



Knowledge... Everywhere

Chemistry

# Chemical Kinetics

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The branch of physical chemistry which deals with the rate at which the chemical reactions occur, the mechanism by which the chemical reactions take place and the influence of various factors such as concentration, temperature, pressure, catalyst etc., on the reaction rates is called the chemical kinetics.

## 1. Chemical reactions.

On the basis of reaction rates, the chemical reactions have been classified into the following three groups:-

(1) **Very fast or instantaneous reactions:** These reactions occur at a very fast rate generally these reactions involve ionic species and known as ionic reactions.

These reactions take about  $10^{-14}$  or  $10^{-16}$  seconds for completion. Its rate can be measured by employing special methods. So, it is almost impossible to determine the rates of these reactions.

Examples: (i)  $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$  (Precipitation reaction)  
(Ppt.)

(ii)  $HCl + NaOH \rightarrow NaCl + H_2O$  (Neutralization reaction)  
(acid) (base) (Salt)

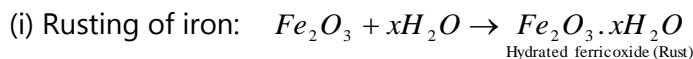
(2) **Moderate reaction:** These type of reactions proceed with a measurable rates at normal temperature. In this a large number of bonds have to be broken in reactants molecules and a large number of new bonds have to be formed in product molecules. Mostly these reactions are molecular in nature.

- Examples:
- (i) Decomposition of  $H_2O_2$ :  $2H_2O_2 \rightarrow 2H_2O + O_2$
  - (ii) Decomposition of  $N_2O_5$ :  $2N_2O_5 \rightarrow 2N_2O_4 + O_2$
  - (iii) Hydrolysis of ester:  $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$
  - (iv) Reaction of NO with chlorine:  $NO + Cl_2 \rightarrow NOCl_2$
  - (v) Inversion of cane sugar in aqueous solution:  $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$   
Glucose Fructose
  - (vi)  $2FeCl_3(aq.) + SnCl_2 \rightarrow 2FeCl_2(aq.) + SnCl_4(aq.)$
  - (vii)  $NO_2 + CO \rightarrow NO + CO_2$
  - (viii) Decolourisation of acidified potassium permanganate with sodium oxalate.

(3) **Very slow reactions:** These reactions are extremely slow and take months together to show any measurable change. The rate of such type of reactions are very slow. So, it is also very difficult to determine the rate of these reactions.

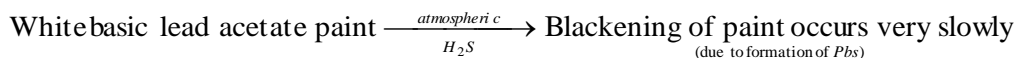


Examples:

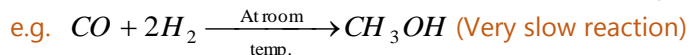


(ii) Reaction between  $H_2$  and  $O_2$  to form  $H_2O$  at ordinary temperature in absence of catalyst.

(iii) Reaction of atmospheric  $H_2S$  on basic lead acetate paint.



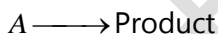
Note: The chemical reactions can be slowed down or speed up by changing conditions under which they occur.



The reaction can be speeded up by maintaining temperature around  $400^\circ C$ , pressure about 300 atm and using a catalyst containing ZnO and  $Cr_2O_3$ .

## 2. Rate of reaction.

"The rate (speed or velocity) of reaction is the rate of change in concentration of reactants or products in unit time."



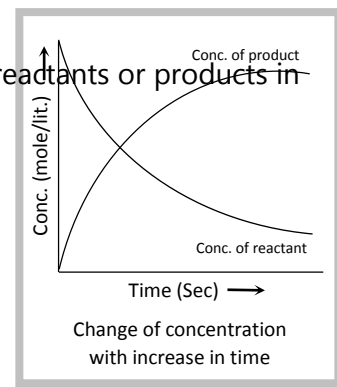
When,  $t = 0$  a

0

Where  $a$  is the initial concentration and  $(a-x)$  is concentration of reactant after time  $t$  and  $x$  will be the concentration of product after time  $t$ .

After,  $t = t$

$(a-x)$  x



$$\text{Rate of reaction} = \frac{\text{Total change in concentration of reactants or products}}{\text{Change in time (in sec.)}}$$

If  $dx$  is the change in concentration in time interval  $dt$  then,

The reaction rate for reactants =  $-\frac{dx}{dt}$ ; the reaction rate for products =  $+\frac{dx}{dt}$

- The negative sign indicates that the concentration of reactant **decreases** with time.
- The positive sign indicates that the concentration of products **increases** with time.
- The concentration change may be positive or negative but the rate of reaction is always **positive**.
- The rate of chemical reaction decreases as the reaction proceeds.
- The concept of mechanical speed or velocity cannot be used in measuring rate of reaction. Rate of reaction depends on molar concentration.



(1) **Types of rate of reactions:** There are two types of rate of reactions.

(i) **Average rate of reaction:** The average rate is defined as the change in the concentration (active mass) of reactants or products over a long time interval.

Consider the general chemical reaction,  $aA + bB + \dots \longrightarrow cC + dD + \dots$

**Average rate = Amount of reactant consumed (or product formed)/time interval.**

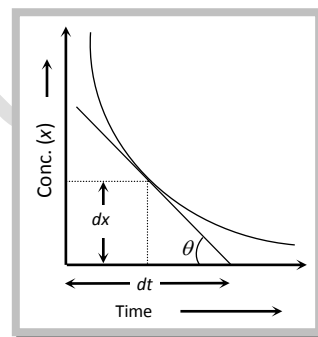
$$\text{Average rate} = -\frac{\Delta[A]}{a\Delta t} = -\frac{\Delta[B]}{b\Delta t} \dots = +\frac{\Delta[C]}{c\Delta t} = +\frac{\Delta[D]}{d\Delta t} = +\dots$$

The average rate over the time interval  $\Delta t$  approaches the instantaneous rate as  $\Delta t$  approaches zero.

(ii) **Instantaneous rate of reaction:** The instantaneous rate of reaction gives the tendency of the reaction at a particular instant. The term  $\Delta t$  becomes smaller and eventually approaches zero, then the rate of reaction at a particular moment called the instantaneous rate ( $R_t$ ) is given by,

$$\text{Instantaneous rate} = (\text{Average rate})_{\Delta t \rightarrow 0}$$

$$R_t = \left( \frac{-\Delta[A]}{\Delta t} \right)_{\Delta t \rightarrow 0} = \left( \frac{\Delta[B]}{\Delta t} \right)_{\Delta t \rightarrow 0} \text{ or } R_t = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$



Where,  $d[A]$ ,  $d[B]$  and  $dt$  being infinitesimally small changes in the concentration of  $A$  and  $B$ , that of time respectively. Instantaneous rate of reaction at any instant of time is obtained by finding the slope of the tangent to the curve (which is obtained by plotting concentration of any suitable reactant or product versus time) at the point corresponding to that instant of time. Rate of reaction =

$$\tan \theta = \frac{dx}{dt}$$

(2) **Unit of rate of reaction:** Unit of rate of reaction =  $\frac{\text{Unit of concentration}}{\text{Unit of time}} = \text{mole liter}^{-1} \text{time}^{-1}$

(i) If reactants and products are in gaseous state then the pressure may be taken in place of concentration thus rate will have unit of  $\text{atm sec}^{-1}$  or  $\text{atm min}^{-1}$

(ii) The unit of time can be second, minute, hours, days and years so the unit of rate of reaction may be expressed as follows:  $\text{mol/liter sec}$  ( $\text{moll}^{-1} \text{s}^{-1}$ ) or  $\text{mol/liter min}$  ( $\text{moll}^{-1} \text{min}^{-1}$ ) or  $\text{mol/liter hour}$  ( $\text{moll}^{-1} \text{h}^{-1}$ ) or  $\text{mol/liter day}$  ( $\text{moll}^{-1} \text{d}^{-1}$ ) or  $\text{mol/liter year}$  ( $\text{moll}^{-1} \text{y}^{-1}$ )



### 3. Experimental methods of Rate studies.

Many physical and chemical methods are available for studying the reaction rate:

- (1) **Volume or Pressure measurement:** The reaction rate can be followed by measuring the volume or pressure change provided one or more of the components are gases.
- (2) **Titrimetry:** The reaction course can be followed using acid-base or oxidation-reduction titration if at least one of the components in the reaction is an acid or a base or an oxidizing agent or a reducing agent.
- (3) **Conductometry or Potentiometry:** It is a suitable method based on conductivity or potentiometric measurements if one or more of the ions are present or produced in the reaction.
- (4) **Spectrophotometry :** When a component of the reaction has a strong absorption band at a particular Wavelength region, spectrophotometers could be used for measuring the reaction rate.
- (5) **Polarimetry:** The reaction rate can be studied from the measurements of optical rotation when at least one of the component of a reaction is optically active.

