Chemical Kinetics

1. CLASSIFICATION OF REACTIONS : [IN TERMS OF RATES]

(i) There are certain reactions which are too slow e.g. rusting of iron, weathering of rocks.

(ii) Instantaneous reactions i.e. too fast e.g. Detonation of explosives, acid-base neutralization, precipitation of AgCl by NaCl and $AgNO_3$.

(iii) Neither too fast nor too slow e.g. combination of H_2 and Cl_2 in presence of light, hydrolysis of ethyl acetate catalysed by acid, decomposition of azomethane

2. RATE OF REACTION

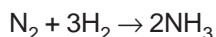The change in concentration of either reactant or product per unit time.

Formula : $v = \pm \dfrac{dc}{dt}$

dc–change in concentration in a small interval dt.

[–] sign is used when we refer to reactant concentration.

[+] sign is used when we refer to product concentration.

Example :

$$N_2 + 3H_2 \rightarrow 2NH_3$$

(i) Rate of formation of ammonia $= + \dfrac{d[NH_3]}{dt}$

(ii) Rate of disappearance of nitrogen $= - \dfrac{d[N_2]}{dt}$

(iii) Rate of disappearance of hydrogen $= - \dfrac{d[H_2]}{dt}$

$$\text{Rate} = + \frac{1}{2}\frac{d[NH_3]}{dt} = - \frac{d[N_2]}{dt} = - \frac{1}{3}\frac{d[H_2]}{dt}$$

$$\text{Thus, Rate} = - \frac{d[N_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$$

or rate of formation of ammonia = Twice the rate of disappearance of nitrogen

i.e. $\dfrac{d[NH_3]}{dt} = \dfrac{2}{3}\left[- \dfrac{d[H_2]}{dt}\right]$
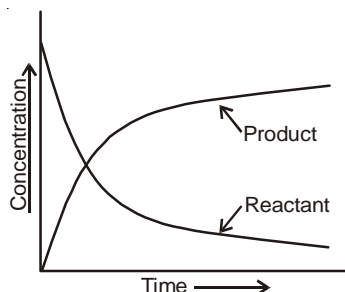
3. AVERAGE VELOCITY OF REACTION

Change in the concentration of reactants or products per unit time is called average reaction velocity. If dc is the change in the concentration of reactants and product in dt time, then

Average velocity $= \pm \dfrac{dc}{dt}$

or   Average velocity = $\dfrac{(-)\text{Change in the concentration of reac}\tan\text{ts}}{\text{Time}}$

$\dfrac{(+)\text{Change in the concentration of products}}{\text{Time}}$

Unit of average velocity = $\dfrac{\text{Unit of concentration}}{\text{Unit of time}}$ = $\dfrac{\text{gram mole}}{\text{Litre}\times\text{Second}}$ = gram mole litre^{-1} second^{-1}

4.   INSTANTANEOUS RATE OF THE REACTION

The rate of reaction determined at specified concentration or specified time is called **instantaneous rate**.

The instantaneous rate of the reaction can be determined by measuring concentration of reactant or product after fixed intervals of time and plotting concentration versus time.
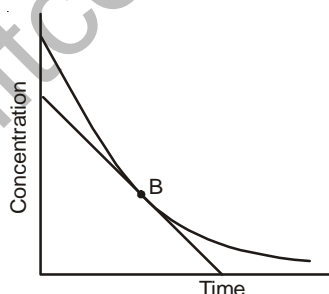
The instantaneous rate at any time is determined by the slope of the tangent at a point on the time-concentration curve corresponding to the specified time. The slope of the tangent at a point is the limiting value of $\dfrac{\Delta c}{\Delta t}$.

$$\lim_{\Delta t\to 0}\frac{\Delta c}{\Delta t} = \frac{dc}{dt}$$

In terms of the concentration of reactant, the rate of the reaction = $- \dfrac{dc}{dt}$

The –sign indicates that the concentration of reactant decreases with time.

In terms of the concentration of product, the rate of the reaction = $+ \dfrac{dc}{dt}$

The +sign indicates that the concentration of product increases with time. In the reaction if at a time t the concentration of product is x and at time t + dt, the concentration becomes x + dx then the reaction rate = $\dfrac{dx}{dt}$

For example the rate of reaction : $N_2 + 3H_2 \quad\quad 2NH_3$

in terms of the concentrations of N_2, H_2 and NH_3 can be expressed as –

$$-\frac{d[N_2]}{dt}, \quad -\frac{1}{3}\frac{d[H_2]}{dt}, \quad +\frac{1}{2}\frac{d[NH_3]}{dt}$$

Ex.1 What should be (a) the rate of disappearance of B and (b) the rate of formation of C, if the rate of disappearance of A for the reaction $A + B \rightarrow 2C$ is 10^{-2} mole/litre/second at a particular temperature ?

Sol. (a) Rate of disappearance of A = Rate of disappearance of B

= 10^{-2} mole/litre/second **Ans.**

(b) Rate of disappearance of A = $\dfrac{1}{2}$ × Rate of formation of C

Rate of formation of C = 2 × Rate of disappearance of A

= 2 × 10^{-2} mole/litre/second **Ans.**

Ex.2 A gaseous reaction : $2A(g) + B(g) \rightarrow 2C(g)$,

Show a decrease in pressure from 120 mm to 100 mm in 10 minutes. The rate of appearance of C is

[1] 2 mm/min [2] 4 mm/min [3] 10 mm/min [4] 12 mm/min. **Ans. [2]**

Sol. Suppose 2p is the pressure of C after 10 min.

