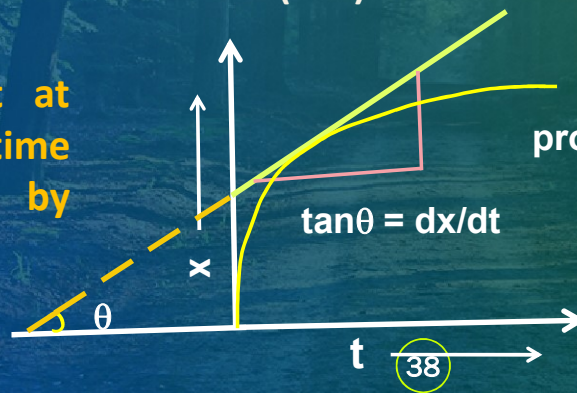


Slope = n

$$\frac{dx}{dt} = k(a-x)^n$$

$$\log(dx/dt) = n \log(a-x) + \log k$$

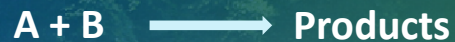
The values of dx/dt at different intervals of time can be determined by plotting x vs t .



(vi) Method of Ratio variation

A complex reaction involving different substances may be studied by appreciably increasing the concentration of the reactant, one at a time and observing the reaction rate over a period.

Consider the reaction:



$$\text{Rate of reaction, } r = \frac{dx}{dt} = k[A]^m [B]^n$$

The index m can be determined by doubling $[A]$, while keeping $[B]$ constant and determining experimentally the change in the rate

$$\frac{\left(\frac{\Delta x}{\Delta t}\right)_2}{\left(\frac{\Delta x}{\Delta t}\right)_1} = \frac{k[A]^m 2^m [B]^n}{k[A]^m [B]^n} = 2^m$$

The same procedure is adopted for evaluating 'n'. **The overall order of reaction = $m+n$**

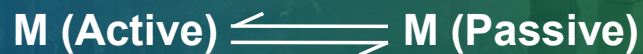


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Arrhenius Equation

According to the hypothesis of Arrhenius:

- (1) All molecules of a system can not take part in chemical reaction.
- (2) Only a certain number of molecules react. These are known as 'active molecules'.
- (3) Other molecules are known as 'passive molecules'.
- (4) An equilibrium exists between both.



- (5) When temperature is raised equilibrium shifts towards active molecules. The number of active molecules increases. Thus, the increase in rate of reaction with increase in temperature is due to an increase in the number of active molecules and not due to the number of collisions.

The basic concept of Arrhenius theory is that "the passive or non-active molecules become active due to the absorption of heat energy.

Derivation of Arrhenius equation

Consider, $A + B \rightleftharpoons C + D$

Rate of forward reaction, $r_f = k_f [A][B]$

Rate of backward reaction, $r_b = k_b [C][D]$

At equilibrium, $r_f = r_b \rightarrow k_f [A][B] = k_b [C][D]$

$$\rightarrow K_c = \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

From thermodynamics, van't Hoff's equation is: $\frac{d \ln K_c}{dT} = \frac{\Delta H}{RT^2}$

where $\Delta H = \text{Heat of reaction} = (E_a)_f - (E_a)_b$

$K_c = \text{Equilibrium constant}$



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$$\rightarrow \frac{d \ln k_f - d \ln k_b}{dT} = \frac{\Delta H}{RT^2}$$

$$\rightarrow \frac{d \ln k_f}{dT} - \frac{d \ln k_b}{dT} = \frac{(E_a)_f}{RT^2} - \frac{(E_a)_b}{RT^2}$$

$$\rightarrow \frac{d \ln k_f}{dT} - \frac{(E_a)_f}{RT^2} = \frac{d \ln k_b}{dT} - \frac{(E_a)_b}{RT^2} = I \text{ (say)}$$

$$\rightarrow \frac{d \ln k_f}{dT} = \frac{(E_a)_f}{RT^2} + I \quad \text{and} \quad \frac{d \ln k_b}{dT} = \frac{(E_a)_b}{RT^2} + I$$

It has been found that I is independent of T and I = 0.

$$\rightarrow \frac{d \ln k_f}{dT} = \frac{(E_a)_f}{RT^2} \quad \text{and} \quad \frac{d \ln k_b}{dT} = \frac{(E_a)_b}{RT^2}$$

These are known as Arrhenius equations. Where E_a = Activation energy.

