

Chapter 11 Chemical Kinetics

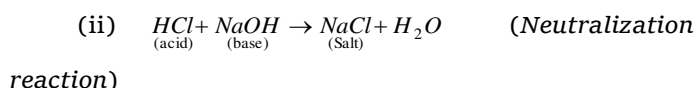
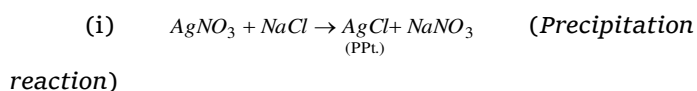
The branch of physical chemistry which deals with the rate at which the chemical reactions occur, the mechanism by which the chemical reactions take place and the influence of various factors such as concentration, temperature, pressure, catalyst etc., on the reaction rates is called the chemical kinetics.

Types of chemical reactions

On the basis of reaction rates, the chemical reactions have been classified into the following three types,

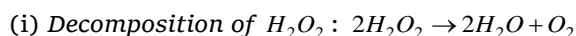
(1) **Very fast or instantaneous reactions** : These reactions occur at a very fast rate generally these reactions involve ionic species and known as ionic reactions. It is almost impossible to determine the rates of these reactions.

Examples



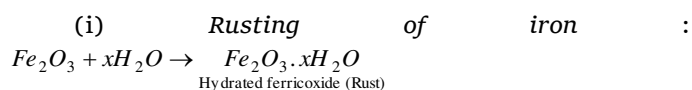
(2) **Moderate reaction** : These reactions proceed with a measurable rates at normal temperature and it is these reactions are studied in chemical kinetics. Mostly these reactions are molecular in nature.

Examples



(3) **Very slow reactions** : These reactions are extremely slow and take months together to show any measurable change.

Examples



Rate of a reaction

The rate (speed or velocity) of a reaction is the change in concentration in per unit time.

$$\frac{\Delta x}{\Delta t} \text{ or } \frac{dx}{dt} = \left(\frac{x_2 - x_1}{t_2 - t_1} \right)$$

where Δx or dx is the concentration change, i.e., $(x_2 - x_1)$ in the time interval Δt or dt , i.e., $(t_2 - t_1)$.

Concentration is generally expressed in active mass, i.e., mole L^{-1}

- The rate measured over a long time interval is called **average rate** and the rate measured for an infinitesimally small time interval is called **instantaneous rate** and

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

- For the reaction $aA + bB \rightarrow cC + dD$

Rate of disappearance of a reactant is negative

$$-\frac{d[A]}{dt} = \text{Rate of disappearance of A}$$

$$-\frac{d[B]}{dt} = \text{Rate of disappearance of B}$$

Rate of formation of a product is positive

$$\frac{d[C]}{dt} = \text{Rate of formation of C}$$

$$\frac{d[D]}{dt} = \text{Rate of formation of } D$$

• In terms of stoichiometric coefficient rate may be expressed as

$$\frac{dx}{dt} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = -\frac{1}{c} \frac{d[C]}{dt} = -\frac{1}{d} \frac{d[D]}{dt}$$

• The rate of reaction is always **positive**.
• The rate of chemical reaction decreases as the reaction proceeds.

• Unit of rate of a reaction = $\frac{\text{Unit of conc.}}{\text{Unit of time}} = \text{mole L}^{-1} \text{time}^{-1}$

In term of gaseous reaction the unit is atm time^{-1} and

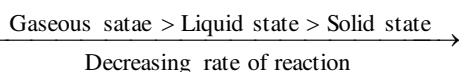
$$\text{Rate in } \text{atm time}^{-1} = \text{Rate in mole L}^{-1} \text{time}^{-1} \times RT$$

Factors affecting rate of a reaction

The rate of a chemical reaction depends on the following things

(1) Nature of reactants

(i) *Physical state of reactants* : This has considerable effect over rate of reaction.



(ii) *Physical size of the reactants* : Among the solids, rate increases with decrease in particle size of the solid.

(iii) Chemical nature of the reactants

(a) 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.

(b) Oxidation-reduction reactions, which involve transfer of electrons, are also slow as compared to the ionic substance.

(c) Substitution reactions are relatively much slower.