Fall in pressure of A = 2p ; Fall in pressure of B = p

Total fall in pressure = (2p + p) – 2p = p = 20 mm

Pressure of C = 2p = 40 mm

Rate of appearance of C = 40/10 = 4 mm/min

Ex.3 The term – $\dfrac{dx}{dt}$ in the rate expression refers to the

[1] concentration of the reactants [2] increase in concentration of the reactants

[3] instantaneous rate of the reaction [4] average rate of the reaction **Ans. [3]**

Sol. It is expression for instantaneous rate

Ex.4 Which of the following expression can be used to describe the instantaneous rate of the reaction ?

$$2A + B \rightarrow A_2B$$

[1] $-\dfrac{1}{2}\dfrac{d[A]}{dt}$ [2] $-\dfrac{d[A]}{dt}$ [3] $\dfrac{1}{2}\dfrac{d[A_2B]}{dt}$ [4] $-\dfrac{1}{2}\dfrac{d[A]}{dt}\cdot\dfrac{d[B]}{dt}$ **Ans. [1]**

Sol. The instantaneous rate of the reaction can be expressed by any of the following expressions

$$-\frac{1}{2}\frac{d[A]}{dt} \text{ or } -\frac{d[B]}{dt} \quad\quad \text{or} \quad\quad \frac{d[A_2B]}{dt}$$

Ex.5 Which of the following will react at the highest rate ?

[1] 1 mol of A and 1 mol of B in a 1 L vessel [2] 2 mol of A and 2 mol of B in a 2 L vessel

[3] 3 mol of A and 3 mol of B in a 3 vessel [4] All would react at the same rate **Ans. [4]**

Sol. Since all have same conc. of reactants, all would react at same rate.

5. FACTORS AFFECTING THE RATE OF REACTION

(i) **Concentration :** Law of mass action enunciates that greater is the conc. of the reactants, the more rapidly the reaction proceeds.

(ii) **Pressure (Gaseous reaction) :** On increasing the pressure, volume decreases and conc. increases and hence the rate.

(iii) **Temperature :** It is generally observed that rise in temperature increases the reaction rate. It has been found that rate is either doubled or tripled for every 10^0 rise in temperature. Temp. coefficient of reaction rate

$$\frac{k_{T+10}}{k_T} \approx 2 \text{ or } 3$$

Where$_{T+10}$ and k_T are rate constants at two temp. differing by 10^0.

(iv) **Nature of the reactants :** The rate depends upon specific bonds involved and hence on the nature of reactants.

(v) **Surface area of the reactants :** In heterogeneous reactions, more powered is the form of reactants, more is the velocity. [as more active centres are provided]

(vi) **Catalyst :** Affects the rate immensely.

Ex.6 For the reaction : $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Given : $\dfrac{d[NO]}{dt} = 3.6 \times 10^{-3}$ mol l^{-1} s^{-1}

Calculate : (i) rate of disappearance of ammonia   (ii) rate of formation of water

Sol. From the eqn. it is clear that

Rate $= -\dfrac{1}{4}\dfrac{d[NH_3]}{dt} = \dfrac{1}{4}\dfrac{d[NO]}{dt} = \dfrac{1}{6}\dfrac{d[H_2O]}{dt}$ Thus : $-\dfrac{1}{4}\dfrac{d[NH_3]}{dt} = \dfrac{1}{4}\dfrac{d[NO_2]}{dt}$

or $-\dfrac{d[NH_3]}{dt} = \dfrac{d[NO_2]}{dt} = 3.6 \times 10^{-3}$ mol l^{-1} s^{-1} Also $\dfrac{1}{4} \cdot \dfrac{d[NO]}{dt} = \dfrac{1}{6} \cdot \dfrac{d[H_2O]}{dt}$

$\dfrac{3}{2} \cdot \dfrac{d[NO]}{dt} = \dfrac{d[H_2O]}{dt}$

$\dfrac{3}{2} \times 3.6 \times 10^{-3} = \dfrac{d[H_2O]}{dt}$

$5.4 \times 10^{-3} = \dfrac{d[H_2O]}{dt}$

6. SPECIFIC REACTION RATE

Applying law of mass action to the reaction :

$$m_1A + m_2B \rightarrow n_1C + n_2D$$
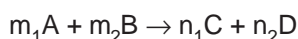
$$\text{Rate} \propto [A]^{m_1} [B]^{m_2}$$

$$\text{or } v = k [A]^{m_1} [B]^{m_2}$$

This equation is known as rate law. Where k is the proportionality constant and is called

       (i) Velocity constant

or   (ii) Velocity coefficient

or   (iii) Specific reaction rate.

On putting [A] = [B] = 1, where have : v = k

Hence specific reaction rate is the rate of the reaction when the concentration of each reactant is taken as unit.

6.1 Unit of Specific Reaction Rate

$v = k\ [A]^{m_1} . [B]^{m_2}$

$\dfrac{conc.}{time} = k\ [conc.]^{m_1+m_2}$

$[conc.]^{[1-(m_1+m_2)]} \times [time]^{-1} = k$

or $k = \left[\dfrac{mole}{litre}\right]^{[1-(m_1+m_2)]} . [second]^{-1}$

7. DISTINCTION BETWEEN RATE AND RATE CONSTANT

Rate of a reaction :

Its units are always mole litre^{-1} time^{-1}.

Rate constant :

Its unit depends upon the order of reaction.

8. RATE LAW

(a) It may also not depend upon the concentration of each reactant or product of the reaction.

Suppose, $mA + nB \rightarrow$ Product

$$\boxed{R \propto [A]^m\ [B]^n}$$

(b) Rate of a chemical reaction is directly proportional to the product of the concentration of reactants.

