CHEMICAL KINETICS

Preface

‘Chemical kinetics ’ is a basic fundamental topic of physical chemistry. Various reactions and the influence of various factors on them can be understood under the heading of this topic. After successful completion of this chapter you should be able to, understand about chemical kinetics and various rates and order of reactions, describe the order and determination of order of reactions, study the molecularity and various theories of rates of reactions, Clear the concept of rate of reaction, rate constant, rate law and law of mass action, describe the factors affecting the rate of reaction and the rate constant, solve all the problems based on it.

This book consists of theoretical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develope better understanding of the chapter and to have better grasping level in the class.

Total No.of questions in Chemical Kinetics are -

In chapter Examples 08

Solved Examples 15

Total No. of questions 23

1. CHEMICAL KINETICS

The branch of physical chemistry which deals with the rate, mechanism of a chemical reaction and influence of various factors such as concentration, temperature, pressure, catalyst on the chemical reaction rates is called **Chemical Kinetics**.

On the basis of their rates, the chemical reactions have been classified into the following three groups -

A. Very fast or Instantaneous reaction : –

These reaction are so fast, they occur as soon as the reactants are brought together.

These are mostly ionic reaction and do not involve any type of bond fission between atoms.

Reason *:*

The ionic reactants are already present in ionic state in their aqueous solution and thus this type of reactions occur very fast or instantaneously due to influence of coulombic forces.

The rate of such type of reactions are very fast. So, it is very impossible to determine the rate of these reactions.

eg. (a) $Ag^+(aq) + NO_3^-(aq) + H^+(aq) + Cl^-(aq) \longrightarrow AgCl(s) + Na^+(aq) + Cl^-(aq)$

(b) $Na^+(aq) + OH^-(aq) + H^+(aq) + Cl^-(aq) \longrightarrow H_2O(\ell) + Na^+(aq) + Cl^-(aq)$

B. Very Slow reaction : –

These reactions are extremely slow and take months together to show any measurable change at room temperature.

The rate of such type of reactions are very slow. So, it is also very difficult to determine the rate of these reactions.

eg. Rusting of Iron.

Reaction of atmospheric H_2S on basic lead acetate paint.

$$2H_2 + O_2 \xrightarrow{\text{Room temperature}} 2H_2O$$

$$C + O_2 \xrightarrow{\text{Room temperature}} CO_2$$

$$CO + 2H_2 \xrightarrow{\text{Room temperature}} CH_3OH$$

C. Moderate reactions : –

The reactions which takes place at moderate and measurable rates at room temperature and these reactions are studied in chemical kinetics.

Most of these reactions are molecular in nature.

eg. $2H_2O_2 \longrightarrow 2H_2O + O_2$

$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$

$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

$NO_2 + CO \longrightarrow NO + CO_2$

$2FeCl_3(aq) + SnCl_2 \longrightarrow 2FeCl_2(aq) + SnCl_4(aq)$

and decolourisation of acidified potassium permanganate with sodium oxalate.

1.1 Importance or Use of Chemical Kinetics :

(a) To predict the rate of particular reaction under specified condition.

(b) To predict the mechanism of reaction.

2. RATE OF REACTION

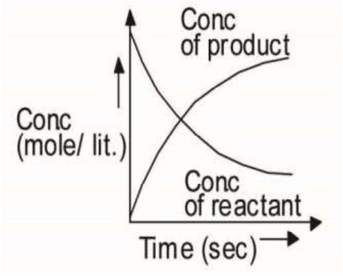
Rate of a reaction defined as the ratio of change in concentration of reactant or product to the time required to produce that change i.e.

$$\boxed{\text{Rate of reaction} = \frac{\text{Total change in concentration of reactants / products}}{\text{Change in time (in sec.)}}}$$

	A $\longrightarrow$	Product P
t = 0, Initial	a	0
t = t	(a – x)	x

$$\text{Rate of reaction} = \pm \frac{dx}{dt}$$

Here, the (+)ve sign indicates that the concentration of product increases and the (–)ve sign indicates that concentration of reactants decreases.



Rate of a reaction is directly proportional to the active mass of reactant.

$$\frac{dx}{dt} \propto (a - x)$$

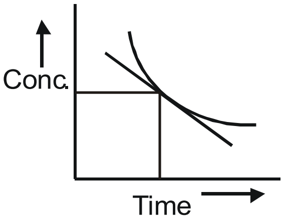
$$\frac{dx}{dt} = K(a - x)$$

Here, K = rate constant.

It (K) is also known as specific rate constant when active mass of reactant is 1.

2.1 Instantaneous Rate of Reaction :

Slope at any point of the curve indicates instantaneous rate of reaction.



A. Rate of Reaction in the form of a Chemical reaction : –

Let us consider a reaction –

$m_1A + m_2B + ...$
$\longrightarrow n_1P + n_2Q + n_3R + ...$

Rate of reaction

$$= -\frac{1}{m_1}\frac{d[A]}{dt} = -\frac{1}{m_2}\frac{d[B]}{dt}$$

$$= \frac{1}{n_1}\frac{d[P]}{dt} = \frac{1}{n_2}\frac{d[Q]}{dt}$$

eg. $N_2 + 3H_2 \longrightarrow 2NH_3$

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

2.2. Rate law :

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

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

(c) Rate law cannot be deduced from the equation for a given reaction. It can be determind by experiments only.

(d) The rate law may not bear a simple relationship with the stoichiometric equation.

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

(f) It may also not depend upon the concentration of each reactant or product of the reaction.
Suppose, $mA + nB \longrightarrow$ Product

$$R \propto [A]^m [B]^n$$

Examples based on Rate of Reaction

Ex.1 Following reaction was carried out at 300 K.