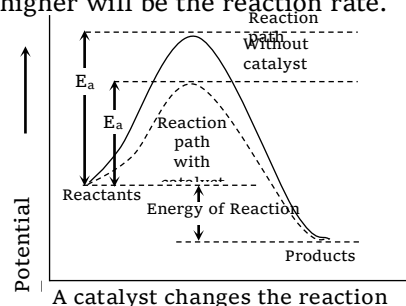
(2) **Effect of temperature** : The rate of chemical reaction generally increases on increasing the temperature. The rate of a reaction becomes almost double or tripled for every 10°C rise in temperature.

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

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

(3) **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.

(4) **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.



(5) **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.

The radiant energy initiates the chemical reaction by supplying the necessary activation energy required for the reaction.

Law of mass action and Rate constant

The rate at which a substance reacts is directly proportional to its active mass and the rate at which a reaction proceeds is proportional to the product of the active masses of the reacting substances.

• For a reaction, $aA + bB \rightarrow \text{product}$

$$\text{Rate} = \left(\frac{dx}{dt}\right) \propto [A]^a [B]^b ; \left(\frac{dx}{dt}\right) = k[A]^a [B]^b$$

Where k is called **rate constant** or **velocity constant**.

$$\text{When } [A] = [B] = 1 \text{ mol / litre, then } \frac{dx}{dt} = k$$

Thus, rate constant k is also called **specific reaction rate**.

• The value of rate constant depends on, nature of reactant, temperature and catalyst. It is independent of concentration of the reactants.

$$\bullet \text{ Unit of rate constant} = \left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \text{sec}^{-1} = \left[\frac{\text{mol}}{\text{litre}}\right]^{1-n} \times \text{sec}^{-1}$$

Where n = order of reaction.

Rate law : Molecularity and Order of a reaction

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

Example : $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ (Unimolecular)

$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ (Bimolecular)



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 conc. terms in rate law

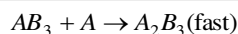
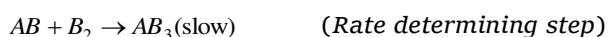
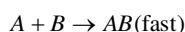
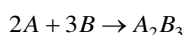
For the reaction $xA + yB \rightarrow \text{Products}$

The rate law is $\text{Rate} = [A]^x [B]^y$

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.)

• Molecularity of a reaction is derived from the mechanism of the given reaction. Molecularity can not be greater than three because more than three molecules may not mutually collide with each other.

• Molecularity of a reaction can't be zero, negative or fractional. order of a reaction may be zero, negative, positive or in fraction and greater than three. Infinite and imaginary values are not possible.

• When one of the reactants is present in the large excess, the second order reaction conforms to the first order and is known as **pseudo unimolecular reaction**. (Table 11.1)

Table : 11.1 Order and molecularity of some reaction

S. No.	Chemical equation	Molecularity	Rate law	Order w.r.t.		
				First reactant	Second reactant	Overall
1.	$aA + bB \rightarrow \text{product}$	$a + b$	$\left(\frac{dx}{dt}\right) = k[A]^a[B]^b$	a	b	$a + b$
2.	$aA + bB \rightarrow \text{product}$	$a + b$	$\left(\frac{dx}{dt}\right) = k[A]^2[B]^0$	2	zero, if B is in excess	2
3.	$2H_2O_2 \xrightarrow{Pt, \Delta} 2H_2O + O_2$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[H_2O_2]$	1*	----	1
4.	$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[CH_3COOC_2H_5]$	1*	Zero, if H_2O is in excess	1
5.	$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+}$ Sucrose $C_6H_{12}O_6 + C_6H_{12}O_6$ Glucose Fructose	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[C_{12}H_{22}O_{11}]$	1*	Zero, if H_2O is in excess	1
6.	$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[(CH_3)_3CCl]$	1*	Zero, if OH^- does not take part in slow step	1
7.	$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[CH_3Cl][OH^-]$	1	1	2
8.	$C_6H_5N_2Cl \xrightarrow{\Delta} C_6H_5Cl + N_2$	1 (Unimolecular)	$\left(\frac{dx}{dt}\right) = k[C_6H_5N_2Cl]$	1	----	1
9.	$CH_3CHO \xrightarrow{\Delta} CH_4 + CO$	1 (Unimolecular)	$\left(\frac{dx}{dt}\right) = k[CH_3CHO]^{3/2}$	1.5	----	1.5
10.	$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$	5	$\left(\frac{dx}{dt}\right) = k[H_2O_2][I^-]$	1	1 (H^+ is medium)	2
11.	$2O_3 \rightarrow 3O_2$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[O_3]^2[O_2]$	1	-1 with respect to O_2	1

*Pseudo-unimolecular reactions.