(c) The rate law represents the experimentally observed rate of reaction which depends upon the slowest step of the reaction.

(d) Rate law cannot be deduce from the equation for a given reaction. It can be find by experiments only.

(e) The rate law may not bear a simple relationship for the stoichiometric equation.

(f) It may not depend upon the concentration of species, which do not appear in the equation for the over all reaction.

Ex.7 In the reaction, A + 2B → 6C + 2D, if the initial rate $-\dfrac{d[A]}{dt}$ at t = 0 is 2.6 × 10^{-2} m sec^{-1}, what will be the value

of $-\dfrac{d[B]}{dt}$ at t = 0 ?

[1] 8.5 × 10^{-2} m sec^{-1} [2] 2.5 × 10^{-2} m sec^{-1} [3] 5.2 × 10^{-2} m sec^{-1} [4] 7.5 × 10^{-2} m sec^{-1} **Ans. [3]**

Sol. From the reaction it is evident that when a mole of A is reacting, 2 moles of B must react. Hence the decrease in the concentration of B must be twice that of A

$$\therefore \qquad -\dfrac{d[B]}{dt} = 2\left[-\dfrac{d[A]}{dt}\right]$$

$$= 2 \times 2.6 \times 10^{-2}$$

$$= 5.2 \times 10^{-2}\ sec^{-1}$$

Ex.8 The dimensions of rate constant of a second order reaction involves :

[1] time and concentration

[2] neither time nor concentration

[3] time only

[4] concentration only

Ans. [1]

Sol. $k = \dfrac{Rate}{[A]^2} = \dfrac{molL^{-1}s^{-1}}{(moll^{-1})^2} = \dfrac{s^{-1}}{mol\,L^{-1}} = (mol\,L^{-1})^{-1}s^{-1}$

Ex.9 The rate constant of a reaction has same units as the rate of reaction. The reaction is of

[1] zero order   [2] first order   [3] second order   [4] none of these   **Ans. [1]**

Sol. For a zero order reaction, $r = k[A]^0$. Thus the units of k are the same as that of rate of reaction.

Ex.10 The rate constant of nth order has units

[1] $litre^{1-n}mol^{1-n}sec^{-1}$ [2] $mol^{1-n}litre^{1-n}sec$ [3] $mol^{1-n^2}litre^{n^2}sec^{-1}$ [4] $mol^{1-n}litre^{n-1}sec^{-1}$ **Ans. [4]**

Sol. For an nth order reaction : rate = k [conc.]^n

$k = \dfrac{rate}{[conc.]^n}$

Units of $k = \dfrac{mol\,L^{-1}\,s^{-1}}{(mol\,L^{-1})^n} = mol^{1-n}\,L^{n-1}\,s^{-1}$

Ex.11 On which of the following factors, the rate constant does not depend ?

[1] Temperature   [2] Concentration   [3] Presence of catalyst   [4] Nature of reactants   **Ans. [2]**

Ans. Rate constant is independent of the conc. of the reactants.

9. ORDER OF REACTION

The order of a reaction may be defined as the sum of the powers to which conc. terms must be raised in an experimentally determined differential rate equation :

For the reaction : $aA + bB \rightarrow$ product

Experimental rate equation : $v = k[A]^p[B]^q$

order with respect to A = p

order with respect to B = q
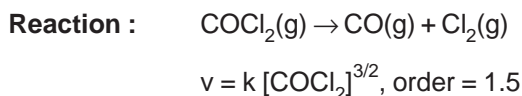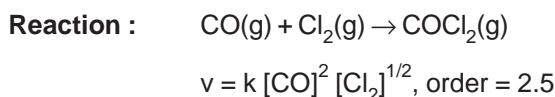
Total order = p + q

p and q may be equal to a and b.

Note : Order may be zero, fractional, integer or negative.

Example :

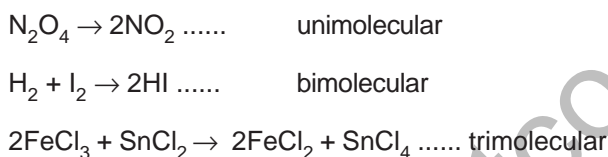| Reaction	Experimental rate equation	order
$H_2 + Cl_2 \rightarrow 2HCl$	$v = k$	zero
$H_2 + Br_2 \rightarrow 2HBr$	$v = k[H_2][Br_2]^{1/2}$	one and half
$H_2 + I_2 \rightarrow 2HI$	$v = k[H_2][I_2]$	two

Examples of fractional order reaction

Reaction : $CO(g) + Cl_2(g) \rightarrow COCl_2(g)$

$v = k\,[CO]^2\,[Cl_2]^{1/2}$, order = 2.5

Reaction : $COCl_2(g) \rightarrow CO(g) + Cl_2(g)$

$v = k\,[COCl_2]^{3/2}$, order = 1.5

10. MOLECULARITY OF A REACTION

''Molecularity is defined as the number of molecules, atoms, or radicals that must collide simultaneously in order for the reaction to take place.'' It is always a whole number and cannot be negative.

In the elementary processes :

Participating species		**Molecularity**
One species participates	.....	unimolecular, 1
Two species participates	.....	bimolecular, 2
Three species participates	.....	trimolecular, 3

Example –

$N_2O_4 \rightarrow 2NO_2$ ...... unimolecular

$H_2 + I_2 \rightarrow 2HI$ ...... bimolecular

$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$ ...... trimolecular

Note : If the reaction takes place in two or more steps then the overall molecularity of the reaction is monitored by the slow or rate determining step.

