

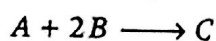
# Chemical Kinetics

## [TOPIC 1] Rate of a Chemical Reaction and Rate Law

**Chemical kinetics** is the branch of chemistry, which deals with the study of the reaction rates, the factors affecting the rate of reactions and the mechanism by which the reactions proceed. Rate of a chemical reaction can be defined as the change in concentration of reactants or products in unit time.

### 1.1 Rate of Disappearance and Rate of Appearance

Rate of a reaction can be expressed in terms of **rate of disappearance** of any of the reactant or **rate of appearance** of any of the product, e.g. for a reaction,



$$\text{Rate of disappearance of } A = \frac{\text{Decrease in concentration of } A}{\text{Time taken}} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{Similarly, rate of disappearance of } B = -\frac{1}{2} \frac{\Delta[B]}{\Delta t}$$

$$\text{Rate of appearance of } C = \frac{\text{Increase in concentration of } C}{\text{Time taken}} = +\frac{\Delta[C]}{\Delta t}$$

where, negative sign indicates that the concentration of reactant is decreasing and positive sign indicates that the concentration of product is increasing.

Unit of rate of a reaction is  $\text{mol L}^{-1} \text{s}^{-1}$  or  $\text{atm s}^{-1}$ .

### Instantaneous Rate

It is defined as the rate of change in concentration of any one of the reactants or products at that particular instant of time.

It is equal to the small change in concentration of reactant or product in small interval of time.

Instantaneous rate,

$$r_{\text{inst}} = \frac{-d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = +\frac{d[C]}{dt}$$

## Average Rate of Reaction

It is the appearance of products or disappearance of reactants over a long time interval.

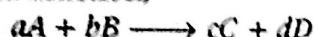
$$\text{Average rate, } r_{av} = \frac{-\Delta[A]}{\Delta t} = -\frac{1}{2} \frac{\Delta[B]}{\Delta t} = + \frac{\Delta[C]}{\Delta t}$$

**NOTE** Rate of a reaction depends upon the experimental conditions such as concentration of the reactants, temperature and catalyst. It also depends upon the nature of reactants.

## 1.2 Rate Law

It is the expression in which rate of reaction is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

Consider a general reaction,



where,  $a$ ,  $b$ ,  $c$  and  $d$  are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is,

$$\text{Rate} = k[A]^x[B]^y \text{ or } -\frac{d[R]}{dt} = k[A]^x[B]^y$$

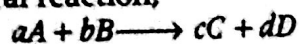
where,  $k$  is rate constant.

- Rate of a reaction decreases with the passage of time as the concentration of reactants decreases. Conversely, rate increases when reactant concentration increases. So, rate of a reaction depends upon the concentration of reactants.
- Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e. theoretically instead it must be determined experimentally.

## Order of a Reaction

The sum of the powers of the concentration of the reactants in the rate law expression is called the **order** of that chemical reaction.

For a general reaction,



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

$$\text{Order of reaction} = (x + y)$$

It is experimentally determined quantity. It may be zero, whole number, fractional or even negative.

## Rate Constant

Rate of reaction is expressed as rate constant, when concentration of each of the reactant is unity.

Reaction	Order	Units of rate constant
Zero order reaction	0	$\text{mol L}^{-1} \text{ s}^{-1}$
First order reaction	1	$\text{s}^{-1}$
Second order reaction	2	$\text{mol}^{-1} \text{ L s}^{-1}$

In case of gaseous reactions, concentration is expressed in terms of pressure, i.e. atmosphere (atm). Rate constant increases with increase in temperature.

## Complex and Elementary Reactions

Reactions which proceed in two or more steps are known as **complex reactions** and each step of a complex reaction is known as **elementary reactions**. The rate of a complex reaction is given by the slowest step called rate determining step amongst these steps.

## Molecularity

It is the number of reacting species taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction. It is a theoretical concept. It is always a whole number value. Its value can never be zero or fractional.

