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# CHEMISTRY

Target : JEE (Main)

CHEMICAL KINETICS

# CHEMICAL KINETICS

## Contents

Topic	Page No.
Theory	01 – 30
Exercise - 1	31 – 37
Exercise - 2	38 – 41
Exercise - 3	41 – 45
Part - I : JEE (Main) /AIEEE Questions	
Part - II : JEE (Adv.)/ IIT-JEE Questions	
Answer Key	46
JEE-MAIN Practice Test Paper	47 – 50
JEE-MAIN Test Paper Answers	51
JEE-MAIN Test Paper Solutions	51 – 53

### JEE(MAIN) SYLLABUS

Rate of a chemical reaction, factors affecting the rate of reactions; concentration, temperature, pressure and catalyst; elementary and complex reactions, order and molecularity of reactions, rate law, rate constant and its units, differential and integral forms of zero and first order reactions, their characteristics and half-lives, effect of temperature on rate of reactions-Arrhenius theory, activation energy and its calculation, collision theory of bimolecular gaseous reactions (no derivation).

### JEE(ADVANCED) SYLLABUS

Rates of chemical reactions; Order of reactions; Rate constant; First order reactions; Temperature dependence of rate constant (Arrhenius equation). Radioactivity: Calculation of decay constant, half life, mean life, unit activity, carbon dating, calculation of earth age.



# Chemical Kinetics

## Introduction :

In the thermodynamics, we have studied whether a reaction will take place or not and if it does then upto what extent (chemical equilibrium). In this chapter we will study about how fast a chemical reaction takes place and what are the different factors affecting this rate of chemical reaction. How to optimise the conditions as to maximise the output in optimum time. The last part of chapter will be dealing with the mechanism of a chemical reaction and catalysis.

## Rate/Velocity of chemical reaction :

The rate of change of concentration with time of different chemical species taking part in a chemical reaction is known as **rate of reaction of that species**.

$$\text{Rate} = \frac{\Delta c}{\Delta t} = \frac{\text{mol/lit}}{\text{sec}} = \text{mol lit}^{-1} \text{time}^{-1} = \text{mol dm}^{-3} \text{time}^{-1}$$

Rate is always defined in such a manner so that it is always a positive quantity.

## Types of Rates of chemical reaction :

For a reaction  $R \longrightarrow P$

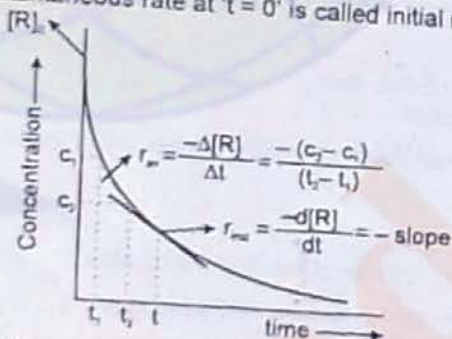
$$\text{Average rate} = \frac{\text{Total change in concentration}}{\text{Total time taken}}$$

$$= \frac{\Delta c}{\Delta t} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

**Instantaneous rate** : rate of reaction at a particular instant

$$R_{\text{instantaneous}} = \lim_{t \rightarrow 0} \left[ \frac{\Delta c}{\Delta t} \right] = \frac{dc}{dt} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Instantaneous rate can be determined by drawing a tangent at time  $t$  on curve drawn for concentration versus time. **Initial Rate** : Instantaneous rate at  $t = 0$  is called initial rate [slope of tangent at  $t = 0$ ].



## Relation between reaction rates of different species involved in a reaction :

For the reaction :  $N_2 + 3H_2 \longrightarrow 2NH_3$

$$\text{Rate of reaction of } N_2 = -\frac{d[N_2]}{dt}$$

$$\text{Rate of reaction of } H_2 = -\frac{d[H_2]}{dt}$$

$$\text{Rate of reaction of } NH_3 = \frac{d[NH_3]}{dt}$$

These rates are not all equal. Therefore by convention the rate of a reaction is defined as

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

**Note** : Rate of reaction value is dependent on the stoichiometric coefficients used in the reaction while rate of any species will be fixed value under given conditions.