11. DIFFERENCE BETWEEN MOLECULARITY AND ORDER OF REACTION

Molecularity	**Order of Reaction**
1. Molecularity can neither be zero nor fractional	1. Order of a reaction can be zero, fractional or integer
2. It is independent of pressure and temperature	2. It depends upon pressure and temperature
3. It is a assigned for each step of mechanism separately	3. It is assigned for overall reaction.
4. It is the number of molecules of reactants concentration terms taking part in elementary step of a reaction.	4. It is sum of power raised or the rate expression.
5. It is a assigned for each step of mechanism separately.	5. Order of a reaction may have negative value.

12. PSEUDO UNIMOLECULAR REACTION

Consider the reaction : $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

Since water is present in large excess, its concentration hardly changes during the course of the reaction. And as such rate depends only on the concentration of ester. The order is one but the molecular is two. Such reactions are called **pseudo unimolecular reaction**.

Ex.12 For a chemical reaction, A → products, the rate of reaction doubles when the concentration of A is increased by 4 times. The order of reaction is

[1] 4   [2] 0   [3] 1/2   [4] 1   **Ans. [3]**

Ans. $r = k[A]^n$ .... (i)   ; $2r = k[4A]^n$ .... (ii)

Dividing (ii) by (i) $\dfrac{2r}{r} = \dfrac{k}{k}\left[\dfrac{4A}{A}\right]^n$

or $2 = 2^{2n}$ or $2n = 1$ or $n = 1/2$

Ex.13 For a hypothetical reaction

A + B → products, the rate law is, $r = k[B][A]^0$, the order of reaction is :
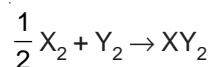
[1] 0   [2] 1   [3] 2   [4] 3   **Ans. [2]**

Sol. $1 + 0 = 1$

Ex.14 The slowest step of a particular reaction is found to be

$$\frac{1}{2}X_2 + Y_2 \rightarrow XY_2$$

The order of the reaction is

[1] 2   [2] 3   [3] 3.5   [4] 1.5   **Ans. [4]**

Sol. $r = k[X_2]^{1/2}[Y_2]^1$ ∴ Order $= 0.5 + 1 = 1.5$

Ex.15 The rate of certain hypothetical reaction A + B + C → products, is given by

$$r = \frac{dA}{dt} = k[A]^{1/2}[B]^{1/3}[C]^{1/4}$$

The order of a reaction is given by

[1] 1   [2] 1/2   [3] 2   [4] 13/12   **Ans. [4]**

Sol.   Order of reaction $= \dfrac{1}{2} + \dfrac{1}{3} + \dfrac{1}{4} = \dfrac{6+4+3}{12} = \dfrac{13}{12}$

13. ZERO ORDER REACTION

Reaction whose rate is not affected by concentration said to be of zero order reaction.

     Example :   **(i)**   Reaction between Acetone and Bromine

                     (ii)   Dissociation of HI on gold surface

(A)   **Unit of Rate Constant –**

$$\boxed{K = mol\ lit^{-1}\ sec^{-1}}$$ Unit of rate of reaction = Unit of rate constant.

(B) **Rate Constant of Zero Order Reaction –**

$$x = Kt$$

The rate of reaction is independent of the concentration of the reaction substance.

(C) **Determination of Half life Period of Zero Order Reaction –**

At $t = t_{1/2}$; $x = \dfrac{a}{2}$

$$t_{1/2} = \dfrac{a}{2K}$$

or $t_{1/2} \propto a$

The half life period is directly proportional to the initial concentration of the reactants.

Ex.16 The rate equation of a reaction is $K[A]^{1/2}[B]^{1/2}[C]^{-1}$. What should be the zero order of the reaction ?

Sol. $n = \dfrac{1}{2} + \dfrac{1}{2} - 1$ (zero)

14. FIRST ORDER REACTION

When the rate of reaction depends only on one concentration term of reactant.

Example – **(i)** All radioactive reactions

(ii) A → Product

(iii) $2NO \rightleftharpoons 2N_2 + O_2$

(iv) $2Cl_2O_7 \rightarrow 2Cl_2 + 7O_2$

(A) **Unit of rate constant of first order reaction**

$$K = (sec)^{-1} \qquad \Delta n = 1$$

(B) **Velocity constant for first order reaction**

$$K = \dfrac{2.303}{t} \log_{10} \dfrac{a}{(a-x)}$$
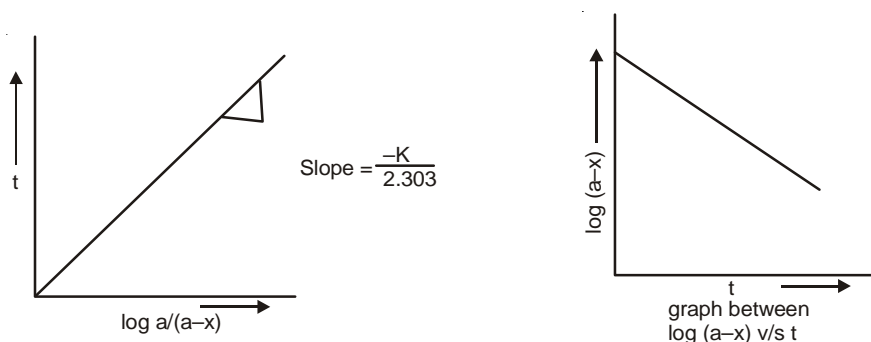
$$t = \dfrac{2.303}{K} \log_{10} \dfrac{a}{(a-x)}$$

where t = time, a = initial concentration at t = 0

(a – x) = concentration after time t

K = Rate constant

(C) **Graphical Representation**

Graph between t v/s $\log \dfrac{a}{(a-x)}$ is a straight line

Slope $= \dfrac{-K}{2.303}$

graph between log (a–x) v/s t

(D)   Half life period of the first Order Reaction

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

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

Ex.17   A first order reaction gets 90% completed in 40 minute. Find out the half-life period of the reaction.