“The energy in excess to the average energy of the molecules at a given temperature which a molecule must have to enter into reaction is known as **activation energy**.”

$$\rightarrow \frac{d \ln k_f}{dT} = \frac{(E_a)_f}{RT^2} \quad \text{and} \quad \frac{d \ln k_b}{dT} = \frac{(E_a)_b}{RT^2}$$

Up on integration: $\ln k_f = -\frac{(E_a)_f}{RT} + \text{constant} \quad \rightarrow \quad k_f = A e^{-(E_a)_f/RT}$

$$\ln k_b = -\frac{(E_a)_b}{RT} + \text{constant} \quad \rightarrow \quad k_b = A e^{-(E_a)_b/RT}$$

In general,

$$k = A e^{-E_a/RT}$$

A = Frequency factor (or)
Collision factor (or)
Pre-exponential factor

Rate constant increases exponentially with temperature.

We have, $\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$

Integrate between proper limits:

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

$$\int_{k_1}^{k_2} d \ln k = \int_{T_1}^{T_2} \frac{E_a}{RT^2} dT$$

$$\therefore \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

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Characteristics of Arrhenius equation

(1) As E_a increases rate constant decreases.

$$k = A e^{-E_a/RT}$$

(2) Larger the E_a , greater the effect of a given temperature T rise on k .

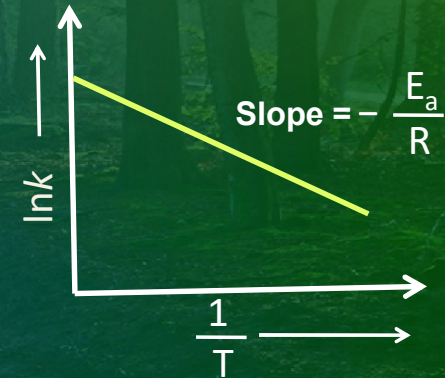
(3) At lower temperature, increase in temperature causes more change in k ; than at higher temperature.

Determination of Activation energy:

E_a can be calculated by using the following equation:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

E_a can also be evaluated graphically. $\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$



Temperature Coefficient

“The ratio of rate constants of a reaction at two temperatures differing by 10K is known as Temperature coefficient.”

$$\ln \frac{k_{T+10K}}{k_T} = -\frac{E_a}{R} \left[\frac{1}{T+10} - \frac{1}{T} \right]$$

$$\ln \frac{k_{T+10K}}{k_T} = -\frac{E_a}{R} \left[\frac{T - T - 10}{T(T+10)} \right]$$

$$\therefore \ln \frac{k_{T+10K}}{k_T} = \left[\frac{10E_a}{RT(T+10)} \right]$$

At ordinary temperatures (300K), for several reactions, $E_a = 80 \text{ kJmol}^{-1}$

$$\frac{k_{T+10K}}{k_T} = \exp \left[\frac{10 \times 80000}{8.314 \times 300 \times 310} \right] = e^{1.03} = 2.8$$

For most of the reactions the observed value usually lies between 2 and 3.

Activation energy:

Threshold energy: “The minimum amount of energy which must be associated with molecules so that mutual collisions may result a chemical reaction.”

Molecules possessing energy less than threshold energy do not react on collisions.

The number of molecules possessing energy equal to or in excess of threshold energy increase appreciably even with a small rise in temperature. Thus rate of reaction increases.

The excess energy that the reactant molecules having energy less than the threshold energy must acquire in order to react to give the final products is known as **Activation energy**.

Activation energy = Threshold energy – Energy possessed by the molecules initially

The energy barrier has to be crossed before the reactants can yield products. It determines the magnitude of threshold energy.

