

## Chemical Kinetics

For any chemical reaction, chemists try to find out

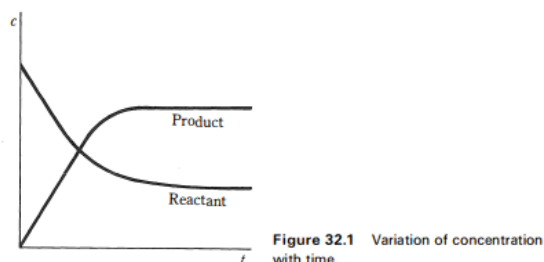
- (a) the feasibility of a chemical reaction which can be predicted by thermodynamics (as you know that a reaction with  $\Delta G < 0$ , at constant temperature and pressure is feasible);
- (b) extent to which a reaction will proceed can be determined from chemical equilibrium;
- (c) speed of a reaction i.e. time taken by a reaction to reach equilibrium.

Thermodynamics tells only about the feasibility and extent of a reaction whereas chemical kinetics tells about the rate of a reaction. For example, thermodynamic data indicate that diamond shall convert to graphite but in reality the conversion rate is so slow that the change is not perceptible at all.

The chemical reactions can be classified into following categories on the basis of their speed:

- (a) **Fast reactions** which proceed at very fast speed and it is practically very difficult to measure the speed of such reactions. Examples of fast reactions include (i) Neutralisation of acids and bases (ii) Organic substitution reactions (iii) Explosive reactions of oxygen with hydrogen and hydrocarbons. The rates of such reactions can be measured by using special methods.
- (b) **Extremely slow reactions** which proceed at a very slow speed and the speed is so slow that it not possible to measure the speed of such reactions. Rusting of iron is very slow reaction.
- (c) **Reaction which precede a measurable speed.** These reactions are utilized in the study of chemical kinetics. Examples are Inversion of cane sugar, saponification of ethyle acetate etc.

**Rate of a reaction:** The rate of a reaction tells us to what speed the reaction occurs. Let us consider a simple reaction  $A \rightarrow B$ , the concentration of A decreases and that of B increases with time.



The rate of a reaction is defined as the change in concentration of any a reaction is defined as the change in concentration of any of reactant or product with time.

As you know during the progress of a reaction the concentration of A keeps on falling with time. The rate of reaction at any given instant is given by the expression

$$r = -d[A]/dt = k[A]$$

where  $-d[A]$  is very small decrease in concentration of A in a very small time interval  $dt$ ,  $C_A$  gives the concentration of the reactant A at a given instant and  $k$  is constant called the rate constant.

Now the concentration of product B increases with time. Hence rate of reaction can also be expressed in terms of increase in concentration of the product B as well. Thus

$$r = d[B]/dt = k[B] \text{ where } dC_B \text{ is very small increase in the concentration of product B in a very small time interval of time } dt.$$

Now it should be clear from the above equations that

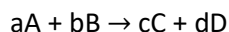
$$r = -d[A]/dt = d[B]/dt = k[A]$$

and for a reaction  $A + B \rightarrow M + N$

the rate can be expressed

$$r = -d[A]/dt = -d[B]/dt = d[M]/dt = d[N]/dt = k[A][B]$$

Now let us consider a reaction



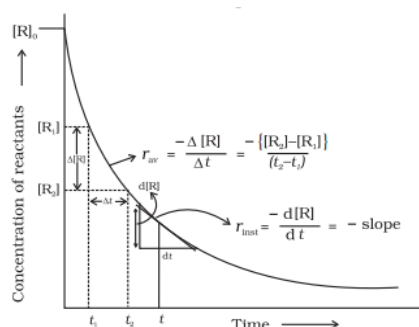
we can write rate expression as follows:

$$r = -1/a \, d[A]/dt = -1/b \, d[B]/dt = 1/c \, d[C]/dt = 1/d \, d[D]/dt = k [A]^a [B]^b$$

### Average and Instantaneous Rate of Reaction and its Calculation:

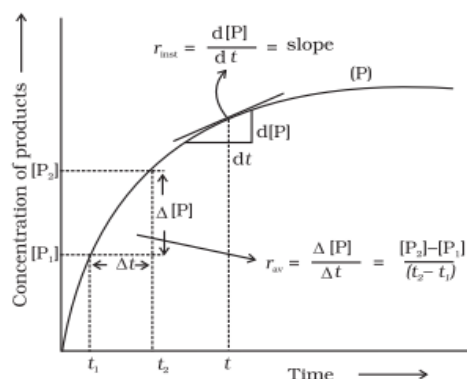
The change in concentration of any of the reactants or any of the product per unit time over a specified interval of time is called the **average rate of reaction**. Average rate of reaction  $P \rightarrow Q$  is given by  $r$ .

$$r_{av} = - \frac{\Delta P}{\Delta t} = + \frac{\Delta R}{\Delta t}$$



Rate of change of concentration of any of the reactants or products at a particular instant of time is called the **instantaneous rate of reaction**, for that particular reaction at that instant of time.

$$r_{inst} = - \frac{dP}{dt} = + \frac{dR}{dt}$$



**Units of rate** Reaction rate has the units of concentration divided by time.

We express concentration in mole/litre but time may be given in any convenient unit second(s), minutes (min) etc.

Therefore, the units of reaction rates may be  $\text{mol L}^{-1}\text{s}^{-1}$ ,  $\text{mol L}^{-1}\text{min}^{-1}$  etc

**Factors affecting the rate of reaction** : There are a number of factors which affect the rate of a reaction, the most important of them are:

(a) **Effect of concentration**: The rate of a chemical reaction is influenced by the no. of collisions per second between the reacting molecules. On increasing the concentration of the reactant, the number of collisions will increase and the rate of reaction will increase and on decreasing the concentration the rate will decrease.