Sol.   Suppose that the initial concentration of reactant (a) = 100   t = 40 minutes

90% of the reaction get completed in 40 minutes.

Therefore,

x = 90

$K_1 = \dfrac{2.303}{t} \ \log \dfrac{a}{a-x}$

$= \dfrac{2.303}{40} \ \log \dfrac{100}{100-90}$

$K_1 = \dfrac{2.303}{40} \ \log 10$

$= \dfrac{2.303}{40} \times 1$

$= 5.757 \times 10^{-2} \ \text{minutes}^{-1}$

$T^{1/2} = \dfrac{0.693}{5.757 \times 10^{-2}} = 10.3 \ \text{minutes}$

Ex.18   Prove with the help of the following data that hydrolysis of H_2O_2 is a first order reaction. Initial concentration in the reaction 25.0.

Sol.

Time, t (in minutes)	10	20	30
V	20.0	15.7	12.5

For a first order reaction, $K_1 = \dfrac{2.303}{t} \log \dfrac{a}{a-x}$;   Here, a = 25

K_1 at t = 10 minutes $= \dfrac{2.303}{10} \ \log \dfrac{25}{20} = \dfrac{2.303}{10} \times 0.0969 = 2.23 \times 10^{-2}$

K_1 at t = 20 minutes $= \dfrac{2.303}{20} \ \log \dfrac{25}{15.7} = \dfrac{2.303}{20} \times 0.2020 = 2.32 \times 10^{-2}$

$$K_1 \text{ at } t = 30 \text{ minutes} = \frac{2.303}{30} \log \frac{25}{12.5} = \frac{2.303}{30} \times 0.3010 = 2.31 \times 10^{-2}$$

Constant value of K_1 shows that hydrolysis of H_2O_2 in aqueous medium is a first order reaction.

Ex.19 Radioactive decay of an atomic nucleus is a first order reaction. Half-life period of radium $[_{88}Ra^{226}]$ is 1590 years. Find out its decay constant.

Sol. $T^{1/2} = \dfrac{0.693}{K_1} = \dfrac{0.693}{T^{1/2}} = \dfrac{0.693}{1590} = 4.358 \times 10^{-4} \ Y^{-1}$

15. SECOND ORDER REACTION

Reaction whose rate is determined by change of two concentration terms said to be a second order reaction.

Example –   **(i)** $S_2O_8^{-2} + 2I^- \rightarrow 2SO_4^{-2} + I_2$

            (ii) $H_2 + I_2 \rightleftharpoons 2HI$
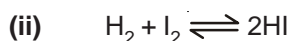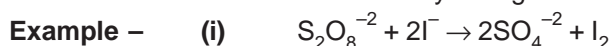
(A)   **Unit of rate Constant**

$$K = mol^{1-\Delta n} \ lit.^{\Delta n - 1} \ sec^{-1}$$

$\Delta n = 2$ $K = mol^{-1} \ lit. \ sec^{-1}$

(B)   **Rate Constant of Second Order Ration**

$$\boxed{K_2 = \frac{1}{t}\left(\frac{x}{a(a-x)}\right)}$$

$$\boxed{t = \frac{1}{K_2}\left(\frac{x}{a(a-x)}\right)}$$

Note : When concentration of A and B are taking different –

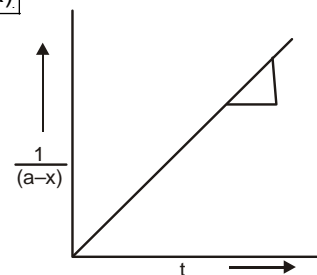then $\boxed{K_2 = \dfrac{2.303}{t(a-b)} \log \dfrac{b(a-x)}{a(b-x)}}$ $\boxed{t = \dfrac{2.303}{K_2(a-b)} \log \dfrac{b(a-x)}{a(b-x)}}$

(C)   **Graphical representation**

Graph between t v/s $\dfrac{1}{(a-x)}$

Slope = K_2

Solp is always (+) ve

(D)   **Half life period of the Second Order Reaction**

$$\boxed{t_{1/2} = \frac{1}{K_2 a}}$$

Half life of second order reaction is depend upon the concentration of the reactants.

$$\boxed{t_{1/2} \propto \frac{1}{a}}$$

Ex.20 Initial concentrations of both the reactants of a second order reaction are equal and 60% of the reaction gets completed in 3000 seconds. How much time will be taken in 20% completion of the reaction ?

Sol. $K_2 = \dfrac{1}{t} \ \dfrac{x}{a(1-x)}$

Suppose, a = 1 $K_2 = \dfrac{1}{3000} \times \dfrac{0.6}{1(1-0.6)} = \dfrac{1}{3000} \times \dfrac{0.6}{0.4}$

Now, for 20% completion

$K_2 = \dfrac{1}{t} \dfrac{x}{a(1-x)}$

$\dfrac{1}{3000} \times \dfrac{0.6}{0.4} = \dfrac{1}{t} \times \dfrac{(0.2)}{1(1-0.2)}$

$\dfrac{1}{3000} \times \dfrac{0.6}{0.4} = \dfrac{1}{t} \times \dfrac{1}{4}$

$t = \dfrac{3000}{0.6} \times \dfrac{0.4}{4}$

t = 500 second

Ex.21 A second order reaction requires 70 minutes to change the concentration of reactants from 0.08 M to 0.01 M. How much time will it require to become 0.04 M.