### 4. Factors affecting Reaction rate.

The rate of a chemical reaction depends on the rate of encounter between the molecules of the reactants which in turn depends on the following things.

- (1) **Effect of temperature on reaction rate:** The rate of chemical reaction generally increases on increasing the temperature.
- (2) **Nature of reactants:**
  - (i) Reactions involving polar and ionic substances including the proton transfer reactions are usually very fast. On the other hand, the reaction in which bonds is rearranged, or electrons transferred are slow.
  - (ii) Oxidation-reduction reactions, which involve transfer of electrons, are also slow as compared to the ionic substance.
  - (iii) Substitution reactions are relatively much slower.

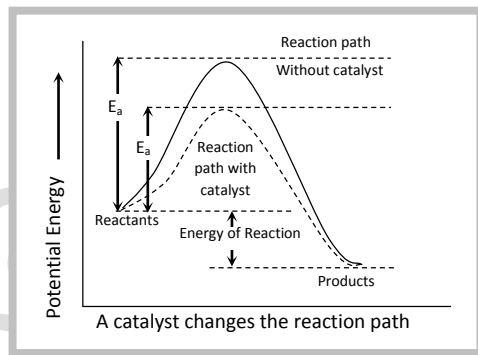


(3) **pH of the medium:** The rate of a reaction taking place in aqueous solution often depends upon the  $H^+$  ion concentration. Some reactions become fast on increasing the  $H^+$  ion concentration while some become slow.

(4) **Concentration of reactants:** The rate of a chemical reaction is directly proportional to the concentration of the reactants means rate of reaction decreases with decrease in concentration.

(5) **Surface area of reactant:** Larger the surface area of reactant, the probability of collisions on the surface of the reactant particles by the surrounding molecules increases and thus rate of reaction increases.

(6) **Presence of catalyst:** The function of a catalyst is to lower down the activation energy. The greater the decrease in the activation energy caused by the catalyst, higher will be the reaction rate. In the presence of a catalyst, the reaction follows a path of lower activation energy. Under this condition, a large number of reacting molecules are able to cross over the energy barrier and thus the rate of reaction increases. Fig. shows how the activation energy is lowered in presence of a catalyst.



(7) **Effect of sunlight:** There are many chemical reactions whose rate are influenced by radiations particularly by ultraviolet and visible light. Such reactions are called photochemical reactions. For example, Photosynthesis, Photography, Blue printing, photochemical synthesis of compounds etc.

$H_2 + Cl_2 \xrightarrow{\text{sunlight } (h\nu)} 2HCl$ : The radiant energy initiates the chemical reaction by supplying the necessary activation energy required for the reaction.

## 5. Rate law, Law of mass action and Rate constant.

(1) **Rate law:** The actual relationship between the concentration of reacting species and the reaction rate is determined experimentally and is given by the expression called rate law.

For any hypothetical reaction,  $aA + bB \rightarrow cC + dD$

Rate law expression may be,  $\text{rate} = k[A]^a[B]^b$

Where a and b are constant numbers or the powers of the concentrations of the reactants A and B respectively on which the rate of reaction depends.



- (i) Rate of chemical reaction is directly proportional to the concentration of the reactants.
- (ii) The rate law represents the experimentally observed rate of reaction, which depends upon the slowest step of the reaction.
- (iii) Rate law cannot be deduced from the relationship for a given equation. It can be found by experiment only.
- (iv) It may not depend upon the concentration of species which do not appear in the equation for the overall reaction.

(2) **Law of mass action:** (Guldberg and Wage 1864) this law relates rate of reaction with active mass or molar concentration of reactants. According to this law, "At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the reactants at that instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reactions."

$$\text{Active mass} = \text{Molar concentration of the substance} = \frac{\text{Number of gram moles of the substance}}{\text{Volume in litres}}$$

$$= \frac{W/m}{V} = \frac{n}{V}$$

Where  $W$  = mass of the substance,  $m$  is the molecular mass in grams, 'n' is the number of g moles and  $V$  is volume in liter.

Consider the following general reaction,  $m_1A_1 + m_2A_2 + m_3A_3 \rightarrow \text{Products}$

$$\text{Rate of reaction} \propto [A_1]^{m_1} [A_2]^{m_2} [A_3]^{m_3}$$

(3) **Rate constant:** Consider a simple reaction,  $A \rightarrow B$ . If  $C_A$  is the molar concentration of active mass of A at a particular instant, then,  $\frac{dx}{dt} \propto C_A$  or  $\frac{dx}{dt} = kC_A$ ; Where  $k$  is a **proportionality constant**, called **velocity constant** or **rate constant** or **specific reaction rate constant**.

At a fixed temperature, if  $C_A = 1$ , then  $\boxed{\text{Rate} = \frac{dx}{dt} = k}$

"Rate of a reaction at unit concentration of reactants is called rate constant."

(i) **The value of rate constant depends on,** Nature of reactant, Temperature and Catalyst  
(It is independent of concentration of the reactants)

(ii) **Unit of rate constant:** Unit of rate constant =  $\left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \text{sec}^{-1}$  or  $= \left[\frac{\text{mol}}{\text{litre}}\right]^{1-n} \times \text{sec}^{-1}$

Where  $n$  = order of reaction





### Difference between Rate law and Law of mass action

Rate law	Law of mass action
It is an experimentally observed law.	It is a theoretical law.
It depends on the concentration terms on which the rate of reaction actually depends	It is based upon the stoichiometry of the equation
Example for the reaction, $aA + bB \rightarrow \text{Products}$	Example for the reaction, $aA + bB \rightarrow \text{Products}$
Rate = $k[A]^m[B]^n$	Rate = $k[A]^a[B]^b$

### Difference between Rate of reaction and Rate constant

Rate of reaction	Rate constant
It is the speed with which reactants are converted into products.	It is proportionality constant.
It is measured as the rate of decrease of the concentration of reactants or the rate of increase of concentration of products with time.	It is equal to rate of reaction when the concentration of each of the reactants is unity.
It depends upon the initial concentration of the reactants.	It is independent of the initial concentration of the reactants. It has a constant value at fixed temperature.

## 6. Order of Reaction.

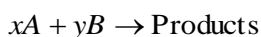
“The order of reaction is defined as the number of atoms or molecules whose concentration change during the chemical reaction.”

Or

“The total number of molecules or atoms whose concentration determine the rate of reaction is known as order of reaction.”

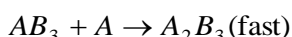
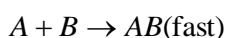
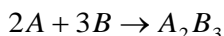


**Order of reaction = Sum of exponents of the concentration terms in rate law**



By the rate law, Rate =  $[A]^x [B]^y$ , then the overall order of reaction.  $n = x + y$ , where x and y are the orders with respect to individual reactants.

If reaction is in the form of reaction mechanism then the order is determined by the slowest step of mechanism.



(Here, the overall order of reaction is equal to two.) An order of a reaction may be zero, negative, positive or in fraction and greater than three. Infinite and imaginary values are not possible.

(1) **First order reaction:** When the rate of reaction depends only on the one concentration term of reactant.

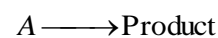
Examples:

- $A \rightarrow \text{product}$
- $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$
- All radioactive reactions are first order reaction.
- Rate of growth of population if there is no change in the birth rate or death rate.
- Rate of growth of bacterial culture until the nutrients are exhausted.

**Exception:**  $H_2O, H^+, OH^-$  and excess quantities are not considered in the determining process of order.

- Examples:
- $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$ ; Order = 1;  $R = k[CH_3COOC_2H_5]$
  - $2A(\text{excess}) + B \rightarrow \text{product}$ ; Order = 1;  $R = k[B]$
  - $2N_2O_5 \rightarrow 4NO_2 + O_2$ ; Order = 1;  $R = k[N_2O_5]$
  - $2Cl_2O_7 \rightarrow 2Cl_2 + 7O_2$ ; Order = 1;  $R = k[Cl_2O_7]$
  - $(CH_3)_3C-Cl + OH^- \rightarrow (CH_3)_3C-OH + Cl^-$ ; Order = 1;  $R = k[(CH_3)_3C-Cl]$

(i) **Velocity constant for first order reaction :** Let us take the reaction



Initially t = 0

a

0



After time  $t = t$   $(a - x)$   $x$

Here, 'a' be the concentration of A at the starting and  $(a - x)$  is the concentration of A after time  $t$  i.e.,  $x$  part has been changed in to products. So, the rate of reaction after time  $t$  is equal to

$$\frac{dx}{dt} \propto (a - x) \text{ or } \frac{dx}{dt} = k(a - x) \text{ or } \frac{dx}{(a - x)} = k \cdot dt \quad \dots(i)$$

integrated rate constant is,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a - x)}$$

.....(ii)

$$t = \frac{2.303}{k} \log_{10} \frac{a}{(a - x)}$$

.....(iii)

(ii) **Half life period of the first order reaction** : when  $t = t_{1/2}$ ;  $x = \frac{a}{2}$ , then eq. (ii) becomes

$$t_{1/2} = \frac{2.303}{k} \log_{10} \frac{a}{\left(a - \frac{a}{2}\right)}; \quad t_{1/2} = \frac{2.303}{k} \log_{10} \frac{a}{a/2}$$

$$t_{1/2} = \frac{2.303}{k} \log_{10} 2 \quad (\because \log 2 = 0.3010); \quad \therefore t_{1/2} = \frac{2.303}{k} \times 0.3010$$

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

Half life period for first order reaction is independent from the concentration of reactant.