(b) **Effect of nature of reactants**: Reactions between polar or ionic molecules occur almost instantaneously. Those reactions in which the bonds are arranged or electrons are transferred takes a comparatively longer time than the reaction between ionic molecules. You can cite the examples of neutralisation reactions or double displacement reactions which are very fast while the oxidation reduction reactions are slower.

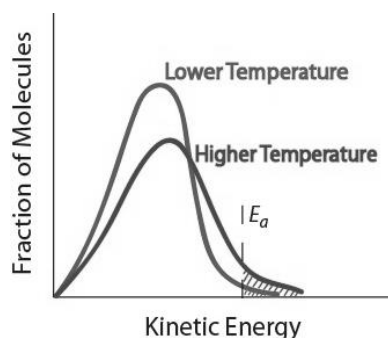
(c) **Effect of catalyst:** A catalyst can increase or decrease the rate of a chemical reaction. For example the combination of hydrogen and oxygen to form water is slow at ordinary temperature, while it proceeds rapidly in presence of platinum.

(d) **Effect of surface area of reactant:** Surface area of reactants is of importance only for heterogeneous reactions. As particle size decreases, surface area for the same mass increases. The smaller particle thus reacts more rapidly than the larger particles. For example, burning of coal dust in air takes place more rapidly than large lump of coal.

(e) **Effect of temperature:** With the exception of few reactions, the rate of reaction is increased considerably with an increase of temperature. Generally the rate of a reaction is almost doubled or tripled by an increase of  $10^{\circ}\text{C}$  in temperature, i.e. the value of temperature coefficient for most of the reactions lies between 2 to 3. Thus,

$$\text{Temperature coefficient} = \frac{K_{t+10}}{K_t} = 2$$

An increase in temperature will raise the average kinetic energy of the reactant molecules. Therefore, a greater proportion of molecules will have the minimum energy necessary for an effective collision



**Law of mass action:** The rate of the chemical reaction at a given temperature is directly proportional to the product of the activities or concentrations of the reactants.

**Thus, for the reaction**

$aA + bB \rightarrow cC + dD$ , the rate expression according to the law of mass action is

$$\text{Rate} = k[A]^a[B]^b$$

**The Rate Constant :** Consider a reaction  $aA + bB \rightarrow cC + dD$ , the rate expression according to the law of mass action is  $\text{Rate} = k[A]^a[B]^b$

where  $k$  is rate constant, velocity constant or specific reaction rate. When  $[A] = [B] = 1$  then  $k = \text{Rate}$ . In general rate constant may be defined as the rate of the reaction when the concentration of each of the reactants is unity. It is characteristic of a particular reaction.

Factors affecting the Rate constant :

(a) Temperature : Variation of rate constant with temperature is given by

$$\text{Arrhenius equation : } k = Ae^{-E_a/RT} \quad (i)$$

$A$  = Constant known as frequency factor

$E_a$  = Energy of activation. Both  $A$  and  $E_a$  are characteristic of a particular reaction.

(b) Catalyst : Presence of positive catalyst lowers the energy of activation and hence influences the rate constant.

**Units of Rate constant :** Units depend upon the order of a reaction.

$$\text{units} = (\text{Concentration})^{1-n} \cdot \text{time}^{-1}$$

$$= (\text{Mol L}^{-1})^{1-n} \cdot \text{time}^{-1} \text{ where } n = \text{order of reaction}$$

Units of rate constant for zero order reaction =  $\text{Mol L}^{-1} \text{time}^{-1}$ .

Units of rate constant for first order reaction =  $\text{time}^{-1}$  etc.

**Characteristics of Rate constant :**

- (I) The value of  $k$  is different for different reactions.
- (II) At fixed temperature the value of  $k$  is constant.
- (III) It is independent of concentration but depends on temperature.
- (IV) The larger the value of  $k$  the faster is the reaction and vice versa.

Difference between Rate and Rate constant of a reaction:

Rate Constant	Rate of reaction
(a) It is equal to rate of reaction when the concentration of reacting species is unity	(a) It is the change in concentration of reactants or products per unit time.
(b) Units depends on order of reaction = $(\text{Mol L}^{-1})^{1-n} \text{ time}^{-1}$ ( $n$ = Order of reaction)	(b) Units are $\text{Mol L}^{-1} \text{ Sec}^{-1}$
(c) It depends upon temperature	(c) It depends upon temperature and concentration

**Rate Law:**

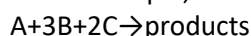
The rate law is the experimentally determined expression for the rate of a reaction and can be used to predict the relationship between the rate of a reaction and the concentrations of reactants and products.

**Order of Reaction:**

The order of a chemical reaction is the sum of powers of the concentration of the reactants in the rate law expression. The order of the reaction is represented by  $n$ . The order of a reaction can be 0, 1, 2, 3, and even a fraction. Order of reaction is an experimental concept.

For the  $\text{N}_2\text{O}_5$  decomposition with a rate law of  $k[\text{N}_2\text{O}_5]$ , this exponent is 1 (and thus is not explicitly shown); this reaction is therefore a first order reaction.

As an example, consider the following reaction,



whose experimental rate law is given by:  $\text{rate} = k[\text{A}][\text{B}]^2$

This reaction is third-order overall, first-order in A, second-order in B, and zero-order in C.

In general For the reaction:  $a\text{A} + b\text{B} \rightarrow \text{P}$ , the rate law expression is as follows:

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

where

- $[\text{A}]$  is the concentration of species A,
- $x$  is the order with respect to species A.
- $[\text{B}]$  is the concentration of species B,
- $y$  is the order with respect to species B
- $k$  is the rate constant.
- $n$  is the reaction order for the whole chemical reaction. This can be found by adding the reaction orders with respect to the reactants. In this case,  $n = x + y$ .