Chemical Kinetics

Solved Examples

Ex.1 From the concentrations of R at different times given below, calculate the average rate of the reaction:

R → P during different intervals of time.					
t/s	0	5	10	20	30
10 <sup>3</sup> × [R]/mol L <sup>-1</sup>	160	80	40	10	2.5

Sol. We can determine the difference in concentration over different intervals of time and thus determine the rate by dividing Δ[R] by Δt

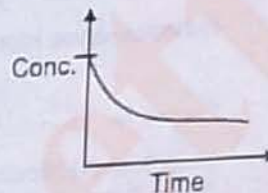
$\frac{[R]_1 \times 10^3}{\text{mol L}^{-1}}$	$\frac{[R]_2 \times 10^3}{\text{mol L}^{-1}}$	$t_2$ s	$t_1$ s	$r_{av} \times 10^3 = \frac{-[R_2 - R_1] \times 10^3}{[t_2 - t_1]}$ mol L <sup>-1</sup> s <sup>-1</sup>
160	80	5	0	16
80	40	10	5	8
40	10	20	10	3
10	2.5	30	20	0.75

Factors affecting rate of chemical reaction :

1. Concentration
2. Temperature
3. Nature of reactants & products
4. Catalyst
5. pH of the solution
6. Dielectric constant of the medium.
7. Radiations/light
8. Pressure
9. Electrical & Magnetic field.

The first four factors generally affect rate of almost all reactions while other factors are specific to some reactions only. The common examples of these reactions are :

- **Concentration** : We know from law of mass action that Rate is proportional to concentration of reactants. So, generally rate of reaction decreases with passage of time, since concentration of reactants decreases.



- **Temperature** :

- **Nature of reactants & Products** :

(a) **Physical state of reactants** :

Gaseous state > Liquid state > Solid state  
Decreasing order of rate of reaction.

(b) **Physical size of reactants** : As we decrease the particle size rate of reaction increases since surface area increases.

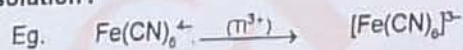
(c) **Chemical nature of reactants** :

- If more bonds are to be broken, the rate of reaction will be slow.
- Similarly bond strength is more, rate of reaction will be slow.

- **Catalyst** :

- Presence of positive catalyst lower down the activation energy hence increases the rate of reaction.
- Presence of negative catalyst increases activation energy hence decreases the rate of reaction.

- **pH of solution** :



This reaction takes place with appreciable rate in acidic medium, but does not take place in basic medium.

- **Dielectric constant of the medium** : More is the dielectric constant of the medium greater will be the rate of ionic reactions.
- **Radiations/light** : Radiation are useful for photochemical reaction.
- **Pressure** : Pressure is important factor for gaseous reaction.
- **Electrical & Magnetic field** : Electric & magnetic fields are rate determining factors if a reaction involves polar species.



### Rate Law (Dependence of rate on concentration of reactants) :

The representation of rate of reaction in terms of the concentration of the reactants is called the rate law. It can only be established by experiments.

Generally rate law expressions are not simple and these may differ for the same reaction on conditions under which the reaction is being carried out.

But for large number of reactions starting with pure reactants we can obtain simple rate laws.

For these reactions :  $\text{Rate} \propto (\text{conc.})^{\text{order}}$

$$\text{Rate} = K (\text{conc.})^{\text{order}} \quad \text{-- differential rate equation or rate expression}$$

Where K = Rate constant = specific reaction rate = rate of reaction when concentration is unity  
unit of K =  $(\text{conc})^{1-\text{order}} \text{ time}^{-1}$

Note : Value of K is a constant for a given reaction, depends only on temperature

### Order of reaction :

Let there be a reaction  $m_1A + m_2B \rightarrow \text{products}$ .

Now, if on the basis of experiment, we find that

$$R \propto [A]^p [B]^q \quad \text{Where } p \text{ may or may not be equal to } m_1 \text{, \& similarly } q \text{ may or may not be equal to } m_2$$

p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and (p + q) is overall order of the reaction.

Note : Order of a reaction can be 'zero' or any whole number, can be a fractional number and it can even be negative with respect to a particular reactant. But overall order is not found to be negative for any reaction till observed.