- For a complex reaction, generally molecularity of the slowest step is same as the order of the overall reaction.
- Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction, molecularity has no meaning.

# [TOPIC 2] Integrated Rate Equations, Pseudo First Order Reaction

## 2.1 Integrated Rate Equations

The differential rate equation is integrated to get a relation between directly measured experimental data, i.e. concentrations at different times and rate constant. The integrated rate equations are different for the reactions of different orders.

### Zero Order Reaction

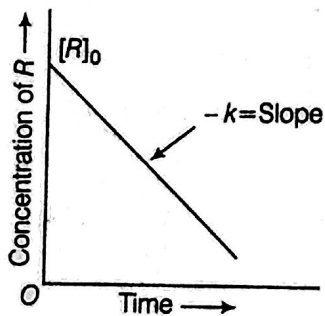
It means that the rate of the reaction is directly proportional to the zero power of the concentration of reactant R,

For the reaction,  $R \rightarrow P$ ,

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0 = k, \quad k = \frac{[R]_0 - [R]}{t}$$

where,  $[R]_0$  is initial concentration of reactant.

A plot of  $[R]$  with time,  $t$  is a straight line with slope =  $-k$ .



Variation in the concentration vs time plot for a zero order reaction

The thermal decomposition of HI on gold surface and the decomposition of gaseous ammonia on a hot platinum surface are the examples of zero order reaction.

### First Order Reaction

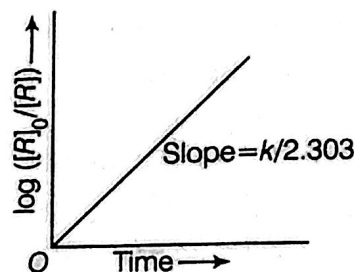
It means that the rate of the reaction is directly proportional to the first power of the concentration of the reactant, R.

For the reaction,  $R \rightarrow P$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R], \quad k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

where,  $[R]_0$  is the initial concentration and  $[R]$  is the concentration of the reactant at time,  $t$ .

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics. A plot of  $\log [R]_0/[R]$  with time,  $t$  for a first order reaction is a straight line with slope =  $\frac{k}{2.303}$ .

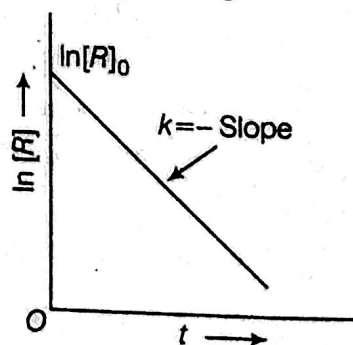


Plot of  $\log [R]_0/[R]$  vs time for a first order reaction

- Rate constant for first order reaction is also given by

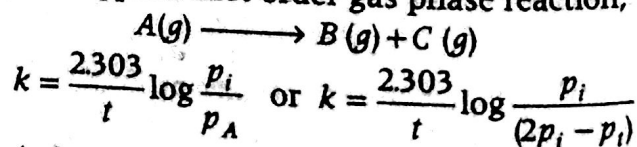
$$k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \Rightarrow \ln [R] = \ln [R]_0 - kt$$

Therefore, the variation in the concentration  $\ln [R]$  vs time ( $t$ ) plot is given below



A plot between  $\ln [R]$  and  $t$  for a first order reaction

- For a typical first order gas phase reaction,



(where,  $p_i$  is the initial pressure of A at time,  $t=0$  and  $p_t$  is the total pressure at time  $t$ .)

## 2.2 Half-life ( $t_{1/2}$ ) of a Reaction

It is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

For a zero order reaction,  $t_{1/2} = \frac{[R]_0}{2k}$

and for first order reaction,  $t_{1/2} = \frac{0.693}{k}$

The half-life of a reaction with  $n$ th order is

$$t_{1/2} \propto \frac{1}{[R]_0^{n-1}}$$

Therefore, for zero order reaction  $t_{1/2} \propto [R]_0$ . For first order reaction  $t_{1/2}$  is independent of  $[R]_0$ . For second order reaction  $t_{1/2} \propto \frac{1}{[R]_0}$  and so on.