**Features of order of reaction :**

- (I) The order of a reaction is experimentally determined quantity.
- (II) It cannot be written from balanced chemical equation.
- (III) It can be written from the rate law equation.
- (IV) Order may be zero, whole number, fractional or negative even

(VI) Reaction with order >3 are rare.

Examples of various order reactions:

1. **Zero order reaction:**

- The photochemical reaction between hydrogen with chlorine,
- decomposition of nitrous oxide over a hot platinum surface,
- decomposition of ammonia in presence of molybdenum or tungsten surface etc.

In such cases Rate=k

2. **First order reaction:**

- Decomposition of Nitrogen Pentoxide:  $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2} \text{O}_2$ , Rate=k[N<sub>2</sub>O<sub>5</sub>]
- Decomposition of ammonium nitrate in aqueous solution:  $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$
- Decomposition of H<sub>2</sub>O<sub>2</sub> in aqueous solution:  $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ .

3. **Second Order reaction:**

Decomposition of HI:  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ , Rate=k[HI]<sup>2</sup>

4. **Third order reaction:**

$2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$ , Rate=k[NO]<sup>2</sup>[Cl<sub>2</sub>]

5. **Fractional order reaction:**

Pyrolysis of acetaldehyde. This reaction has an order of 1.5

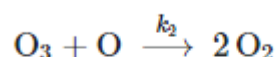
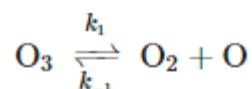
$\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$ , Rate=k[CH<sub>3</sub>CHO]<sup>3/2</sup>

6. **Negative order reaction:**

Decomposition of Ozone into Oxygen is negative order reaction with respect to Oxygen.

$2\text{O}_3 \rightarrow 3\text{O}_2$ , Rate=k[O<sub>3</sub>]<sup>2</sup>[O<sub>2</sub>]<sup>-1</sup>

Explanation:



$$\text{rate} = k_2[\text{O}_3][\text{O}]$$

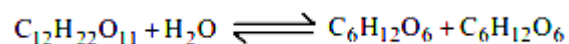
$$k_1[\text{O}_3] = k_{-1}[\text{O}_2][\text{O}]$$

$$\text{rate} = \frac{k_1 k_2}{k_{-1}} [\text{O}_3]^2 [\text{O}_2]^{-1}$$

**Pseudo unimolecular reactions** : Reactions like hydrolysis of an ester or cane sugar, which though bimolecular and yet following the kinetics of first order are called pseudo unimolecular reactions.



$$\text{Rate} = [\text{CH}_3\text{COOC}_2\text{H}_5]$$

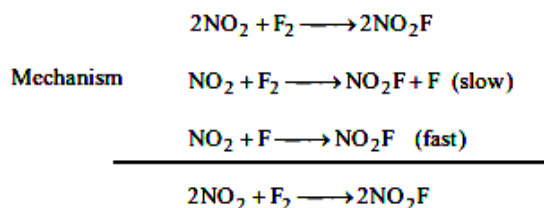


$$\text{Rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

In above reactions the rate is independent of concentration of H<sub>2</sub>O being present in excess. Hence [H<sub>2</sub>O] is constant.

### Rate determining Step:

Some reactions take place in more than one step. Each step has its own rate. The slowest step is called the rate determining step or rate controlling step e.g.



First step is the rate determining step. The rate law equation is always written from slow step

$$\therefore \text{The rate law is given as } \text{rate} = k[\text{NO}_2][\text{F}_2]$$

Remember that reaction intermediate is never shown in rate law equation.

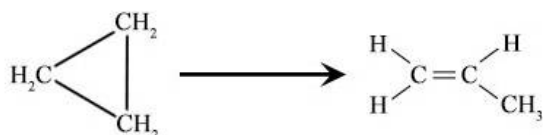
- **Molecularity of reaction:**

molecularity is the number of molecules that come together to react in an elementary (single-step) reaction and is equal to the sum of stoichiometric coefficients of reactants in the elementary reaction with effective collision (sufficient energy) and correct orientation. Depending on how many molecules come together, a reaction can be unimolecular, bimolecular or even trimolecular.

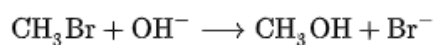
The kinetic order of any elementary reaction or reaction step is equal to its molecularity, and the rate equation of an elementary reaction can therefore be determined by inspection, from the molecularity.

The kinetic order of a complex (multistep) reaction, however, is not necessarily equal to the number of molecules involved. The concept of molecularity is only useful to describe elementary reactions or steps.

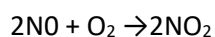
An example of a **unimolecular reaction**, is the isomerization of cyclopropane to propene:



An example of a bimolecular reaction is the  $\text{SN}^2$ -type nucleophilic substitution of methyl bromide by hydroxide ion:



Example of termolecular reaction is:



### Difference Between Molecularity and Order of Reaction:

Order of Reaction	Molecularity of Reaction
1. It is experimentally determined quantity	It is a theoretical concept.
2. It can have integral, fractional or negative	Always integral values only,, never zero or negative values
3. It cannot be obtained from balanced or stoichiometric equation	It can be obtained.
4. It tells about the slowest step in the	It does not tell anything about mechanism

mechanism	
5. It is sum of the powers of the concentration terms in the rate law equation	It is the number of reacting species undergoing simultaneous collision in the reaction.
6. It is changed when one reactant is taken in large excess	It undergoes no change.