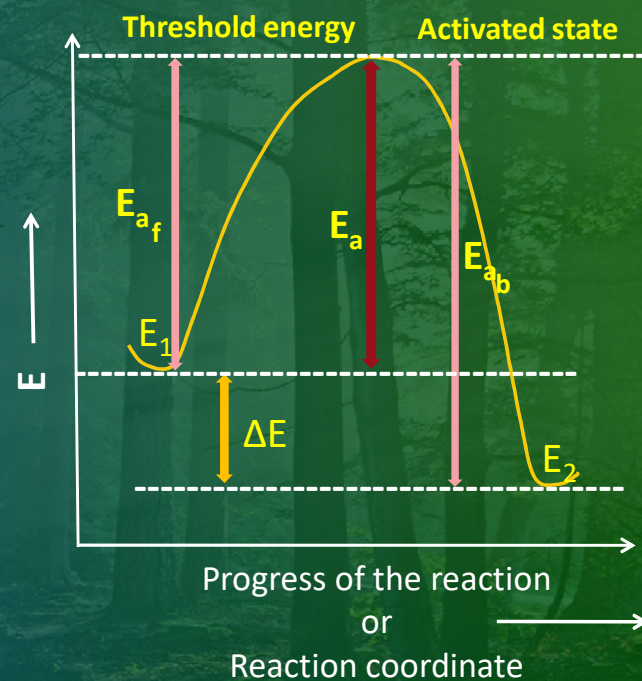
The molecules in the activated state are under condition of acute strain. The bond between atoms of the reacting molecules become very feeble. Thus, the probability of formation of new bonds between atoms of the molecules of the reactants is fairly strong.

$$E_{a_f} = E_a \quad E_{a_b} > E_a$$

$$\text{Heat of reaction, } \Delta E = E_2 - E_1$$

For exothermic reaction, $\Delta E = -ve$

and for endothermic reaction, $\Delta E = +ve$



Effect of Catalyst

A catalyst is a substance which can increase the rate of reaction, but itself remains unchanged in amount and chemical composition at the end of the reaction.

When catalyst is added a new reaction path with lower energy barrier is obtained.

As the energy barrier is reduced in magnitude, a large number of reactant molecules can overcome it. This increases the reaction rate.



Collision Theory of Bimolecular Reactions

Postulates:

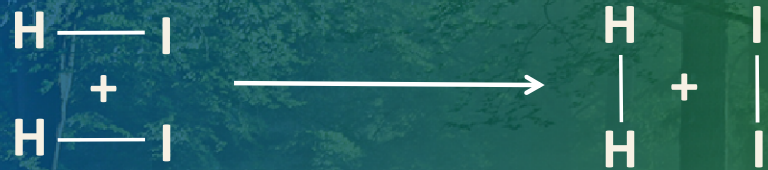
- i. A reaction occurs on the collision of two molecules, only if they possess a certain minimum amount of energy in excess to the normal energy of the molecules.
- ii. The collisions between the molecules other than activated molecules do not lead to chemical reaction at all.
- iii. The minimum energy which should be possessed by the molecules is known as **Threshold energy**.

Threshold energy – Energy possessed by the molecules initially = Activation energy

For a chemical reaction to occur when two molecules collide, it is supposed that molecules must have energy greater than E_1 and the other, than E_2 .

Where, $E_1 + E_2 = E_a = \text{Activation energy}$.

The probability of collisions is, then, given by
$$e^{-(E_1 + E_2)/RT} = e^{-E_a/RT}$$



Both HI molecules collide. Before the bonds between H and I break, new bonds between H and H; I and I will be formed.

If z' is the number of molecules per mL of the gas taking part in binary collisions per second,

then the rate of reaction, $\frac{dx}{dt} = z' e^{-E_a/RT}$

If 'n' number of molecules of the same kind are involved in the bimolecular reaction, then

$$\frac{dx}{dt} = kn^2$$

$$\rightarrow kn^2 = z' e^{-E_a/RT}$$

$$\rightarrow k = \frac{z'}{n^2} e^{-E_a/RT}$$

Here z' is twice the number of molecular collisions per second per mL (z_{11}), as two molecules take part in every collision.

$$\text{Hence, } z' = 2 \times 2n^2d^2 \left(\frac{\pi RT}{M}\right)^{1/2}$$

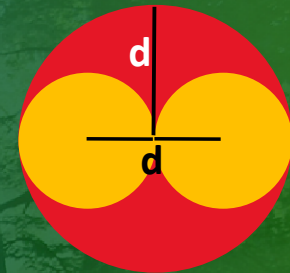
$$\rightarrow z' = 4n^2d^2 \left(\frac{\pi RT}{M}\right)^{1/2}$$

$$\therefore k = 4d^2 \left(\frac{\pi RT}{M}\right)^{1/2} e^{-E_a/RT}$$

$$\text{OR } k = z e^{-E_a/RT}$$

$z = \text{Collision number}$

$d = \text{Collision diameter}$
 $M = \text{Molecular weight}$



The number of molecular collisions by one molecule per second per mL = $\pi d^2 C_{rel} \rho$