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

How is the rate of formation of SO_3 related to the rate of disappearance of O_2 –

(A) $-\frac{\Delta[O_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[SO_3]}{\Delta t}$

(B) $-\frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[SO_3]}{\Delta t}$

(C) $-\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[SO_3]}{\Delta t}$

(D) None of these **(Ans. A)**

Sol. Rate of reaction

$$= -\frac{1}{2}\frac{\Delta[SO_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[SO_3]}{\Delta t}$$

Therefore, rate of disappearance of O_2 is related to rate of formation of SO_3 as -

$$-\frac{\Delta[O_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[SO_3]}{\Delta t}$$

Ex.2 For the reaction

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$, the concentration of NO_2 increases by 2.4×10^{-2} Mol lit.$^{-1}$ in 6 second. What will be the rate of appearance of NO_2 and the rate of disappearance of N_2O_5–

(A) 2×10^{-3} mol lit.$^{-1}$ sec^{-1} , 4×10^{-3} mol lit.$^{-1}$ sec^{-1}

(B) 4×10^{-3} mol lit.$^{-1}$ sec^{-1} , 2×10^{-3} mol lit.$^{-1}$ sec^{-1}

(C) 2×10^{-3} mol lit.$^{-1}$ sec^{-1} , 2×10^{-3} mol lit.$^{-1}$ sec^{-1}

(D) None of these **(Ans. B)**

Sol. Rate of reaction $= -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$

$$= \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t}$$

Since NO_2 is the product, therefore, its concentration when t = 0 is zero.

$\therefore$ Rate of appearance of NO_2 i.e.

$$\frac{\Delta[NO_2]}{\Delta t} = \frac{2.4\times10^{-2}}{6}$$

$= \mathbf{4 \times 10^{-3}\ mol\ lit.^{-1}\ sec^{-1}}$

Thus, rate of reaction $= \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t}$

$= \frac{4\times10^{-3}}{4}$ mol lit.$^{-1}$ sec^{-1}

$= 1 \times 10^{-3}$ mol lit^{-1} sec^{-1}.

$\therefore$ Rate of disappearance of N_2O_5 i.e.

$\frac{\Delta[N_2O_5]}{\Delta t} = 2 \times$ Rate of reaction

$= 2 \times 1 \times 10^{-3}$ mol lit.$^{-1}$ sec^{-1}

$= \mathbf{2 \times 10^{-3}\ mol\ lit.^{-1}\ sec^{-1}}$.

Ex.3 In the reaction , $A + 2B \longrightarrow 6C + 2D$, if the initial rate $-\frac{d[A]}{dt}$ at t = 0 is 2.6×10^{-2} m sec^{-1}, what will be the value of $-\frac{d[B]}{dt}$ at t = 0 ?

(A) 8.5×10^{-2} m sec^{-1}
(B) 2.5×10^{-2} m sec^{-1}
(C) 5.2×10^{-2} m sec^{-1}
(D) 7.5×10^{-2} m sec^{-1} **(Ans. C)**

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

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

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

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

2.3 Unit of Rate constant : –

Let us take a following reaction

$$aA + bB \rightleftharpoons \text{Product}$$

$$r = K[A]^m[B]^n$$

$$\frac{Mol}{lit.\ sec.} = K\left[\frac{Mol}{lit.}\right]^m\left[\frac{Mol}{lit.}\right]^n$$

$$\frac{Mol}{lit.\ sec.} = K\left[\frac{Mol}{lit.}\right]^{m+n}$$

$K = mol^{1-(m+n)}\ lit^{(m+n)-1}\ sec^{-1}$

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

Here, n = order of reaction.

3. FACTORS AFFECTING THE RATE OF REACTION

(a) Concentration of reactants : –

Since we have been observed that the rate of a chemical reaction is directly proportional to the concentration of the reactants means rate of reaction decreases with decreasing in concentration.

(b) Surface area of reactant : –

Larger the surface area of reactant, the probability of collisions on the surface of the reactant particles by the surrounding molecules increases and thus rate of reaction increases.

(c) Presence of catalyst : –

A catalyst increases the rate of the reaction, is does not affect the state of equilibrium. It is because the activation energy for the forward and backward reaction decrease to the same extent.

Characteristics of catalyst are : –

(i) A catalyst remains unchanged chemically at the end of reaction however its physical state may change.

eg. MnO_2 is used as catalyst in granular form for the decomposition of $KClO_3$ is left in powder form at the end of reaction.

(ii) A catalyst never initiate a chemical reaction. It simply influence the rate of reaction.

(iii) A small quantity of catalyst is sufficient to influence the rate of reaction.

(iv) A catalyst does not influence the equilibrium constant of reaction. If simply helps in attaining equilibrium faster.

(v) A catalyst normally does not alter the nature of products in a reaction.

(vi) A catalyst does not make reaction more exothermic as it does not alter the individual energy of reactants.

(vii) Catalyst's activity is more or less specific. A catalyst for one reaction may not necessarily catalyse another reaction.

(d) Effect of sunlight : –

There are many chemical reactions whose rates are influenced by radiations particularly by ultraviolet and visible light. Such reactions are called photochemical reactions.

eg. Photosynthesis, Photography, Blue printing, Photochemical synthesis of compounds etc.

$$H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$$

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

4. ORDER OF REACTION

It may be defined as the sum of all the powers to which the concentration terms are raised as expressed in rate law expression or total number of concentration terms in the experimentally based equation is known as order of reaction.

order of reaction = Sum of exponents of the concentration terms in rate law.

$$xA + yB \longrightarrow \text{Products}$$

By the rate law, Rate = $[A]^x [B]^y$, then the overall order of reaction.

$$\boxed{n = x + y}$$

Where x and y are the orders with respect to individual reactants.

(a) If reaction is in the form of reaction mechanism than the order is determined by the slowest step of mechanism.

$$2A + 3B \longrightarrow A_2B_3$$
$$A + B \longrightarrow AB \text{ (fast)}$$
$$AB + B_2 \longrightarrow AB_3 \text{(slow)}$$
$$AB_3 + A \longrightarrow A_2B_3 \text{ (fast)}$$

Here, the overall order of reaction is equal to two.

(b) An order of a reaction may be possible zero. (–)ve, (+)ve or in fractions.