Sol. For second order reaction

when, (a – x) = 0.01

$K_2 = \dfrac{x}{t.a(a-x)}$

$K_2 = \dfrac{0.07}{70 \times 0.08 \times (0.01)}$ ......(1)

(a – x) = for 0.04

$K_2 = \dfrac{0.04}{t \times 0.08 \times (0.04)}$ ....(2)

From the equation (1) and (2)

$\dfrac{0.07}{70 \times 0.08 \times (0.01)} = \dfrac{0.04}{t \times 0.08 \times (0.04)}$

t = 10 minutes

16. THIRD ORDER REACTION

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

    (i) $2NO + O_2 \rightleftharpoons 2NO_2$

    (ii)   A + B + C → Product
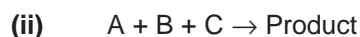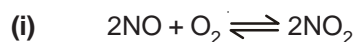
Rate constant of third order reaction

$$\boxed{k = \dfrac{1}{t} \cdot \dfrac{x(2a-x)}{2a^2(a-x)^2}}$$

Half life period $\boxed{t_{1/2} = \dfrac{1}{a^2}}$

Thus, half life is inversely proportional to the square of initial concentration.

17. DETERMINATION OF ORDER OF REACTION

17.1 Integration Method

In this method, value of K is determined by putting values of initial concentration of reactants and change in concentration with time in kinetic equation of first, second and third order reactions. The equation by which constant value of K is obtained is called order of that reaction.

$$K_1 = \frac{2.303}{t} \log \frac{a}{a-x} \qquad \text{(For first order reaction)}$$

$$K_2 = \frac{1}{t} \left[\frac{x}{a(a-x)} \right] \qquad \text{(For second order reaction)}$$

$$K_3 = \frac{1}{2t} \left[\frac{x(2a-x)}{a^2(a-x)^2} \right] \qquad \text{(For third order reaction)}$$

Ex.22 For a reaction, $A \rightarrow B$, it has been found that the order of the reaction is zero with respect to A. Which of the following expression correctly describes the reaction ?

[1] $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$ [2] $[A]_0 - [A] = kt$ [3] $t_{1/2} = \frac{0.693}{k}$ [4] $t_{1/2} \propto \frac{1}{[A]_0}$ **Ans. [2]**

Sol. $-\frac{d[A]}{dt} = k[A]_0, \ -d[A] = kdt$

Integrating from $t = 0$ to $t = t$ $[A]_0 - [A] = kt$

17.2 van't Hoff Differential Method

van't Hoff gave the following relationship between velocity V of nth order reaction and concentration of reactants, C.

$$n = \frac{\log(V_1 / V_2)}{\log(C_1 / C_2)}$$

C_1 and C_2 are two different concentrations, while V_1 and V_2 are their velocities.

17.3 Graphical Method

If a straight line is obtained on drawing a graph between log $(a - x)$ and time or $\frac{dx}{dt}$, then it is first order reaction.

If a straight line is obtained on drawing a graph between $(a - x)^2$ and $\frac{dx}{dt}$, then it is second order reaction.

Ex.23 Which of the following graphs is for a second order reaction ?

Ans. [3]
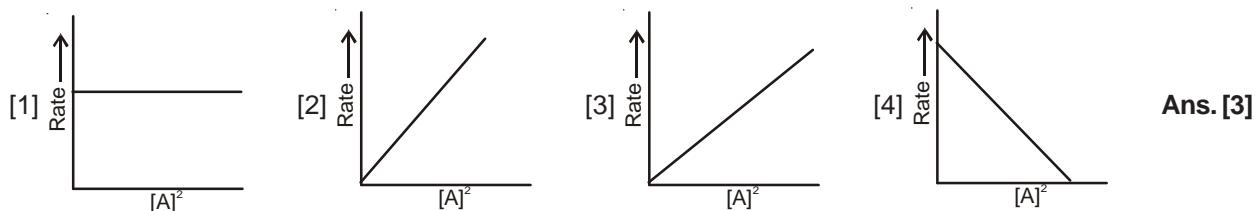
Sol. For second order reaction rate vs $[A]^2$ is a straight line with slope equal to k   rate = $k[A]^2$

If a straight line is obtained on drawing a graph between $(a - x)^3$ and $\frac{dx}{dt}$, then it is third order reaction.

17.4 Half-life Method

Relation between half-life period of a reaction and initial concentration is as follows : $t^{1/2} \propto \dfrac{1}{a^{n-1}}$

For first order reaction (Half life $\propto a$)

For second order reaction (Half life $\propto 1/a$)

For third order reaction (Half life $\propto 1/a^2$)

Ex.24 For a first order reaction, $t_{0.75}$ is 1386 seconds. Therefore, the specific rate constant is

[1] $10^{-1}\ s^{-1}$ [2] $10^{-3}\ s^{-1}$ [3] $10^{-2}\ s^{-1}$ [4] $10^{-4}\ s^{-1}$ **Ans. [2]**

Sol. $t_{0.75} = 1386\ s = 2 \times t_{0.5}$; $t_{0.5} = \dfrac{1386}{2} = 693\ s$; $k = \dfrac{0.693}{693\,s} = 1 \times 10^{-3}\ s^{-1}$

Ex.25 $t_{1/2}$ of first order reactions is given by $\dfrac{0.693}{k}$, $t_{3/4}$ would be equal to
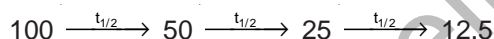
[1] $\dfrac{0.693}{k}$ [2] $\dfrac{0.346}{k}$ [3] $\dfrac{1.386}{k}$ [4] $\dfrac{0.924}{k}$ **Ans. [3]**

