

## Arrhenius Equation

The variation of equilibrium constant of a reaction with temperature is described by Van't Hoff equation of thermodynamics which is as follows:

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$$

If  $k_1$  and  $k_2$  be the rate constants of forward reaction and backward reaction, respectively then  $K_p = k_1/k_2$ . Further,

$\Delta H = E_{a1} - E_{a2}$ . Putting these in the above equation we get,

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_2}{dT} = \frac{E_{a1}}{RT^2} - \frac{E_{a2}}{RT^2}$$

Splitting into two parts

$$\frac{d \ln k_1}{dT} = \frac{E_{a1}}{RT^2} + Z \quad (\text{For FR})$$

$$\frac{d \ln k_2}{dT} = \frac{E_{a2}}{RT^2} + Z \quad (\text{For BR})$$

where  $Z$  is constant

Arrhenius sets  $Z$  equal to zero and without specifying FR and BR, he gave the following equation called Arrhenius equation.

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

From this equation it is evident that rate of change of logarithm of rate constant with temperature depends upon the magnitude of energy of activation of the reaction. Higher the  $E_a$  smaller the rate of change of logarithm of rate constant with temperature. That is, rate of the reaction with low  $E_a$  increases slowly with temperature while rate of the reaction with high  $E_a$  increases rapidly with temperature. It is also evident that rate of increase of logarithm of rate constant will go on decreasing with increase of temperature.

Integrating Equation 4 assuming  $E_a$  to be constant we get,

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

$$\text{or } \ln \frac{k}{A} = -\frac{E_a}{RT}$$

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

Equation (iii) is integrated form of **Arrhenius** equation. The constant A called pre-exponential factor is the frequency factor since it is somewhat related with collision frequency. It is a constant for a given reaction. From Equation (iii) it is evident that as  $T \rightarrow \infty$ ,  $k \rightarrow A$ . Thus, the constant A is the rate constant of reaction at infinity temperature. The rate constant goes on increasing with temperature.

So, when T approaches infinity, k will be maximum. That is to say, A is the maximum rate constant of a reaction.

It is also to be noted that the exponential term i.e.  $e^{-E_a/RT}$  measures the fraction of total number of molecules in the activated state or fraction of the total number of effective collisions. If  $n_{E_a}$  and n be the number of molecules of reactant in the activated state and the total number of molecules of the reactant present in the reaction vessel respectively, then

$$\frac{n_{E_a}}{n} = e^{-E_a/RT}$$

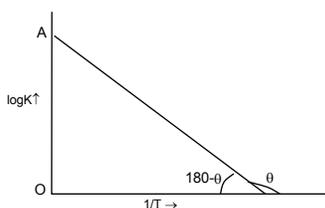
Equation (ii) may also be put as

$$\log k = \left( -\frac{E_a}{2.303R} \right) \frac{1}{T} + \log A \quad \dots(\text{iv})$$

Since  $\frac{E_a}{2.303R}$  and  $\log A$  both are constants for a given reaction. So from equation (iv) it is

evident that a plot of  $\log k$  vs.  $\frac{1}{T}$  will be a straight line of the slope equal to  $-\frac{E_a}{2.303R}$  and

intercept equal to  $\log A$  as shown below.



$$\frac{-E_a}{2.303R} = \tan \theta = -\tan(180 - \theta) = -\frac{OA}{OB}$$

$$\therefore E_a = \frac{OA}{OB} \times 2.303R$$

Thus, from this plot  $E_a$  and A both can be determined accurately.

If  $k_1$  be the rate constant of a reaction at two different temperature  $T_1$  and  $T_2$  respectively then from equation (iv), we may write

$$\log k_1 = -\frac{E_a}{2.303R} \cdot \frac{1}{T_1} + \log A \quad \text{and} \quad \log k_2 = -\frac{E_a}{2.303R} \cdot \frac{1}{T_2} + \log A$$

Subtracting former from the latter we get

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

With the help of this equation it is possible to calculate  $E_a$  of a reaction provided, rate constants of reaction at two different temperatures are known. Alternatively one can calculate rate constant of a reaction at a given temperature provided that rate constant of the reaction at some other temperature and also  $E_a$  of the reaction is known.

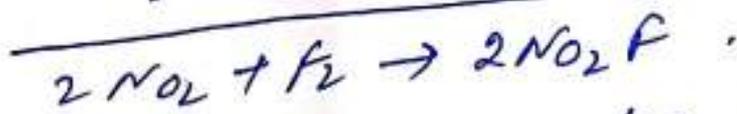
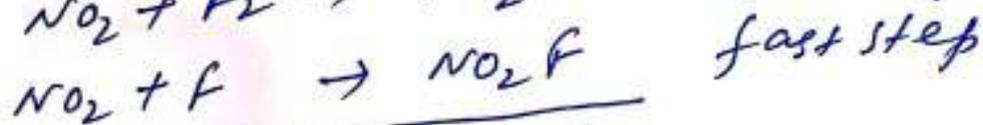
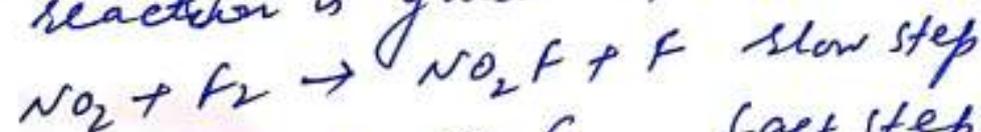
To understand the concept of order, let us discuss the following few examples;

(i)  $\text{NO}_2$  and  $\text{F}_2$  react as follows;



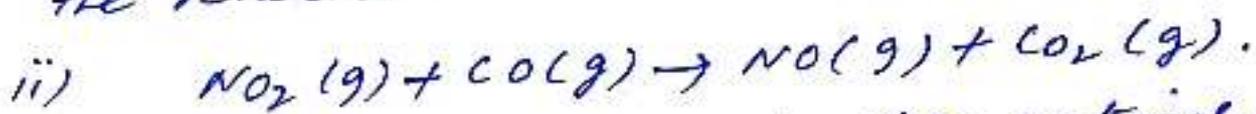
According to law of mass action; the rate of the above reaction is given by  
 $R = k \cdot [\text{NO}_2]^2 [\text{F}_2]^1$ ; i.e. rate varies with square of the concentration of  $\text{NO}_2$  & with first power of  $\text{F}_2$ .

\* But experimental observations reveal that the reaction is proportional to the product of the concentrations of  $\text{NO}_2$  and  $\text{F}_2$ .  
 thus  $R = k \cdot [\text{NO}_2]^1 [\text{F}_2]^1$  i.e. the overall order of this reaction is  $1+1=2$ . To understand the deviance of exponents of  $\text{NO}_2$  &  $\text{F}_2$  from stoichiometry, it is proposed that the reaction occurs in more than one step & rate depends on the slowest step; i.e. rate determining step. The mechanism of the above reaction is given as;

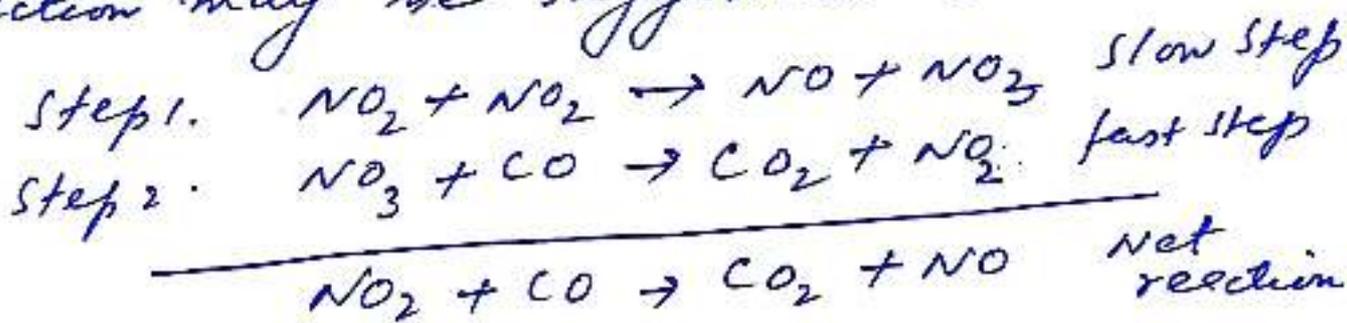


Since rate depends upon the slowest step hence rate of the above reaction is  
 $R = k \cdot [\text{NO}_2]^1 [\text{F}_2]^1$ . This is called rate law. Each of the steps is called

an elementary process is all the steps taken together give the mechanism of the reaction.



The experimental observations reveal that the rate of the reaction is proportional to the square of the concentration of nitrogen peroxide. This indicates that the rate determining step in the mechanism of this reaction must be independent of the concentration of CO. Keeping in view the above fact, the mechanism of the reaction may be suggested as



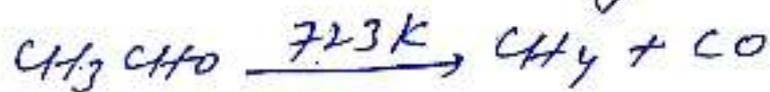
Although the above reaction proceeds through two steps, but the rate of the overall reaction is determined by the first step which is the slower of the steps. Hence experimentally observed rate of the reaction is given by the expression

$$\text{Rate} = k [\text{NO}_2] [\text{NO}_2]$$

$$\Rightarrow \text{Rate} = k [\text{NO}_2]^2$$

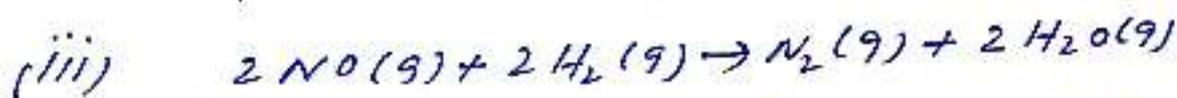
Further it may be mentioned here

that the order of a reaction may not always be a whole number. for example, at  $450^{\circ}\text{C}$  ( $723\text{K}$ ), acetaldehyde decomposes as



Experimentally, it is found that  
Rate of reaction  $\propto [\text{CH}_3\text{CHO}]^{1.5}$

Thus, order of the reaction is  $1\frac{1}{2}$  or 1.5



Kinetic experiment carried out at  $1100\text{K}$  upon this reaction has shown the following rate data.