**Integrated Rate Laws:** The integrated rate law expresses the concentration of reacting species with time. This information is obtained by integrating the corresponding differential rate law.

**Zero-order Reaction:** For a zero-order reaction

$A \rightarrow \text{product}$

the rate of reaction is  $r = -\frac{d[A]}{dt} = k[A]^0 = k$

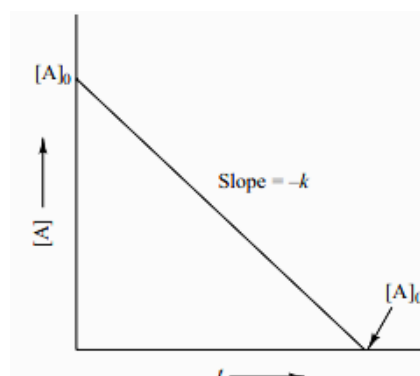
The unit of  $k$  is that of rate reaction  $r$ , that is  $\text{mol L}^{-1} \text{s}^{-1}$ .

If  $[A]_0$  and  $[A]_t$  are the concentrations at  $t = 0$  and  $t = t$ , respectively, we have

$$\int_{[A]_0}^{[A]_t} d[A] = - \int_0^t dt$$

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

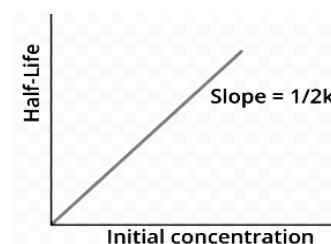
The variation of  $[A]$  with time is linear with slope equal to  $-k$



**Half-Life:** The half-life period of a reaction is the time required for the concentration of reactant to decrease to half of its original concentration, i.e. at  $t = t_{1/2}$ ,  $[A]_t = [A]_0 / 2$ . Thus, the above equation becomes

$$[A]_0/2 = [A]_0 - k t_{1/2} \text{ i.e. } t_{1/2} = [A]_0/2k$$

that is, half-life period is directly proportional to the initial concentration of the reactant.



**Time of completion** of the reaction Here  $[A]_t = 0$ .

$$\text{Hence } t_{\text{completion}} = [A]_0/k$$

**First-Order Reaction:** For a first order reaction

$A \rightarrow \text{product}$

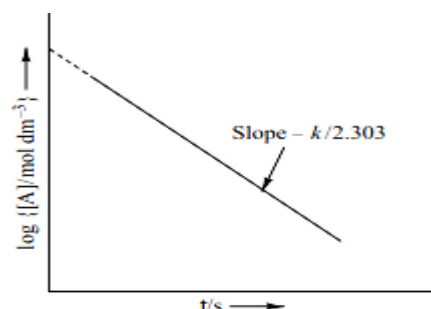
the rate of reaction is  $r = -\frac{d[A]}{dt} = k[A]$

The unit of  $k$  is (unit of  $r$ /unit of  $[A]$ ), i.e.  $\text{s}^{-1}$ . If  $[A]_0$  and  $[A]_t$  are the concentrations at  $t = 0$  and  $t = t$ , respectively, then

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

This gives  $\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt$

or  $\ln ([A]_t/c^0) = \ln ([A]_0/c^0) - kt$



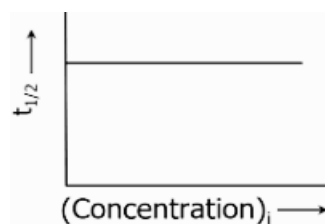
where  $c^0 = 1 \text{ M}$ . The variation of  $\ln ([A]_t / c^0)$  or  $(\log ([A]_t / c^0))$  with time is linear with slope equal to  $-k$  (or  $-k/2.303$ )

**Half-Life** : At  $t = t_{1/2}$ ,  $[A]_t = [A]_0/2$ . Hence

$$\ln \left( \frac{[A]_0/2}{[A]_0} \right) = -k t_{1/2}$$

or

$$t_{1/2} = \frac{\ln 2}{k} = \frac{2.303 \log 2}{k} = \frac{0.693}{k}$$



Thus, half-life period is independent of the initial concentration of the reactant and has a constant value dependent only on the rate constant.

**Note** In fact, the time required for any definite fraction (say, 1/2, 1/3, 1/4, etc.) to occur is independent of the initial concentration of the reactant.

**Illustration** The half-life of a first-order reaction is 2.0 min. The time taken to reduce the initial concentration to 12.5% is

$$\begin{array}{c} 100\% \xrightarrow{t_{1/2}} 50\% \xrightarrow{t_{1/2}} 25\% \xrightarrow{t_{1/2}} 12.5\% \\ \hline 3t_{1/2} = 3 \times 2.0 \text{ min} = 6.0 \text{ min} \end{array}$$

- Rate equation expressed in terms of pressure:**

For a reaction involving gaseous species, concentration terms may be replaced by partial pressures. Let the reaction  $A \rightarrow \text{products}$  be started with the pressure  $p_0$  of A. If  $\Delta n_g$  is the change in stoichiometric number of gaseous species, then

$$\begin{array}{ccc} A & \rightarrow & \text{products} \\ p_0 - p & & (\Delta v_g + 1)p \end{array}$$

$$p_{\text{total}} = (p_0 - p) + (\Delta v_g + 1)p = p_0 + (\Delta v_g)p.$$

This gives

$$p = (p_{\text{total}} - p_0) / \Delta v_g,$$

and

$$p_0 - p = p_0 - \frac{p_{\text{total}} - p_0}{\Delta v_g} = \frac{(\Delta v_g + 1)p_0 - p_{\text{total}}}{\Delta v_g}$$