In general (for a first order reaction only),

$$N = N_0 \left(\frac{1}{2}\right)^n$$

where,  $N_0$  = initial amount of reactant

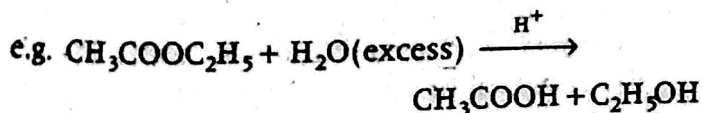
$N$  = amount of reactant left after time,  $t$

$$n = \frac{\text{Total time, } (t)}{\text{Half - life } (t_{1/2})}$$

## 2.3 Pseudo First Order Reactions

Pseudo first order reactions are not truly first order but show first order kinetics under certain conditions. e.g. inversion of cane sugar and acidic hydrolysis of an ester. These reactions are bimolecular but have order one.

In other words, we can say that when a reaction is first order wrt each of the two reactants then, it becomes pseudo first order, when one of the reactants is taken in excess.



**NOTE** The relation between half-life period of a reactant and its initial concentration for a reaction of  $n$ th order is  $t_{1/2} = \frac{1}{k[R]_0^{n-1}}$

## [TOPIC 3] Temperature Dependence of the Rate and Collision Theory

### 3.1 Temperature Dependence of the Rate

The rate of reaction is dependent on temperature. This is expressed in terms of temperature coefficient. Most of the chemical reactions are accelerated by increase in temperature.

#### Temperature Coefficient

It is the ratio of rate constant at temperature 308 (298 + 10) K to the rate constant at temperature 298 K.

$$\text{Temperature coefficient} = \frac{\text{Rate constant at 308 K}}{\text{Rate constant at 298 K}}$$

It is observed that for a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.

#### Arrhenius Equation

The temperature dependence of rate of a chemical reaction is expressed by **Arrhenius equation**.

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

where,  $A$  = frequency factor,

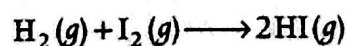
$E_a$  = activation energy (in J/mol),

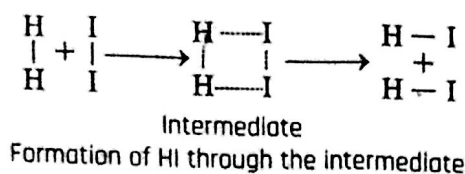
$R$  = gas constant and

$T$  = temperature

#### Arrhenius Theory

Arrhenius theory state that product are formed through the intermediates or activated complex.





## Activation energy ( $E_a$ )

It is given by the energy difference between activated complex and the reactant molecules. It is the energy needed to form the intermediate called **activated complex** or it is the extra energy contained by the reactant molecules that results into effective collision between them to form the products.

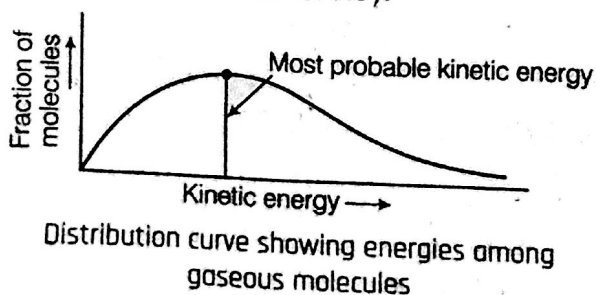
## Threshold Energy

It is the minimum energy which the colliding molecules must have for effective collisions, i.e. those collisions which lead to the formation of product molecules.