Experiment no	$[\text{NO}]$	$[\text{H}_2]$	Rate
1	$5 \times 10^{-3}$	$2.5 \times 10^{-3}$	$3 \times 10^{-5}$
2	$1 \times 10^{-2}$	$2.5 \times 10^{-3}$	$1.2 \times 10^{-4}$
3	$1 \times 10^{-2}$	$5 \times 10^{-3}$	$2.4 \times 10^{-4}$

Let order w.r.t  $[\text{NO}_2]$  be  $m$  & w.r.t  $[\text{H}_2]$  be  $n$  & ~~that~~ thus  $R = k[\text{NO}]^m[\text{H}_2]^n$

From exp. 1 & 2  $\frac{3 \times 10^{-5}}{1.2 \times 10^{-4}} = \frac{k(5 \times 10^{-3})^m (2.5 \times 10^{-3})^n}{k(10^{-2})^m (2.5 \times 10^{-3})^n}$

$$\Rightarrow \frac{1}{4} = \left(\frac{5 \times 10^{-3}}{10^{-2}}\right)^m = \left(\frac{5}{10}\right)^m = \left(\frac{1}{2}\right)^m$$

$$\Rightarrow \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^m \Rightarrow \boxed{m=2}$$

From exp 2 and 3 we have

$$\frac{1.2 \times 10^{-4}}{2.4 \times 10^{-4}} = \frac{k [10^{-2}]^m \times [2.5 \times 10^{-3}]^n}{k [10^{-2}]^m \times [5 \times 10^{-3}]^n}$$

$$\Rightarrow \frac{1.2}{2.4} = \left( \frac{2.5 \times 10^{-3}}{5 \times 10^{-3}} \right)^n$$

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

$$\Rightarrow n = 1$$

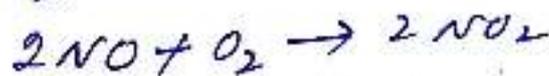
$$\text{Since } R = k [\text{NO}]^m [\text{H}_2]^n,$$

$$\Rightarrow R = k [\text{NO}]^2 [\text{H}_2]$$

this means, that the overall order of the reaction is 3 & order w.r.t  $[\text{NO}]$  is 2 and order w.r.t  $[\text{H}_2] = 1$

iv) Reactions involving intermediates in equilibrium with reactants.

Consider the reaction of NO and  $\text{O}_2$  to produce  $\text{NO}_2$ .



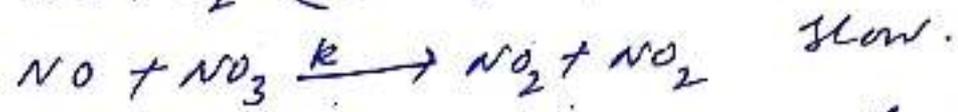
The rate of the reaction has been found to be

$$R = k' [\text{NO}]^2 [\text{O}_2]$$

To account for this, the following mechanism has been proposed.

Dividing  
2 by 3  
In equality  
bases are  
same,  
powers are  
also same.

$k'$  is a  
new const  
ant)



Let  $k$  be the rate constant of the slow step  
Since rate depends on the slow step, hence

$R = k[\text{NO}][\text{NO}_3]$ . But since  $\text{NO}_3$  is an intermediate whose net rate of formation is zero & hence can't be kept in the rate law. Let  $K$  be the equilibrium constant of the fast step, then

$$K = \frac{[\text{NO}_3]}{[\text{NO}][\text{O}_2]} \Rightarrow [\text{NO}_3] = K[\text{NO}][\text{O}_2]$$

Substituting the value of  $[\text{NO}_3]$  in above rate equation, we have

$$R = k[\text{NO}] + K[\text{NO}][\text{O}_2]$$

$$\Rightarrow R = k + k[\text{NO}]^2[\text{O}_2]$$

Put  $k + k = k'$  (another constant)

$$\text{hence } R = k'[\text{NO}]^2[\text{O}_2]$$

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## Theories of Reaction Rates:

Two main theories to explain the rates of chemical reactions are :

1. Collision theory.
2. Transition state theory or the theory of absolute reaction rates.

### 1. Collision Theory

This theory was put forward by Max Trautz and Willian Lewis in 1916-18. It is based on kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and the reaction occurs when molecules collide with each other.

For a collision to occur at least two molecules must collide therefore we consider *bimolecular reactions*.

Later in the discussion we shall take up *unimolecular reactions* also.

### Collision theory of bimolecular reactions

Collision theory of bimolecular gaseous reactions proposes quantitative calculation of rate of reactions. It is based on the following postulates :

- (i) The products are formed only when the reactant molecules collide with each other.
- (ii) Only those collisions are effective in which the molecules possess sufficient energy of activation as well proper orientation.

Each collision is not effective to bring about the reaction. Only a fraction of total number of molecules is effective in bringing about the chemical reaction.

If  $f$  is the fraction of the molecules having activation energy and  $z$  is the number of bimolecular collisions per unit volume per second (*i.e.* collision frequency) between the reactant molecules, then the rate of a bimolecular reaction is given by

$$\text{Rate} = z \times f \quad \dots(1)$$

From Maxwell-Boltzmann law of distribution of energy, the fraction of total molecules which possess energy equal to or more than activation energy  $E_a$  is given as

$$f = \frac{\Delta n}{N} = e^{-E_a/RT} \quad \dots(2)$$

where  $\Delta n$  is the number of activated molecules and  $N$  is the total number of molecules. The factor  $e^{-E_a/RT}$  is called *Boltzmann factor*. Substituting the value of  $f$  into equation (1) we get

$$\text{Rate} = -\frac{dn_A}{dt} = z \times e^{-E_a/RT} \quad \dots(3)$$

The rate equations from collision theory are derived for two different cases :

**Case 1.** When bimolecular collisions occur between similar molecules

Consider a bimolecular gaseous reaction



The molecules are considered to be rigid and hard spheres. It is assumed that there are no forces of attraction or repulsion between them. From kinetic theory of gases, the collisions per unit volume per unit time is given by

$$z_{AA} = \frac{1}{\sqrt{2}} \pi v \sigma_A^2 n_A^2 \quad \dots(4)$$

where  $\sigma_A$  is the diameter of molecule A,  $n_A$  is the number of molecules of A per unit volume of the container.

From kinetic theory of gases, the value of average velocity  $v$  is given as

$$v = \sqrt{\frac{8kT}{\pi m_A}} \quad \dots(5)$$

where

$m_A$  = Mass of a single molecule A

$k$  = Boltzmann constant

$T$  = Absolute temperature

Substituting the value of  $v$  in equation (4) we get

$$z_{AA} = \frac{1}{\sqrt{2}} \pi \sigma_A^2 n_A^2 \sqrt{\frac{8kT}{\pi m_A}} = 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi kT}{m_A}} \quad \dots(6)$$

To obtain above equation in terms of molar mass of A we write  $k = R/N$  and  $m_A = \frac{M_A}{N}$  where  $M_A$  is the molar mass of A,  $N$  is the Avogadro's number and  $R$  is the gas constant.

$$z_{AA} = 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi(R/N)T}{M_A/N}} = 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}} \quad \dots(7)$$

Substituting this value of  $z_{AA}$  in equation (3) we get

$$\text{Rate} = -\frac{dn_A}{dt} = 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}} \times e^{-E_a/RT} \text{ collisions cm}^{-3} \text{ s}^{-1} \quad \dots(8)$$

Since each collision involves two similar molecules, the rate of reaction in terms of molecules of A reacting per  $\text{cm}^3$  per second is given as

$$\text{Rate} = -dn_A / dt = 2 \times \left( 2\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}} e^{-E_a/RT} \right) \text{ molecules cm}^{-3} \text{ s}^{-1}$$

$$\boxed{\text{Rate} = 4\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}} e^{-E_a/RT} \text{ molecules cm}^{-3} \text{ s}^{-1}} \quad \dots(9)$$

In general, for a bimolecular reaction  $A + A \longrightarrow \text{Products}$ , the reaction rate is

$$\text{Rate} = k n_A^2 \quad \dots(10)$$

where  $k$  is the rate constant.

Comparing equations (9) and (10) we get

$$k = 4\sigma_A^2 \sqrt{\frac{\pi RT}{M_A}} e^{-E_a/RT} \text{ molecules cm}^{-3} \text{ s}^{-1} \quad \dots(11)$$

Using this value of  $k$ , we can determine the frequency factor  $A$  in Arrhenius equation. Compare equation (11) with Arrhenius equation

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

we get

$$A = 4\sigma_A^2 \sqrt{\frac{\pi RT}{M_A}} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad \dots(12)$$

The rate equation (9), the rate constant equation (11) and the frequency factor equation (12) can be expressed in terms of *molar concentrations* as follows :

The concentration of  $A$  is expressed in moles per litre as

$$[A] = \frac{n_A \times 10^3}{N} \text{ moles L}^{-1}, \text{ where } N \text{ is Avogadro's number.}$$

or

$$n_A = \frac{[A] \times N}{10^3}$$

$\therefore$

$$dn_A = \frac{N}{10^3} \times d[A]$$

or

$$d[A] = \frac{10^3}{N} \times dn_A$$

Therefore, the reaction rate is given as

$$-\frac{d[A]}{dt} = -\frac{10^3}{N} \left( \frac{dn_A}{dt} \right) = \frac{10^3}{N} \left( -\frac{dn_A}{dt} \right) \quad \dots(13)$$

Substituting the value of  $(-dn_A/dt)$  from equation (9) into equation (13), we get

$$-\frac{d[A]}{dt} = \frac{10^3}{N} \left[ 4\sigma_A^2 n_A^2 \sqrt{\frac{\pi RT}{M_A}} \times e^{-E_a/RT} \right]$$

Substituting for  $n_A = \frac{[A]N}{10^3}$  in above equation, we get

$$-\frac{d[A]}{dt} = \frac{10^3}{N} \left[ 4\sigma_A^2 \frac{[A]^2 N^2}{10^3 \times 10^3} \sqrt{\frac{\pi RT}{M_A}} \times e^{-E_a/RT} \right]$$

or

$$\text{Rate} = 4\sigma_A^2 \frac{[A]^2 N}{10^3} \sqrt{\frac{\pi RT}{M_A}} e^{-E_a/RT} \text{ moles L}^{-1} \text{ s}^{-1} \quad \dots(14)$$

Comparing equation (14) with a general rate law equation

$$\text{Rate} = k [A]^2$$

We get

$$k = 4\sigma_A^2 \frac{N}{10^3} \sqrt{\frac{\pi RT}{M_A}} \times e^{-E_a/RT} \text{ L mol}^{-1} \text{ s}^{-1} \quad \dots(15)$$