Examples showing different values of order of reactions :

Reaction	Rate law	Order
$2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$	$R = K [\text{N}_2\text{O}_5]^1$	1
$5\text{Br}^-(\text{aq}) + \text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\ell) + 3\text{H}_2\text{O}(\ell)$	$R = K [\text{Br}^-] [\text{BrO}_3^-] [\text{H}^+]^2$	$1 + 1 + 2 = 4$
$\text{H}_2(\text{Para}) \rightarrow \text{H}_2(\text{ortho})$	$R = K [\text{H}_2(\text{Para})]^{3/2}$	3/2
$\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$	$R = K [\text{NO}_2]^2 [\text{CO}]^0$	$2 + 0 = 2$
$2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$	$R = K [\text{O}_3]^2 [\text{O}_2]^{-1}$	$2 - 1 = 1$
$\text{H}_2 + \text{Cl}_2 \xrightarrow{h\nu} 2\text{HCl}$	$R = K [\text{H}_2]^0 [\text{Cl}_2]^0$	$0 + 0 = 0$

The reaction (2) does not take place in one single step. It is almost impossible for all the 12 molecules of the reactants to be in a state of encounter simultaneously. Such a reaction is called **complex reaction** and takes place in a sequence of a number of **elementary reactions**. For an elementary reaction the sum of stoichiometric coefficients = order of the reactions. But for complex reactions order is to be experimentally calculated.



## Solved Examples

**Ex.2** The reaction  $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{NOCl}(\text{g})$  is second order in NO and first order in  $\text{Cl}_2$ . In a volume of  $2 \text{ dm}^3$ , 5 mole of nitric oxide and 2 mol of  $\text{Cl}_2$  were brought together, and the initial rate was  $2.4 \times 10^{-3} \text{ mole dm}^{-3} \text{ s}^{-1}$ . What will be the rate when half of the chlorine has reacted ?

**Ans.**  $4.32 \times 10^{-4} \text{ M sec}^{-1}$

**Sol.**  $2\text{NO} + \text{Cl}_2 \longrightarrow 2\text{NOCl}$

5      2

5-2    1          2

$$R = k \left(\frac{5}{2}\right)^2 \times \left(\frac{2}{2}\right)^1$$

$$2.4 \times 10^{-3} = k \left(\frac{25}{4}\right)$$

$$K = \frac{4 \times 2.4 \times 10^{-3}}{25} \quad R_1 = \frac{4 \times 2.4 \times 10^{-3}}{25} \left[\frac{3}{2}\right]^2 \left[\frac{1}{2}\right]$$

$$R = \frac{4 \times 2.4 \times 10^{-3}}{25} \times \frac{9 \times 1}{8} = 4.32 \times 10^{-4} \text{ M sec}^{-1}$$

### Integrated rate laws :

#### (a) Zero Order Reactions :

For a zero order reaction

General rate law is, Rate =  $k [\text{conc.}]^0 = \text{constant}$

If  $C_0$  is the initial concentration of a reactant and  $C_t$  is the concentration at time 't' then

$$\text{Rate} = k = \frac{C_0 - C_t}{t} \quad \text{or} \quad kt = C_0 - C_t \quad \text{or} \quad C_t = C_0 - kt$$

Unit of K = same as that of Rate =  $\text{mol lit}^{-1} \text{ sec}^{-1}$ .

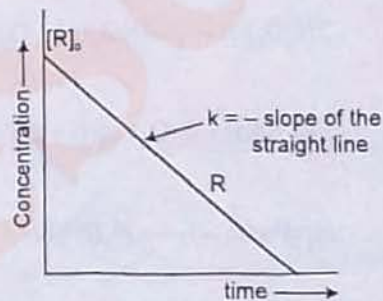
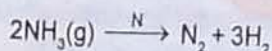
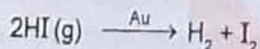
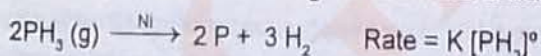
$$\text{Time for completion} = \frac{C_0}{k}$$

$$t_{1/2} \text{ (half life period)} \quad \text{at } t_{1/2}, C_t = \frac{C_0}{2}, \text{ so } kt_{1/2} = \frac{C_0}{2} \Rightarrow t_{1/2} = \frac{C_0}{2k}$$

$$\therefore t_{1/2} \propto C_0$$

#### Examples of zero order reactions :

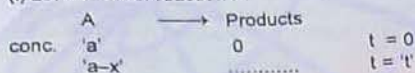
Generally decomposition of gases on metal surfaces at high concentrations follow zero order kinetics.