Table : 11.2 Rate constant and other parameters of different order reactions

Order	Rate constant	Unit of rate constant	Effect on rate by changing conc. to m times	(Half-life period) $T_{50} =$
0	$k_0 = \frac{x}{t}$	conc. time ⁻¹ (mol L ⁻¹ s ⁻¹)	No change	$\frac{a}{2k_0}$
1	$k_1 = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$, $C = C_0 e^{-k_1 t}$ $N = N_0 e^{-k_1 t}$, $k_1 = \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{(a - x_1)}{(a - x_2)}$	time ⁻¹ (s ⁻¹)	m times	$\frac{0.693}{k_1}$
2	$k_2 = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right] = \frac{x}{ta(a-x)}$ (for the case when each reactant has equal concentration) $k_2 = \frac{2.303}{t(a-b)} \log_{10} \left[\frac{b(a-x)}{a(b-x)} \right]$ (for the case when both reactants have different concentration)	conc ⁻¹ time ⁻¹ (mol L ⁻¹) s ⁻¹ L mol ⁻¹ s ⁻¹	m^2 times	$\frac{1}{k_2 a}$
3	$k_3 = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$	conc ⁻² time ⁻¹ (mol L ⁻¹) ⁻² s ⁻¹ L ² mol ⁻² s ⁻¹	m^3 times	$\frac{3}{2k_3 a^2}$
n	$k_n = \frac{1}{(n-1)t} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$; $n \geq 2$	conc ⁽¹⁻ⁿ⁾ time ⁻¹ (mol L ⁻¹) ⁽¹⁻ⁿ⁾ s ⁻¹ L ⁽ⁿ⁻¹⁾ mol ⁽¹⁻ⁿ⁾ s ⁻¹	m^n times	$\frac{2^{n-1} - 1}{(n-1)k_n (a)^{n-1}}$

Methods for determination of order of a reaction**(1) Integration method** (Hit and Trial method)

(i) The method can be used with various sets of a , x and t with integrated rate equations.

(ii) The value of k is determined and checked for all sets of a , x and t .

(iii) If the value of k is constant, the used equation gives the order of reaction.

(iv) 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.

$$t_{1/2} \propto a^{1-n}; \quad t_{1/2} = k a^{1-n}; \quad \log t_{1/2} = \log k + (1-n) \log a$$

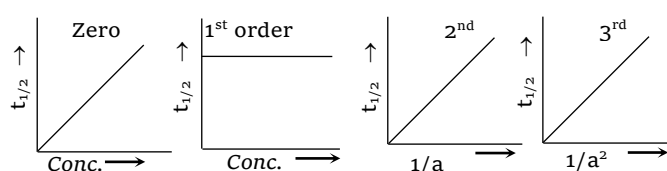
A plotted graph of $\log t_{1/2}$ vs $\log a$ gives a straight line with slope $(1-n)$, determining the slope we can find the order n . If half-life at different concentration is given then,

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

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

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

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.

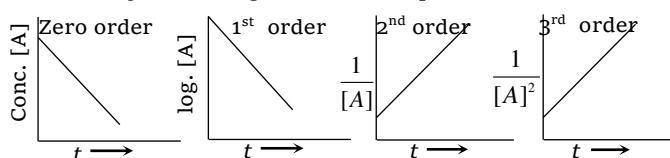
(i) If the plot of $\log(a-x)$ Vs t is a straight line, the reaction follows first order.

(ii) If the plot of $\frac{1}{(a-x)}$ Vs t is a straight line, the reaction follows second order.

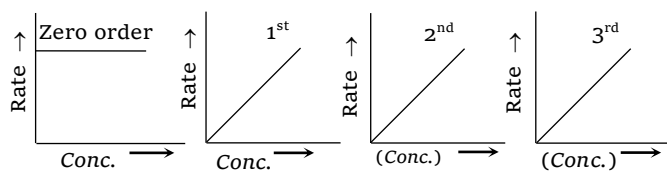
(iii) If the plot of $\frac{1}{(a-x)^2}$ Vs t is a straight line, the reaction follows third order.