Time for completion of  $n^{\text{th}}$  fraction,  $t_{1/n} = \frac{2.303}{K} \log \frac{1}{\left(1 - \frac{1}{n}\right)}$

(iii) **Unit of rate constant of first order reaction** :  $k = (\text{sec})^{-1}$

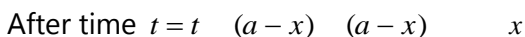
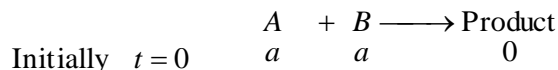
(2) **Second order reaction**: Reaction whose rate is determined by change of two concentration terms is said to be a second order reaction. For example,

- $CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$
- $S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$

(i) **Calculation of rate constant**:  $2A \longrightarrow \text{product}$  or  $A + B \longrightarrow \text{product}$



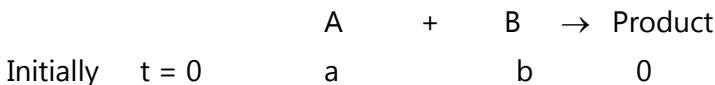
When concentration of  $A$  and  $B$  are same.



$$\frac{dx}{dt} = k[A][B] = k[a-x][a-x]$$

$$\frac{dx}{dt} = k[a-x]^2; \text{ Integrated equation is } \boxed{k = \frac{1}{t} \cdot \frac{x}{a(a-x)}}; \quad \boxed{t = \frac{1}{k} \cdot \frac{x}{a(a-x)}}$$

When concentration of  $A$  and  $B$  are taken different



$$\frac{dx}{dt} = k[a-x].[b-x], \text{ Integrated equation is,}$$

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

(ii) **Half-life period of the second order reaction:** When  $t = t_{1/2}; x = \frac{a}{2}; t_{1/2} = \frac{1}{k} \left( \frac{\frac{a}{2}}{a \times (a - \frac{a}{2})} \right) = \frac{1}{ka}$

Half-life of second order reaction depends upon the concentration of the reactants.  $\boxed{t_{1/2} \propto \frac{1}{a}}$

(iii) **Unit of rate constant:**  $k = \text{mol}^{1-\Delta n} \text{ lit}^{\Delta n-1} \text{ sec}^{-1}; \Delta n = 2, k = \text{mol}^{-1} \text{ lit. sec}^{-1}$  (Where  $\Delta n$  = order of reaction)

(3) **Third order reaction:** A reaction is said to be of third order if its rate is determined by the variation of three concentration terms. When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as



(i) **Calculation of rate constant:**  $\frac{dx}{dt} = k(a-x)^3$ , integrated equation is  $k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$

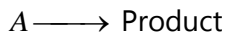
(ii) **Half-life period of the third order reaction:** Half-life period =  $\frac{3}{2a^2k}$ ;  $t_{1/2} \propto \frac{1}{a^2}$ ; Thus, half-life is inversely proportional to the square of initial concentration.

(iii) **Unit of rate constant:**  $k = \left(\frac{\text{mol}}{\text{litre}}\right)^{-2} \text{time}^{-1}$  or  $k = \text{litre}^2 \text{mol}^{-2} \text{time}^{-1}$

(4) **Zero order reaction:** Reaction whose rate is not affected by concentration or in which the concentration of reactant do not change with time are said to be of zero order reaction. For example,

- $H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$
- Dissociation of HI on gold surface.
- Reaction between acetone and bromine.
- The formation of gas at the surface of tungsten due to adsorption.

(i) **Calculation of Rate Constant:** Let us take the reaction



Initially  $t = 0$        $a$                $0$

$$\frac{dx}{dt} = k[A]^0, \quad \frac{dx}{dt} = k; \quad dx = k \cdot dt$$

Integrated rate equation,  $k = \frac{x}{t}$ ; the rate of reaction is independent of the concentration of the reacting substance.

(ii) **Half-life period of zero order reaction:** When  $t = t_{1/2}$ ;  $x = \frac{a}{2}$ ;  $t_{1/2} = \frac{a}{2k}$  or  $t_{1/2} \propto a$ ; the half-life period is directly proportional to the initial concentration of the reactants.

(iii) **Unit of Rate constant:**  $k = \frac{\text{mole}}{\text{lit. sec.}}$ ; Unit of rate of reaction = Unit of rate constant.



Note: In general, the units of rate constant for the reaction of  $n^{\text{th}}$  order are:

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

$$\frac{\text{mol L}^{-1}}{\text{s}} = k(\text{mol L}^{-1})^n \text{ or } k = (\text{mol L}^{-1})^{1-n} \text{ s}^{-1}$$

**Units of rate constants for gaseous reactions:** In case of gaseous reactions, the concentrations are expressed in terms of pressure in the units of atmosphere. Therefore, the rate has the units of atm per second. Thus, the unit of different rate constants would be:

(i) Zero order reaction :  $\text{atm s}^{-1}$

(ii) First order reaction :  $\text{s}^{-1}$

(iii) Second order reaction:  $\text{atm}^{-1} \text{ s}^{-1}$

(iv) Third order reaction:  $\text{atm}^{-2} \text{ s}^{-1}$

In general, for the gaseous reaction of  $n^{\text{th}}$  order, the units of rate constant are  $(\text{atm})^{1-n} \text{ s}^{-1}$

Modified expressions for rate constants of some common reactions of first order

Reaction	Expression for rate constant
$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$	$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$ <p>Here <math>V_t</math> = volume of <math>O_2</math> after time <math>t</math> and <math>V_\infty</math> = volume of <math>O_2</math> after infinite time.</p>
$NH_4NO_2(aq) \longrightarrow 2H_2O + N_2$	<p>Same as above, here <math>V_t</math> and <math>V_\infty</math> are volumes of <math>N_2</math> at time <math>t</math> and at infinite time respectively.</p>
$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$	$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$ <p>Here <math>V_0</math> and <math>V_t</math> are the volumes of <math>KMnO_4</math> solution used for titration of same volume of reaction mixture at zero time (initially) and after time <math>t</math>.</p>
$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$	$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$ <p>Here <math>V_0, V_t</math> and <math>V_\infty</math> are the volumes of <math>NaOH</math> solution used for titration of same volume of reaction mixture after time, <math>0, t</math> and infinite time respectively.</p>
$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$ <small><i>d</i>-Sucrose                      <i>d</i>-Glucose                      <i>l</i>-Fructose</small>	$k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$



(After the reaction is complete the equimolar mixture of glucose and fructose obtained is laevorotatory)

Here,  $r_0$ ,  $r_t$  and  $r_\infty$  are the polarimetric readings after time 0,  $t$  and infinity respectively.

Examples of reactions having different orders

Examples	Rate Law	Order
<b>First order reaction</b>		
$2H_2O_2 \longrightarrow 2H_2O + O_2$	$r = k [H_2O_2]$	1
$C_2H_5Cl \longrightarrow C_2H_4 + HCl$	$r = k [C_2H_5Cl]$	1
$2N_2O_5 \longrightarrow 4NO_2 + O_2$	$r = k [N_2O_5]$	1
$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$	$r = k [SO_2Cl_2]$	1
$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$	$r = k [ester][H_2O]^0$	1
$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$	$r = k [sugar][H_2O]^0$	1
All radioactive decay	$r = k [radioactive\ species]$	1
<b>Second order reactions</b>		
$NO + O_3 \longrightarrow NO_2 + O_2$	$r = k [NO][O_3]$	2
$2NO_2 \longrightarrow 2NO + O_2$	$r = k [NO_2]^2$	2
$H_2 + I_2 \longrightarrow 2HI$	$r = k [H_2][I_2]$	2
$CH_3COOC_2H_5 + OH^- \longrightarrow CH_3COO^- + C_2H_5OH$	$r = k [CH_3CO_2C_2H_5][OH^-]$	2
$C_2H_4 + H_2 \longrightarrow C_2H_6$	$r = k [C_2H_4][H_2]$	2
$2N_2O \longrightarrow 2N_2 + O_2$	$r = k [N_2O]^2$	2
$2CH_3CHO \longrightarrow 2CH_4 + 2CO$	$r = k [CH_3CHO]^2$	2
<b>Third order reactions</b>		
$2NO + O_2 \longrightarrow 2NO_2$	$r = k [NO]^2[O_2]$	3
$2NO + Br_2 \longrightarrow 2NOBr$	$r = k [NO]^2[Br_2]$	3
$2NO + Cl_2 \longrightarrow 2NOCl$	$r = k [NO]^2[Cl_2]$	3
$Fe^{2+} + 2I^- \longrightarrow FeI_2$	$r = k [Fe^{2+}][I^-]^2$	3
<b>Zero order reactions</b>		
$H_2 + Cl_2 \longrightarrow 2HCl$ (over water)	$r = k [H_2]^0 [Cl_2]^0$	0
$2NH_3 \xrightarrow{Pt} N_2 + 3H_2$	$r = k [NH_3]^0$	0
<b>Fractional order reactions</b>		
Para $H_2 \longrightarrow$ ortho $H_2$	$r = k [para\ H_2]^{1.5}$	1.5