Chemical Kinetics

(b) First Order Reactions :

(i) Let a 1<sup>st</sup> order reaction is



Let  $\frac{dx}{dt}$  be the rate of reaction at time 't'

$\therefore \frac{dx}{dt} = k(a-x)^1$  or  $\frac{dx}{a-x} = k dt.$

On solving  $t = \frac{2.303}{k} \log \frac{a}{a-x}$   $k = \frac{2.303}{t} \log \frac{C_0}{C_1}$

$$k = \frac{2.303}{t} \log \frac{C_0}{C_1}$$

Wilhemy formula :  
 $C_t = C_0 e^{-kt}$

Interval formula :  
 $k = \frac{2.303}{(t_2 - t_1)} \log \frac{C_1}{C_2}$

If any substance is growing/increasing following first order kinetics then :

$$k = \frac{2.303}{t} \log \left( \frac{a+x}{a} \right)$$

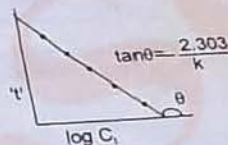
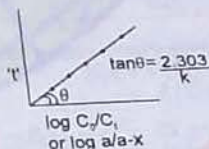
where a is initial concentration of the substance and x is the increment in its concentration after time t.

Half life time ( $t_{1/2}$ )  $k = \frac{2.303}{t_{1/2}} \log \frac{2C_0}{C_0} \Rightarrow t_{1/2} = \frac{2.303 \log 2}{k} = \frac{0.693}{k}$

$\therefore$  Half life period for a 1<sup>st</sup> order reaction is a constant quantity.

Graphical Representation :

$$t = -\frac{2.303}{k} \log C_1 + \frac{2.303}{R} \log C_0$$



First order growth reaction :

For bacteria multiplication or virus growth use following concept

Consider a growth reaction

Time Population (or colony)

0 a  
dt (a+x)

$\frac{dx}{dt} = k(a+x)$  or  $\frac{dx}{(a+x)} = k dt$

on integration

$\log_e (a+x) = kt + C$   
at  $t=0; x=0 \Rightarrow C = \log_e a$

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

or  $k = -\frac{2.303}{t} \log_{10} \left( \frac{a}{(a+x)} \right)$

or

$$k = \frac{2.303}{t} \log_{10} \left( \frac{a+x}{a} \right)$$

Chemical Kinetics

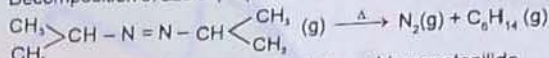
Generation time :

At  $t =$  generation time,  $x = a$

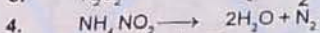
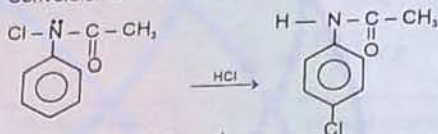
$$t = \frac{0.693}{k}$$

Examples of 1<sup>st</sup> order reactions :

1. Decomposition of azoisopropane

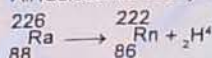


2. Conversion of N-chloro acetanilide into p-chloroacetanilide



5. Radioactive decay

• All radioactive decays are always first order kinetics.