(iv) In general, for a reaction of n th order, a graph of $\frac{1}{(a-x)^{n-1}}$ Vs t must be a straight line.

Plots from integrated rate equations



Plots of rate Vs concentrations [Rate = $k(\text{conc.})^n$]



(4) **Van't Hoff differential method** : The rate of reaction varies as the n^{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,

$$\frac{-dC_1}{dt} = kC_1^n \quad \text{and} \quad \frac{-dC_2}{dt} = kC_2^n$$

Taking logarithms,

$$\log_{10} \left(\frac{-dC_1}{dt} \right) = \log_{10} k + n \log_{10} C_1 \quad \dots (i)$$

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

Subtracting equation (ii) from (i),

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

$\frac{-dC_1}{dt}$ 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).

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, 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, 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, Rate = $k[A]^2[B][C]^0$

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

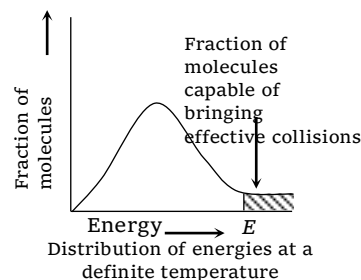
Theories of reaction rate

(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, $\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$. 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.

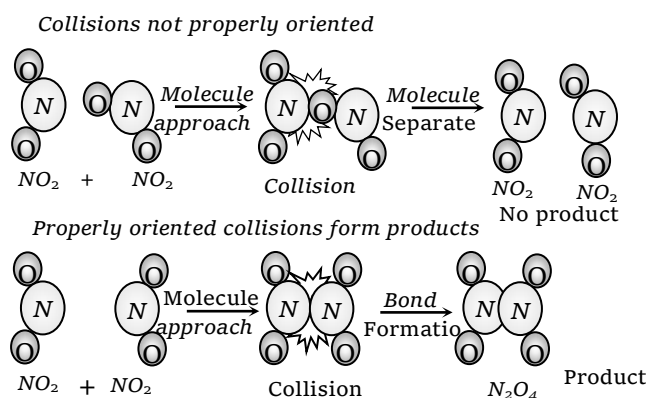


Fig. 11.1

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

(a) For a reaction to occur, there must be collisions between the reacting species.

(b) Only a certain fraction of the total number of collisions is effective in forming the products.

(c) 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 :

(a) The number of collisions per unit volume per second (Collision frequency, Z) between the reacting species

(b) 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

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.

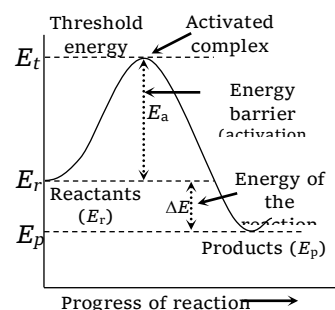
(a) **Zero activation energy** = Fraction of effective collision (f) will be very large = Very fast reaction (Instantaneous reaction).

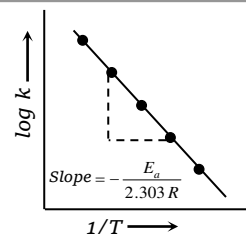
(b) **Low activation energies** = Fraction of effective collision (f) will be large = Fast reactions.

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

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

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**.





(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, Rate \propto 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 (ΔH) 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 $E_a^r > E_a^f$.

Arrhenius equation

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

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

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 litre.

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,

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

The value of activation energy (E_a) increases, the value of k decreases and therefore, the reaction rate decreases.

When $\log k$ plotted against $1/T$, 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 ,

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

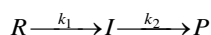
where k_1 and k_2 are rate constant at temperatures T_1 and T_2 respectively ($T_2 > T_1$).