The number of molecular collisions per second per mL $z_{11} = \pi d^2 C_{rel} \rho^2$

Collision cross section = πd^2

Relative velocity, $C_{rel} = \sqrt{2} \langle C \rangle$

$\langle C \rangle = \text{Average velocity} = (2RT/\pi M)^{1/2}$

$\rho = \text{Number density} = n/v$

$$\textcircled{51} \text{ where, } z = 4d^2 \left(\frac{\pi RT}{M}\right)^{1/2}$$

“**Collision number** is the number of collisions per second when there is only one mole of reactant per unit volume.”

$$k = 4d^2 \left(\frac{\pi RT}{M} \right)^{1/2} e^{-E_a/RT}$$

$$\rightarrow \ln k = \ln \left[4d^2 \left(\frac{\pi RT}{M} \right)^{1/2} \right] - \frac{E_a}{RT}$$

$$\rightarrow \frac{d}{dT} (\ln k) = \frac{1}{2T} + \frac{E_a}{RT^2} \quad \text{Since, } \frac{E_a}{RT^2} \gg \frac{1}{2T}$$

$$\rightarrow \frac{d}{dT} (\ln k) = \frac{E_a}{RT^2}$$

This is identical with Arrhenius equation.

If the bimolecular reaction involves two molecules of different species, then

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$$z = d^2 \left[8\pi RT \left(\frac{M_1 + M_2}{M_1 M_2} \right) \right]^{1/2}$$



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Limitations

There are certain reactions where the experimental and calculated values of E_a differ.

Ex: Reaction between C_2H_5OH and $(CH_3CO)_2O$; combination of two molecules of ethylene etc.

In polymerization of Ethylene, the reaction occurs only once in 2000 collisions between activated molecules.

In polymerization of 1,3 – butadiene, the reaction occurs only once in about 10,000 collisions between activated molecules.

Steric Factor

There are certain reactions where the experimental and calculated values of E_a differ.

For reactions between complicated molecules, the observed rate is found to be much smaller than the theoretically predicated rate.

This discrepancy is explained by the fact that the colliding molecule is treated as a hard sphere having no internal energy.



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- Again the spherical model ignores the dependence of the effectiveness of a collision on the relative orientation of colliding molecules.
- Also the activation energy has been treated as though it were related entirely to translational motion, ignoring the effect of rotational and vibrational motions.

For these reasons, collision theory is only to reactions between very simple gaseous molecules.

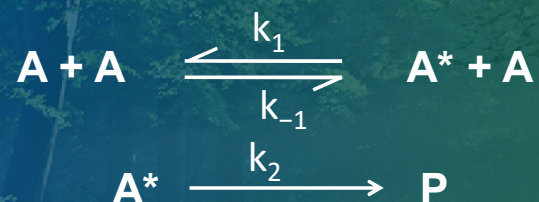
∴ Steric factor 'p' is introduced into equation for the bio molecular rate constant in order to take account of the orientational requirement.

$$\therefore k = pz e^{-E_a/RT}$$

The Steric factor is equal to the fraction of molecular collisions in which the molecules A and B possess the relative orientation necessary for the reaction.

Lindemann Theory of Unimolecular Reactions

According to Lindemann theory, a unimolecular reaction $A \longrightarrow P$, proceeds via following **mechanism**:



Here A^* is the energized A molecule which has acquired sufficient vibrational energy to enable it to isomerise or decompose.

A^* is simply a molecule in higher vibrational energy level and not activated molecule.

In the first step, the kinetic energy of second molecule is transferred in to the vibrational energy of the first during collision. The second molecule need not to be the same molecule. It could be a product molecule or a foreign molecule present in the system. However, it does not appear in the stoichiometry.

A^* can either be de-energised back to A in which the vibrational energy is transferred to the kinetic energy of A or be decomposed or isomerised to products; in which the excess vibrational energy is used to break the appropriate chemical bonds.