On comparing equation (15) with Arrhenius equation

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

We get

$$A = 4\sigma_A^2 \frac{N}{10^3} \sqrt{\frac{\pi RT}{M_A}} \text{ L mol}^{-1} \text{ s}^{-1} \quad \dots(16)$$

**Case 2. When the bimolecular collisions occur between dissimilar molecules**

Consider a bimolecular reaction



The no. of binary collisions  $Z_{AB}$  per unit volume per unit time between molecules A and B are given by

$$Z_{AB} = \sigma_{AB}^2 \sqrt{\frac{8\pi kT}{\mu}} n_A n_B \quad \dots(17)$$

where  $\sigma_{AB}$  is the distance of closest approach or the effective molecular diameter for collision between molecules A and B. It is equal to the mean of the molecular diameters  $\left(\frac{\sigma_A + \sigma_B}{2}\right)$ ,  $n_A$  and  $n_B$  are the number of molecules of A and B per unit volume and  $\mu$  is the reduced mass and is given by

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$$

or

$$\frac{1}{\mu} = \frac{m_A + m_B}{m_A m_B}$$

or

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

Hence equation (17) is written as

$$Z_{AB} = \sigma_{AB}^2 \sqrt{8\pi kT \left(\frac{m_A + m_B}{m_A m_B}\right)} n_A n_B \quad \dots(18)$$

The collision number  $Z_{AB}$  in terms of molar masses can be expressed by substituting the following in the equation (18)

$$m_A = \frac{M_A}{N}, m_B = \frac{M_B}{N} \text{ and } k = \frac{R}{N}$$

where R is gas constant, N is Avogadro's number,  $M_A$  and  $M_B$  are molar masses of A and B respectively.

Equation (18) becomes

$$\begin{aligned} Z_{AB} &= \sigma_{AB}^2 \sqrt{\frac{8\pi \left(\frac{R}{N}\right) T \left(\frac{M_A}{N} + \frac{M_B}{N}\right)}{\frac{M_A}{N} \times \frac{M_B}{N}}} n_A n_B \\ &= \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} n_A n_B \end{aligned}$$

According to collision theory, the rate of reaction in terms of molecules of A and B reacting per  $\text{cm}^3$  per second is

$$\text{Rate} = -\frac{dn_A}{dt} = -\frac{dn_B}{dt} = Z_{AB} \times e^{-E_a/RT}$$

Substituting value of  $Z_{AB}$

$$\text{Rate} = -\frac{dn_A}{dt} = -dn_B/dt = \sigma_{AB}^2 \sqrt{8\pi RT \left( \frac{M_A + M_B}{M_A M_B} \right)} n_A n_B e^{-E_a/RT} \quad \dots(19)$$

The units of rate are molecules  $\text{cm}^{-3} \text{s}^{-1}$

Also the rate is given as

$$\text{Rate} = k n_A n_B \quad \dots(20)$$

where  $k$  is the rate constant for the reaction comparing equations (19) and (20) we get

$$k = \sigma_{AB}^2 \sqrt{8\pi RT \left( \frac{M_A + M_B}{M_A M_B} \right)} e^{-E_a/RT} \quad \dots(21)$$

The units of  $k$  are molecules  $\text{cm}^{-3} \text{s}^{-1}$

On comparing equation (21) with Arrhenius equation i.e.

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

We get

$$A = \sigma_{AB}^2 \sqrt{8\pi RT \left( \frac{M_A + M_B}{M_A M_B} \right)} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad \dots(22)$$

To express the rate equation (20), rate constant equation (21) and frequency factor equation (22) in terms of molar concentrations of A and B we proceed as follows:

$$[A] = \frac{n_A}{N} \times 10^3 \text{ moles L}^{-1} \text{ or } n_A = \frac{N \times [A]}{10^3} \quad \dots(23)$$

$$\therefore dn_A = \frac{N}{10^3} d[A] \quad \text{or} \quad d[A] = \frac{10^3}{N} dn_A$$

$$\therefore \frac{d[A]}{dt} = \frac{10^3}{N} \times \frac{dn_A}{dt}$$

$$\text{Similarly, } [B] = \frac{n_B}{N} \times 10^3 \text{ moles L}^{-1} \text{ or } n_B = \frac{N}{10^3} \times [B] \quad \dots(24)$$

$$\therefore dn_B = \frac{N}{10^3} d[B] \quad \text{or} \quad d[B] = \frac{10^3}{N} dn_B$$

$$\therefore \frac{d[B]}{dt} = \frac{10^3}{N} \frac{dn_B}{dt}$$

The reaction rate is

$$\begin{aligned} \text{Rate} &= -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -\frac{10^3}{N} \times \frac{dn_A}{dt} \\ &= \frac{10^3}{N} \times \left( -\frac{dn_A}{dt} \right) \quad \dots(25) \end{aligned}$$

Substituting value of  $\left( -\frac{dn_A}{dt} \right)$  from equation (19) into equation (25), we get

$$\text{Rate} = \frac{10^3}{N} \sigma_{AB}^2 \sqrt{8\pi RT \left( \frac{M_A + M_B}{M_A M_B} \right)} n_A n_B e^{-E_a/RT}$$

Substituting values of  $n_A$  and  $n_B$  from equations (23) and (24) in above equation, we get

$$\text{Rate} = \frac{10^3}{N} \sigma_{AB}^2 \sqrt{8\pi RT \left( \frac{M_A + M_B}{M_A M_B} \right)} \frac{N}{10^3} [A] \times \frac{N[B]}{10^3} \times e^{-E_a/RT}$$

$$\text{Rate} = \frac{N}{10^3} \sigma_{AB}^2 \sqrt{8\pi RT \left( \frac{M_A + M_B}{M_A M_B} \right)} [A] [B] e^{-E_a/RT} \text{ mol}^{-1} \text{ s}^{-1} \quad \dots(26)$$

Comparing this equation (26) with general rate equation

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

We get

$$k = \frac{N}{10^3} \sigma_{AB}^2 \sqrt{8\pi RT \left( \frac{M_A + M_B}{M_A M_B} \right)} e^{-E_a/RT} \text{ L mol}^{-1} \text{ s}^{-1} \quad \dots(27)$$

On comparing equation (26) with Arrhenius equation

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

We get

$$A = \frac{N}{10^3} \sigma_{AB}^2 \sqrt{8\pi RT \left( \frac{M_A + M_B}{M_A M_B} \right)} \text{ L mol}^{-1} \text{ s}^{-1} \quad \dots(28)$$

### Modification of Collision Theory

The collision theory predicts accurately the rate constant for bimolecular reactions involving simple molecules in gas phase and in solution.

However, for reactions involving *complex molecules* or for bimolecular reactions at high pressure the observed reaction rate is lower than the theoretically calculated value.

To explain this, it was suggested that the *orientation* of the molecules at the time of collision must also be considered. To account for this, a factor  $p$ , known as *probability* or *steric factor* is introduced and the equation for the rate constant is modified as

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

The probability factor varies from reaction to reaction and can have any value between 1 and  $10^{-9}$ . It accounts for the fact collision between activated molecules is not the only requirement for the reaction to occur. For an effective collision, suitable orientation of the colliding molecules is also essential for the reaction to occur. By introducing a correction factor  $p$ , the equations (16) and (28) get modified as follows :

For biomolecular reactions having *similar molecules*

$$A = p \times 4 \sigma_A^2 \frac{N}{10^3} \sqrt{\frac{\pi RT}{M_A}} \text{ L mol}^{-1} \text{ s}^{-1} \quad \dots(29)$$

For bimolecular reactions having *dissimilar molecules*

$$A = p \times \frac{N}{10^3} \sigma_{AB}^2 \sqrt{8\pi RT \left( \frac{M_A + M_B}{M_A M_B} \right)} \text{ L mol}^{-1} \text{ s}^{-1} \quad \dots(30)$$

Substituting the values of constants  $N$ ,  $\pi$  and  $R$  equation (29) becomes

$$A = (3.893 \times 10^{29}) \times p \sigma_A^2 \sqrt{\frac{T}{M_A}} \text{ L mol}^{-1} \text{ s}^{-1} \quad \dots(31)$$

and equation (30) becomes

$$A = (2.753 \times 10^{29}) \times p \sigma_{AB}^2 \sqrt{T \left( \frac{M_A + M_B}{M_A M_B} \right)} \text{ L mol}^{-1} \text{ s}^{-1} \quad \dots(32)$$

This modification of collision theory has its own limitation as follows :

There is no method available for estimating  $p$  theoretically with the help of collision theory. To bridge the gap between theoretically calculated values and experimental values another theory called *transition state theory* has been proposed.

### Limitations of collision theory:

Although collision theory of reaction rates is satisfactorily applicable to simple gaseous reactions, it fails in many cases such as rapid chain reactions, reactions involving complex molecules etc. The theory suffers from following weaknesses:

1) The collision theory does not help in calculation of the orientation factor ' $p$ '. No attempt has been made to correlate the value of ' $p$ ' with the structure and properties of reacting molecules. As we move from simple atomic reactions to complex reactions the value of  $p$  has been found to vary from unity to  $10^9$ . This wide variation in the value of ' $p$ ' has not been explained, in terms of collision theory.

2) The reacting molecules acquire activation energy from translational, potential, vibrational and rotational motions. However, the molecules in collision theory have been treated as hard spheres undergoing elastic collisions and in term  $e^{-E_{act}/RT}$  only the translational energy involving two degrees of freedom has been considered. The whole kinetic energy is not taken in to account.

3) The actual distance at which the reaction is supposed to occur is actually different from collision diameter taken in the collision theory.

4) The collision theory is silent on the breaking and making of bonds involved in the reaction.