Mechanism of the reaction

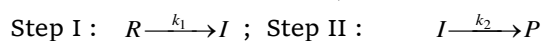
(1) Reaction involving first order consecutive reactions

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

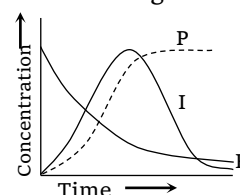
(ii) For example, reactants (R) are first converted to intermediate (I) which is then converted to product (P) as



Therefore, the reaction takes place in two steps, both of which are first order i.e.,

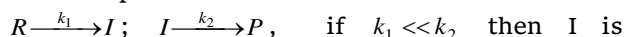


This means that I is produced by step I and consumed by step II. In these reactions, each stage will have its own rate and rate constant the reactant concentration will always decrease and product concentration will always increase as shown in fig.



Concentration profile of reactants (R), intermediate (I) and products (P) as a

(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



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

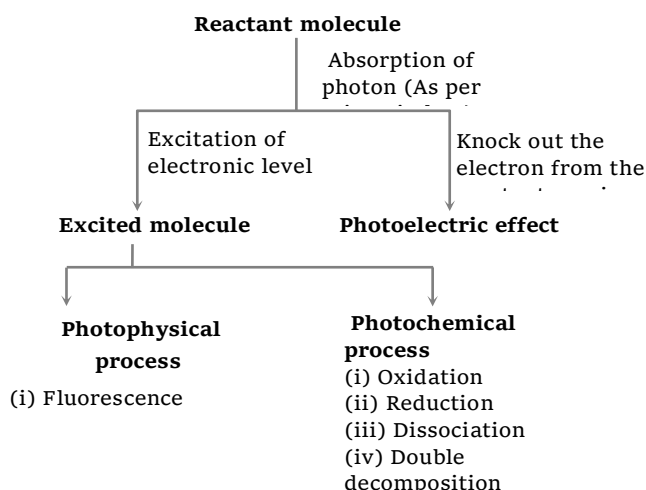
NO_2 and SO_2 , NO_2 is consumed in the following two reactions, $2NO_2 \xrightarrow{k_1} N_2O_4$; $NO_2 + SO_2 \xrightarrow{k_2} NO + SO_3$

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

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

Photochemical reaction

Absorption of radiant energy by reactant molecules brings in photophysical 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 λ , more E/Photon). A reaction-taking place in UV light may not occur on exposure to yellow light (lower λ and lesser E/Photon)

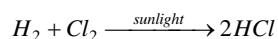
(iv) The rate of photochemical reactions depend upon the intensity of radiation's absorbed.

(v) The ΔG values for light initiated reactions may or may not be **negative**.

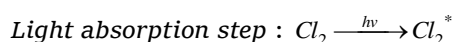
(vi) The temperature does not have marked effect on the rate of light initiated reactions.

(2) Mechanism of some photochemical reactions

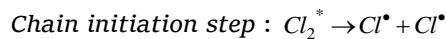
(i) **Photochemical combination of H_2 and Cl_2** : A mixture of H_2 and Cl_2 on exposure to light give rise to the formation of HCl , showing a chain reaction and thereby producing 10^6 to 10^8 molecules of HCl per photon absorbed.



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.



.....(i)

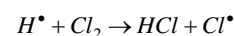


.....(ii)

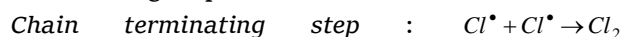
The chlorine free radical then combines with H_2 molecule to form HCl and H^\bullet free radical. The H^\bullet free radical so formed again combines with another Cl_2 molecule to give HCl and Cl^\bullet free radical back resulting into chain propagation step.



.....(iii)



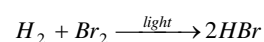
The combination of two Cl^\bullet free radicals leads to chain terminating step.



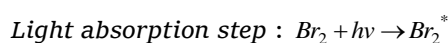
.....(iv)

(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 .



Mechanism

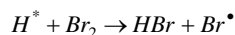


.....(i)



.....(ii)

Chain propagation step : $Br^* + H_2 \rightarrow HBr + H^*$
.....(iii)



.....(iv)

Chain termination step : $Br^* + Br^* \rightarrow Br_2$ (v)

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 (ϕ) 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) Photoetching in electronic industry
- (v) Many polymerization reactions.
- (vi) Modern printing technology
- (vii) Free radical combinations to obtain many compounds.

Tips & Tricks

✍ Different reactions have different rates because their activation energies are different. Lesser the activation energy faster is the reaction.