$CO + Cl_2 \longrightarrow COCl_2$	$r = k [CO]^2 [Cl_2]^{1/2}$	2.5
$COCl_2 \longrightarrow CO + Cl_2$	$r = k [COCl_2]^{3/2}$	1.5
$CH_3CHO \longrightarrow CH_4 + CO$	$r = k [CH_3CHO]^{3/2}$	1.5
<b>Negative order reaction</b>		
$2O_3 \longrightarrow 3O_2$	$r = k [O_3]^2 [O_2]^{-1}$	-1 with respect to $O_2$ . Overall order = 1

## 7. Methods for Determination of Order of a reaction.

### (1) Substitution method in integrated rate equation (Hit and Trial method)

- The method can be used with various sets of  $a$ ,  $x$  and  $t$  with integrated rate equations.
- The value of  $k$  is determined and checked for all sets of  $a$ ,  $x$  and  $t$ .
- If the value of  $k$  is constant, the used equation gives the order of reaction.
- If all the reactants are at the same molar concentration, the kinetic equations are:

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)} \quad \text{(For first order reactions)}$$

$$k = \frac{1}{t} \left[ \frac{1}{a} - \frac{1}{a-x} \right] \quad \text{(For second order reactions)}$$

$$k = \frac{1}{2t} \left[ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right] \quad \text{(For third order reactions)}$$

### (2) Half-life method: This method is employed only when the rate law involved only one concentration term.

$t_{1/2} \propto a^{1-n}$ ;  $t_{1/2} = ka^{1-n}$ ;  $\log t_{1/2} = \log k + (1-n) \log a$ , a plotted graph of  $\log t_{1/2}$  vs  $\log a$  gives a straight line with slope  $(1-n)$ , determining the slope we can find the order  $n$ . If half-life at different concentration is given then.

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

$$\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2 = (n-1) [\log_{10} a_2 - \log_{10} a_1]$$



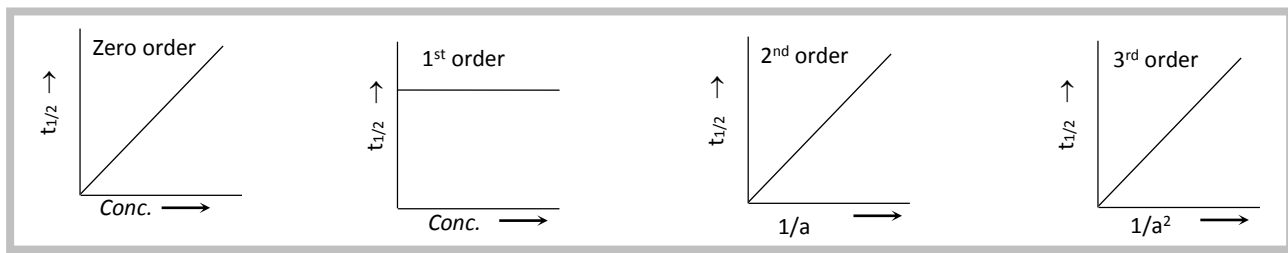


$$n = 1 + \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{(\log_{10} a_2 - \log_{10} a_1)}$$

This relation can be used to determine order of reaction

'n'

**Plots of half-lives Vs concentrations ( $t_{1/2} \propto a^{1-n}$ )**



(3) **Graphical method:** A graphical method based on the respective rate laws, can also be used.

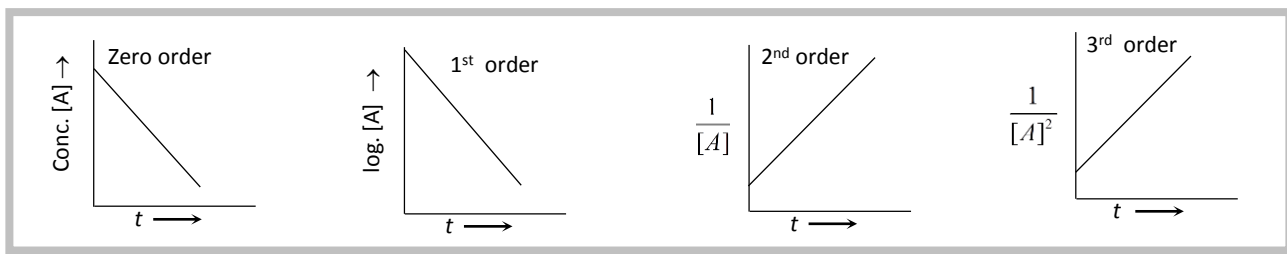
- (i) If the plot of  $\log(a - x)$  Vs  $t$  is a straight line, the reaction follows first order.
- (ii) If the plot of  $\frac{1}{(a - x)}$  Vs  $t$  is a straight line, the reaction follows second order.
- (iii) If the plot of  $\frac{1}{(a - x)^2}$  Vs  $t$  is a straight line, the reaction follows third order.
- (iv) In general, for a reaction of nth order, a graph of  $\frac{1}{(a - x)^{n-1}}$  Vs  $t$  must be a straight line.

**Graphical determination of order of the reaction**

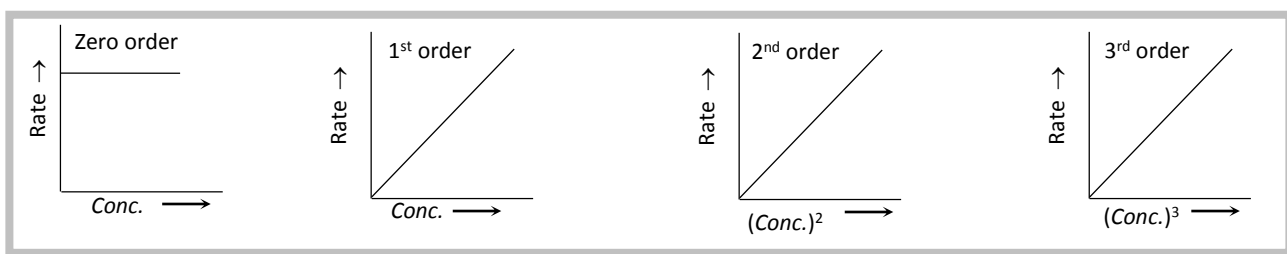
Order	Equation	Straight line plot		Slope	Intercept on Y-axis
		Y- axis	X-axis		
Zero	$x = k_0 t$	$x$	$t$	$k_0$	0
First	$\log_{10}(a - x) = \frac{-k_1 t}{2.303} + \log_{10} a$	$\log_{10}(a - x)$	$t$	$\frac{-k}{2.303}$	$\log_{10} a$
Second	$(a - x)^{-1} = k_2 t + a^{-1}$	$(a - x)^{-1}$	$t$	$k_2$	$a^{-1}$
$n^{\text{th}}$	$(a - x)^{1-n} = (n - 1)k_n t + a^{1-n}$	$(a - x)^{1-n}$	$t$	$(n - 1)k_n$	$a^{1-n}$



Plots from integrated rate equations



Plots of rate Vs concentrations [Rate = k (conc.)<sup>n</sup>]



(4) **Van't Haff differential Method:** The rate of reaction varies as the  $n^{\text{th}}$  power of the concentration where ' $n$ ' is the order of the reaction. Thus for two different initial concentrations  $C_1$  and  $C_2$  equation, can be written in the form,  $\frac{-dC_1}{dt} = kC_1^n$  and  $\frac{-dC_2}{dt} = kC_2^n$

Taking logarithms,  $\log_{10} \left( \frac{-dC_1}{dt} \right) = \log_{10} k + n \log_{10} C_1$  .....(i)

and  $\log_{10} \left( \frac{-dC_2}{dt} \right) = \log_{10} k + n \log_{10} C_2$  .....(ii)

Subtracting equation (ii) from (i),

$$n = \frac{\log_{10} \left( \frac{-dC_1}{dt} \right) - \log_{10} \left( \frac{-dC_2}{dt} \right)}{\log_{10} C_1 - \log_{10} C_2}$$
 .....(iii)

$\frac{-dC_1}{dt}$  and  $\frac{-dC_2}{dt}$  are determined from concentration Vs time graphs and the value of ' $n$ ' can be determined.