## 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 :

$$k = \frac{1}{t} [a - (a-x)] \quad (\text{For zero order reactions}) \quad \text{where } k = \text{rate constant, } a = \text{initial concentration of reactant and } (a-x) \text{ is the concentration of reactant at time } t.$$

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

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

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

(2) **Half-life method** : This method is employed only when the rate law involved only one concentration term. In general for a reaction of  $n$ th order, the expression for half life time is:

$$t_{1/2} \propto \frac{1}{a^{n-1}} \quad \text{where } a \text{ is initial rxn concentration and } n \text{ is order of the reaction.}$$

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

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

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

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

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

Remember:

For Zero Order rxn.  $t_{1/2} \propto a$

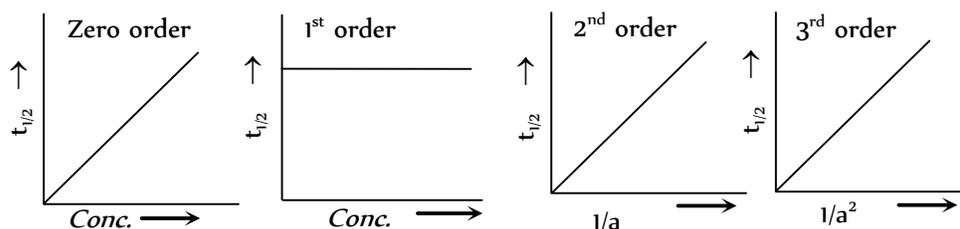
for 1st order rxn.  $t_{1/2} = 0.693/k$  (independent of conc.)

for 2nd order rxn.  $t_{1/2} \propto 1/a$

for 3rd order rxn.  $t_{1/2} \propto 1/a^2$

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) For zero order rxn, rate eqn. is:

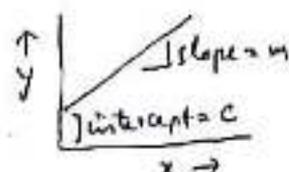
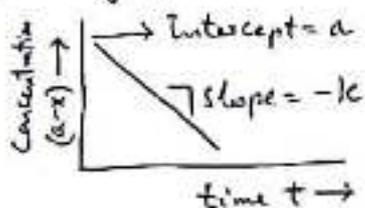
$$k = \frac{1}{t} [a - (a-x)]$$

where  $k$  = rate constant  
 $a$  = initial concn. of reactants  
 $(a-x)$  = concentration of reactant after time  $t$ .

$$\text{or } kt = a - (a-x)$$

$$\text{or } \frac{(a-x)}{1} = \frac{-k}{m} t + \frac{a}{c} \quad \text{--- The eqn. is in the form of linear eqn. } y = mx + c$$

Plotting a graph between  $(a-x)$  vs time  $t$



Eqn for linear eqn.  $y = mx + c$ .

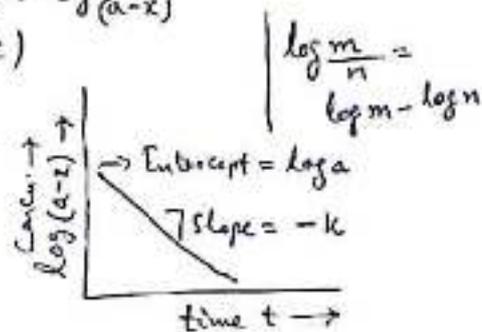
(ii) for 1st order rxn, rate eqn. is:

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

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

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

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



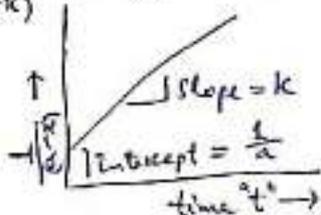
(iii) for 2nd order rxn, rate eqn. is:-

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

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

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

$$y = mx + c$$

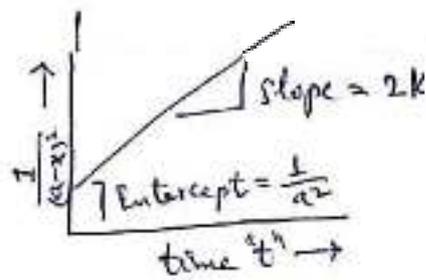


(iv) for 3rd order rxn, rate eqn. is:

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

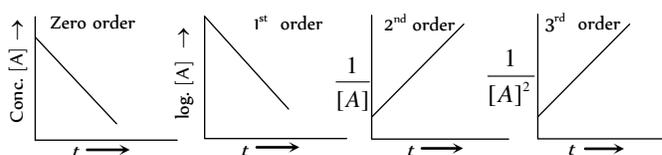
$$\text{or } 2kt = \frac{1}{(a-x)^2} - \frac{1}{a^2}$$

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



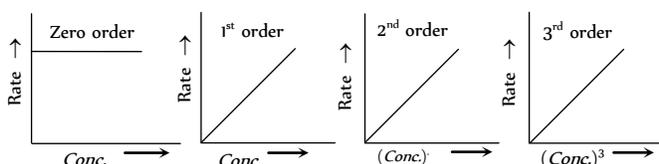
- (i) If the plot of  $(a - x)$  Vs  $t$  is a straight line, the reaction follows zero order.
- (ii) If the plot of  $\log(a - x)$  Vs  $t$  is a straight line, the reaction follows first order.
- (iii) If the plot of  $\frac{1}{(a - x)}$  Vs  $t$  is a straight line, the reaction follows second order.
- (iv) If the plot of  $\frac{1}{(a - x)^2}$  Vs  $t$  is a straight line, the reaction follows third order.
- (v) 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**



$$[A] = (a - x)$$

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



(4) **Van't Hoff differential method** : The method was devised by Van't Hoff. According to this method, the rate  $r$  of the  $n^{th}$  order reaction is given by:

$$r = k C^n \quad \dots\dots(i)$$

Taking logs, we have

$$\log r = \log k + n \log C \quad \dots\dots(ii)$$

Thus, if the plot of  $\log r$  Versus Concentration  $\log C$  gives a straight line, then slope gives value of  $n$  and intercept gives  $\log k$ , Fig 1.

Thus for two different initial concentrations  $C_1$  and  $C_2$  equation, can be written in the form:

$$\frac{-dC_1}{dt} = kC_1^n \text{ and } \frac{-dC_2}{dt} = kC_2^n \text{ here, } r_1 = \frac{-dC_1}{dt}; r_2 = \frac{-dC_2}{dt}$$

Taking logarithms,

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

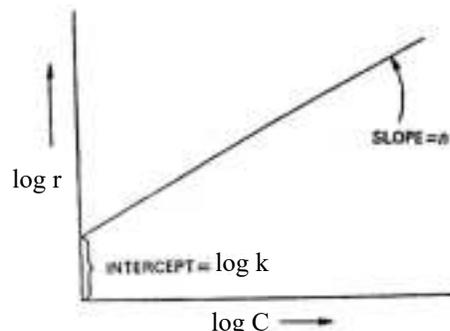


Fig. 1  $\log r$  Vs  $\log C$  for the  $n$ th Order reaction.

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

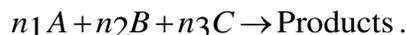
Subtracting equation (ii) from (i),

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

$\frac{-dC_1}{dt}$  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,



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,  $\text{Rate} \propto [A]^2$  *i.e.*, order with respect to *A* is 2.

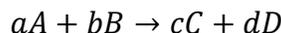
(ii) Keeping the concentrations of *A* and *C* constant, if concentration of *B* is doubled, the rate of reaction is also doubled. This means that,  $\text{Rate} \propto [B]$  *i.e.*, order with respect to *B* is 1.

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

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

# Differential and Integrated Rate Laws

Rate laws describe the progress of the reaction; they are mathematical expressions which describe the relationship between reactant rates and reactant concentrations. In general, if the reaction is:



We can write the following expression:

$$\text{rate} = k[A]^m[B]^n$$

Where:

$k$  is a proportionality constant called *rate constant* (its value is fixed for a fixed set of conditions, specially temperature).

$m$  and  $n$  are known as *orders of reaction*. As it can be seen from the above expression, these orders of reaction indicate the degree or extent to which the reaction rate depends on the concentration of each reactant. We can say the following about these orders of reaction:

1. In general, they are not equal to the coefficients from the balanced equation. Remember: they are determined experimentally (unless a reaction is what we call an *elementary reaction*, but they are the exception).
2. Each reactant has its own (independent) order of reaction.
3. Orders of reaction are often times a positive number, but they can also be zero, a fraction and in some instances a negative number.
4. The *overall reaction order* is calculated by simply adding the individual orders ( $m + n$ ).

As it turns out, rate laws can actually be written using two different, but related, perspectives. Which are these two perspectives? What information does each provide? Read along and you will find out. One more thing – I must insist: it is not possible to predict the rate law from the overall balanced chemical reaction; rate laws must be determined experimentally.

## Differential vs Integrated Rate Laws

**Differential rate laws** express the *rate of reaction as a function of a change in the concentration* of one or more reactants *over a particular period of time*; they are *used to describe what is happening at the molecular level* during a reaction. These rate laws help us determine the overall mechanism of reaction (or process) by which the reactants turn into products. *E.g.:*

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

On the other hand, **integrated rate laws** express the reaction *rate as a function of the initial concentration and a measured (actual) concentration of one or more reactants after a specific amount of time (t) has passed*; they are *used to determine the rate constant and the reaction order from experimental data*. *E.g.* (when  $n = 1$ ):

$$\ln[A] = -kt + \ln[A]_0$$

Where  $[A]_0$  is the initial concentration of the reactant and  $[A]$  is the concentration after a time  $t$  has passed.

Although calculus is not needed for this class, on the next page you will see how to obtain the integrated rate laws for zero, first and second order rate laws because they provide important information. You do not need to memorize the method nor the equations.

## Zeroth order reactions ( $n = 0$ )

The differential form of the rate law is (notice the presence of the negative sign since the reactant disappears):

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

In order to be able to integrate with ease, we can use a technique called separation of variables to get:

$$d[A] = -kdt$$

(notice how each side has a different, unique variable)

Now we can integrate both sides over the desired interval:

$$\int_{[A]_0}^{[A]} d[A] = -k \int_{t_0}^t dt$$

( $[A]_0$  and  $t_0$  are initial conditions, whereas  $[A]$  refers to the concentration after a time  $t$  has passed)

Notice how  $-k$  comes out of the integral since it is a constant. Also, recall from calculus that (you can always check a table of integrals if you don't remember):

$$\int dx = x \quad (\text{a constant } C \text{ is added, but we do not need it since we know the limits})$$

Which leads to (after evaluating over the limits, which means upper limit minus lower limit):

$$[A] \Big|_{[A]_0}^{[A]} = -kt \Big|_{t_0}^t \quad \Rightarrow \quad [A] - [A]_0 = -k(t - t_0)$$

We consider (actually define)  $t_0 = 0$ , and so the equation can take the form:

$$[A] = -kt + [A]_0$$

Which looks like:

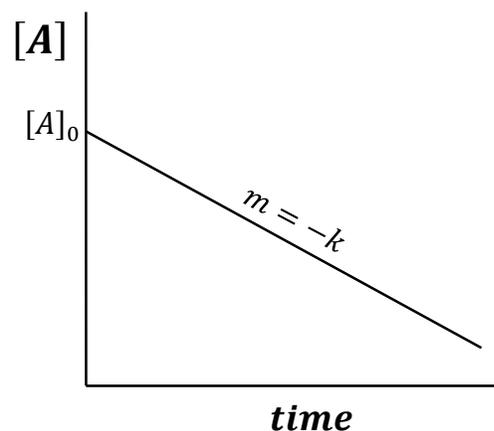
$$y = mx + b$$

Where:

$$y = [A] \quad ; \quad m = -k \quad ; \quad x = t \quad ; \quad b = [A]_0$$

If you think of it, this is a very interesting scenario! Why? If we keep plotting  $[A]$  vs  $t$  for a longer and longer period of time, we will get to a point at which the concentration  $[A]$  will become negative (since we have a negative slope); nevertheless, we are well aware of the fact that there is no such thing as a negative concentration, so, what is wrong here?