4.1 First order reaction : –

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

eg. (a) $H_2O_2 \longrightarrow H_2O + \frac{1}{2} O_2$

(b) $A \longrightarrow$ Product

(c) All radioactive reactions.

Exceptions :

H_2O, H^+, OH^- and excess quantities are not considered in the determining process of order.

eg. (1) $CH_3COOC_2H_5 \rightarrow CH_3COOH + C_2H_5OH$

order = 1 $\quad r = K\,[CH_3COOC_2H_5]$

(2) $2A(\text{excess}) + B \longrightarrow$ Product

order = 1 $\quad r = K\,[B]$

(3) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

order = 1 $\quad r = K\,[N_2O_5]$

(4) $2Cl_2O_7 \longrightarrow 2Cl_2 + 7O_2$

order = 1 $\quad r = K\,[Cl_2O_7]$

(5) $(CH_3)_3\text{–}C\text{–}Cl + OH^- \rightarrow (CH_3)_3C - OH + Cl^-$

order = 1 $\quad r = K\,[(CH_3)_3\,C - Cl]$

A. Unit of rate constant of first order reaction:

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

B. Velocity constant for first order reaction:

let us take the reaction

	A ⟶	Product
t = 0	a	0
After time t	(a – x)	x

Here, ‘a’ be the concentration of A at the start and (a – x) is the concentration of A after time taken t. i.e. x part of a has been changed in the product. So, the rate of reaction after time t is equal to

$$\frac{dx}{dt} \propto (a - x)$$

$$\text{or} \quad \frac{dx}{dt} = K(a - x)$$

$$\text{or} \quad \frac{dx}{(a - x)} = K\,.dt$$

upon integration of above equation

$$\int \frac{dx}{(a - x)} = \int K\,.\,dt$$

$$-\log_e (a - x) = Kt + C$$

$$\text{at, } t = 0, \quad x = 0$$

$$C = -\log_e a$$

on putting the value of ‘C’

$$-\log_e (a - x) = Kt - \log_e a$$

$$\log_e a - \log_e (a - x) = Kt$$

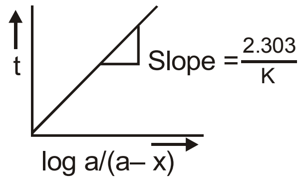
$$\log_e \frac{a}{(a - x)} = Kt$$

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

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

C. Graphical Representation :

Graph between t vs. log $\frac{a}{(a - x)}$ is a straight line.



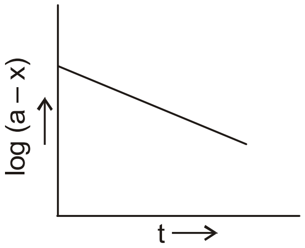
For graph between log (a – x) vs. time (t)

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

$$t = \frac{2.303}{K} [\log_{10} a - \log_{10} (a - x)]$$

$$[\log a - \log (a - x)] = \frac{K}{2.303} t$$

or $\log(a-x) = \frac{-K}{2.303}t + \log a$



graph between
log (a – x) vs. t

$$\boxed{\text{slope} = \frac{-K}{2.303}}$$

D. Determination of Half life period of the first order reaction : –

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

$$t_{1/2} = \frac{2.303}{K}\log\frac{a}{\left(a-\frac{a}{2}\right)}$$

$$t_{1/2} = \frac{2.303}{K}\log\frac{a}{a/2}$$

$$t_{1/2} = \frac{2.303}{K}\log 2$$

$\because$ $\log 2 = 0.3010$

$$\therefore\ t_{1/2} = \frac{2.303}{K} \times 0.3010$$

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

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

4.2 Second Order Reaction : –

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

eg. $CH_3CHO \longrightarrow CH_4 + CO$

$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$

$S_2O_8^{-2} + 2I^- \longrightarrow 2SO_4^{-2} + I_2$

A. Unit of rate constant : –

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

n = order of reaction

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

B. Calculation of rate constant : –

$$2A \longrightarrow \text{Product}$$

$$A + B \longrightarrow \text{Product}$$

(i) When concentration of A and B taking same.

$$A + B \longrightarrow \text{Product}$$

	A	B	Product
t = 0	a	a	a
t = t	(a – x)	(a – x)	x

$$\frac{dx}{dt} = K_2\,[A]\,[B]$$

$$= K_2\,[a-x]\,[a-x]$$

$$\frac{dx}{dt} = K_2\,[a-x]^2$$

on taking the integration of above equation -

$$\int\frac{dx}{[a-x]^2} = \int K_2 dt$$

$$\frac{1}{(a-x)} = K_2 t + C$$

at $t = 0$; $x = 0$

$$C = \frac{1}{a}$$

on putting the value of C on the above equation-

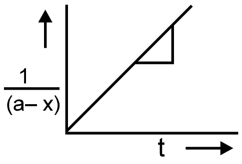
$$K_2 t = \frac{1}{(a-x)} - \frac{1}{a}$$

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

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

C. Graphical representation : –

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



slope = K_2

slope will always be (+) ve

D. Determination of half life period of the Second Order Reaction : –

at $t = t_{1/2}$; $x = \frac{a}{2}$

$$t_{1/2} = \frac{1}{K_2}\left(\frac{\frac{a}{2}}{a \times (a - \frac{a}{2})}\right)$$

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

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

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

4.3 Zero Order Reaction : –

Reaction whose rate is not affected by concentration or in which the concentration of reactant do not change with time are said to be of zero order reaction.

eg. (i) $H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$

(ii) Dissociation of HI on gold surface.

(iii) Reaction between Acetone and Bromine.

A. Unit of Rate constant : –

$$\boxed{K = \frac{\text{mole}}{\text{lit. sec.}}}$$

Unit of rate of reaction = Unit of rate constant.