The integrated rate law is

$$\ln \left( \frac{p_0 - p}{p_0} \right) = -kt \quad \text{i.e.} \quad \ln \left( \frac{(\Delta v_g + 1)p_0 - p_{\text{total}}}{\Delta v_g p_0} \right) = -kt$$

If  $p_\infty$  is the pressure at infinite time, where the reaction is almost completed, we will have

$$p_\infty = (\Delta v_g + 1)p_0$$

with this, the rate law becomes

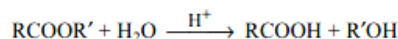
$$\ln \left( \frac{p_\infty - p_{\text{total}}}{p_\infty - p_0} \right) = -kt$$

**Illustration** For the reaction  $(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3 (\text{g}) \rightarrow 2 \text{CH}_3\text{COCH}_3(\text{g}) + \text{C}_2\text{H}_6(\text{g})$ , we have  
di-tertiarybutyl peroxide

$$\Delta v_g = 2 + 1 - 1 = 2; \quad p_\infty = (\Delta v_g + 1)p_0 = 3p_0. \quad \text{The rate law becomes } \ln \left( \frac{3p_0 - p_{\text{total}}}{2p_0} \right) = -kt$$

- Rate equation expressed in terms of volume of titrant:**

The acid hydrolysis of an ester



may be studied by titrating the product RCOOH against an alkali solution. It  $V_t$  and  $V_\infty$  are the volume of alkali solution required for the neutralization of RCOOH at time  $t$  and infinite time respectively, then

$$[\text{Ester}]_0 = V_\infty \text{ and } [\text{Ester}]_t = V_\infty - V_t$$

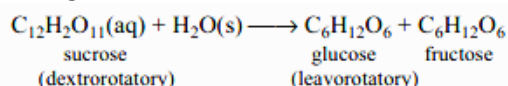
Hence, the rate law becomes

$$\ln \left( \frac{[\text{Ester}]_t}{[\text{Ester}]_\infty} \right) = \ln \left( \frac{V_\infty - V_t}{V_\infty} \right) = -kt$$



- **Rate equation expressed in terms of Rotation of plane polarized light:**

The inversion of cane sugar, which follows first order kinetics is



The reaction can be followed by measuring the rotation of plane polarized light. If  $\theta_t$  and  $\theta_\infty$  are the respective angles of rotation at time  $t$  and at the end of reaction, then

$$[\text{sucrose}]_0 \propto \theta_\infty - \theta_0 \quad \text{and} \quad [\text{sucrose}] \propto \theta_\infty - \theta_t$$

Hence, the rate law is

$$\ln \left( \frac{[\text{sucrose}]_0}{[\text{sucrose}]_t} \right) = \ln \left( \frac{\theta_\infty - \theta_0}{\theta_\infty - \theta_t} \right) = -kt$$

**First order growth kinetics :** It is used in population growth and bacteria multiplication

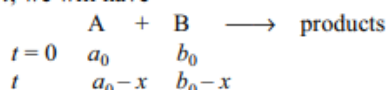
$$k = \frac{2.303}{t} \log \frac{a+x}{a}$$

where  $a$  is initial population and  $(a+x)$  population after time  $t$

**Second-Order Reactions :** For a second-order reactions  $A + B \rightarrow \text{products}$ , the rate law is

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

Let  $a_0$  and  $b_0$  be the initial concentrations of A and B, respectively, at let  $x$  be the extent of reaction divided by constant volume, at time  $t$ , we will have



Since,  $-\frac{d[A]}{dt} = -\frac{d(a_0 - x)}{dt} = \frac{dx}{dt}$ , we write the rate law as

$$\frac{dx}{dt} = k(a_0 - x)(b_0 - x)$$

The integrated expression is

$$\log \left( \frac{b_0 - x}{a_0 - x} \right) = \log \left( \frac{b_0}{a_0} \right) + \left( \frac{b_0 - a_0}{2.303} \right) kt$$

**Special Case** If  $[A]_0 = [B]_0$  then the rate expression becomes

$$-\frac{d[A]}{dt} = k[A]^2$$

The integrated expression is  $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$

**Half- Life Period** Equation (16) gives

$$\frac{1}{[A]_0/2} - \frac{1}{[A]_0} = kt_{1/2} \quad \text{i.e.} \quad t_{1/2} = \frac{1}{k[A]_0}$$

that is, half-life period is inversely proportional to the initial concentration of the reactant.

**Methods to Determine Order and Rate Constant :**

- **Integration Method:** In this method, the data are substituted in the integrated rate equations for different-order reactions. The equation which gives almost a constant value of rate constant decides the order of the reaction.
- **Graphical Method:** In this method, the data are plotted according to the different integrated rate equations to yield a straight line. The rate constant of the reaction is obtained from the slope of the resultant straight-line plot.
- **Half-Life Method :** This method can be employed only when the rate law involves only one concentration term. For  $t_{0.5} = 0.693/k$  and it is independent of the initial concentration of the reactant. For the second order  $t_{0.5} \propto 1/[A]_0$  and so on.

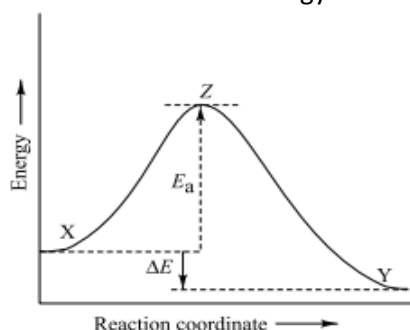
- **Van't Hoff's Differential Method** :In this method, the order of a reaction with respect to each of its reactants can be determined. A number of kinetic experiments are carried out by varying the initial concentration of only one species keeping all others constant. From the variation in the rate of reaction, the order of the reaction with respect to the species whose concentration is varied is determined. The experiment is repeated this way with the variation of concentration of other species one by one.
- **Ostwald Isolation Method** :In this method, the concentrations of all species except one are taken in large amounts. During the course of the reaction, the variation in these excess concentration terms is negligible and thus remain virtually constant. These constant terms can be merged with the rate constant and, thus, the rate of reaction depends only on one term which is not taken in the excess amount. In this manner the experiment is repeated taking one term each time not in excess and all other terms in excess amounts and the rate of reaction with respect to the species not taken in large amounts is determined as in the case of the van't Hoff differential method.