Solved Examples

Ex.3 Calculate  $\frac{t_{0.75}}{t_{0.50}}$  for a 1<sup>st</sup> order reaction

Sol.  $k = \frac{2.303}{t_{1/4}} \log \frac{C_0}{\frac{1}{4}C_0} = \frac{2.303}{t_{1/2}} \log \frac{C_0}{\frac{C_0}{2}} \Rightarrow \frac{t_{1/4}}{t_{1/2}} = \frac{\log 4}{\log 2} = \frac{2 \log 2}{\log 2} = 2$

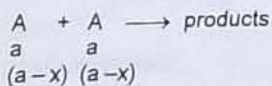
Ex.4 At least how many half-lives should elapse for a 1<sup>st</sup> order reaction A  $\rightarrow$  products so that the reaction is at least 95% completed? ( $\log 2 = 0.3$ )

- (1) 4 (2) 5 (3) 6 (4) 7

Sol. (2)  $100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25 \xrightarrow{t_{1/2}} 12.5 \xrightarrow{t_{1/2}} 6.25 \xrightarrow{t_{1/2}} 3.125$   
 0% 50% 75% 87.5% 93.75% 96.875%

(c) Second order reaction :

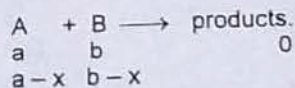
2<sup>nd</sup> order Reactions  
Two types



$\therefore \frac{dx}{dt} = k(a-x)^2$   
 $\Rightarrow \int_0^x \frac{dx}{(a-x)^2} = \int_0^t k dt$

$\Rightarrow \left( \frac{-1}{(a-x)} \right)_0^x = kt$

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



Rate law

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

$\int_0^x \frac{dx}{(a-x)(b-x)} = \int_0^t k dt$

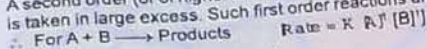
$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$



Chemical Kinetics

(d) Pseudo first order reaction :

A second order (or of higher order) reactions can be converted into a first order reaction if the other reactant is taken in large excess. Such first order reactions are known as pseudo first order reactions.



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

Now if 'B' is taken in large excess  $b \gg a$ .

$$\therefore k = \frac{2.303}{-bt} \log \frac{(a-x)}{a} \Rightarrow k = \frac{2.303}{bt} \log \frac{a}{a-x}$$

'b' is very large can be taken as constant

$$\Rightarrow kb = \frac{2.303}{t} \log \frac{a}{a-x} \Rightarrow k' = \frac{2.303}{t} \log \frac{a}{a-x}$$

- $k'$  is pseudo first order rate constant
- $k'$  will have units of first order.
- $k$  will have units of second order.
- Examples of Pseudo 1<sup>st</sup> order reactions :

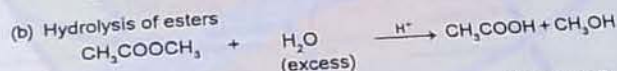
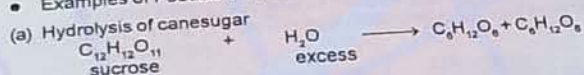
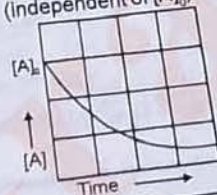
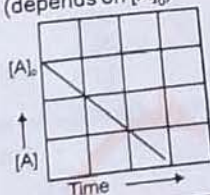
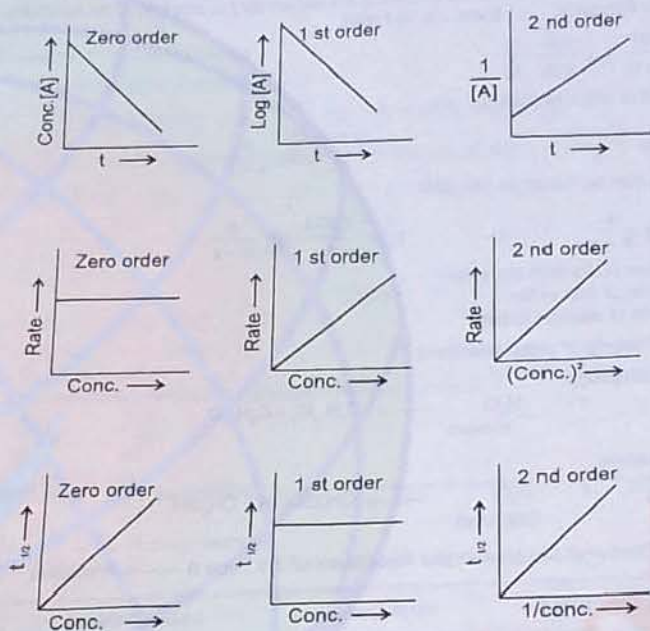