B. Calculation of Rate Constant : –

Let us take the reaction

$$\begin{array}{lcl} & A \longrightarrow & \text{Product} \\ t = 0, & a & 0 \end{array}$$

$$\frac{dx}{dt} = K\,[A]^o$$

$$\frac{dx}{dt} = K$$

$$dx = K \,.\, dt$$

On putting the intigration of the above equation,

$$\int dx = \int K \,.\, dt$$

$$x = Kt + C$$

at $t = 0$; $x = 0$

$$C = 0$$

$$\boxed{x = Kt}$$

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

C. Determination of Half life period of Zero Order Reaction : –

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

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

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

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

Examples based on Different order of reaction

Ex.4 The first order rate constant for the decomposition of N_2O_5 is 6.2×10^{-4} second^{-1}. What will be the half life period in second for this decomposition.

(A) 1117.74 seconds (B) 117.74 seconds

(C) 1177.74 seconds (D) None

(Ans. A)

Sol. We know that for a first order reaction,

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

$$\therefore \quad t_{1/2} = \frac{0.693}{6.2 \times 10^{-4}}$$

$$= \mathbf{1117.74\ seconds}$$

Ex.5 The half life time for the decomposition of a substance dissolved in CCl_4 is 2.5 hour at 30ºC. How much of the substance will be left after 10 hours, if the initial weight of the substance is 160 gm–

(A) 20 gm (B) 30gm

(C) 40 gm (D) 10 gm

(Ans. D)

Sol. No. of half life periods

$$= \frac{\text{Total time}}{\text{Time of one half life period}}$$

$$= \frac{10}{2.5} = 4$$

Now we know that the quantity left after ‘n’ half-life periods

$$= (1/2)^n \times \text{Initial quantity}$$

$$= (1/2)^4 \times 160$$

$$= \frac{160}{2 \times 2 \times 2 \times 2} = \mathbf{10\ gm}$$

Ex.6 A first order reaction was started with a decimolar solution of the reactant. After 8 minutes and 20 seconds, its concentration was found to be M/100. Determine the rate constant of the reaction –

(A) 4.6×10^{-3} sec^{-1}

(B) 16.6×10^{-3} sec^{-1}

(C) 24.6×10^{-3} sec^{-1}

(D) 40.6×10^{-3} sec^{-1} **(Ans. A)**

Sol. Here $a = 0.1$ M

$$a - x = \frac{M}{100} = 0.01 \text{ M}$$

$$t = 8 \text{ minutes } 20 \text{ seconds}$$
$$= 500 \text{ seconds}$$

Substituting the values in the first order reaction.

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$= \frac{2.303}{500} \log \frac{0.1}{0.01}$$

$$= \frac{2.303}{500} \log 10$$

$$= \frac{4.606}{1000} \times 1$$

$$= \mathbf{4.6 \times 10^{-3}\ sec^{-1}}$$

Ex.7 87.5% of a radioactive substance disintegrates in 40 minutes. What is the half life of the substance–

(A) 13.58 min	(B) 135.8 min
(C) 1358 min	(D) None

(Ans. A)

Sol. Determination K by substituting the respective values.

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$= \frac{2.303}{40} \log \frac{a}{a - 0.875a}$$

$$= \frac{2.303}{40} \log \frac{a}{0.125a}$$

$$= \frac{2.303}{40} \log 8$$

$$= 0.051 \text{ min}^{-1}$$

$$\therefore\ t_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.051} = \mathbf{13.58\ min}$$

Ex.8 A second order reaction with two reactants is started with 0.1 m concentration of each reactant. It is 20% complete in 500 seconds. How much time it take to go 60% completion–

(A) 5000 seconds	(B) 3000 seconds
(C) 2000 seconds	(D) 4000 seconds

(Ans. B)

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

Since a = 0.1 so for 20% completion x would be 20% of initial concentration.

i.e. $a = 0.1$

$$\therefore\ x = \frac{20}{100} \times 0.1 = 0.02$$

$$K_2 = \frac{1}{500} \times \frac{0.02}{0.1(0.1-0.02)} = \frac{1}{200}$$

For 60% completion,

$$x = \frac{60}{100} \times 0.1 = 0.06$$

$$K_2 = \frac{1}{t} \times \frac{0.06}{0.1(0.1-0.06)}$$

$$\text{or } \frac{1}{200} = \frac{1}{t} \times \frac{0.06}{0.1(0.1-0.06)}$$

or **t = 3000 sec**.

5. DETERMINATION OF ORDER OF REACTION

5.1 Substitution Method in integrated Rate Equation : –

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

(ii) The value of K determine and check for all sets of a, x and t.

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

(iv) If all the reactants are at the same molar concentration, the kinetic equations are : –

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

for first order reactions

$$K = \frac{1}{t}\left[\frac{1}{a} - \frac{1}{a-x}\right]$$

for second order reactions

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

for third order reactions

5.2 Half life method :

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

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

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 than,

$$(t_{1/2}) \propto \frac{1}{a_1^{\,n-1}}, \qquad (t_{1/2}) \propto \frac{1}{a_2^{\,n-1}},$$

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

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

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

5.3 Graphical method :

A graphical method based on the respective rate, which be used.

If the plot of log (a – x) vs 't' is a straight line, the reaction follows first-order.

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

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

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

5.4 Vant Haff Differential Method : –

In this method the order of the given reaction with respect to each of its reactant can be determined-

For the reaction

$$pA + qB \rightarrow \text{Product}$$

$$\text{Rate law } \frac{dx}{dt} = k\,[A]^p\,[B]^q$$

If concentration B is kept constant and new rate constant $k^1 = k\,[B]^q \Rightarrow \frac{dx}{dt} = k'\,[A]^p$

$$\left(\frac{dx}{dt}\right)_1 = k_1\,[A_1]^P = R_1$$

$$\text{If} \quad \left(\frac{dx}{dt}\right)_2 = k_1\,[A_2]^P = R_2$$

$$\frac{R_1}{R_2} = \left[\frac{A_1}{A_2}\right]^P$$

$$\log_{10}\frac{R_1}{R_2} = P\log\left[\frac{A_1}{A_2}\right]$$

a graph can be plot between $\log\left(\frac{R_1}{R_2}\right)$ Vs

$\log\left(\frac{A_1}{A_2}\right)$ is a straight line of slop -P

6. MOLECULARITY

(a) The total number of moles or atom or ion or molecules or reacting species in a fundamental chemical reaction is known as molecularity of the reaction or the total number of molecules present in the reactants of a balanced chemical equation is known as molecularity of the reaction. for eg.