**Collision Theory** : Chemical reaction occurs as a result of effective collisions between reacting molecules. For this two things are important.

- (I) Proper orientation of reacting molecules.
- (II) Possession of certain minimum amount of energy by reacting molecules

**Threshold Energy** : The minimum amount of energy possessed by the reacting molecules to have effective collisions, resulting in the formation of product, is called threshold energy.

**Activation Energy ( $E_a$ )** : The excess energy over and above the average potential energy possessed by reacting molecules to have effective collisions resulting in the formation of product is known as activation energy. **Activation Energy = threshold energy – average energy of reactants** For fast reaction the activation energy is low. For slow reaction the activation energy is high.



**Collision Frequency (z)** : Total number of collisions which occur among the reacting molecules per second per unit volume is called collision frequency. Its value is given by

$$z = \sqrt{2} \pi \bar{v} \sigma^2 n^2$$

$\bar{v}$  = average velocity,  $\sigma$  = molecular diameter in cm.,

$n$  = number of molecules per cc.

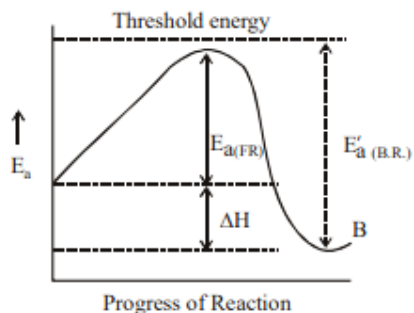
**Rate of Reaction from Collision theory** : It is given by Rate of reaction =  $f \times z$

Where,  $z$  = collision frequency

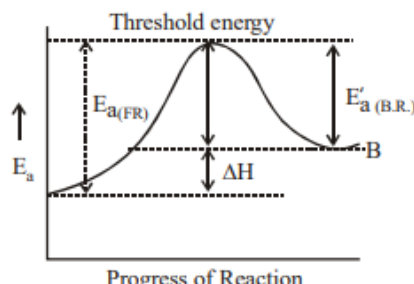
$f$  = fraction of effective collisions =  $\frac{\Delta n}{N} = e^{-E_a/RT}$

$$\therefore \text{Rate (k)} = Z e^{-E_a/RT}$$

### Graphical Representation of Exothermic Reactions



### Graphical Representation of Endothermic Reactions



**Temperature Dependence of Rate constant:** The rate constant, hence the rate of reaction, increases with increase in temperature. It is found that this increase is about 2 to 3 times with an increase of  $10^\circ\text{C}$  of the reaction. The Arrhenius equation relating the rate constant,  $k$  with kelvin temperature,  $T$ , is

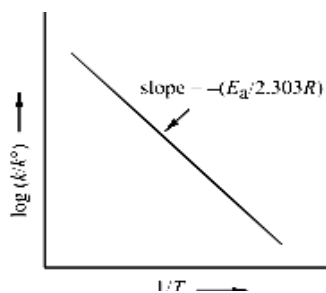
$$k = Ae^{-E_a/RT}$$

where  $A$  is known as pre-exponential factor. Its unit is the same as that of rate constant  $k$ , i.e.  $(\text{mol}^{-1} \text{dm}^3) \text{ s}^{-1}$  where  $n$  is the order of reaction,  $R$  is a gas constant ( $= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $E_a$  is known as energy of activation. Writing the above equation in the logarithm form, we have

$$\ln \left( \frac{k}{k^0} \right) = \ln \left( \frac{A}{k^0} \right) - \frac{E_a}{R} \frac{1}{T}$$

or  $\log \left( \frac{k}{k^0} \right) = \log \left( \frac{A}{k^0} \right) - \frac{E_a}{2.303R} \frac{1}{T}$

where  $k^0$  represents the unit of rate constant  $k$ , so that the quantities  $k/k^0$  and  $A/k^0$  become unitless. According to the above equation,  $\log (k/k^0)$  varies linearly with  $1/T$  with slope equal to  $-E_a/(2.303 R)$  and intercept equal to  $\log (A/k^0)$ .

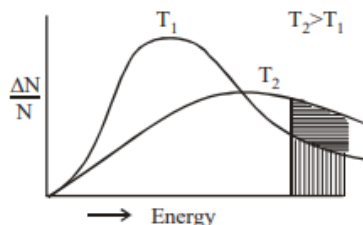


For the two sets of data at two different temperatures, we have

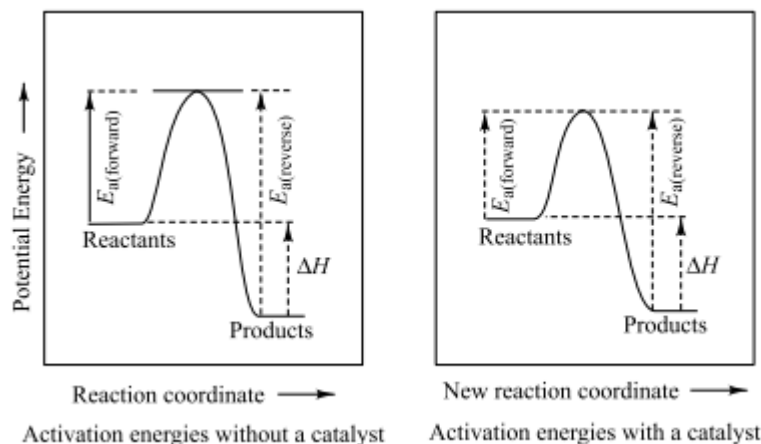
$$\log \left( \frac{k_2}{k_1} \right) = -\frac{E_a}{2.303R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

### Graphical representation of the effect of temperature on rate of reaction:

Fraction of the molecules having energy equal to activation energy is shown by shaded portion. The fraction of such molecules become almost double for  $10^\circ\text{C}$  rise of temperature and the rate of reaction almost doubles for  $10^\circ\text{C}$  rise of temperature.