Table : Characteristics of First-and Second-Order Reactions of the Type  $A \rightarrow \text{Products}$

	Zero Order	First-Order	Second-Order	$n^{\text{th}}$ order
Differential Rate law	$-\frac{\Delta A}{\Delta t} = k[A]^0$	$-\frac{\Delta[A]}{\Delta t} = k[A]$	$-\frac{\Delta[A]}{\Delta t} = k[A]^2$	$-\frac{\Delta A}{\Delta t} = k[A]^n$
(Integrated Rate law)	$[A]_t = [A]_0 - kt$	$\ln [A]_t = -kt + \ln [A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{(A_t)^{n-1}} - \frac{1}{(A_0)^{n-1}} = (n-1)kt$
Linear graph	$[A]_t$ versus $t$	$\ln [A]$ versus $t$	$\frac{1}{[A]}$ versus $t$	$\frac{1}{(A_t)^{n-1}}$ v/s $t$
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$ (depends on $[A]_0$ )	$t_{1/2} = \frac{0.693}{k}$ (Independent of $[A]_0$ )	$t_{1/2} = \frac{1}{k[A]_0}$ (depends on $[A]_0$ )	$t_{1/2} \propto \frac{1}{(A_0)^{n-1}}$



Graphical comparison of different orders



Methods to determine order of a reaction :

(A) Initial rate method :

- By comparison of different initial rates of a reaction by varying the concentration of one of the reactants while others are kept constant

$$r = k [A]^a [B]^b [C]^c \quad \text{if } \begin{matrix} [B] = \text{constant} \\ [C] = \text{constant} \end{matrix}$$

then for two different initial concentrations of A we have

$$r_{01} = k [A_0]_1^a \quad r_{02} = k [A_0]_2^a$$

$$\Rightarrow \frac{r_{01}}{r_{02}} = \left( \frac{[A_0]_1}{[A_0]_2} \right)^a$$

or in log form we have

$$a = \frac{\log(r_{01}/r_{02})}{\log([A_0]_1/[A_0]_2)}$$

Chemical Kinetics

Solved Examples

Ex. 6 The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below:

t/s	0	100	200	300
p/Pa	$4.00 \times 10^7$	$3.50 \times 10^7$	$3.00 \times 10^7$	$2.5 \times 10^7$

Determine the order of reaction, its rate constant and half-life period.

Sol. It can be seen that rate of reaction between different time intervals is

$$0-100 \text{ s, rate} = \frac{(4.00 - 3.50) \times 10^7 \text{ Pa}}{100} = 5 \text{ Pa/s}$$

$$100-200 \text{ s, rate} = \frac{(3.50 - 3.00) \times 10^7 \text{ Pa}}{100} = 5 \text{ Pa/s}$$

$$200-300 \text{ s, rate} = \frac{(3.00 - 2.50) \times 10^7 \text{ Pa}}{100} = 5 \text{ Pa/s}$$

We notice that the rate remains constant and therefore, reaction is of zero order. Alternatively, if we plot  $p$  against  $t$ , it is a straight line again indicating it is a zero order reaction.

$$k = \text{rate} = 5 \text{ Pa/s}$$

$$t_{1/2} = \frac{\text{initial concentration or pressure}}{2k} = \frac{4.00 \times 10^7 \text{ Pa}}{2 \times 5 \text{ Pa/s}} = 4000$$

(B) Integrated rate law method

It is method of fit and trial. By checking where the kinetic data (experimental data) best fits into which integrated rate law, we determine the order. It can also be done graphically.

Solved Examples

Ex. 6 The rate of decomposition of  $\text{N}_2\text{O}_5$  in  $\text{CCl}_4$  solution has been studied at 318 K and the following results have been obtained

t/min	0	135	342	683	1680
c/M	2.08	1.91	1.87	1.35	0.57

Find the order of the reaction and calculate its rate constant. What is the half-life period?