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$ (Unimolecular)

$NO + O_3 \longrightarrow NO_2 + O_2$ (Bimolecular)

$2NO + O_2 \longrightarrow 2NO_2$ (Trimolecular)

(b) Molecularity of a reaction can't be Zero, (–)ve or in fraction.

(c) Molecularity of a reaction is derived from the mechanism of the given reaction.

for eg.

$$A_2 + \frac{3}{2}B_2 \longrightarrow A_2B_3$$

step I $2A \longrightarrow A_2$ — Bimolecular

step II $A_2 + \frac{1}{2}B_2 \longrightarrow A_2B$ — Trimolecular

step III $A_2B + B_2 \longrightarrow A_2B_3$ — Bimolecular

Pseudo – Unimolecular Reaction :

Those reaction which may have order of reaction is one while molecularity of reaction 2 or more than two (2).

eg. $2N_2O_5 \longrightarrow 4NO_2 + O_2$

order = 1

molecularity = 2

6.1 Difference between Molecularity and Order of Reaction

S.No.	Molecularity	Order of Reaction
1	It is the number of molecules of reactants concentration terms taking part in elementary step of a reaction.	It is sum of power raised on the rate expression
2	Molecularity is a theoretical value and is derived from mechanism	Order of a reaction is an experiment value derived from rate expression
3	Molecularity can neither be zero nor fraction	Order of a reaction can be zero fractional for integer.
4	It is a assigned for each step of mechanism separately.	Order of a reaction may have negative value.
5	It is a assigned for each step of mechanism separately.	It is as signed for overall reaction.
6	It is independent of pressure and temperature	It depends upon pressure and temperature.

7. THEORY OF RATE OF REACTION

7.1 Collision Theory : –

A. Collision frequency (Z) : –

Number of collision between reacting molecules per second in per unit volume is called collision frequency.

$$\therefore \quad Z = \frac{1}{\sqrt{2}} \pi\sigma^2 u_{av} (N^*)^2$$

where σ = collision diameter

u_{av} = average velocity = $\sqrt{\frac{8RT}{\pi M}}$

N^* = no. of molecules per unit volume

$$\therefore Z \propto \sqrt{\frac{8RT}{\pi M}} \text{ or } \therefore Z \propto \sqrt{T}$$

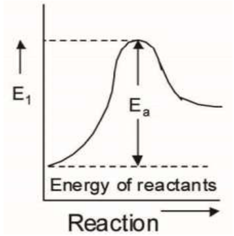
Since collision frequency (Z) is directly proportional to the square root of absolute temperature (T). With the increase in temperature, the average velocity of the reacting molecules increases. Which results in the increase in no. of collisions per unit time (Z).

B. Effective Collisions :

Those collisions which is completed between reactant molecules by which reactants can be converted into products is called effective collision.

(a) Energy barrier :

Minimum energy required for the reacting molecules to get converted into product is known as energy barrier. It is also called as threshold energy.

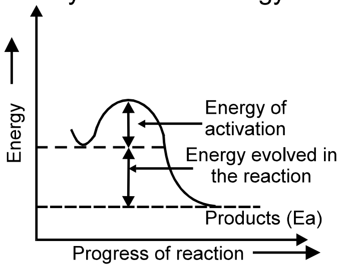


(b) Orientation barrier : –

Orientation barrier said to be to gain the energy barrier which is required to the effective collision between reacting molecules for may be forming of new bonds and to break old bonds.

7.2 Activation Energy Theory : –

(a) For a reaction to take place molecules of reactants must collide with each other. Out of these collisions only those collision result in the formation of products which possess energy equal to or more than the certain minimum energy called **threshold energy**. Collisions of the molecules possessing energy less than the threshold energy do not form products. It means between reactants and products there is an energy barrier which must be crossed before the reactants are converted into products. The energy required for crossing this energy is supplied by the kinetic energy of the molecules.



The minimum extra energy over and above the average potential energy of the reactants which must be supplied to the reactants to enable them to cross over the energy barrier between reactants and products is called **Activation energy**. Activation energy = [Threshold energy] – [Average energy of the reactants]

$$E_a = E_{th} - E_{reactant}$$

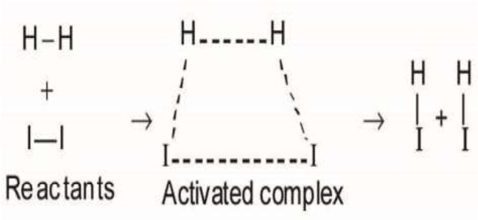
For fast reaction : Activation energies are low

For slow reaction : Activation energies are high

(b) Activated complex or Transition state : –

During a chemical reaction certain bonds are broken and certain new bonds are formed. The breaking of bonds requires energy whereas the formation of bonds results in the release of energy.

eg.



In the reactions or hydrogen with iodine from hydrogen iodide, when a molecule of hydrogen approaches that of iodine, H–H and I–I bonds starts forming.

In the beginning breaking of bonds predominates and therefore, energy of the system starts increasing till it reaches a maxima.

After this the energy starts decreasing because process of bond formation predominates and finally leads to the products hydrogen iodide. The arrangement of atoms corresponding to energy maxima (threshold) is called transition state or activated complex.

8. DIFFERENCE BETWEEN RATE OF REACTION & RATE CONSTANT

S.No.	Rate of reaction	Reaction rate constant
1	Rate of reaction is called as the change in concentration of the reactant or product per unit time	Rate constant is the proportionality constant in the rate law equation. When molar concentration of reactants is taken as unity, its value is equal to rate of reaction
2	Rate of reaction varies with concentration of the reactant	Since it is proportionality constant for a particular reaction, it is independent of the concentration of the reactant.
3	Rate of reaction increases with increase in temperature	Rate constant value also varies directly with the temperature.
4	The units of rate of reaction is mole litre^{-1} time^{-1}	The units of reaction rate constant depends upon the order of reaction I.e. its unit differs according to order to reaction.