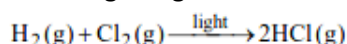
**Effect of catalyst on Rate of Reaction :** A catalysed reaction provides a new pathway or a mechanism by which the potential energy barrier between the reactants and products is lowered. The graphical representation is as follows :



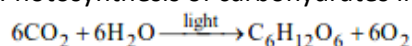
**Main characteristics of a catalyst:**

- A catalyst is a substance that increases the rate of a reaction.
- In a reaction, catalyst goes through a cycle in which it is used up and regenerated so that it is used over and over again.
- A catalyst, though involved in a reaction, does not appear in the over-all chemical equation. Its presence is shown by writing it over the arrow connecting reactants and products.
- A catalyst operates by providing an alternate path that has a lower energy of activation for the reaction .
- A catalyst lowers the energies of activation of both the forward and reverse reactions without affecting the enthalpy of reaction. This leads to increase in the rate of both forward and backward reactions and thereby helps attaining the equilibrium position of the reaction more rapidly.
- A catalyst does not change the equilibrium constant of a reaction. Thus, the relative concentrations of reactants and products at equilibrium are not affected by the use of a catalyst.

**Photochemical Reactions :** Reactions which take place by the absorption of radiations of suitable wavelength e.g.



Photosynthesis of carbohydrates in plants takes place in presence of chlorophyll and sunlight.



**Free Energy Change in photochemical reactions :** The free energy change of a photochemical reaction may not be negative. In the synthesis of carbohydrates and formation of HCl,  $\Delta G$  is +ve.

**Photosensitization :** Certain molecules absorb light energy and transfer it to another molecule which may undergo a reaction. The process is called photosensitisation and the substance doing so is called photosensitizer e.g. chlorophyll acts as photosensitizer in photosynthesis.

**Vision :** It is a first photochemical reaction in which the compound, called *retinal*, present in the eye undergoes geometrical isomerism by absorbing a photon of light.

**Chemiluminescence :** Emission of light in a chemical reaction at ordinary temperature is called chemiluminescence.

**Fluorescence :** The absorption of energy and instantaneous re-emitting of the energy is called fluorescence.

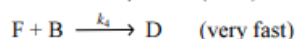
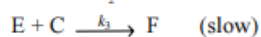
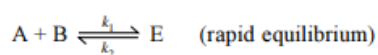
**Phosphorescence :** The continuous glow of some substances even after the cutting of source of light is called phosphorescence e.g. ZnS.

**Bioluminescence :** The phenomenon of chemiluminescence exhibited by certain living organisms is called bioluminescence e.g. light emission by fire flies.

### MULTIPLE CHOICE QUESTIONS:

1. The rate constant does not depend upon
  - a) temperature
  - b) concentration of reactants and products
  - c) activation energy
  - d) catalyst
2. The units of rate constant and rate of reaction are identical for
  - a) zero order reaction
  - b) first order reaction
  - c) second order reaction
  - d) reversible reaction
3. The order of an elementary reaction
  - a) is equal to its molecularity
  - b) cannot be predicted
  - c) depends upon temperature
  - d) depends on the experimental condition
4. The reaction  $2A + B \rightarrow D + E$  involves the following mechanism  
 $A \rightarrow B$  (fast)  
 $B \rightarrow C$  (slow)  
 $A + C \rightarrow D + E$   
The rate expression would be
  - a)  $k[A]^2[B]$
  - b)  $k[B]$
  - c)  $k[A]$
  - d)  $k[A][B]$
5. The half-life of a reaction  $A \rightarrow B$  varies as the inverse of concentration of A. The order of the reaction would be
  - a) 0
  - b) 1
  - c) 2
  - d) 3
6. If  $k_f$  and  $k_b$  are the rate constants of forward and backward reactions in an equilibrium reaction, the equilibrium constant of the reaction is given by
  - a)  $K_{eq} = k_f / k_b$
  - b)  $K_{eq} = k_b / k_f$
  - c)  $K_{eq} = k_f k_b$
  - d)  $K_{eq} = 1 / k_f k_b$

7. The reaction  $A + 2B + C \rightarrow D$  occurs by the following mechanism



- $r = k [C]$
  - $r = k [A] [B]^2 [C]$
  - $r = k [D]$
  - $r = k [A] [B] [C]$
8. For the reaction  $5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2(aq) + 3H_2O(l)$ , if the rate of disappearance of  $Br^-$  is  $2.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ , the rate of appearance of  $Br_2$  will be
- $2.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$
  - $1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$
  - $1.25 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$
  - $3.0 \text{ mol L}^{-1} \text{ s}^{-1}$
9. In a kinetic study, the plot of [reactant] versus time is a straight line with a negative slope. The reaction follows
- zero-order kinetics
  - first-order kinetics
  - second-order kinetics
  - fractional-order kinetics
10. A substance (initial concentration  $a$ ) reacts according to zero order kinetics. The time it takes for the completion of the reaction is
- $a/k$
  - $a/2k$
  - $k/a$
  - $2k/a$
11. For a first order reaction the ratio of times for 99.9% completion and half of the reaction is
- 8
  - 9
  - 10
  - 12
12. For the first order decomposition of  $N_2O_5$  it is found that



Which of the following is true?