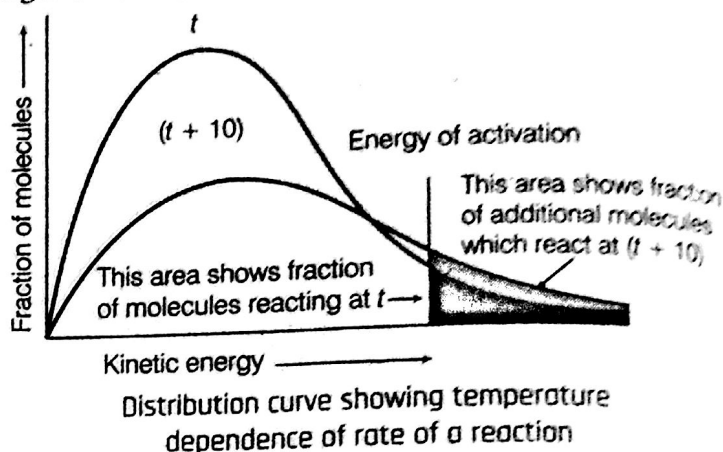
## 3.2 Maxwell Boltzmann Distribution Curve

According to **Ludwig Boltzmann** and **James Clark Maxwell**, the **distribution of kinetic energy** may be described by plotting the fraction of molecules ( $N_E/N_T$ ) with a given kinetic energy, ( $E$ ) vs kinetic energy, where,  $N_E$  is the number of molecules with energy  $E$  and  $N_T$  is the total number of molecules, this is called Maxwell's distributions of energies, represented by the figure given below.

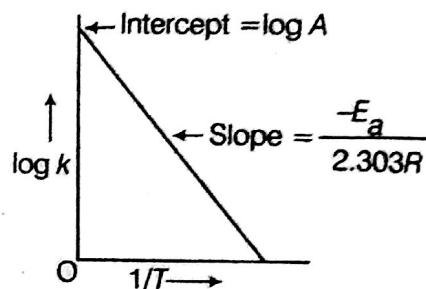
The peak of the curve corresponds to the most probable kinetic energy (kinetic energy of maximum fraction of molecules).



When the temperature is raised, the maximum of the curve moves to higher energy value (shown in figure below) and the curve broadens out.



Taking logarithm of both sides, **Arrhenius equation** becomes



A plot between  $\log k$  and  $1/T$

$$\log k = \log A - \frac{E_a}{2.303 RT}$$

A plot of  $\log k$  with  $\frac{1}{T}$  gives a straight line with slope =  $-\frac{E_a}{2.303 R}$  and intercept =  $\log A$  as given

above. If  $k_2$  and  $k_1$  are rate constants at temperature  $T_2$  and  $T_1$ , respectively

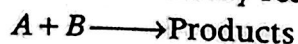
$$\text{then } \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 \cdot T_2} \right]$$

The rate of a chemical reaction alters by the presence of a **catalyst**. It alters the rate by providing alternative path of lower or higher activation energy to the reactants. A catalyst does not change the enthalpy ( $\Delta_r H$ ), Gibb's energy ( $\Delta G$ ) of reaction and the equilibrium constant of a reaction. It only helps in attaining the equilibrium faster.

## 3.3 Collision Theory

According to the **collision theory**, rate of reaction depends on the collision frequency and effective collisions. The number of collisions per second per unit volume of the reaction mixture is known as **collision frequency** ( $Z$ ).

For a bimolecular elementary reaction,



$$\text{Rate} = Z_{AB} e^{-E_a/RT}$$

where,  $Z_{AB}$  represents the **collision frequency** of reactants  $A$  and  $B$  and  $e^{-E_a/RT}$  represents the **fraction of molecules** with energies equal to or greater than  $E_a$ .

The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed. A collision of correctly oriented particles will be effective if the kinetic energy of collision  $\geq$  activation energy ( $E_a$ ).

According to **collision theory**, another factor  $P$  called steric factor, which refers to the orientation of molecules which collide, is important and contributes to effective collision.

$$\text{Rate} = P Z_{AB} e^{-E_a/RT}$$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.