9. DIFFERENCE BETWEEN RATE LAW AND LAW OF MASS ACTION

S. No.	Rate Law	Law of Mass action
1	It is an experimentally observed law.	It is a theoretical law.
2	It depends on the concentration terms on which the rate of reaction actually depends eg. for the reaction, aA + b B $\rightarrow$ Products Rate law, Rate = k[A]^m [B]^n	It is based upon the stoichiometry of the equation eg. for the reaction, aA + b B $\rightarrow$ Product Rate = k[A]^a [B]^b

10. FACTORS AFFECTING THE RATE CONSTANT

(A) Arrhenius equation :

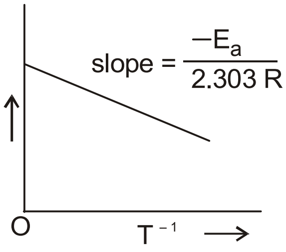
Variation of rate constant k with temperature T (K) is give by Arrhenius eqn.

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

$$\log_e k = \log_e A - \frac{E_a}{RT}$$

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303\ RT}$$

where A is called the frequency factor or the pre-expontential factor. Collectively A and E_a are called the Arrhenius parameters of the reaction.



When $T \rightarrow \infty$, $k = Ae^o = A$

A plot (fig.) between $\log_{10}$ k and $\left(\frac{1}{T}\right)$ of above equ. is a straight line of

$$\text{slope} = \frac{-E_a}{2.303\ R}$$

hence $E_a = 2.303 \times R \times \text{slope}$

(B) Effect of temperature :

(i) When $\Delta H = 0$ $\log K_1 = \log K_2$

$K_2 = K_1$ No change in rate constant

(ii) When $\Delta H > 0$ It is endothermic reaction

So, $T_2 > T_1$

$\log K_2 > \log K_1$

$K_2 > K_1$

In endothermic reaction with the increase in temperature, rate constant is also increases.

(iii) When, $\Delta H < 0$ It is exothermic reaction.

So, $T_1 > T_2$

$\therefore \quad \log K_2 < \log K_1 \quad ; \; K_2 < K_1$

In exothermic reaction with the increase in temperature, rate constant decreases.

(b) Temperature coefficient : –

The ratio of specific rate constant of reaction at two temperature separated by 10ºC is known as the temperature coefficient.

$$\text{Temperature Coefficient} = \frac{K \text{ at } (t + 10^\circ C)}{K \text{ at } t^\circ C} = \frac{K_{35^\circ C}}{K_{25^\circ C}}$$

The temperature coefficient for most of the reactions varies between 2 and 3 i.e. the rate of reaction becomes double for 10ºC rise in temperature.

(C) Effect of Catalyst :

Positive catalyst increases the rate of reaction while, the negative catalyst decreases.

SOLVED EXAMPLES

Ex.1 Dinitrogen pentaoxide decomposes as follows-

$N_2O_5 \rightarrow 2NO_2 + ½\ O_2$

If $-\dfrac{d[N_2O_5]}{dt} = k'\ [N_2O_5]$

$$\frac{d[NO_2]}{dt} = k''\ [N_2O_5]$$

$$\frac{d[O_2]}{dt} = k'''\ [N_2O_5]$$

Derive a relation in k', k" and K"'.

(A) $\dfrac{k'}{2} = \dfrac{k''}{3} = \dfrac{k'''}{4}$ (B) $(k')^2 = k'' = k'''$

(C) $2k' = k'' = 2k'''$ (D) $k' = \dfrac{k''}{2} = 2k'''$

Ans. [D]

Sol. For the given change

$$\frac{-d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = 2\frac{d[O_2]}{dt}$$

on substituting values in given

$$k'\ [N_2O_5] = \frac{1}{2}\ k''\ [N_2O_5] = 2K'''\ [N_2O_5]$$

or $2k' = k'' = 4k'''$

Ex.2 The rate of change in concentration of C in the reaction $2A + B \rightarrow 2C + 3D$ was reported as 1.0 mol litre^{-1} sec^{-1}. Calculate the reaction rate -

(A) 0.05 mol litre^{-1}. sec^{-1}

(B) 0.01 mol. litre^{-1} sec^{-1}

(C) 0.5 mol litre^{-1} sec^{-1}

(D) None of these

Ans. [C]

Sol. We have

$$-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

$$= \frac{1}{2}\frac{d[C]}{dt} = \frac{1}{3}\frac{d[D]}{dt}$$

= rate of reaction.

$$\therefore \frac{d[C]}{dt} = 1.0 \text{ mol litre}^{-1} \text{ sec}^{-1}$$

$$\therefore \frac{d[A]}{dt} = -\frac{d[C]}{dt} = -1.0 \text{ mol litre}^{-1} \text{ sec}^{-1}$$

or $\dfrac{d[B]}{dt} = -\dfrac{1}{2}\dfrac{d[C]}{dt} = -\dfrac{1}{2} \times 1$

$= -0.5$ mol litre^{-1} sec^{-1}

or $\dfrac{d[D]}{dt} = \dfrac{3}{2}\dfrac{d[C]}{dt} = \dfrac{3}{2} \times 1$

$= 1.5$ mol litre^{-1} sec^{-1}

Also

$$\because \text{Rate} = \frac{1}{2}\frac{d[C]}{dt}$$

$$\therefore \text{Rate} = \frac{1}{2} \times 1 = 0.5 \text{ mol litre}^{-1} \text{ sec}^{-1}$$

Ex.3 For a reaction 3A → products, it is found that the rate of reaction doubles, if concentration of A is increased four times, calculate order of reaction -