In actuality, nothing is wrong! What we can conclude is that a zero-order reaction model can be applied to describe a reaction just for a limited amount of time; we know the system must, at some point, change into a different kinetics model.



One more thing. The half-life is defined as the time it takes for half of the initial amount of reactant to disappear (*i.e.* a reduction of 50% its original amount). If we replace this idea on the integrated rate law we get:

$$\frac{1}{2}[A]_0 = -kt_{1/2} + [A]_0 \quad ; \quad t_{1/2} = \frac{[A]_0}{2k}$$

This means the half-life depends on the initial concentration of reactant and the rate constant.

## First order reactions ( $n = 1$ )

The differential form of the rate law is:

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

After separating the variables we get:

$$\frac{d[A]}{[A]} = -kdt$$

Now we can integrate both sides over the desired interval:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_{t_0}^t dt$$

Recall from calculus that (or check a table of integrals):

$$\int \frac{1}{x} dx = \ln x \quad \text{and} \quad \int dx = x \quad (\text{definite integrals})$$

The above formulas lead to (after evaluating over the limits):

$$\ln[A] \Big|_{[A]_0}^{[A]} = -kt \Big|_{t_0}^t \quad \Rightarrow \quad \ln[A] - \ln[A]_0 = -k(t - t_0)$$

We consider  $t_0 = 0$ , and the equation can take the form:

$$\ln[A] = -kt + \ln[A]_0$$

Which looks like:

$$y = mx + b$$

Where:

$$y = \ln[A] \quad ; \quad m = -k \quad ; \quad x = t \quad ; \quad b = \ln[A]_0$$

This means that if we plot  $\ln[A]$  vs  $t$ , we get a line with a slope that is the negative of the rate constant. Also, using the laws of logarithms, we get:

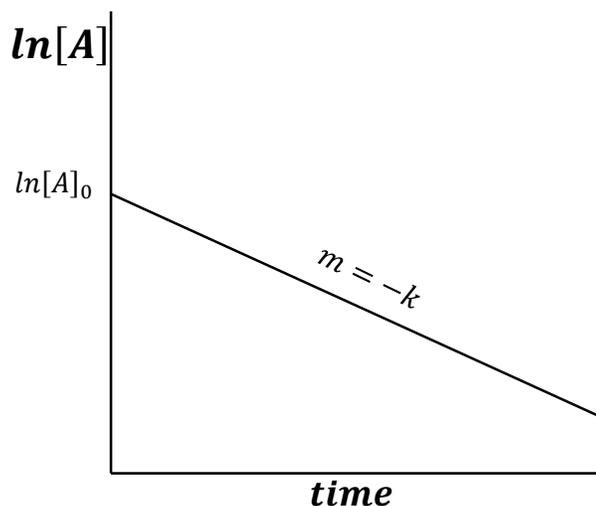
$$\ln[A] - \ln[A]_0 = \ln \frac{[A]}{[A]_0} = -kt$$

What is the time it takes for half of the initial concentration to disappear (the half-life or  $t_{1/2}$ )?

$$@ t = t_{1/2} \quad \Rightarrow \quad [A] = \frac{1}{2} [A]_0$$

$$\ln \frac{[A]}{[A]_0} = -kt \quad \text{or} \quad \ln \frac{[A]_0}{[A]} = kt_{1/2} \quad (\text{reverse sign})$$

$$kt_{1/2} = \ln \frac{[A]_0}{\frac{1}{2} [A]_0} \quad ; \quad t_{1/2} = \frac{\ln 2}{k} \cong \frac{0.693}{k}$$



The equation above means the half-life or  $t_{1/2}$  for a first order reaction is a constant. Check the graph for  $[A]$  vs  $t$  (from which you can calculate the half-life) on your textbook. **Getting ahead:** we will see this half-life equation again in the nuclear chemistry chapter, although in its exponential form, which is:

$$[A] = [A]_0 e^{-kt}$$

## Second order reactions ( $n = 2$ )

The differential form of the rate law is:

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

We separate the variables and integrate over the interval:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k \int_{t_0}^t dt$$

Recall from calculus that (or check a table of integrals):

$$\int x^n dx = x^{n+1}(n+1) \quad (\text{definite integral}); \quad \text{where } n = -2, \quad \text{so: } \int x^2 dx = x^{-1}(-1)$$

The above formulas lead to (after evaluating over the limits):

$$-\frac{1}{[A]} \Big|_{[A]_0}^{[A]} = -kt \Big|_{t_0}^t \quad \Rightarrow \quad \frac{1}{[A]_0} - \frac{1}{[A]} = -k(t - t_0)$$

Notice above how the limits seem changed due to the presence of a  $-1$  on the left side. If  $t_0 = 0$ , then:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Which, again, looks like:

$$y = mx + b$$

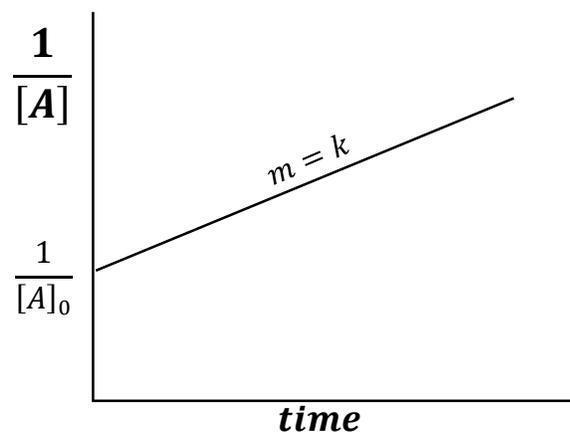
Where:

$$y = \frac{1}{[A]} \quad ; \quad m = k \quad ; \quad x = t \quad ; \quad b = \frac{1}{[A]_0}$$

Which means that if we plot  $\frac{1}{[A]}$  vs  $t$ , we get a line with a slope that is the rate constant itself (not its negative!).

What is the time it takes for half of the initial concentration to disappear (the half-life or  $t_{1/2}$ )?

$$\begin{aligned} @ t = t_{1/2} &\Rightarrow [A] = \frac{1}{2}[A]_0 \\ \frac{1}{[A]} &= \frac{1}{\frac{[A]_0}{2}} = \frac{2}{[A]_0} = kt + \frac{1}{[A]_0} \\ t_{1/2} &= \frac{1}{k[A]_0} \end{aligned}$$



Notice that, as it was the case with the half-life for the zeroth order reaction, the half-life for the second order reaction also depends (albeit in a different way) from the initial concentration of the reactant (as well as on the rate constant); for this reason, the concept of half-life for second (and zeroth order) reactions are far less useful. However, the inverse relation of the half-life on the initial concentration suggests the following:

1. With a high initial concentration of reactant, we have a higher probability of the two reactant molecules interacting to form product; consequently, the reactant will be consumed in a shorter period of time.
2. Since the half-life is longer when initial concentrations are low, species following a second order kinetics may exist for a longer period of time if their initial concentrations are small.

## FACTORS AFFECTING THE RATE OF A CHEMICAL REACTION

The various factors which influences the rate of reaction are

- (i) Concentration of reactants
- (ii) Temperature of reactants
- (iii) Nature of reacting substances
- (iv) Presence of catalyst
- (v) Exposure to radiations

### 1. Concentration of the reactants

Greater is the concentration of reactants, more will be the chances of collisions between the reacting particles, consequently, larger is the rate of the reaction. For gaseous reactants as the concentration is related to the pressure, therefore, greater is the pressure more will be number of molecules per unit volume and consequently, greater will be the rate of encounters between the molecules.

### 2. Effect of temperature on reaction rate

The rates of almost all reactions increase with the increase in temperature. In most of the cases the rate of the reaction becomes almost double for every 10° rise of temperature. This is also expressed in the terms of **Temperature co-efficient**. Which is the ratio of rate constant of the reaction at two temperatures differing by 10°. The two temperature generally selected are 298K and 308 K. Thus

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

### Explanation of the effect of temperature

According to collision theory of reaction rates.

Rate of a reaction =  $f \times z$

Where  $f$  = no. of effective collision

$z$  = frequency of collision

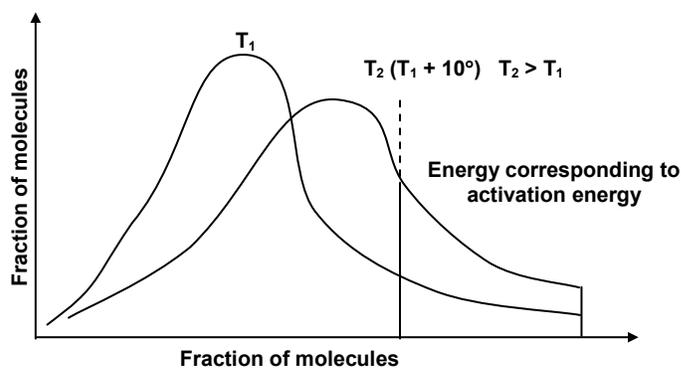
Thus, the increase in rate is due to either of the above factors is  $f$  or  $z$  or due to both of these.

It may be observed that the increase in the total number of collision per unit volume per unit time (collision frequency) is not so much responsible for the higher reaction rate as is the increase in the fraction of effective collisions. Let us, for eg, calculate the increase in collision frequency when temperature increases from 298 to 308 K. As we know that collision frequency is directly proportional to the square root of absolute temperature, therefore, the rate of collision frequencies at these temperatures follows as

$$\frac{Z_{308}}{Z_{298}} = \sqrt{\frac{308}{298}} = 1.016$$

From the above ratio it is clear that there is a insignificant increase in the collision frequency. Hence it can not explain the observed increase in the ratio of the reaction with increase in temperature.