(5) **Ostwald's isolation method** (Initial rate method): This method can be used irrespective of the number of reactants involved e.g., consider the reaction,  $n_1A + n_2B + n_3C \rightarrow \text{Products}$ .

This method consists in finding the initial rate of the reaction taking known concentrations of the different reactants (A, B, C). Now the concentration of one of the reactants is changed (say that of A) taking the concentrations of other reactants (B and C) same as before. The initial rate of the reaction is determined again. This gives the rate expression with respect to A and hence the order with respect to A. The experiment is repeated by changing the concentrations of B and taking the same concentrations of A and C and finally changing the concentration of C and taking the same concentration of A and B. These will give rate expressions with respect to B and C and hence the orders with respect to B and C respectively. Combining the different rate expressions, the overall rate expression and hence the overall order can be obtained.

Suppose it is observed as follows:

(i) Keeping the concentrations of B and C constant, if concentration of A is doubled, the rate of reaction becomes four times. This means that,  $\text{Rate} \propto [A]^2$  i.e., order with respect to A is 2

(ii) Keeping the concentrations of A and C constant, if concentration of B is doubled, the rate of reaction is also doubled. This means that,  $\text{Rate} \propto [B]$  i.e., order with respect to B is 1

(iii) Keeping the concentrations of A and B constant, if concentration of C is doubled, the rate of reaction remains unaffected. This means that rate is independent of the concentration of C i.e., order with respect to C is zero. Hence the overall rate law expression will be,  $\text{Rate} = k[A]^2 [B] [C]^0$

$\therefore$  Overall order of reaction = 2 + 1 + 0 = 3.



## 8. Molecularity of Reaction.

"It is the sum of the number of molecules of reactants involved in the balanced chemical equation".

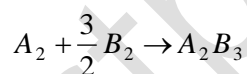
Or

"It is the minimum number of reacting particles (Molecules, atoms or ions) that collide in a rate determining step to form product or products".

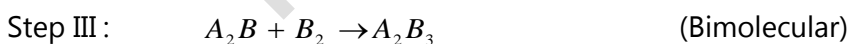
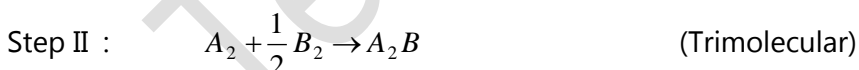
- Molecularity of a complete reaction has no significance and overall kinetics of the reaction depends upon the rate determining step. Slowest step is the rate-determining step. This was proposed by **Van't Hoff**.



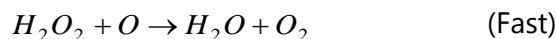
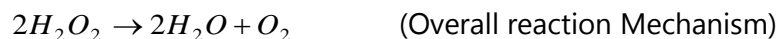
- Molecularity of a reaction can't be Zero, negative or fractional.
- Molecularity of a reaction is derived from the mechanism of the given reaction.
- Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.



Mechanism



Example: Decomposition of  $H_2O_2$



Rate =  $K[H_2O_2]$ ; the reaction is Unimolecular



(1) **Pseudo Unimolecular Reaction:** Reaction whose actual order is different from that expected using rate law expression are called **pseudo-order reaction**. For example,  $RCl + H_2O \rightarrow ROH + HCl$

**Expected rate law:**  $Rate = k[RCl][H_2O]$ ; Expected order =  $1 + 1 = 2$

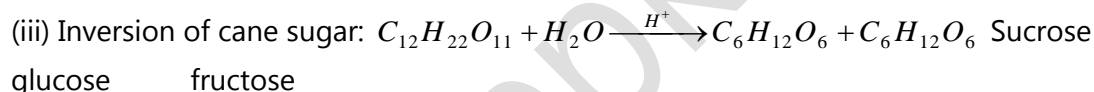
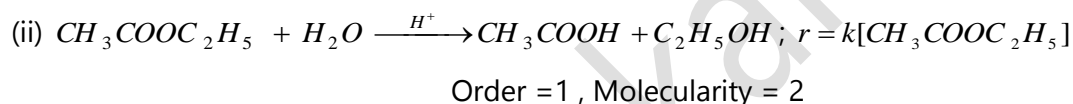
**Actual rate law:**  $Rate = k[RCl]$ ; Actual order = 1

Because of water is taken in excess amount; therefore, its concentration may be taken constant. The reaction is therefore, pseudo first order. Similarly the acid catalyzed hydrolysis of ester, viz.,



Those reactions which may have order of reaction as one while Molecularity of reaction 2 or more than two are as follows:

Examples: (i)  $2N_2O_5 \rightarrow 4NO_2 + O_2$ ; Order = 1; Molecularity = 2



Order = 1, Molecularity = 2



## Difference between Molecularity and Order of reaction

Molecularity	Order of Reaction
It is the number of molecules of reactants terms taking part in elementary step of a reaction.	It is sum of the power of the concentration terms of reactants in the rate law expression.
Molecularity is a theoretical value	Order of a reaction is an experimental value
Molecularity can neither be zero nor fractional.	Order of a reaction can be zero, fractional for integer.
Molecularity has whole number values only i.e., 1, 2, 3, etc.	Order of a reaction may have negative value.
It is assigned for each step of mechanism separately.	It is assigned for overall reaction.
It is independent of pressure and temperature.	It depends upon pressure and temperature.

## 9. Theories of Reaction rate.

Some theories, which explain the reaction rate, are as follows:

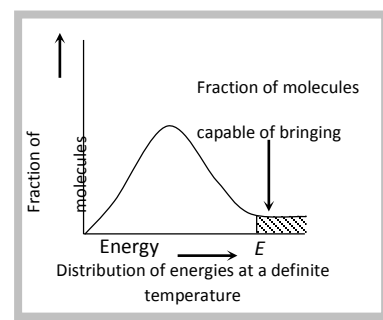
### (1) Collision theory

(i) The basic requirement for a reaction to occur is that the reacting species must collide with one another. This is the basis of **collision theory** for reactions.

(ii) The number of collisions that takes place per second per unit volume of the reaction mixture is known as **collision frequency** (Z). The value of collision frequency is very high of the order of  $10^{25}$  to  $10^{28}$  in case of binary collisions.

(iii) Every collision does not bring a chemical change. The collisions that actually produce the product are **effective collisions**. The effective collisions, which bring chemical change, are few in comparison to the total number of collisions. The collisions that do not form a product are **ineffective elastic collisions**, i.e., molecules just collide and disperse in different directions with different velocities.

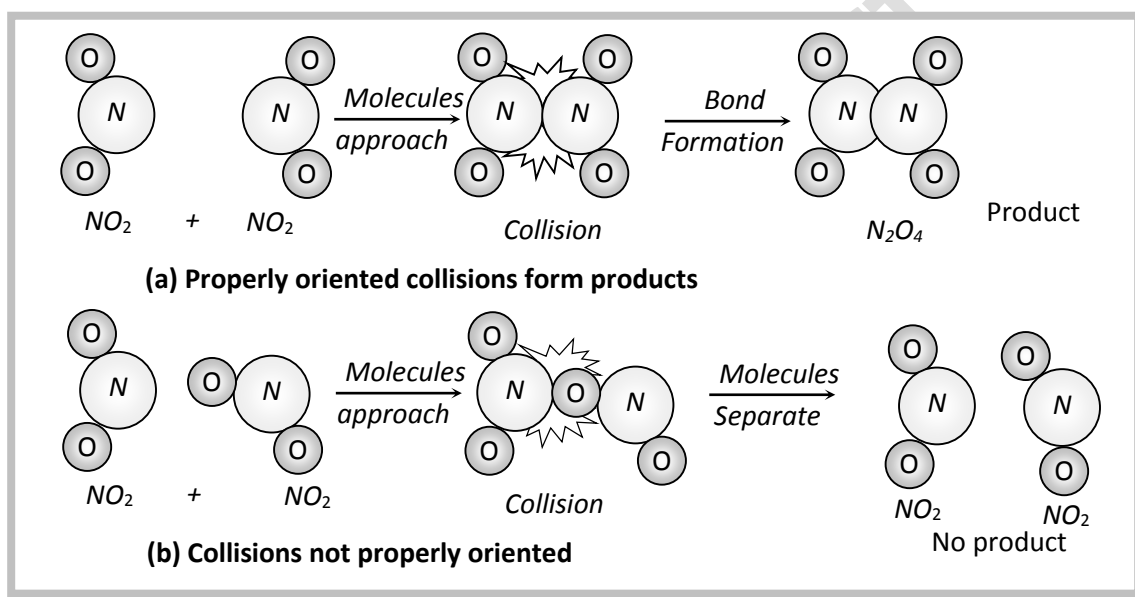
(iv) For a collision to be effective, the following two barriers are to be cleared



(a) Energy barrier: "The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as **threshold energy**".

- In the graph 'E' corresponds to minimum or threshold energy for effective collision.
- There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy to cross the energy barrier.