In the Lindemann mechanism, a time lag exists between the energisation of A to A^* , and the decomposition or isomerisation of A^* to P . During this time lag, A^* can either be de-energised back to A .

According to the stationary or steady state principle, whenever a short-lived reaction intermediate occurs, its rate of formation can be taken as equal to its rate of disappearance.

Here A^* is short-lived species.

$$\text{Its rate of formation} = k_1[A]^2$$

$$\text{Rate of decomposition} = k_{-1}[A^*][A] + k_2[A^*]$$

Applying steady state approximation,

$$k_1[A]^2 = k_{-1}[A^*][A] + k_2[A^*]$$

$$\rightarrow [A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

$$\therefore \text{Rate of reaction, } -\frac{d[A]}{dt} = r = k_2[A^*]$$

$$\therefore r = \frac{k_1k_2[A]^2}{k_{-1}[A] + k_2}$$

At High pressure:

$$\rightarrow k_{-1}[A] \gg k_2$$

$\rightarrow k_2$ can be neglected.

$$\therefore r = \frac{k_1k_2}{k_{-1}} [A] \rightarrow r = k[A]$$

Thus if concentration of A is high, reaction is of first order.

At Low pressure:

$$\rightarrow k_2 \gg k_{-1}[A]$$

$\rightarrow k_{-1}[A]$ can be neglected.

$$\therefore r = \frac{k_1k_2}{k_2} [A]^2 \rightarrow r = k_1[A]^2$$

Thus if concentration of A is low, the reaction becomes order.

Limitations

(i) The experimental rate is defined as, $r = k_{\text{uni}} [A]$

$$\text{We have, } r = \frac{k_1 k_2 [A]^2}{k_{-1} [A] + k_2} \rightarrow k_{\text{uni}} [A] = \frac{k_1 k_2 [A]^2}{k_{-1} [A] + k_2}$$

$$\rightarrow k_{\text{uni}} \equiv k = \frac{k_1 k_2 [A]}{k_{-1} [A] + k_2}$$

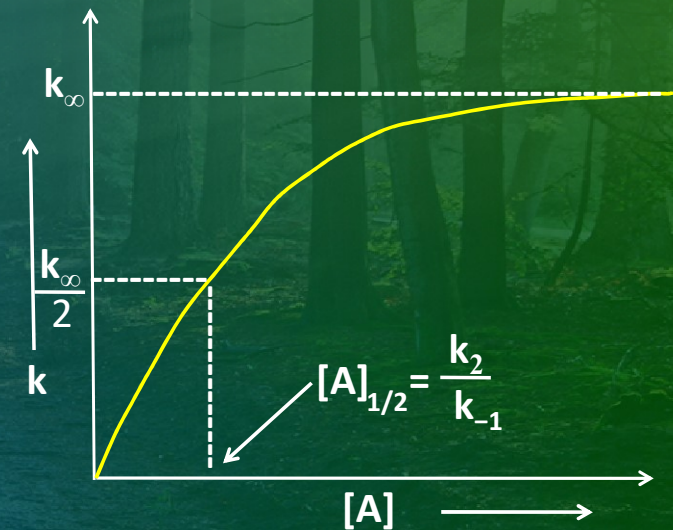
$$\rightarrow k = \frac{k_1 k_2}{k_{-1} + \frac{k_2}{[A]}}$$

where, k = First order rate constant

The rate constant, k , is a constant in the higher concentration range but falls at lower concentrations.

$$\text{when, } k_{-1} [A] = k_2 \rightarrow k = \frac{k_{\infty}}{2}$$

And the corresponding concentration = $[A]_{1/2}$ (58)



$$k = \frac{k_1 k_2 [A]}{k_{-1}[A] + k_2}$$

when, $k_{-1}[A] = k_2 \rightarrow k = \frac{k_1 k_2 [A]_{1/2}}{k_{-1}[A]_{1/2} + k_{-1}[A]_{1/2}}$

$$\rightarrow k = \frac{k_1 k_2}{2k_{-1}} = \frac{k_\infty}{2}$$

Where $k_\infty = \frac{k_1 k_2}{k_{-1}}$

$$\therefore \frac{k_\infty}{2} = \frac{k_1 [A]_{1/2}}{2}$$

$$\rightarrow k_\infty = k_1 [A]_{1/2}$$

Thus, $[A]_{1/2} = \frac{k_\infty}{k_1} = \frac{k_2}{k_{-1}}$

The value of k_∞ is an experimental quantity. Using collision theory, $k_\infty = z_1 e^{-E_1/RT}$

Experimentally, however, it was found that the values of $[A]_{1/2}$ were always smaller than those estimated in this way. Thus error must lie in calculation of k_1 rather than k_∞ .