Sol. It can be shown that the rate of the reaction. We now try integrated first order equation i.e.  $k = \frac{\ln(c_0/c)}{t}$

t/min	c/M	$k = \frac{\ln(c_0/c)}{t} \text{ min}^{-1}$
0	2.08	$6.32 \times 10^{-4}$
135	1.91	$6.30 \times 10^{-4}$
339	1.68	$6.32 \times 10^{-4}$
683	1.35	$6.32 \times 10^{-4}$
1680	0.72	$6.31 \times 10^{-4}$

It can be seen that the value of  $k$  is almost constant for all the experimental results and hence it is first order reaction with  $k = 6.31 \times 10^{-4} \text{ min}^{-1}$ .

$$t_{1/2} = \frac{0.69}{6.31 \times 10^{-4} \text{ min}^{-1}} = 1.094 \times 10^5 \text{ min}^{-1}$$

Graphical method: Alternatively, if we draw a graph between  $\ln c$  against  $t$ , we obtain a straight line with slope =  $-k$ .

Chemical Kinetics

(C) Method of half lives :

- The half lives of each order is unique so by comparing half lives we can determine order

for  $n^{\text{th}}$  order reaction  $t_{1/2} \propto \frac{1}{[R_0]^{n-1}}$

$$\frac{t_{1/2}}{t'_{1/2}} = \frac{(R_0')^{n-1}}{(R_0)^{n-1}}$$

Solved Examples

Ex.7 In the reduction of nitric gas with hydrogen, the reaction was found to be 50% complete in 210 seconds when the initial pressure of the mixture was 200 mm. In a second experiment the time of half reaction was 140 seconds when the initial pressure was 300 mm. Calculate the total order of the reaction.

Sol. For a  $n^{\text{th}}$  order reaction ( $n \neq 1$ ),  $t_{1/2} \propto \frac{1}{C_0^{n-1}}$

$$\frac{210}{140} = \left(\frac{300}{200}\right)^{n-1} \quad n = 2$$

(D) Ostwald's Isolation method :

- This method is useful for reaction which involve a large number of reactants. In this method, the concentration of all the reactants are taken in large excess exception that of one, so if

$$\text{rate} = k [A]^a [B]^b [C]^c = k_0 [A]^a$$

Then value of 'a' can be calculated by previous methods and similarly 'b' and 'c' can also be calculated.

Methods to monitor the progress of the reaction :

(A) Pressure measurement :

Progress of gaseous reaction can be monitored by measuring total pressure at a fixed volume & temperature.

This method can applied for those reaction also in which a gas is produced because of decomposition of a solid or liquid. We can get an idea about the concentration of reacting species at a particular time by measuring pressure.

- The pressure data can be given in terms of
  - Partial pressure of the reactant
  - Total pressure of the reaction system
  - Pressure at only some points of time

Solved Examples

Ex.8 Find the expression for K in terms of  $P_0$ ,  $P_t$  and n

Sol. Let there is a 1<sup>st</sup> order reaction,  $A(g) \rightarrow nB(g)$

Let initial pressure at time t	$P_0$	0	$t = 0$
	$P_A = (P_0 - x)$	$nx$	$t = t$
	-	$nP_0$	$t = \infty$

$$\therefore P_t (\text{Total pressure at time 't'}) = P_0 - x + nx = P_0 + (n - 1) x$$

$$\therefore x = \frac{P_t - P_0}{n - 1}$$

Chemical Kinetics

$$\therefore P_A = P_0 - \frac{P_t - P_0}{n-1} = \frac{P_0 n - P_t}{n-1}$$

$$\therefore a \propto p_0 \quad \& \quad a-x \propto P_A = \frac{nP_0 - P_t}{n-1}$$

$$\therefore k = \frac{2.303}{t} \log \frac{P_0(n-1)}{nP_0 - P_t} \quad \text{or} \quad K = \frac{2.303}{t} \log \frac{P_\infty - P_0}{P_\infty - P_t}$$

Final total pressure after infinite time =  $P_t = nP_0$

- Formula is not applicable when  $n = 1$ , the value of  $n$  can be fractional also.
- Do not remember the formula but derive it for each question.