(b) Orientation barrier: The colliding molecules should also have proper orientation so that the old bonds may break and new bonds are formed. For example,  $NO_2(g) + NO_2(g) \rightarrow N_2O_4(g)$ . during this reaction, the products are formed only when the colliding molecules have proper orientation at the time of collisions. These are called effective collisions.



(v) Thus, the main points of **collision theory** are as follows,

- For a reaction to occur, there must be collisions between the reacting species.
- Only a certain fraction of the total number of collisions is effective in forming the products.
- For effective collisions, the molecules should possess sufficient energy as well as orientation.

(vi) The fraction of effective collisions, under ordinary conditions may vary from nearly zero to about one for ordinary reactions. Thus, the rate of reaction is proportional to:

- The number of collisions per unit volume per second (Collision frequency, Z) between the reacting species
- The fraction of effective collisions (Properly oriented and possessing sufficient energy), f



i.e.,  $\text{Rate} = \frac{-dx}{dt} = f \times Z$ ; where  $f$  is fraction of effective collision and  $Z$  is the collision frequency.

(vii) The physical meaning of the activation energy is that it is the minimum relative kinetic energy which the reactant molecules must possess for changing into the products molecules during their collision. This means that the fraction of successful collision is equal to  $e^{-E_a/RT}$  called **Boltzmann factor**.

(viii) It may be noted that besides the requirement of sufficient energy, the molecules must be properly oriented in space also for a collision to be successful. Thus, if  $Z_{AB}$  is the collision frequency,  $P$  is the **orientation factor** (Steric factor) then,  $k = PZ_{AB} \cdot e^{-E_a/RT}$ . If we compare this equation with Arrhenius equation.  $k = A e^{-E_a/RT}$

We know that pre-exponential form 'A' in Arrhenius equation is,  $A = PZ_{AB}$ .

### Concept of activation energy

(i) The excess energy (Over and above the average energy of the reactants) which must be supplied to the reactants to undergo chemical reactions is called **activation energy** ( $E_a$ ),

$$E_a = E_{(\text{Threshold energy})} - E_{(\text{Reactants})}$$

### Activation energy = Threshold energy – Average kinetic energy of the reacting molecules.

(a) Zero activation energy = Fraction of effective collision ( $f$ ) will be very large = Very fast reaction (Instantaneous reaction).

(b) Low activation energies = Fraction of effective collision ( $f$ ) will be large = Fast reactions.

(c) High activation energies = Fraction of effective collision ( $f$ ) will be small = Slow reaction.

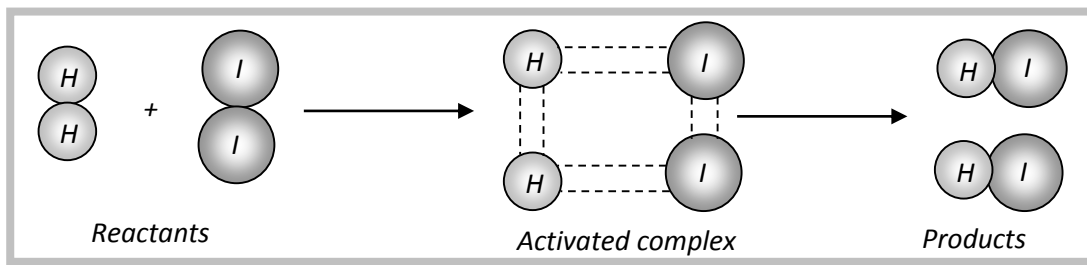
(ii) When the colliding molecules possess the kinetic energy equal to activation energy, the atomic

Configuration of species formed at this stage is different from the reactants as well as products. This stage is called the **activated state** or **transition state** and specific configuration of this state is called **activated complex**. In other words, we can say that, A collision between high energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster called the



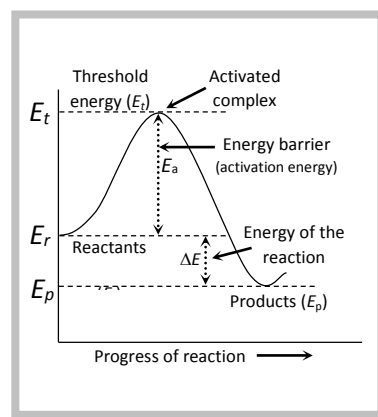
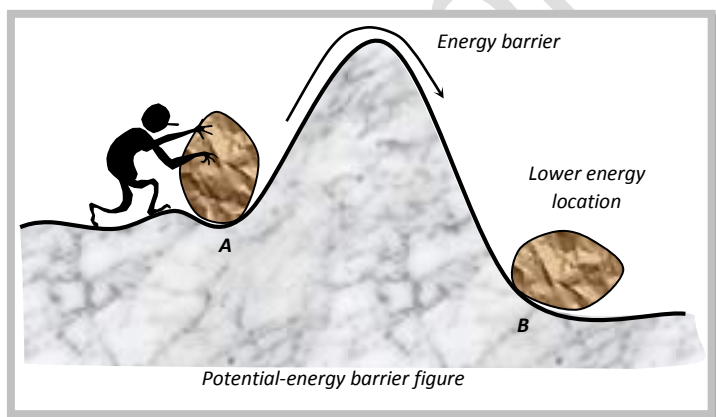


**activated complex.** The life span of an activated complex is very small. Thus, the activated complex breaks either into reactants again or new substances, i.e., products.



(iii) The activation energy ( $E_a$ ) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products.

(iv) According to the concept of activation energy, the reactants do not change directly into the products. The reactant first absorb energy equal to activation energy and form activated complex. At this state, the molecules must have energy at least equal to the threshold energy. This means that the reaction involves some energy barrier which must be overcome before products are formed. The energy barrier is known as **activation energy barrier**.



Note: The activation energy is found to increase with the lowering of temperature i.e., at lower temperatures the activation energy tends to increase.



## (2) Transition state theory

(i) According to transition state theory the activated complex is supposed to be in equilibrium with the reactant molecules.

(ii) Once the transition state is formed it can either return to the initial reactants or proceeds to form the products.

(iii) Assuming that once formed the transition state proceeds to products we can say that rate is proportional to concentration of transition state. Mathematically,  $\text{Rate} \propto \text{Transition state}$ ; **Rate = Constant  $\times$  Transition state**

(iv) The activation energy for the forward reaction, ( $E_a^f$ ) and the activation energy for the reverse reaction ( $E_a^r$ ) are related to the enthalpy ( $\Delta H$ ) of the reaction by the equation  $\Delta H = E_a^f - E_a^r$ .

(a) For endothermic reactions,  $\Delta H > 0$ , so that  $E_a^r < E_a^f$

(b) For exothermic reaction,  $\Delta H < 0$ , so that  $E_a^r > E_a^f$ .

Note: Exothermic reaction requires less activation energy than the endothermic reaction. Therefore an exothermic reaction proceeds at a faster rate than the endothermic reaction.

Kinetic stability of fuels: Combustion of fuels is highly exothermic reaction yet these can be safely stored in contact with oxygen or air. The stability of fuels is due to high activation energy of these combustion reactions.  $E_a$  cannot be zero (if suppose  $E_a = 0$  then according to Arrhenius equation  $k = A$  i.e., every collision between molecules leads to be chemical reaction. This is not true.)

## 10. Dependence of reaction rate on temperature.

A general approximate rule or the effect of temperature on reaction rates is that the rate of a reaction becomes almost double for every  $10^\circ C$  rise in temperature. This is also called temperature coefficient.

**Temperature coefficient.** Temperature coefficient of a reaction is defined as the ratio of rate constants at two temperatures differing by (generally  $25^\circ C$  and  $35^\circ C$ ) 10.

$$\text{Temperature coefficient } t = \frac{k \text{ at } (t + 10^\circ C)}{k \text{ at } t^\circ C} = \frac{k_{35^\circ C}}{k_{25^\circ C}} \quad \text{Or} \quad \text{Temperature coefficient } t = \frac{k_{t+10}}{k_t}$$

The temperature coefficient for most of the reactions lies between 2 and 3 i.e. the rate of reaction increase by a factor of 2 to 3, for every  $10^\circ C$  rise in temperature.



## 11. Arrhenius equation and Calculation of activation energy.

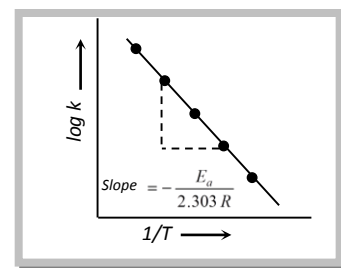
Arrhenius proposed a quantitative relationship between rate constant and temperature as,

$$k = A e^{-E_a/RT} \quad \dots(i)$$

The equation is called **Arrhenius equation** in which constant A is known as **frequency factor**. This factor is related to number of binary molecular collision per second per liter.  $E_a$  Is the activation energy.  $T$  is the absolute temperature and  $R$  is the gas constant. Both A and  $E_a$  are collectively known as **Arrhenius parameters**. Taking logarithm equation (i) may be written as,

$$\log k = \log A - \frac{E_a}{2.303 RT} \quad \dots(ii)$$

The value of activation energy ( $E_a$ ) increases, the value of  $k$  decreases and therefore, the reaction rate decreases. When  $\log k$  plotted against  $\frac{1}{T}$ , we get a straight line. The intercept of this line is equal to  $\log A$  and slope equal to  $-\frac{E_a}{2.303 R}$ . Therefore  $E_a = -2.303 R \times \text{slope}$ .