✍ The reaction, $NO + \frac{1}{2} O_2 \rightarrow NO_2$, exhibits a small negative temperature coefficient and the rate of reaction decreases with increase of temperature.

✍ Fuels in contact with oxygen do not burn by themselves. This is because they need activation energy (provided by the flame) to initiate the reaction. Thus, fuels are thermodynamically unstable (ΔG is -ve) but kinetically stable.

✍ Quantum efficiency of the photochemical reaction, $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$ is very high while that of $H_2 + Br_2 \xrightarrow{h\nu} 2HBr$, is very low. This is because

after the chain initiating step ($X_2 \xrightarrow{h\nu} 2X$)

$Cl + H_2 \rightarrow HCl + H$ is exothermic whereas

$Br + H_2 \rightarrow HBr + H$ is endothermic.

✍ **Drapper's effect** : $H_2 + Cl_2 \rightarrow 2HCl$, Such reactions are accompanied by the increase in the volume. This is called Drapper's effect. The reason is that the reaction is exothermic and heat released raises the temperature and gas expands resulting in the increase in volume.

✍ **Actinometer** : A device which is used to measure the intensity of radiation is known as actinometer. e.g., Uranyl oxalate actinometer.

✍ Amount of the substance left after 'n' half lives

$$= \frac{A_0}{2^n}$$

✍ Free energy change (ΔG) for thermochemical reactions is always negative but remember, ΔG for photochemical reaction may not always be negative. It may be +ve also because a part of the light energy absorbed is converted into the free energy of the products.

✍ Negative catalysts or inhibitors are those substances which decrease the rate of a reaction.

✍ Example of fourth order reaction,
 $4KClO_3 \rightarrow 3KClO_4 + KCl$

✍ **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 photochemical reaction absorbs only one quantum of radiation.

✍ Kinetics of fast reactions can be studied by (i) Relaxation method (ii) Flash photolysis technique etc.

✍ Enzyme catalysed reactions are faster than metal catalysed reactions, the former has lower activation energy.

Ordinary Thinking

Objective Questions

Rate of a reaction

1. The rate of a chemical reaction
 [MP PMT 1973; CPMT 1982]
 (a) Increases as the reaction proceeds
 (b) Decreases as the reaction proceeds

- (c) May increase or decrease during the reaction
(d) Remains constant as the reaction proceeds
2. The rate of a reaction that not involve gases is not dependent on [CPMT 1988; AFMC 1995]
(a) Pressure (b) Temperature
(c) Concentration (d) Catalyst
3. The rate at which a substance reacts depends on its [MP PMT 1987; BHU 1999; KCET 2005]
(a) Atomic weight (b) Equivalent weight
(c) Molecular weight (d) Active mass
4. The rate law for the reaction
 $RCl + NaOH(aq) \rightarrow ROH + NaCl$ is given by Rate
 $= K_1[RCl]$. The rate of the reaction will be [IIT 1988]
(a) Doubled on doubling the concentration of sodium hydroxide
(b) Halved on reducing the concentration of alkyl halide to one half
(c) Decreased on increasing the temperature of the reaction
(d) Unaffected by increasing the temperature of the reaction
5. If doubling the concentration of a reactant 'A' increases the rate 4 times and tripling the concentration of 'A' increases the rate 9 times, the rate is proportional to [AIIMS 1991]
(a) Concentration of 'A'
(b) Square of concentration of 'A'
(c) Under root of the concentration of 'A'
(d) Cube of concentration of 'A'
6. The rate of chemical reaction at constant temperature is proportional to
(a) The amount of products formed
(b) The product of masses of the reactants
(c) The product of the molar concentration of the reactants
(d) The mean free path of the reaction
7. The concentration of a reactant decreases from 0.2 M to 0.1 M in 10 minutes. The rate of the reaction is
(a) 0.01 M (b) 10^{-2}
(c) $0.01 \text{ mol dm}^{-3} \text{ min}^{-1}$ (d) $1 \text{ mol dm}^{-3} \text{ min}^{-1}$
8. When a reaction is progressing
(a) The rate of the reaction goes on increasing
(b) The concentration of the products goes on decreasing
(c) The concentration of the reactants goes on decreasing
(d) The reaction rate always remains constant