(A) 1 (B) 1/2

(C) 2 (D) 3 **Ans. [B]**

Sol. Rate = k [Reactant]^n

if [Reactant] = a ; rate = r_1

if [Reactant] = 4a ; rate = $2r_1$

$\Rightarrow r_1 = k\ [4a]^n$

$2r_1 = k\ [4a]^n$

$$\therefore \frac{1}{2} = \left[\frac{1}{4}\right]^n$$

$$\therefore n = \frac{1}{2}$$

Ex.4 A first order reaction takes 69.3 minute for 50% completion. How much time will be needed for 80% completion -

(A) 160.97 minute (B) 170.97 minute

(C) 150.97 minute (D) 0 minute

Ans. [A]

Sol. $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{69.3}$

now $k = \dfrac{2.303}{t} \log \dfrac{100}{20}$

$$t_{80\%} = \frac{2.303}{0.693} \times 69.3 \log 5$$

$t_{80\%} = 160.97$ minute

Ex.5 The reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ shows an increase in concentration of NO_2 by 20×10^{-3} mol litre^{-1} in 5 second calculate the rate of appearance of NO_2 -

(A) 2×10^{-3} mol litre^{-1} sec^{-1}

(B) 4×10^{-3} mol litre^{-1} sec^{-1}

(C) 1×10^{-3} mol litre $^{-1}$ sec^{-1}

(D) None of these **Ans. [B]**

Sol. Increase in concentration of NO_2

$= 20 \times 10^{-3}$ mol litre^{-1} time taken = 5 sec

$\therefore$ Rate of appearance of NO_2

$$= \frac{\Delta[NO_2]}{\Delta t}$$

$$= \frac{20 \times 10^{-3}}{5}$$

$$= \mathbf{4 \times 10^{-3}\ mol\ litre^{-1}\ sec^{-1}}$$

Ex.6 For the reaction $2N_2O_5\ (g) \rightarrow 4NO_2\ (g) + O_2\ (g)$ the concentration of NO_2 increases by 2.4×10^{-2} Mol lit^{-1} in 6 seconds. Calculate the rate of appearance of NO_2 and the rate of disappearance of N_2O_5 -

(A) 4×10^{-3} mol lit^{-1} sec^{-1}, 2×10^{-3} mol lit^{-1} sec^{-1}

(B) 2×10^{-3} mol lit^{-1} sec^{-1}, 4×10^{-3} mol lit^{-1} sec^{-1}

(C) 3×10^{-3} mol lit^{-1} sec^{-1}, 3×10^{-3} mol lit^{-1} sec^{-1}

(D) None of these **Ans. [A]**

Sol. Rate of reaction, $-\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t}$

Since, NO_2 is the product, therefore, its concentration when t = 0 is zero.

$\therefore$ Rate of appearance of NO_2 i.e.

$$\frac{\Delta[NO_2]}{\Delta t} = \frac{2.4 \times 10^{-2}}{6}$$

$$= \mathbf{4 \times 10^{-3}\ mol\ lit^{-1}\ sec^{-1}}$$

Thus, rate of reaction $= \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t}$

$$= \frac{4 \times 10^{-3}}{4} \text{ mol lit}^{-1}\text{ sec}^{-1}$$

$$= 1 \times 10^{-3} \text{ mol lit}^{-1}\text{ sec}^{-1}$$

$\therefore$ Rate of diapearance of N_2O_5

i.e. $\frac{\Delta[N_2O_5]}{\Delta t} = 2 \times$ Rate of reaction

$$= 2 \times 1 \times 10^{-3} \text{ mol lit}^{-1}\text{ sec}^{-1}$$

$$= \mathbf{2 \times 10^{-3}\ mol\ lit^{-1}\ sec^{-1}}$$

Ex.7 For the chemical reaction $3O_2 \longrightarrow 2O_3$, the rate of formation of O_3 is 0.04 mole lit^{-1} sec^{-1}. Determine the rate of disappearance of O_2 -

(A) 0.04 mol lit^{-1} sec^{-1}

(B) 0.08 mol lit^{-1} sec^{-1}

(C) 0.10 mol lit^{-1} sec^{-1}

(D) 0.06 mol lit^{-1} sec^{-1} **Ans. [D]**

Sol. $\frac{d[O_3]}{dt} = 0.04$ mol lit^{-1} sec^{-1}

We know, Rate

$$= -\frac{1}{3}\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[O_3]}{dt}$$

$$-\frac{d[O_2]}{dt} = \frac{3}{2} \times \frac{d[O_3]}{dt} = \frac{3}{2} \times 0.04$$

$$= \mathbf{0.06\ mol\ lit^{-1}\ sec^{-1}}.$$

Ex.8 For the reaction $2NO\ (g) + H_2(g) \longrightarrow N_2O\ (g) + H_2O\ (g)$, at 900 K. following data are observed.

Initial pressure of NO (atm)	Initial pressure of H_2 (atm)	Rate
0.15	0.40	0.02
0.075	0.40	0.005
0.150	0.02	0.10

Find out the rate law and order of reaction -

(A) $k[P_{NO_2}]^2 [P_{H_2}]^1$, 3

(B) $k[P_{NO_2}]^2 [P_{H_2}]^1$, 2

(C) $k[P_{NO_2}]^2 [P_{H_2}]^1$,1

(D) $k[P_{NO_2}]^2 [P_{H_2}]^1$,0 **Ans. [A]**

Sol. Rate law equation in terms of pressure is

$$\text{Rate} = k[P_{NO_2}]^m [P_{H_2}]^n$$

Substituting the given data in rate law equation we get,

(i) $0.02 = (0.15)^m\ [0.4]^n$

(ii) $0.005 = (0.075)^m\ [0.4]^n$

(iii) $0.010 = (0.15)^m\ [0.2]^n$

Divide equation (i) by (ii)

$$\frac{0.02}{0.005} = \frac{k[0.15]^m [0.4]^n}{k[0.075]^m [0.4]^n}$$

or $4 = [2]^m \quad \therefore \quad m = \mathbf{2}$

Divide equation (i) by (iii)

$$\frac{0.02}{0.01} = \frac{k[0.15]^m [0.4]^n}{k[0.15]^m [0.2]^n}$$

or $2 = (2)^n$ ∴ n **= 1**

Rate law, $r = k[P_{NO_2}]^2 [P_{H_2}]^1$

Order of reaction **= 2 + 1 = 3**

Ex.9 The half life time for the following reaction are

(i) $H^+ + OH^- \rightarrow H_2O$ $t_{1/2} = 10^{-12}$ sec.

