CHEMISTRY

IIT- JEE

THEORY

EXAMPLES

EXERCISES

SOLUTION & TIPS

- CHEMICAL KINETICS 2nd
- NUCLEAR CHEMISTRY
- ELECTRO CHEMISTRY 3rd
- SOLID - STATE 1st
- SOLUTIONS
- SURFACE CHEMISTRY

CAREER POINT

TOTAL LEARNING SOLUTION PROVIDER

Where **Care** leads to **Career**

NUCLEAR CHEMISTRY

ELECTRO CHEMISTRY

SOLID-STATE

SOLUTIONS

SURFACE CHEMISTRY

— CHEMICAL KINETICS —

IIT-JEE Syllabus

1. Rate of chemical reactions

2. Order of reactions

3. Rate constant, Concentration and Temperature effect

4. Kinetics of first order reactions

5. Arhenious equations

*** Students are advised to solve the questions of exercises in the same sequence or as directed by the faculty members.

Index : Preparing your own list of Important/Difficult Questions

Instruction to fill

(A) Write down the Question Number you are unable to solve in **column A** below, by Pen.

(B) After discussing the Questions written in **column A** with faculties, strike off them in the manner so that you can see at the time of Revision also, to solve these questions again.

(C) Write down the Question Number you feel are important or good in the **column B**.

EXERCISE NO.	COLUMN :A Questions I am unable to solve in first attempt	COLUMN :B Good/Important questions
1		10/
2		
3		
4		
5		

Advantages

1. It is advised to the students that they should prepare a question bank for the revision as it is very difficult to solve all the questions at the time of revision.

2. Using above index you can prepare and maintain the questions for your revision.

CHEMICAL KINETICS

KEY CONCEPTS

1. Introduction

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 rate of chemical reaction is called **Chemical Kinetics**.
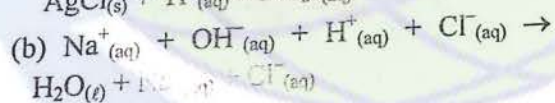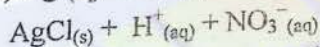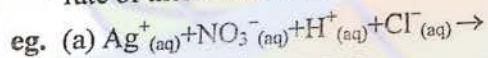
2. Types of Reactions

On the basis of their rates, the chemical reactions have been classified into the following three types.

2.1 Very fast or Instantaneous reaction :

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

(ii) These are mostly ionic reaction and do not involve any type of bond fission and formation between atoms.
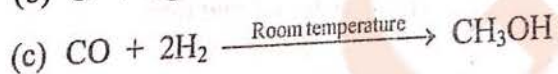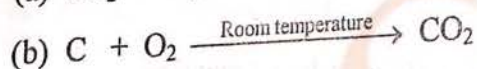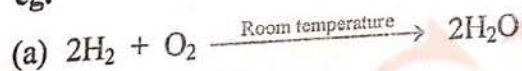
Reason :

(i) 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 columbic forces among ions.

(ii) The rate of such type of reactions are very fast. So, it is very difficult to determine the rate of these reactions.

eg. (a) $Ag^+_{(aq)} + NO_3^-_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \rightarrow$
$AgCl_{(s)} + H^+_{(aq)} + NO_3^-_{(aq)}$

(b) $Na^+_{(aq)} + OH^-_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \rightarrow$
$H_2O_{(\ell)} + Na^+_{(aq)} + Cl^-_{(aq)}$

2.2 Very Slow reaction :

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

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

eg.

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

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

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

(d) Rusting of iron

2.3 Moderate reactions :

(i) These are the reactions which takes place at moderate and measurable rates at room temperature and only these reactions are studied in chemical kinetics.