- $k = k'$
- $k < 2k'$
- $k = 3k'$
- $k = 2k'$

13. The half-life period and the initial concentration for a reaction are as follow:

$t_{1/2}/s$	420	294	735
$a/\text{mmHg}$	350	500	200

The order of the reaction is

- zero
  - one
  - two
  - three
14. The activation energy for a reaction which doubles the rate when the temperature is raised from 300 K to 310 K is
- 50.6 kJ mol<sup>-1</sup>
  - 53.6 kJ mol<sup>-1</sup>
  - 56.6 kJ mol<sup>-1</sup>
  - 59.6 kJ mol<sup>-1</sup>
15. For an exothermic reaction  $A \rightarrow B$ , the activation energy is 65 kJ mol<sup>-1</sup> and enthalpy of reaction is 42 kJ mol<sup>-1</sup>. The activation energy for the reaction  $B \rightarrow A$  would be
- 23 kJ mol<sup>-1</sup>
  - 107 kJ mol<sup>-1</sup>
  - 65 kJ mol<sup>-1</sup>
  - 42 kJ mol<sup>-1</sup>
16. The activation energy of a reaction is 65.8 kJ mol<sup>-1</sup>, on changing the temperature from 2°C to 27°C, its rate constant changes by
- Two times
  - Five times
  - Eight times
  - Eleven times
17. The use of a catalyst helps in
- increasing the rate of forward reaction only
  - increasing the rate of backward reaction only
  - increasing the rates of both forward and backward reactions
  - increasing the relative amounts of products
18. Consider an endothermic reaction  $X \rightarrow Y$  with the activation energies  $E_b$  and  $E_f$  for the backward and forward reactions, respectively. In general
- $E_b = E_f$
  - No definite relation between  $E_f$  and  $E_b$
  - $E_b < E_f$
  - $E_b > E_f$
19. For the non-stoichiometric reaction  $2A + B \rightarrow C + D$ , the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial concentration of A	Initial concentration of B	Initial rate of formation of C in mol L <sup>-1</sup> s <sup>-1</sup>
0.1 M	0.1 M	$1.2 \times 10^{-3}$
0.1 M	0.2 M	$1.2 \times 10^{-3}$
0.2 M	0.1 M	$2.4 \times 10^{-3}$

The rate law for the formation of C is

- $d[C]/dt = k[A]$
- $d[C]/dt = k[A][B]$
- $d[C]/dt = k[A]^2[B]$
- $d[C]/dt = k[A][B]^2$

20. For the reaction,  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ , the rate equation can be expressed in term of

$$-\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5] \quad \text{and} \quad \frac{d[\text{NO}_2]}{dt} = k'[\text{N}_2\text{O}_5]$$

The constant  $k$  and  $k'$  are related as

- $k = k'$
  - $2k = k'$
  - $k = 2k'$
  - $k = 4k'$
21. Higher order ( $>3$ ) reactions are rare due to
- low probability of simultaneous collision of all the reacting species
  - increase in entropy and activation energy as more molecules are involved.
  - shifting of equilibrium towards reactants due to elastic collisions
  - loss of active species on collisions
22. The rate constant of a reaction is  $1.5 \text{ mol}^{-3/2} \text{ L}^{3/2} \text{ s}^{-1}$ , the order of the reaction is
- 1
  - 1.5
  - 2.5
  - 3.0
23. The half-life of a reaction  $\text{A} \rightarrow \text{product}$  is found to be inversely proportional to  $[\text{A}]_0^{1/2}$ . The order of the reaction is
- 1
  - 1.5
  - 2.5
  - 3.0
24. A living plant disintegrates at the rate of 15 disintegrates per minute per gram of the carbon. After  $1.94 \times 10^3 \text{ y}$  the rate of disintegration was 12 disintegrates per minute. The half-life period of carbon is (Given:  $\log(0.8) = -0.097$ )
- 5270 y
  - 5730 y
  - 6026 y
  - 6750 y

25. The kinetic data for the reaction at 298 K  $\text{OCl}^- + \text{I}^- \xrightarrow{\text{OH}^-} \text{OI}^- + \text{Cl}^-$  is as follows:

$\frac{[\text{OCl}^-]}{\text{mol dm}^{-3}}$	$\frac{[\text{I}^-]}{\text{mol dm}^{-3}}$	$\frac{[\text{OH}^-]}{\text{mol dm}^{-3}}$	$\frac{10^{-4} \times d[\text{OI}^-]/dt}{\text{mol dm}^{-3} \text{ s}^{-1}}$
0.0017	0.0017	1.0	1.75
0.0034	0.0017	1.0	3.50
0.0017	0.0034	1.0	3.50
0.0017	0.0017	0.5	3.50

The rate law for the formation of  $\text{OI}^-$  is

- $r = k [\text{OCl}^-][\text{I}^-]$
- $r = k [\text{OCl}^-]^2$
- $r = k [\text{I}^-]^2[\text{OCl}^-]$
- $r = k [\text{OCl}^-][\text{I}^-]/[\text{OH}^-]$



**Answer Key:**

<b>Question</b>	<b>Answer</b>
1	b
2	a
3	a
4	b
5	c
6	a
7	d
8	b
9	a
10	a
11	c
12	a
13	c
14	b
15	a
16	d
17	c
18	c
19	a
20	b
21	a
22	c
23	b
24	c
25	d