Rate constants for the reaction at two different temperatures  $T_1$  and  $T_2$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad \dots(iii)$$

Where  $k_1$  and  $k_2$  are rate constant at temperatures  $T_1$  and  $T_2$  respectively ( $T_2 > T_1$ ).

**Note:** Generally rate of reaction increases with increase in temperature but remember for the reaction  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ ; the rate decreases slightly with increase in temperature because it has small negative temperature coefficient.

When  $E_a = 0$ , the rate of reaction becomes independent of temperature ( $E_a =$  activation energy)



## 12. Mechanism of the reaction.

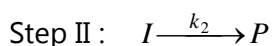
- The study of reaction pathway or mechanism of a reaction is very important aspect of kinetics of reaction.
- In some reactions, intermediates formed which accumulate during the early period of the reaction, reach to the maximum concentration and then react and give the final products.
- The necessary condition for a mechanism is that it must lead to the correct law.

### (1) Reaction involving first order consecutive reactions

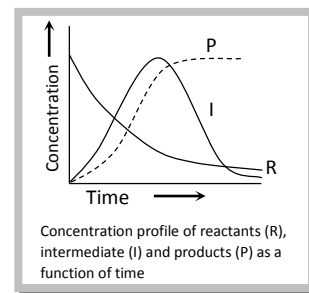
(i) In such reactions, the reactions form a stable intermediate compound before they are finally converted into the products.

(ii) For example, reactants ( $R$ ) are first converted to intermediate ( $I$ ) which is then converted to product ( $P$ ) as

$R \xrightarrow{k_1} I \xrightarrow{k_2} P$ ; Therefore, the reaction takes place in two steps, both of which are first order i.e.,



This means that  $I$  is produced by step I and consumed by step II. In these reactions, each stage will have its own rate and rate constant the reactant concentration will always decrease and product concentration will always increase as shown in fig.



(2) **Reaction involving slow step:** When a reaction occurs by a sequence of steps and one of the step is slow, then the rate determining step is the slow step. For example in the reaction

$R \xrightarrow{k_1} I; I \xrightarrow{k_2} P$ , if  $k_1 \ll k_2$  then  $I$  is converted into products as soon as it is formed, we can say that

$$\frac{-d[R]}{dt} = \frac{d[P]}{dt} = k_1[R]$$

(3) **Parallel reactions:** In such type of reactions the reactants are more reactive, which may have different orders of the reactions taking place simultaneously. For example, in a system containing  $NO_2$  and  $SO_2$ ,  $NO_2$  is consumed in the following two reactions,  $2NO_2 \xrightarrow{k_1} N_2O_4$ ;  
 $NO_2 + SO_2 \xrightarrow{k_2} NO + SO_3$

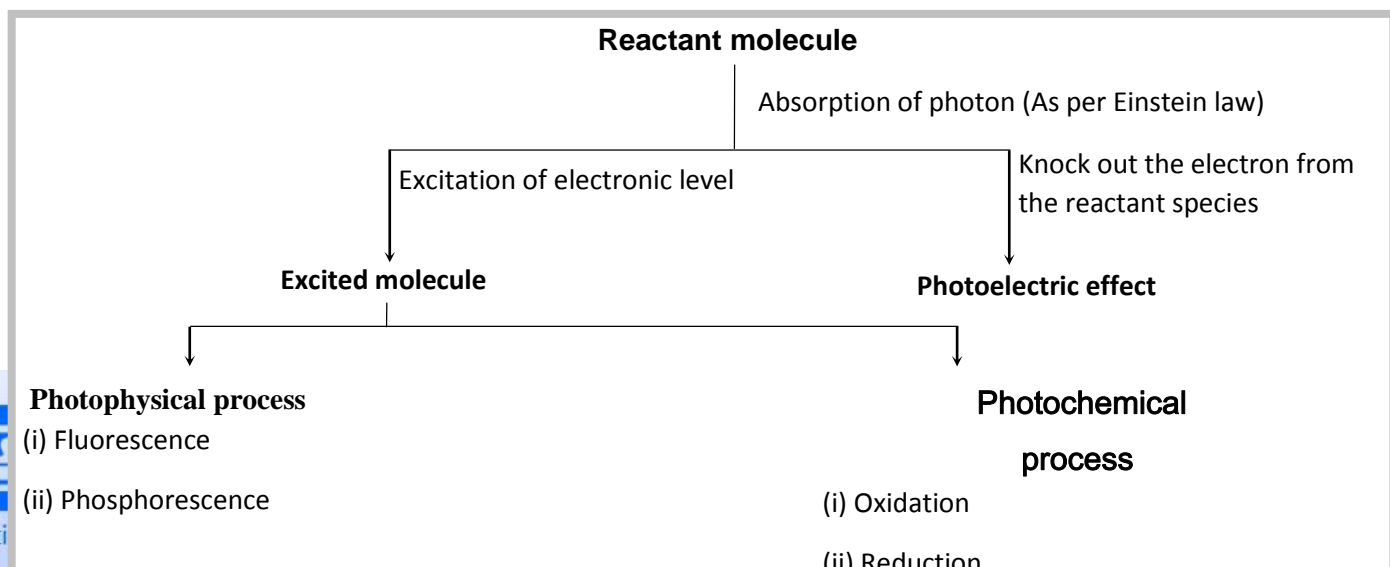


The rate of disappearance of  $NO_2$  will be sum of the rates of the two reactions *i.e.*,

$$-\frac{d[NO_2]}{dt} = 2k_1[NO_2]^2 + k_2[NO_2][SO_2]$$

### 13. Photochemical reactions:

Absorption of radiant energy by reactant molecules brings in photo physical as well as photochemical changes. According to **Einstein's law** of photochemical equivalence, the basic principle of photo processes, each reactant molecule is capable of absorbing only one photon of radiant energy. The absorption of photon by a reactant molecule may lead to any of the photo process.



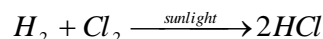
The chemical reactions, which are initiated as a result of absorption of light, are known as **photochemical reactions**. In such cases, the absorbed energy is sufficient to activate the reactant molecules to cross the energy barrier existing between the reactants and products or in other words, energy associated with each photon supplies activation energy to reactant molecule required for the change.

### (1) Characteristics of photochemical reactions

- (i) Each molecule taking part in a photo process absorbs only one photon of radiant energy thereby increasing its energy level by  $h\nu$  or  $\frac{hc}{\lambda}$
- (ii) Photochemical reactions do not occur in **dark**.
- (iii) Each photochemical reaction requires a definite amount of energy which is characteristic of a particular wavelength of photon. For example, reactions needing more energy are carried out in presence of UV light (lower  $\lambda$ , more E/Photon). A reaction-taking place in UV light may not occur on exposure to yellow light (lower  $\lambda$  and lesser E/Photon)
- (iv) The rate of photochemical reactions depend upon the intensity of radiation's absorbed.
- (v) The  $\Delta G$  values for light initiated reactions may or may not be **negative**.
- (vi) The temperature does not have marked effect on the rate of light initiated reactions.

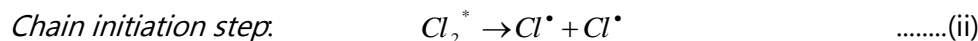
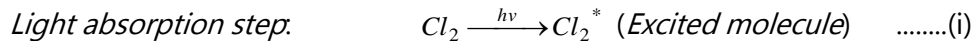
### (2) Mechanism of some photochemical reactions

- (i) **Photochemical combination of  $H_2$  and  $Cl_2$** : A mixture of  $H_2$  and  $Cl_2$  on exposure to light give rise to the formation of  $HCl$ , showing a chain reaction and thereby producing  $10^6$  to  $10^8$  molecules of  $HCl$  per photon absorbed.

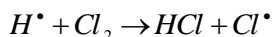
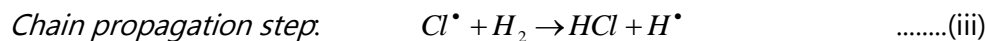


The mechanism leading to very high yield of  $HCl$  as a result of chemical change can be as follows. Chlorine molecules absorb radiant energy to form an excited molecule which decomposes to chlorine free radicals ( $Cl$ ) to give chain initiation step.