Solved Examples

**Ex.9** For the decomposition of azoisopropane at 270°C it was found that at  $t = 0$ , the total pressure was 33.15 mm of Hg and after 3 minutes the total pressure was found to be 46.3 mm of Hg. Calculate the value of 'k' for this reaction.

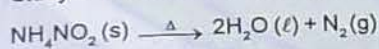
**Sol.**  $k = \frac{2.303}{3} \log \frac{33.15(2-1)}{2 \times 33.15 - 46.3} = 0.1684 \text{ min}^{-1}$

(B) Volume measurement :

(i) By measuring the volume of product formed we can monitor the progress of reactions.

Solved Examples

**Ex.10** Study of a reaction whose progress is monitored by measuring the volume of a escaping gas.



**Sol.** Let,  $V_t$  be the volume of  $\text{N}_2$  collected at time 't'  
 $V_\infty$  = be the volume of  $\text{N}_2$ , collected at the end of the reaction.

$$a \propto V_\infty$$

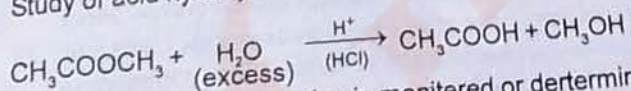
$$(a-x) \propto V_\infty - V_t$$

$$\therefore k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

(ii) By titration method : By measuring the volume of titrating agent we can monitor amount of reactant remaining or amount of product formed at any time. It is the titre value . Here the milliequivalents or millimoles are calculated using valence factors.

Solved Examples

**Ex.11** Study of acid hydrolysis of an ester.



The progress of this reaction is monitored or determined by titrating the reaction mixture at different time intervals against a standard solution of NaOH using phenolphthalein as indicator. Find out rate constant of the reaction in terms of volume of NaOH consumed at  $t = 0$ ,  $V_0$ , at  $t = \infty$ ,  $V_\infty$  & at time  $t$ ,  $V_t$ .



Chemical Kinetics

**Arrhenius theory of reaction rate :**

It was developed by max Trautz and William lewis. It gives insight in to the energetics and mechanistic aspects of reactions. It is based upon kinetic theory of gases.

**Arrhenius** proposed a theory of reaction rate which states as follows :

○ A chemical reaction takes place due to the collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z).

○ Every collision does not bring a chemical change. The collision that actually produce the products are effective collision. For a collision to be effective the following two barriers are to be effective the following two barriers are to be cleared.

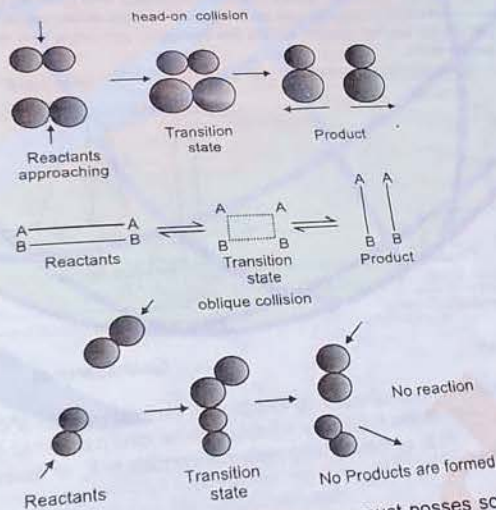
● **Energy barrier :**

The minimum amount of energy which the colliding molecules must posses as to make the chemical reaction to occur is known as threshold energy.

"The minimum amount of extra energy required by reactant molecules to participate in a reaction is called activation energy ( $E_a$ )"

● **Orientation barrier :**

Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper direction to make collision effective. Following diagrams can explain importance of suitable direction for collision.



- Collision to be effective the colliding molecules must posses some certain minimum energy called threshold energy of the reaction.
- Reactant molecules having energy equal or greater than the threshold are called active molecules and those having energy less than the threshold are called passive molecules.
- At a given temperature there exists a dynamic equilibrium between active and passive molecules. The process of transformation from passive to active molecules being endothermic, increase of temperature increases the number of active molecules and hence the reaction.
- Concept of energy of activation ( $E_a$ )  
 $\text{Passive molecules} \rightleftharpoons \text{Active molecules}, \Delta H = +ve$

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