Let us now consider the effect of increase in temperature on the number of effective collisions.



Energy distribution at different temperature

Now, as we know that the rise in temperature increases the kinetic energy of the molecules. ( $\therefore K.E \propto T$ ) therefore the energy distribution curve gets flattened and shifts towards higher energy region. A close reveals examination of the curves in the graph clearly reveals that the fraction of molecules possessing higher kinetic energy i.e. energy greater than threshold energy, as indicated by shaded portion becomes almost double and therefore, the rate of reaction almost doubles for  $10^\circ$  rise in temperature. Thus, increase in the rate of reaction with increase in temperature is mainly due to increase in no. of collisions which are energetically effective.

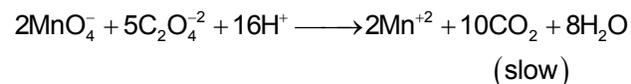
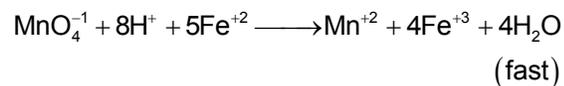
#### Note:

The reaction rate dependence on temperature can also explained by Vant Hoff's equation.

$$\text{Log} \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

#### Nature of reacting substance

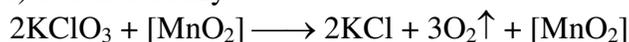
The nature of reacting substances affect, the rates significantly. For e.g. the oxidation of ferrous ( $\text{Fe}^{+2}$ ) by  $\text{KMnO}_4$  in acidic medium is practically instantaneous. On the other hand, oxidation of oxalate ions ( $\text{C}_2\text{O}_4^{-2}$ ) by  $\text{KMnO}_4$  in acidic medium is comparatively much slower.



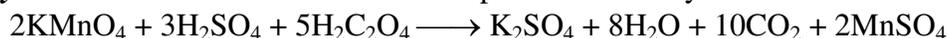
#### Catalyst

A catalyst is a substance, which increases the rate of a reaction without itself being consumed at the end of the reaction, and the phenomenon is called catalysis. There are some catalysts which decrease the rate of reaction and such catalysts are called negative catalyst. Obviously, the catalyst accelerating the rate will be positive catalyst. However, the term positive is seldom used and catalyst itself implies positive catalyst.

Catalyst are generally foreign substances but sometimes one of the product formed may act as a catalyst and such catalyst is called "*auto catalyst*" and the phenomenon is called auto catalysis. Thermal decomposition of  $\text{KClO}_3$  is found to be accelerated by the presence of  $\text{MnO}_2$ . Here  $\text{MnO}_2$  (foreign substance) acts as a catalyst.

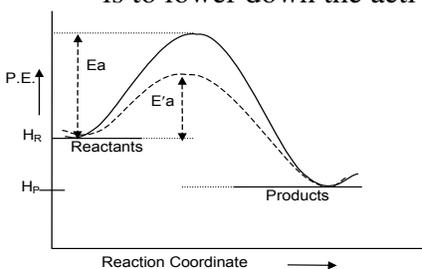


MnO<sub>2</sub> can be recovered in the same composition and mass at the end of the reaction. In the permanganate titration of oxalic acid in the presence of bench H<sub>2</sub>SO<sub>4</sub> (acid medium), it is found that the titration in the beginning there is slow discharge of the colour of permanganate solution but after sometime the discharge of the colour become faster. This is due to the formation of MnSO<sub>4</sub> during the reaction which acts as a catalyst for the same reaction. Thus, MnSO<sub>4</sub> is an “*auto catalyst*” for this reaction. This is an example of auto catalyst.



### General characteristics of catalyst

- A catalyst does not initiate the reaction. It simply fastens it.
- Only a small amount of catalyst can catalyse the reaction.
- A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant and hence  $\Delta G^0$ . It simply lowers the time needed to attain equilibrium. This means if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst also the reaction will go to 75% of completion before the attainment of equilibrium but the time needed for this will be less than 20 minutes.
- A catalyst drives the reaction through a different route for which energy barrier is of shortest height and hence  $E_a$  is of lower magnitude. That is, the function of the catalyst is to lower down the activation.



$E_a$  = Energy of activation in absence of catalyst.  
 $E'_a$  = Energy of activation in presence of catalyst.  
 $E_a - E'_a$  = lowering of activation energy by catalyst.

If  $k$  and  $k_{\text{cat}}$  be the rate constant of a reaction at a given temperature  $T$ , and  $E_a$  and  $E'_a$  are the activation energies of the reaction in absence and presence of catalyst, respectively, the

$$\frac{k_{\text{cat}}}{k} = \frac{Ae^{-E'_a/RT}}{Ae^{-E_a/RT}}$$

$$\frac{k_{\text{cat}}}{k} = e^{(E_a - E'_a)/RT}$$

Since  $E_a > E'_a$  so  $k_{\text{cat}} > k$ . the ratio  $\frac{k_{\text{cat}}}{k}$  gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature and this depends upon  $E_a - E'_a$ . Greater the value of  $E_a - E'_a$ , more number of times  $k_{\text{cat}}$  is greater than  $k$ .

The rate of reaction in the presence of catalyst at any temperature  $T_1$  may be made equal to the rate of reaction in absence of catalyst but for this sake we will have to raise the temperature. Let this temperature be  $T_2$  then

$$e^{-E'_a/RT_1} = e^{-E_a/RT_2}$$

or  $\frac{E'_a}{T_1} = \frac{E_a}{T_2}$

## Initial Rate Method

- In this method initial rate of reaction is determined by varying the concentration of one of the reactants while others are kept constant

- $R = k[A]^x[B]^y[C]^z$

- if  $[B]$  &  $[C] = \text{Constant}$

then for two different initial concentrations of A we have

$$R_{0_1} = k[A_0]_1^a$$

and

$$R_{0_2} = k[A_0]_2^a$$

$$\Rightarrow \frac{R_{0_1}}{R_{0_2}} = \left( \frac{[A_0]_1}{[A_0]_2} \right)^n$$

## Graphical Method

- This method can be used when there is only one reactant.
- If the plot of  $\log [A]$  vs  $t$  is a straight line, the reaction follows first-order .
- If the plot of  $1/[A]$  vs  $t$  is a straight line, the reaction follows second order.
- If the plot of  $1/[A]^2$  is a straight line , the reaction follows third order.
- Generally, for a reaction of  $n$ th order, a graph of  $1/[A]^{n-1}$  vs  $t$  must be a straight line.
- Here  $[A]$  is the concentration of reactant at any given time of the reaction (other  $t = 0$ ).  $[A] = (a-x)$  where  $a$  is the initial concentration and  $x$  is the extent of reaction at time  $t$ .

Refer to the following video for Determination of Order of a Reaction

## Half Life Method

- This method is used only when the rate law involved by only one concentration term.

$$t_{(1/2)} \propto a^{1-n}$$

$$t_{(1/2)} = k' 1/a^{n-1}$$

$$\log t_{(1/2)} = \log k' + (1-n)a$$

- Graph of  $\log t_{1/2}$  vs  $\log a$ , gives a straight line with slope  $(1-n)$  , where 'n' is the order of the reaction.
- Determining the slope we can find the order n.
- If half life at different concentrations is given then.

$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}}$$

and

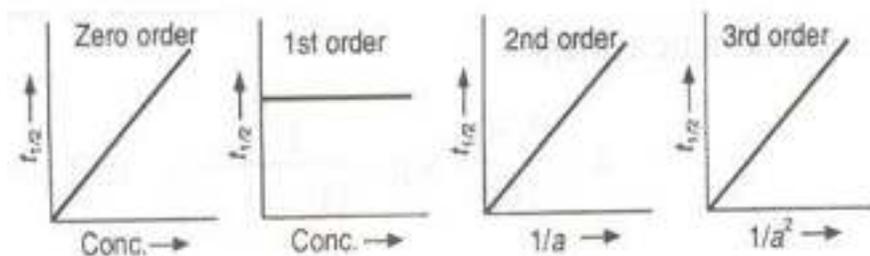
$$(t_{1/2})_2 \propto \frac{1}{a_2^{n-1}}$$

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

Taking logarithm and rearranging

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

- Plots of half-lives concentration ( $t_{1/2} \propto a^{1-n}$ ):



- This relation can be used to determine order of reaction 'n'

## Van't Hoff Differential Method

- As we know that, the rate of a reaction varies as the nth power of the concentration of the reactant where 'n' is the order of the reaction.
- Thus, for two different initial concentrations  $C_1$  and  $C_2$ , equations can be written in the form

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

and

$$\log\left(\frac{dC_2}{dt}\right) = \log k + n \log C_2 \quad \dots(ii)$$

Taking logarithms,

Subtracting Eq. (ii) from (i),

$$\log\left(\frac{dC_1}{dt}\right) - \log\left(\frac{dC_2}{dt}\right) = n(\log C_1 - \log C_2)$$

or

$$n = \frac{[\log(-dC_1/dt) - \log(-dC_2/dt)]}{[\log C_1 - \log C_2]} \quad \dots(iii)$$

- $-dc_1/dt$  and  $-dc_2/dt$  are determined from concentration vs. time graphs and the value of 'n' can be determined.

## Solved Example

Question:

From the following data show that the decomposition of hydrogen peroxide in aqueous solution is a first - order reaction. What is the value of the rate constant?

Time in minutes	0	10	20	30	40
Volume V in ml	25.0	20.0	15.7	12.5	9.6

where V is the number of ml of potassium permanganate required to decompose a definite volume of hydrogen peroxide solution.

**Solution:**

The equation for a first order reaction is

The volume of  $\text{KMnO}_4$  used, evidently corresponds to the undecomposed hydrogen peroxide.

Hence the volume of  $\text{KMnO}_4$  used, at zero time corresponds to the initial concentration a and the volume used after time t, corresponds to (a - x) at that time. Inserting these values in the above equation, we get

when t = 10 min.  $k_1 = 2.23/10 \log (25/20) = 0.022318 \text{ min}^{-1} = 0.000372 \text{ s}^{-1}$

when t = 20 min.  $k_1 = 2.23/20 \log (25/12) = 0.023265 \text{ min}^{-1} = 0.0003871 \text{ s}^{-1}$

when t = 30 min.  $k_1 = 2.23/30 \log (25/12.5) = 0.02311 \text{ min}^{-1} = 0.000385 \text{ s}^{-1}$

when t = 40 min.  $k_1 = 2.23/40 \log (25/19.6) = 0.023932 \text{ min}^{-1} = 0.0003983 \text{ s}^{-1}$

The constancy of k, shows that the decomposition of  $\text{H}_2\text{O}_2$  in aqueous solution is a **first order** reaction.