Sol. $t_{3/4} = 2(t_{1/2}) = \dfrac{2 \times 0.693}{k} = \dfrac{1.386}{k}$

Ex.26 The $t_{1/2}$ of a first order reaction is found to be 2 minutes. The percentage of the reactant left after 360 seconds is :

[1] 12.5 [2] 25 [3] 15 [4] 7.5 **Ans. [1]**

Sol. 360 seconds = 6 min = 3 half-lives

$100 \xrightarrow{\ t_{1/2}\ } 50 \xrightarrow{\ t_{1/2}\ } 25 \xrightarrow{\ t_{1/2}\ } 12.5$

17.5 Ostwald Isolation Method

This method is used to find out the order of complex reactions. If nA, nB and nC molecules of substance A, B and C, respectively, are present in a reaction, then nA + nB + nC will be the order of reaction.

When B and C are in excess, the order of reaction will be nA.

When A and B are in excess, the order of reaction will be nC.

When A and C are in excess, the order of reaction will be nB.

Ex.27 When the initial concentration of a reaction was doubled, its half life become half, What should be the order of the reaction ?

Sol. Rate law for product of a reaction is as follows :

$$\text{Rate} = K[A]^n \qquad \text{and} \qquad \dfrac{t_{0.5}}{t_{\frac{0.5}{2}}} = \left[\dfrac{2a}{a}\right]^{n-1}$$

$$2 = [2]^{n-1} \qquad ; \qquad n - 1 = 2$$

$$n = 2$$

18. TEMPERATURE EFFECT

The rate of reaction is dependent on temperature. This is expressed in terms of temperature coefficient which is a ratio of two rate constants differing by a temperature of 10^0. Generally the temperature selected are 298K and 308K. It is mathematically expressed as,

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

According to collision theory the reaction rate depends on collision frequency and effective collisions.

For a molecule to have effective collision it should fulfill two conditions :

(i) Proper orientation   (ii) Sufficient energy

It is observed that the reaction rate doubles for 10^0 rise in temperature from 298K to 308K. This is presumably because the effective collisions double for 10^0 rise in temperature from 298K to 308K. It must be noted that only reactions whose activation energy falls in the range of 50—55kJ are found to double their rate for this range of temperature. **The value of temperature coefficient for most of the reactions lies between 2 to 3.**

19. ARRHENIUS EQUATION

Arrhenius derived a mathematical expression to give a quantitative relationship between rate constant and temperature. The expression is

$$k = A.e^{-Ea/RT}$$

(Here, A = frequency factor; Ea = activation energy ; R = gas constant and T = temperature). The doubling of reaction rate for 10^0 rise in temperature from 298K to 308K can also be explained by calculating rate constant for the above temperature. Since Ea for majority of reactions falls in range 50—55kJ mol^{-1} therefore the rate of reaction doubles for all such reactions when the temperature is increased from 298K to 308K.

If k_1 and k_2 are rate constants at temperature T_1 and T_2 then

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

Ex.28 Value of rate constant for a first order reaction at 500 K is 1.60×10^{-5} second^{-1}, whereas at 600 K, it is 6.36×10^{-3} second^{-1}. Find out the activation energy of the reaction.

Sol. $\log\left(\dfrac{K_1}{K_2}\right) = \dfrac{-E_a}{2.303\,R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

$\log 1.60 \times 10^{-5} - \log 6.36 \times 10^{-3}$

$= \dfrac{-E_a}{2.303 \times 8.314}\left[\dfrac{1}{500} - \dfrac{1}{600}\right]$

$5.241 - 3.8035 = \dfrac{E_a}{19.15} \times \dfrac{1}{3000}$ $E_a = 2.5999 \times 19.15 \times 3000$

$E_a = 1.49 \times 10^5$

Ex.29 An exothermic reaction, $X \rightarrow Y$, has an activation energy 30 kJ mol^{-1}. If energy change (ΔE) during the reaction is -20kJ, then the activation energy for the reverse reaction is

[1] -30kJ   [2] 20 kJ   [3] 50 kJ   [4] 10 kJ   **Ans. [3]**

Sol. $\Delta E = E_{a_{(f)}} - E_{a_{(b)}}$; $-20 = 30 - E_{a_{(b)}}$; $E_{a_{(b)}} = 50$ kJ

Ex.30 An endothermic reaction, $A \rightarrow B$, has an activation energy as x kJ mol^{-1} of A. If energy change of the reaction is y kJ, the activation energy of reverse reaction is

[1] $- x$ [2] $x - y$ [3] $x + y$ [4] $y - x$ **Ans. [2]**

Sol. $\Delta E = E_{a_{(f)}} - E_{a_{(b)}}$; $y = x - E_{a_{(b)}}$; $E_{a_{(b)}} = x - y$

Ex.31 Which of the following relations is correct ?

[1] $k = A\, e^{Ea/RT}$ [2] $\ln k - \ln A = \dfrac{E_a}{RT}$ [3] $\ln A - \ln k = \dfrac{E_a}{RT}$ [4] $\ln A - \ln k = -\dfrac{E_a}{RT}$ **Ans. [3]**

Sol. $k = Ae^{-Ea/RT}$

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

Ex.32 Which of the following expression give the effect of temperature on the rate constant ?