(ii) Most of these reactions are molecular in nature.

eg. (a) $2H_2O_2 \rightarrow 2H_2O + O_2$

(b) $2N_2O_5 \rightarrow 2N_2O_4 + O_2$

(c) $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

(d) $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

(e) $NO_2 + CO \rightarrow NO + CO_2$

(f) $2FeCl_3$ (aq) $+ SnCl_2 \rightarrow 2FeCl_2$ (aq) $+ SnCl_4$ (aq)
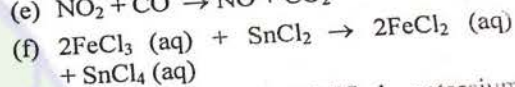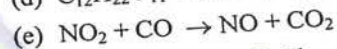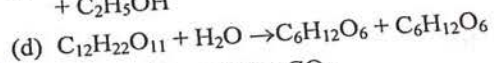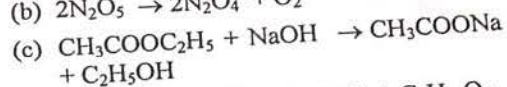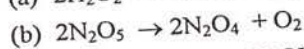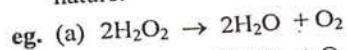
(g) decolorization of acidified potassium permanganate with sodium oxalate.

3. Rate of reaction

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

Rate of reaction

$$= \frac{\Delta c}{\Delta t} = \frac{\text{change in concentration of reactant or product (in mol L}^{-1})}{\text{time (in second)}}$$

Consider following reaction

$$A \longrightarrow \text{Products}$$
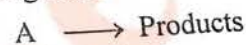
$$t = 0 \qquad a \text{ mol L}^{-1}$$

$$t = t \text{ sec } (a - x) \text{ mol L}^{-1} \times \text{ mol L}^{-1}$$

average rate of reaction $= \dfrac{x}{t}$

Note :

(i) Normally, the rate of reaction changes with time and hence it should be expressed as instantaneous rate as, $r = \dfrac{dx}{t}$

(ii) Graphically rate of reaction can be determined by curve between concentration and time

$$r_{(inst.)} = \lim_{\Delta t \to 0} \left(\frac{\Delta c}{\Delta t} \right)$$

$$= \frac{dc}{dt}$$
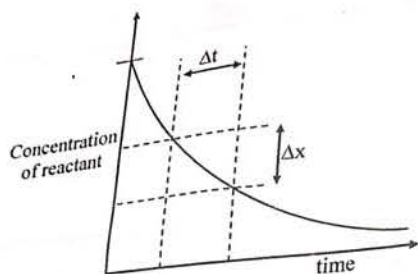
The slope of the above curve gives rate of reaction.

i.e. $\tan\theta = \frac{\Delta x}{\Delta t}$ = rate of reaction

(iii) Unit for rate of reaction is mole L^{-1} sec^{-1}.

(iv) The change is concentration of different reaction components, in the same time, may differ according to the balanced chemical reaction and hence the rate is normaly expressed as change in concentration per unit time per mol of that substance.

Consider a general reaction.

$$m_1A + m_2B \to n_1P + n_2Q$$
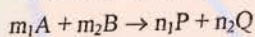
$$\text{rate of reaction} = -\frac{1}{m_1}\frac{d[A]}{dt} = -\frac{1}{m_2}\frac{d[B]}{dt}$$

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

e.g. $N_2 + 3H_2 \longrightarrow 2NH_3$

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

Note : Here, –ve sign represent the decrease in concetration with time and +ve sign, increase in concetration with time.

3.1 Classification of rate of reaction :

Rate of reaction can be classified into two categories

(i) **Average rate of reaction :**

Rate measured for a definite time interval is called average rate of reaction.

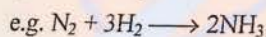$$\text{rate}_{(avg)} = \frac{c_2 - c_1}{t_2 - t_1} \text{ where } c_2 \& c_1 \text{ are }$$

concentration at time t_2 & t_1 respectively

(ii) **Instantaneous rate of reaction :**

Rate measured for an infinitesimilly small time interval is called instantaneous rate of reaction.

3.2 Reaction life time : It is defined as the time taken by the reaction to proceed almost completely.

3.3 Half life time : It is defined as the time taken by reaction to proceed to 50% completion i.e. concentration of reactant decreases to half of its initial value. It is denoted by $t_{1/2}$ or t_{50}.