(ii) $N_2O_5\,(aq) \xrightarrow{328\text{ K}} 2NO_2\,(g) + 1/2\, O_2\,(g)$
$t_{1/2} = 89$ min.

(iii) $CH_3COOC_2H_5\,(l) + H_2O\,(l) \xrightarrow{H^+}$
$CH_3COOH\,(l) + C_2H_5OH\,(l)$
$t_{1/2} = 1000$ days

(iv) $[Cr(H_2O)_6]^{3+} + I^-(aq) \rightarrow [Cr(H_2O)_5\, I]^{2+} + H_2O$
(I) $t_{1/2} = 2000$ yr

which is (a) fast reaction (b) slow reaction (c) moderate rate reaction -

(A) i, iv, (ii, iii) (B) i, ii, (iii, iv)
(C) i, iii, (iv, ii) (D) i, ii, (iv, iii)

Ans. [A]

Sol. Half life time is a measure of rate of reaction. Shorter the half life time, faster is the reaction. Therefore, reaction (i) is reaction. Reaction (iv) is slow reaction. and reactions (ii) and (iii) are moderate rate reactions.

Ex.10 In a first order reaction A → Products, the ratio of a and (a – x) was found to be 8 after 60 minutes. Calculate the rate of the reaction in moles of A reacted per minute, If its concentration is 0.1 mole litre^{-1} -

(A) 5.566×10^{-3} mole litre^{-1} min^{-1}
(B) 3.466×10^{-3} mole litre min
(C) 4.366×10^{-3} mole litre^{-1} min^{-1}
(D) 3.466×10^{-3} mole litre^{-1} min^{-1}

Ans. [D]

Sol. $K = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{60}\log 8$

$= 3.466 \times 10^{-2}$ min^{-1}

Rate of reaction, $\frac{dx}{dt} = K[A]$

$= 3.466 \times 10^{-2} \times 0.1$

= 3.466×10^{-3} mole litre^{-1} min^{-1}

Ex.11 In the reaction of NO by H_2 it was observed that equimolecular mixture of gases at 500 mm was half changed in 100 seconds. In another experiment with an initial pressure of 250 mm, the reactions was half completed in 200 seconds. Calculate the order of reaction-

(A) 1 (B) 2
(C) 3 (D) 4 **(Ans. [B]**

Sol. Since, $t_{1/2} \propto \frac{1}{a^{n-1}}$,

So $\frac{t_1}{t_2} = \left[\frac{a_2}{a_1}\right]^{n-1} = \left[\frac{p_2}{p_1}\right]^{n-1}$

Here $p_1 = 500$ mm, $p_2 = 250$ mm,
$t_1 = 100$ sec, $t_2 = 200$ sec. Thus

$$\frac{100}{200} = \left[\frac{250}{500}\right]^{n-1}$$

or $n = 2$

i.e. Order of reaction **= 2nd**.

Ex.12 A study of chemical kinetics of the reaction A + B → Products, gave the following data at 25ºC.

Experiment	[A]	[B]	d [Products]dt
1	1.0	0.15	4.20×10^{-6}
2	2.0	0.15	8.40×10^{-6}
3	1.0	0.20	5.60×10^{-6}

Calculate the rate law -

(A) K [A] (B) K [B]
(C) K [A] [B] (D) None of these

Ans. [C]

Sol. Doubling the concentration of A increases the rate by two times. Raising the concentrating of B by 4/3 times increases the rate of B by 4/3 times. Thus the reaction is of first order with respect to both A and B. So rate law **= K [A] [B]**.

Ex.13 The values of rate constant for the decomposition of N_2O_5,

$$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$$

are 3.50×10^{-5} and 5×10^{-3} at 27ºC and 67ºC, respectively. Calculate the energy of activation -

(A) 14.8 k Cal/Mol (B) 24.8 k Cal/Mol
(C) 28.8 k Cal/Mol (D) 34.8 k Cal/Mol

Ans. [C]

Sol. Given

$k_2 = 5 \times 10^{-3}$, $T_2 = 67 + 273 = 340$ K

$k_1 = 3.50 \times 10^{-5}$, $T_1 = 27 + 273 = 300$ K

$R = 2 \times 10^{-3}$ kcal mol^{-1} k^{-1}

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

$$2.303 \log \frac{5 \times 10^{-3}}{3.5 \times 10^{-5}}$$

$$= \frac{E_a}{R} \left[\frac{340 - 300}{340 \times 300}\right]$$

E_a = 25 kcal/Mole

Ex.14 An exothermic reaction A $\longrightarrow$ B has an activation energy of 17kJ per mole of A. The heat of the reaction is 40 kJ. Calculate the activation energy for the reverse reaction B $\longrightarrow$ A -

(A) 60 kJ (B) 57 kJ

(C) 75 kJ (D) 90 kJ **Ans. [B]**

Sol. For the reaction A $\longrightarrow$ B.

Activation energy $(E_a)_f = 17$ kJ,

$\Delta H = -40$ kJ

$\because \Delta H = (E_a)_f - (E_a)_b$

$-40 = 17 - (E_a)_b$

$(E_a)_b = 40 + 17 =$ **57 kJ**.

Ex.15 An endothermic reaction X $\longrightarrow$ Y has an activation energy of 175 kJ mol^{-1} and the heat of reaction is 85 kJ. Find the activation energy of the reaction Y → X -

(A) 70 (B) 80

(C) 90 (D) 100 **Ans. [C]**

Sol. $\Delta H = 85$ kJ ; $(E_a)_f = 175$ kJ

$\because \Delta H = (E_a)_f - (E_a)_b$

$85 = 175 - (E_a)_b$

$\therefore (E_a)_b = 175 - 85$ **= 90 kJ**