[1] $\ln A = RT \ln E_a - \ln k$ [2] $\ln k = \ln A - E_a/RT$

[3] $k = AE_a/RT$ [4] None of these   **Ans. [2]**

Sol. The effect of temperature on rate constant is quantitatively given by Arrhenius equation

$$k = Ae^{-Ea/RT} \text{ on } \ln k = \ln A - E_a/RT$$

Ex.33 The plot of log k vs $\dfrac{1}{T}$ helps to calculate

[1] Energy of activation   [2] Rate constant of the reaction

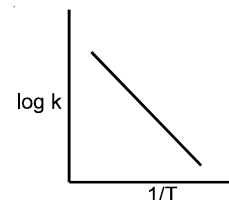[3] Order of the reaction   [4] Energy of activations as well as the frequency factor

Ans. [4]

Sol. According to Arrhenius equation : $\log k = \log A - \dfrac{E_a}{2.303} \cdot \dfrac{1}{T}$

Plot of log k vs. $\dfrac{1}{T}$ is straight line

Slope $= -\dfrac{E_a}{2.303R}$

Intercept $= \log A$

19.1 Effect of Nature Reactants

The reaction rate depends on the physical state of reactants (physical nature) and the activation energy of reactants (chemical nature). In general

(i) smaller the particle size, more is the surface area it provides, for the reaction and more is the rate of reaction.

(ii) low activation energy reactions are fast whereas,

(iii) high activation energy reactions are slow reactions.

19.2 Effect of Presence of a Catalyst

The rate of reaction enhances by the presence of a catalyst. A catalyst is specific in nature and accelerates the rate by providing alternative path of lower activation energy to the reactants.

19.3 Activated Complex Theory

According to this theory when activation energy is supplied to a reaction it absorbs to form intermediate activated complex. An activated complex is a high energy, unstable intermediate which exists very briefly. Once formed it immediately decomposes to form products of lower energy state or more stability.

For an exothermic reaction, the activation energy plot is shown here.

Activation energy = Threshold energy – Energy of colliding molecules

Effective collisions are those in which colliding molecules must have

(i) energy equal to or greater than the threshold energy

(ii) proper orientation
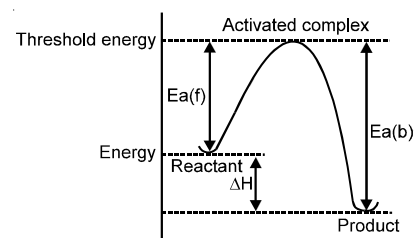
20. EXPOSURE OF RADIATIONS

Certain reactions are found to occur on exposure to visible radiation. Such reactions are called photochemical reactions.

The rate of a photochemical reaction is affected by the intensity of light whereas temperature has little effect.

Free energy change (ΔG) of a photochemical reaction may not be negative as a part of the light energy absorbed by the reactants changes into free energy by the products.

eg. ΔG is possible for the reaction

$$H_2 + Cl_2 \longrightarrow 2HCl$$

21. PHOTOSENSITIZER

It is substance which when added to a reaction mixture helps to initiate the photochemical reaction without undergoing any chemical change itself. This phenomenon is known as photosensitization. e.g. chlorophyll acts as photosensitizer in the photosynthesis.

22. VISION

Vision involves geometrical isomerisation of a compound retinal (an unsaturated aldehyde) present in the eye by absorbing the light falling on it - a photochemical reaction.

23. QUANTUM YIELD OR QUANTUM EFFICIENCY OF A PHOTOCHEMICAL REACTION

$$\phi = \frac{\text{number of reactant molecules reacting in a given time}}{\text{number of photon (quanta) of light absorbed in the same time}}$$

Different photochemical reaction have different values of quantum efficiency depending upon their mechanisms. For example photosynthesis of HBr has low value of while photosynthesis of HCl has very high value of ϕ.

(i) In the Arrhenius equation the quantity $e^{-Ea/RT}$ is known as **Boltzmann factor.**

(ii) **Autocatalysis** is a phenomenon in which the product formed is itself a catalyst and thereof enhances the rate

: $2MnO_4^- + 6H^+ + (COOH)_2 \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Mn^{2+} ions formed catalyse the reaction.

(iii) **Promoters** are substances which do not act as catalyst but enhance the efficiency of a catalyst.

(iv) **Negative catalyst** or **inhibitors** are those substance which decrease the rate of a reaction.

(v) Catalyst can be poisoned by many substances.

24. TABLE OF FORMULAE

Type of reaction	Integrated rate equation	Unit of rate constant	Half-life period	$t^{3/4}$ life period
Zero order reaction	$-\dfrac{\Delta[A]}{\Delta t} = k_0[A]^0$ Differential form $\dfrac{dx}{dt} = k$	Concentration time^{-1}	$t^{1/2} = \dfrac{a}{2K_0}$	--
First order reaction	$k_1 = \dfrac{2.303}{t}\log_{10}\dfrac{a}{(a-x)}$	Time^{-1}	$t^{1/2} = \dfrac{0.693}{K_1}$	$t^{3/4} = 2 \times \dfrac{0.693}{K_1} = \dfrac{1.382}{K_1}$
Second order reaction	$k_2 = \dfrac{2.303}{t(a-b)}\log\dfrac{b(a-x)}{a(b-x)}$ Differential form $\dfrac{dx}{dt} = k(a-x)^2$	Mole^{-1}litre time^{-1}	$t^{1/2} = \dfrac{1}{K_2 a}$	$t^{3/4} = \dfrac{3}{K_2 a}$
Third order reaction	$k_3 = \dfrac{1 \times (2a-x)}{t2a^2(a-x)^2}$ Differential form $\dfrac{dx}{dt} = k(a-x)^3$	Litre^{2}mole^{-2}time^{-1}	$t^{1/2} = \dfrac{3}{K_3 a}\dfrac{1}{2}$	---

25. IMPORTANT GRAPHICAL REPRESENTATION