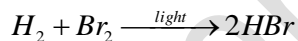
The chlorine free radical then combines with  $H_2$  molecule to form  $HCl$  and  $H^\bullet$  free radical. The  $H^\bullet$  free radical so formed again combines with another  $Cl_2$  molecule to give  $HCl$  and  $Cl^\bullet$  free radical back resulting into chain propagation step.



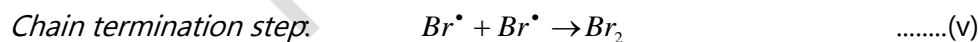
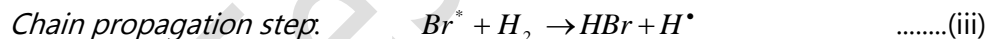
The combination of two  $Cl^\bullet$  free radicals leads to chain terminating step.



(ii) **Photochemical combination of  $H_2$  and  $Br_2$**  : The combination of  $H_2$  and  $Br_2$  to form  $HBr$  in presence of light is also an example of chain reaction like photochemical combination of  $H_2$  and  $Cl_2$ . Here two  $Br_2$  molecules absorb photon, however, in spite of chain reaction only one molecule of  $HBr$  is formed for each 100 photon absorbed by 100 molecules of  $Br_2$ . The mechanism of reaction is given below.



**Mechanism:**



The lower values of  $HBr$  formation per photon of light absorbed has been attributed to the fact that step (III) is highly endothermic and thus before step (III) can take place most of the bromine free radicals recombine as per step (V) to give  $Br_2$  molecule and thus providing less feasibility for step (IV) i.e. steps regenerating free radicals. Also the decomposition of  $HBr$  increases with increase in temperature.

(3) **Quantum yield** (or quantum efficiency): The quantum efficiency or yield ( $\phi$ ) of a photochemical reaction may be expressed as,  $\phi = \frac{\text{No. of molecules reacted or product formed}}{\text{No. of photon absorbed}}$



(4) **Application of photochemistry:** Photochemistry has significant role in our daily life. Some of the photochemical reactions commonly known as cited below.

- |   |   |
|---|---|
| (i) Photosynthesis in plants                              | (ii) Photography                          |
| (iii) The formation and destruction of ozone layer        | (iv) Photo etching in electronic industry |
| (v) Many polymerization reactions.                        | (vi) Modern printing technology           |
| (vii) Free radical combinations to obtain many compounds. |   |

(5) **Damaging effect of photochemistry:** As already discussed, the destruction of ozone layer by chloro-fluorocarbon is due to photochemical decomposition of these compounds. The fading away of colors in colored fabrics is due to the photochemical decomposition of coloring material (i.e. dyes) used in printing technology.

Note: Generally ultraviolet or visible radiations are used for carrying out such type of reactions because their photons possess energies approximately of the order of 420 kJ per mol which is comparable to mole of the bond energy.

Thus UV radiation energy is capable of breaking the bonds. On the other hand IR radiations are generally not used because their photons possess energy of the order of 60 kJ per mole which is quite less for breaking the bonds.

Destruction of ozone layer: The formation and dissociation of ozone keeps a balance of ozone and oxygen in the ozone layer. However the diffusion of chloro-fluorocarbon such as  $CFCl_3$  and  $CF_2Cl_2$  into the ozone layer are destroying the ozone.  $Cl_2 + h\nu \rightarrow CF_2 \dot{Cl} + \dot{Cl}$ ;  $\dot{Cl} + O_3 \rightarrow \dot{Cl}O + O_2$ ;  $\dot{Cl}O + O_3 \rightarrow \dot{Cl} + 2O_2$ . Chloro-fluorocarbons are used as aerosol repellents and as refrigerants.

Hence, ozone layer which acts as an umbrella for earth is being continuously destroying by the harmful UV radiation's coming from the sun.

## 14. Study of fast reactions.

Rates of chemical reactions differ from very slow to very fast. The rates of moderate speed reactions lying in between these two extreme reactions. However, rates of some instantaneous reactions are so fast that they occur within  $10^{-12}$  second or in even less time. For example.





- **Neutralization** reactions have half-life of  $10^{-10}$  sec ;  $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$
- **Photosynthesis** has half-life of  $10^{-12}$  sec ;  $6CO_2 + 6H_2O \xrightarrow[hv]{\text{chlorophyll}} C_6H_{12}O_6 + 6O_2$
- **Some precipitation** reactions have very short half-life;  $AgNO_3 + KCl \rightarrow AgCl \downarrow + KNO_3$
- **Isomerization** of retinal in vision has half-life of  $10^{-12}$  sec

Rates of such reactions cannot be studied by ordinary methods because change in concentration cannot be measured during this short interval of time. However, modern techniques such as flow methods, relaxation methods, flash photolysis, laser technique and spectrophotometric methods are used to study such fast reactions.

(1) **Photosynthesis in plants:** Plants obtain their food for growth by the combination of  $CO_2$  and  $H_2O$  in presence of chlorophyll and light (a fast reaction) which leads to the preparation of carbohydrate and this phenomenon is known as **photosynthesis**. The studies on photosynthesis involve flash photolysis technique. The following mechanism has been proposed for photosynthesis. First step of the reaction mechanism involves the excitation of chlorophyll molecule by absorbing photon of red light. The excited chlorophyll molecule transfers its energy in the form of an electron to nearby reactant molecule A within  $10^{-12}$  second. The reactant molecule which accepts this energy is known as **electron acceptor**.



The electron acceptor (A) transfer this electron to another electron acceptor molecule (B).  $A + B \rightarrow A + B^- + E$

The process leads to release of energy which is used for the series of reaction to yield the synthesis of energy rich molecule of carbohydrates from  $CO_2$  and water.  $6CO_2 + 6H_2O \xrightarrow{\text{Energy}} C_6H_{12}O_6 + 6O_2$

(2) **Isomerization of retinal in vision:** The mechanism involves two steps

- The retinal molecule (a light sensitive molecule present in the retina of eye) gets excited on exposure to light and undergoes geometrical isomerization and the energy absorbed is stored as chemical energy. The process takes place within  $10^{-12}$  sec .
- As soon as the first step gets completed, the retinal is converted back into its original form within  $10^{-12}$  sec and the energy released is used to send signals to the brain which ultimately causes the sensation of vision.



### Differences between Photochemical and Thermochemical reactions

Photochemical reactions	Thermochemical reactions
These reactions are initiated by light radiation.	These reactions are initiated by heat energy.
They cannot occur in dark.	They do occur in dark.
Temperature does not have any significant effect on the rates of such reactions and temperature coefficient is low.	The temperature does have a marked effect on the rates of these reactions and temperature coefficient is generally high.
The value of $\Delta G$ may be +ve or -ve.	$\Delta G$ is -ve for such reactions.

### Important tips

- ☞ **Chemiluminescence:** It is the emission of light in chemical reaction at ordinary temperature e.g., the light emitted by **glow worms** (fire flies) is due to the oxidation of a protein Luciferin present in them.
- ☞ **Fluorescence and Phosphorescence:** There are some substances which when exposed to light or radiation, absorbs light and immediately start re-emitting the energy. The glow continue as long as the source of light is there. Such substances are called fluorescent substances and phenomenon as fluorescence e.g., **fluorite** ( $CaF_2$ ), fluorescein dye etc.  
On the other hand, there are some substances which continue to glow for some time even after the source of light is cut off. Such substances are called phosphorescent substances and phenomenon as phosphorescence e.g., **Zinc sulphide** and sulphides of other alkaline earth metals.
- ☞ **Bioluminescence:** Certain living organisms emit light and show the phenomenon of chemiluminescence. It is known as Bioluminescence e.g., light emission in fire flies.
- ☞ Example of fourth order reaction,  $4KClO_3 \rightleftharpoons 3KClO_4 + KCl$
- ☞ **Grothus-Draper law:** When light falls on a substance, a part of light is absorbed, a part is reflected and a part is transmitted. Only that part of light which is absorbed causes a particular reaction to occur.
- ☞ **Stark's Einstein law of photochemical equivalence:** According to this law, every atom or molecule taking part in a photochemical reaction absorbs only one quantum of radiation. ( $E = h\nu$ ). The energy absorbed by one mole of reacting molecules is known as one Einstein.
- ☞ Free energy ( $\Delta G$ ) for thermochemical reactions is always negative but remember,  $\Delta G$  for photochemical reactions may not always be negative. It is because a part of the light energy absorbed by the reactants



is converted into free energy of the products. In the following photochemical reactions for which  $\Delta G$  is positive and still they are spontaneous

- (a) Ozonisation of oxygen
- (b) Synthesis of carbohydrates
- (c) Decomposition of HCl to  $H_2$  and  $Cl_2$

☞ There are some substances which when added to a reaction mixture helps to start the photochemical reaction but do not undergo any chemical change are called photosensitizer and this process is called photosensitization. A photosensitizer simply acts as a carrier of energy. For example (i) Dissociation of  $H_2$  in the presence of mercury vapors. (ii) Photosynthesis in presence of chlorophyll.

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