The average value of the rate constant is **0.0003879 s<sup>-1</sup>**.

## # Test Your Knowledge

**Question 1:**

In which of the following methods initial rate of reaction is determined by varying the concentration of one of the reactants while others are kept constant

- a. Graphical method
- b. Initial rate method
- c. Half life method
- d. Van'thoff method

**Question 2:**

If the plot of  $1/[\text{A}]^2$  is a straight line , the reaction follows

- a. zero order
- b. first order
- c. second order
- d. third order

**Question 3:**

$\log t(1/2) =$

- a.  $\log k' - (1-n)a$
- b.  $\log k' + (1-n)a$

c.  $-\log k' + (1-n)a$

d.  $\log k' / (1-n)a$

**Question 4:**

Which of the following methods is used only when the rate law involved by only one concentration term?

a. Graphical method

b. Initial rate method

c. Half life method

d. Van'thoff method

**Answer Key:**

Q.1	Q.2	Q.3	Q.4
b	d	b	c

**Related Resources**

Derivation of rate equations for second order  
(two reactants): The general equation for  
such reactions may be written as



Suppose the initial concentration of A =  $a \text{ mol l}^{-1}$

& the initial concentration of B =  $b \text{ mol l}^{-1}$ .

Let  $x \text{ mol l}^{-1}$  of A reacts in time 't', then  
the amount of B that would react in  
the same time would also be  $x \text{ mol l}^{-1}$

At time t, concentration =  $(a-x) \text{ mol l}^{-1}$   
of A

& concentration of B =  $(b-x) \text{ mol l}^{-1}$ .

Applying law of mass action, we get

$$R = k[A][B]$$

$$\Rightarrow R = k(a-x)(b-x)$$

$$\Rightarrow \frac{dx}{dt} = k(a-x)(b-x) \quad \text{--- (1)}$$

where k is the rate constant. Eq.

(1) may be rewritten as

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

using partial fractions, L.H.S  
may be written as

$$\frac{1}{(a-b)} \left\{ \frac{1}{(b-x)} - \frac{1}{(a-x)} \right\} dx$$

Initial  
concent-  
ration  
means  
concent-  
ration  
at  $t=0$

R when  
expressed  
in products  
 $= \frac{dx}{dt}$

& rate at  
any time  
t would  
be proport  
ional to  
concent.

of A & B  
left behind  
at time 't'

Hence  $\frac{1}{(a-b)} \left\{ \frac{1}{(b-x)} - \frac{1}{(a-x)} \right\} dx = k \cdot dt \quad (2)$

Integrating equation (2) we get

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

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

where I is constant of integration

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

$$\Rightarrow \frac{1}{(a-b)} \left[ \ln \frac{(a-x)}{(b-x)} \right] = kt + I \quad (3)$$

at  $t=0$ ,  $x=0$  i.e. at initial time (at start of reaction; concentration of product is zero).

$$\Rightarrow \frac{1}{(a-b)} \left[ \ln \frac{a}{b} \right] = k \times 0 + I$$

$$\Rightarrow I = \frac{1}{(a-b)} \cdot \ln \left( \frac{a}{b} \right)$$

Putting the value of I in (3)

we get

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

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

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

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

$$\left. \begin{aligned} \int \frac{1}{x} \cdot dx &= \ln x \\ \int \frac{1}{(a-x)} \cdot dx &= \ln(a-x) \\ &\times \text{coefficient} \\ &\text{of } x \\ \text{coefficient} \\ \text{of } x &= -1 \\ &= -\ln(a-x) \\ \ln m - \ln n &= \ln \frac{m}{n} \end{aligned} \right\}$$

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

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

$$\text{or } k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad \text{--- (4)}$$

The above =n is the equation of rate constant for a second order reaction which involves two different reactants & whose different amounts reacts at time  $t = 0$ .

Equation (04) gets modified if one of the reactant is present in excess. Suppose reactant A is present in excess then "a" will be very large as compared to b so that  $(a - b) = a$  and  $(a - x) = a$

Substituting the values of  $(a - b)$  and  $(a - x)$  in equation (04) we get:

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

or  $k = \frac{2.303}{ta} \log \frac{b}{(b-x)}$

or  $k \times a = \frac{2.303}{t} \log \frac{b}{(b-x)} \quad \dots\dots\dots (05)$

As a is taken in excess therefore it remains almost constant therefore equation (05) can be written as :

$$k' = \frac{2.303}{t} \log \frac{b}{(b-x)} \quad \dots\dots\dots (06)$$

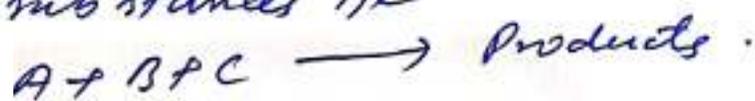
where  $k' = k \times a = \text{constant}$

Equation (06) is an equation of rate constant for the first order reaction. The bimolecular reactions in which one of the reactant is taken in excess are called pseudounimolecular reactions. These reactions follow first order kinetics.

## Derivation of Integrated Rate Equation for Third Order Reaction:

"Reactions of Third order": A reaction is said to be of third order, if the rate of the reaction depends upon three concentration terms. For a third order reaction, three possibilities arise;

i) Reactions involving three molecules of different substances i.e.



ii) Reactions involving two molecules of one substance and one molecule of another substance i.e.



iii) Reactions involving all the three molecules of the same substance i.e.



But as per syllabus, we have to study the kinetics of third order reaction involving one type of reactant.



Let  $a \text{ mol l}^{-1}$  be the initial concentration of A at  $t = 0$ , and let  $x \text{ mol l}^{-1}$  be the concentration of product formed at time  $t = t$ , then the concentration of A left behind at  $t = t$  is  $(a-x) \text{ mol l}^{-1}$ .

$$\text{then } \frac{dx}{dt} \propto [A]^3 \text{ i.e. } \frac{dx}{dt} \propto (a-x)^3$$

$$\Rightarrow \frac{dx}{dt} = k(a-x)^3 \Rightarrow \frac{dx}{(a-x)^3} = k \cdot dt \quad (1)$$

where  $k$  is the rate constant for the third order reaction

Integration of Equation (1) gives

$$\int \frac{dx}{(a-x)^3} = k \int dt + I$$

where  $I$  is the integration constant

$$\Rightarrow \int (a-x)^{-3} \cdot dx = kt + I$$

$$\Rightarrow \frac{(a-x)^{-3+1}}{-3+1} \cdot \text{coefficient of } x = kt + I$$

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

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

$$\left| \int x^n = \frac{x^{n+1}}{n+1} \right.$$

To determine the value of  $I$ , we use boundary conditions i.e. at  $t=0$ ;  $x=0$

$$\Rightarrow \frac{1}{2(a-0)^2} = k \times 0 + I$$

$$\Rightarrow \frac{1}{2a^2} = I$$

Substituting the value of  $I$  in eq (2) we get

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

$$\Rightarrow kt = \frac{1}{2(a-x)^2} - \frac{1}{2a^2} \quad \text{--- (3)}$$

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

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

$$\Rightarrow kt = \frac{1}{2} \left[ \frac{a^2 - \{a^2 - 2ax + x^2\}}{a^2(a-x)^2} \right]$$

$$\Rightarrow kt = \frac{1}{2} \left[ \frac{a^2 - a^2 + 2ax - x^2}{a^2(a-x)^2} \right]$$

$$\Rightarrow kt = \frac{1}{2} \left[ \frac{2ax - x^2}{a^2(a-x)^2} \right]$$

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

$$k = \frac{1}{2t} \left[ \frac{x(2a-x)}{a^2(a-x)^2} \right] \text{ --- (4)}$$

Equation 4 represents the rate equation of third Order Reactions involving three molecules of a single reactant.

Alternatively, Equation 4 may be written in the form:

If the initial concentration of A is  $C_0$  at  $t = 0$  and at time  $t$  the concentration of A is  $C_t$

$$\text{i.e } a = C_0 \text{ ----- (5)}$$

$$(a-x) = C_t \text{ ----- (6)}$$

$$\text{therefore, } (a-x) - a = C_t - C_0$$

$$\text{or } -x = C_t - C_0$$

$$\text{or } x = C_0 - C_t \text{ ----- (7)}$$

$$(2a-x) = 2C_0 - (C_0 - C_t) = C_0 + C_t \text{ ----- (8)}$$

Putting the values of  $a$ ,  $(a-x)$ ,  $x$  and  $(2a-x)$  from equations (5), (6), (7) and (8) into equation (4), we get:

$$k = \frac{1}{2t} \left[ \frac{x(2a-x)}{a^2(a-x)^2} \right] \text{ --- (4)}$$

$$k = \frac{1}{2t} \left[ \frac{(C_0 - C_t)(C_0 + C_t)}{C_0^2 C_t^2} \right]$$

$$k = \frac{1}{2t} \left[ \frac{C_0^2 - C_t^2}{C_0^2 C_t^2} \right]$$

$$k = \frac{1}{2t} \left[ \frac{1}{C_t^2} - \frac{1}{C_0^2} \right] \text{ ----- (9)}$$

# Kinetics of Photochemical decomposition of Hydrogen Iodide (HI):



Photodecomposition of hydrogen iodide occurs on exposure to radiation of wavelength range 207-282 nm. The mechanism for the reaction proposed by Warburg is as follows:

Primary step (Photo-activation):



Secondary steps:



Overall reaction:-



The rate of decomposition of HI is given as

$$-\frac{d[\text{HI}]}{dt} = k_1 I_a + k_2 [\text{H}\cdot] [\text{HI}] \quad \dots\dots (1) \quad (\text{where } I_a = \text{Intensity of the absorbed light, Rate } \propto I_a)$$