Thus we should modify k_1 so that it is larger than $k_\infty = z_1 e^{-E_1/RT}$

(ii) We have,

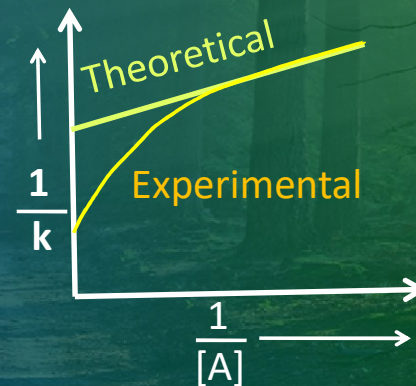
$$k = \frac{k_1 k_2 [A]}{k_{-1} [A] + k_2}$$

$$\frac{1}{k} = \frac{k_{-1} [A] + k_2}{k_1 k_2 [A]}$$

$$\rightarrow \frac{1}{k} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1 [A]}$$

$1/k$ vs $1/[A]$ should give a straight line.

But deviation is observed.



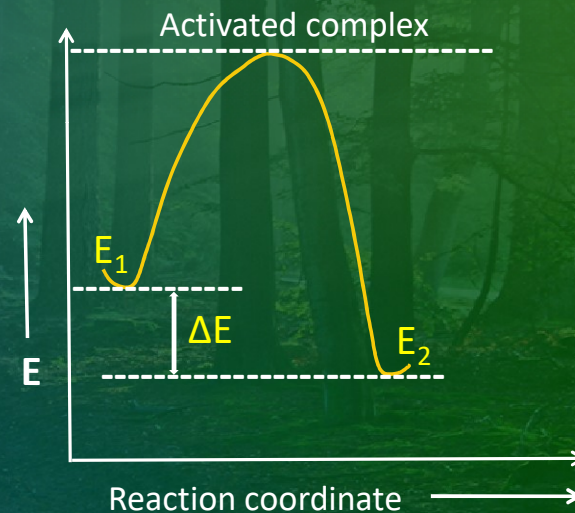
Qualitative Treatment of Transition State Theory

According to TST, the rate of reaction is the number of activated complexes passing per second over the top of potential energy barrier.

Postulates

(i) As the reacting molecules approach to each other, there is a continuous series of changes in bond distance. These changes are accompanied by energy changes.

(ii) The reactant molecules are changed into an energy rich intermediate called activated complex or transition state.



(iii) The activated complex may be formed by some loose association or bonding of reactant molecules with necessary rearrangement of valence bonds and energy.

If it is a unimolecular reaction, rearrangement of atoms and redistribution of energy produce activated complex.

(iv) The activated complex, though unstable, has a transient existence. It is treated formally as a definite molecule with an independent entity.

The activated complex remains in equilibrium with the reactants and its potential energy is minimum. Finally the activated complex decomposes into products.

(v) The activation energy is the additional energy which the reacting molecule must acquire to form the activated complex.

Comparison of TST with Collision Theory

(i) From TST,
$$k = \frac{RT}{N_A h} e^{-\Delta H^*/RT} e^{-\Delta S^*/R}$$

Where, ΔH^* = Standard enthalpy change, i.e.,
Standard heat of activation.

ΔS^* = Standard entropy of activation.

From Collision theory,
$$k = pz e^{-E_a/RT}$$

$$\rightarrow pz = \frac{RT}{N_A h} e^{-\Delta S^*/R} \quad [\because E_a = \Delta H^*]$$

$$\rightarrow p = \frac{RT}{N_A zh} e^{-\Delta S^*/R}$$

Thus, Steric factor p is related to entropy of activation.

(ii) In Collision theory, no account is taken of the internal motions of the reactant molecules, where as, in TST, account is taken of the internal degrees of freedom of reactant molecules.

(iii) The concept of entropy of activation in TST is very useful for qualitative purposes. Thus for bimolecular processes, this is an advantage over collision theory.