Applying steady state approximation to  $[\text{H}\cdot]$ , we have

$$\frac{d[\text{H}\cdot]}{dt} = k_1 I_a - k_2 [\text{H}\cdot] [\text{HI}] = 0 \quad \dots\dots (2)$$

$$\therefore k_2 [\text{H}\cdot] [\text{HI}] = k_1 I_a \quad \dots\dots (3)$$

Substituting from equation (3) into equation (1), we get

$$-\frac{d[\text{HI}]}{dt} = 2k_1 I_a$$

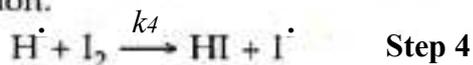
Quantum yield of this reaction is given as

$$\begin{aligned} \phi &= \frac{\text{Rate of disappearance of HI}}{\text{Rate of absorption of light}} \\ &= -\frac{d[\text{HI}]/dt}{k_1 I_a} \quad \dots\dots (4) \end{aligned}$$

Putting the values, we get

$$\phi = \frac{2k_1 I_a}{k_1 I_a} = 2 \quad \dots\dots (5)$$

Thus the quantum yield is 2. The quantum yield decreases as the reaction proceeds. This is due to the secondary reaction.



which gains speed as the reaction proceeds. This can be explained kinetically if step 4 is also included into the mechanism of photodissociation of HI. Then the steady state approximation for  $[\text{H}\cdot]$  gives.

$$\frac{d[\text{H}\cdot]}{dt} = k_1 I_a - k_2 [\text{H}\cdot] [\text{HI}] - k_4 [\text{H}\cdot] [\text{I}_2] = 0 \quad \dots(6)$$

$$\therefore [\text{H}\cdot] = \frac{k_1 I_a}{k_2 [\text{HI}] + k_4 [\text{I}_2]} \quad \dots(7)$$

Substituting value of [H] from equation (7) into equation (1), we get

$$\begin{aligned} -\frac{d[\text{HI}]}{dt} &= k_1 I_a + k_2 [\text{HI}] \frac{k_1 I_a}{k_2 [\text{HI}] + k_4 [\text{I}_2]} \\ &= k_1 I_a \left[ 1 + \frac{1}{1 + (k_4 [\text{I}_2] / k_2 [\text{HI}])} \right] \\ -\frac{d[\text{HI}]}{I_a dt} &= k_1 + \frac{k_1}{1 + (k_4 [\text{I}_2] / k_2 [\text{HI}])} \end{aligned} \quad \dots(8)$$

Equation (8) shows that as the reaction proceeds  $[\text{I}_2]$  increases, therefore, the quantum yield decreases.

Photochemical decomposition HBr is also similar to that of HI and quantum yield is also 2.

## Effect of temperature on reaction rate:

The rates of almost all reactions increase with the increase in temperature. In most of the cases the rate of the reaction becomes almost double for every 10° rise of temperature. This is also expressed in the terms of **Temperature co-efficient**. Which is the ratio of rate constant of the reaction at two temperatures differing by 10°. The two temperature generally selected are 298K and 308 K. Thus

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

### Explanation of the effect of temperature

According to collision theory of reaction rates.

Rate of a reaction =  $f \times z$       where  $f$  = no. of effective collision,  $z$  = frequency of collision.

Thus, the increase in rate is due to either of the above factors  $f$  or  $z$  or due to both of these.

It may be observed that the increase in the total number of collision per unit volume per unit time (collision frequency) is not so much responsible for the higher reaction rate as is the increase in the fraction of effective collisions. Let us, for eg, calculate the increase in collision frequency when temperature increases from 298 to 308 K. As we know that collision frequency is directly proportional to the square root of absolute temperature, therefore, the rate of collision frequencies at these temperatures follows as:

$$\frac{Z_{308}}{Z_{298}} = \sqrt{\frac{308}{298}} = 1.016$$

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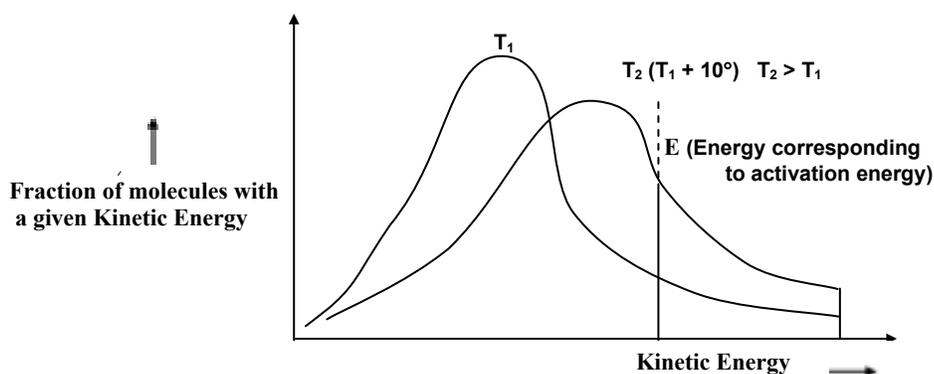


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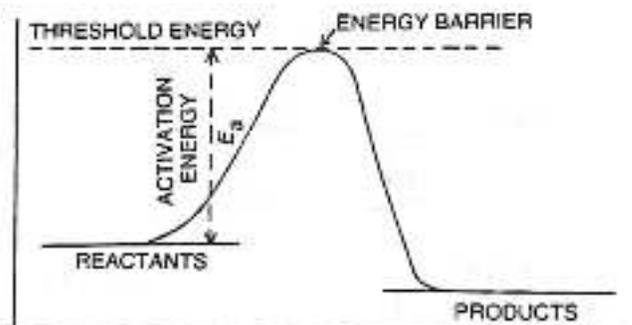
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**Note:**

The reaction rate dependence on temperature is explained by Arrhenius equation.

$$\text{Log} \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

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An exothermic reaction.

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## EFFECT OF TEMPERATURE ON RATE OF REACTION-ARRHENIUS EQUATION

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Taking logarithms on both sides of equation (1), we get

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If  $k_1$  and  $k_2$  are the rate constants for the reaction at two different temperatures  $T_1$  and  $T_2$  respectively.

$$\text{Then,} \quad \ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \dots(3)$$

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$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \quad \dots(5)$$

Thus, knowing the values of rate constants  $k_1$  and  $k_2$  at two different temperatures  $T_1$  and  $T_2$ , the value of activation energy  $E_a$  can be calculated. Equation (5) can also be used

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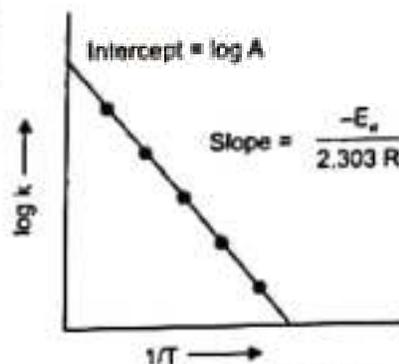


Fig. 1. Plot of  $\log k$  Vs  $1/T$  to calculate  $E_a$ .

### Example:

**Example 1.** The rate constant of reaction is  $2.46 \times 10^{-5} \text{ sec}^{-1}$  at 273 K and  $1.63 \times 10^{-5} \text{ sec}^{-1}$  at 303 K. Calculate the energy of activation of the reaction.

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$$T_1 = 273 \text{ K}, T_2 = 303 \text{ K}$$

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We know,

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

Substituting the value in the above equation,

$$\log \frac{1.63 \times 10^{-5}}{2.46 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.314} \left[ \frac{303 - 273}{303 \times 273} \right]$$

$$E_a = \frac{2.303 \times 8.314 \times 273 \times 303}{30} \log \frac{1.63 \times 10^{-5}}{2.46 \times 10^{-5}}$$

$$= 96510 \text{ J mol}^{-1}$$

$$= 96.51 \text{ kJ mol}^{-1}$$

## Effect of temperature on reaction rate:

The rates of almost all reactions increase with the increase in temperature. In most of the cases the rate of the reaction becomes almost double for every  $10^\circ$  rise of temperature. This is also expressed in the terms of **Temperature co-efficient**. Which is the ratio of rate constant of the reaction at two temperatures differing by  $10^\circ$ . The two temperature generally selected are 298K and 308 K. Thus

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

### Explanation of the effect of temperature

According to collision theory of reaction rates.

Rate of a reaction =  $f \times z$       where  $f$  = no. of effective collision,  $z$  = frequency of collision.

Thus, the increase in rate is due to either of the above factors  $f$  or  $z$  or due to both of these.

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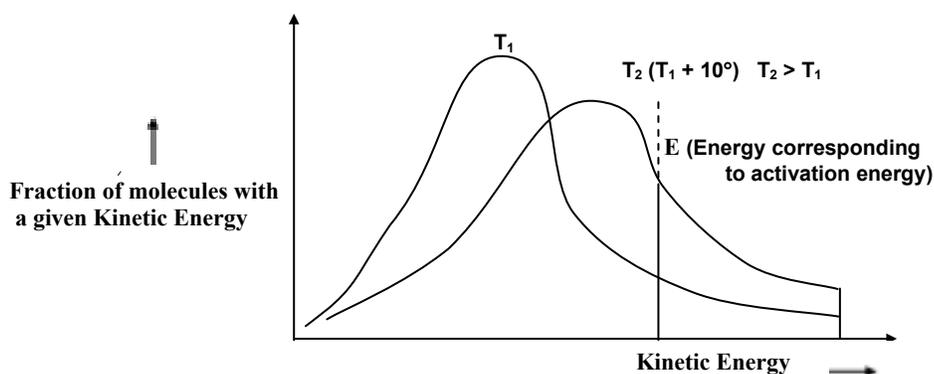


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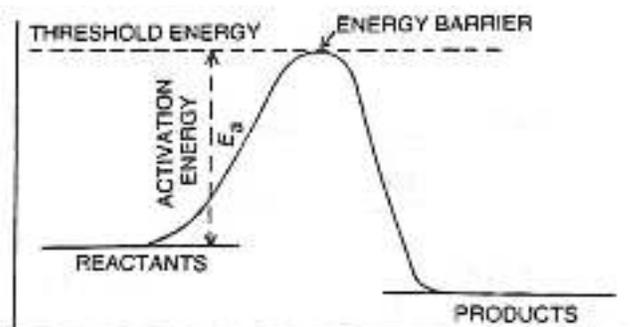
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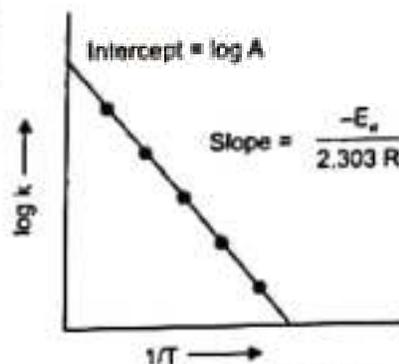


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