3.4 Generation time : In biological processes time taken by certain virus or bacteria to double its population or colony is called generation time.

4. Rate Law & Rate Constant

At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the active masses of the reactants raised to the exerimentally determined powers. Consider a general reaction

$$aA + bB \longrightarrow \text{products}$$
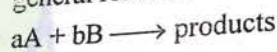
$$\text{rate} \propto [A]^x [B]^y ; \qquad \text{rate} = k [A]^x [B]^y$$

Here k is velocity constant or rate constant or specific rate of reaction & x and y are experimently determined values.

If $[A] = [B] = 1$ $\qquad$ or $\qquad$ rate = k

So rate constant is defined as rate of reaction when concentration of all reactants is taken unity.

4.1 Factors affecting rate constant :

Value of rate constant depends on following factors

(i) Temperature

(ii) Catalyst

Note :– Above factors will be discussed after collision theory.

4.2 Units of rate constant :

Unit of rate constant

$$= \left[\frac{1}{\text{unit of conc.}} \right]^{n-1} \times \text{time}^{-1}$$

$$= \left[\frac{\text{litre}}{\text{mole}} \right]^{n-1} \times \text{second}^{-1}$$

where n is the order of reaction

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4.3 Difference between rate of reaction and rate constant :

Rate of reaction	Reaction rate constant
1. Rate of reaction is called as the change in the concentration of the reactant or product per unit time.	1. Rate constant is the proportionality constant in 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	2. Since it is proportionality constant for a particular reaction, it is independent of the concentration of the reactant.
3. The units of rate of reaction is mole litre^{-1} time^{-1} irrespective to the order of reaction.	3. The units of reaction rate constant depends upon the order of reaction i.e. its unit differs according to order of reaction.

5. Molecularity of Reaction

(i) For elementary or single step reactions the molecularity is defined as the number of molecules of reactants involved in the balanced stoichiometric equation.

Eg. $PCl_5 \rightarrow PCl_3 + Cl_2$ (Unimolecular)

$2HI \rightarrow H_2 + I_2$ (Bimolecular)

$2SO_2 + O_2 \rightarrow 2SO_3$ (Trimolecular)

(ii) But for multi step reactions the molecularity is defined as the minimum number of reacting particles (molecules, atoms or ions) taking part in slowest step or rate determining step (RDS) of chemical reaction.

(a) eg.

$H_2O_2 \rightarrow H_2O + O$ (Slow)

$O + O \rightarrow O_2$ (Fast)

$2H_2O_2 \rightarrow 2H_2O + O_2$ (Unimolecular)

(b) eg.

$NO_2 + F_2 \rightarrow NO_2F + F$ (Slow)

$NO_2 + F \rightarrow NO_2F$ (Fast)

$2NO_2 + F_2 \rightarrow 2NO_2F$ (Bimolecular)

Note :

(i) Molecularity is theoretical concept.

(ii) Molecularity can not be zero, negative or fractional.

(iii) Molecularity can not be more than 3.

6. Order of Reaction

Consider a general reaction

$aA + bB + cC \rightarrow$ Product

Let rate of reaction depends on the product of concentrations of A, B and C raised to the power α, β and γ respectively. So we can write rate law for above reaction.

rate = $k[A]^\alpha [B]^\beta [C]^\gamma$ (k is rate constant)

Here sum of power of concentration terms involved in rate law expression is called order of reaction or overall order of reaction.
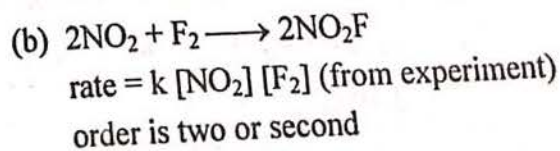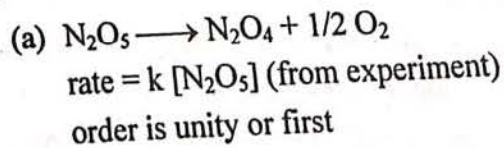
$\alpha + \beta + \gamma =$ order (n)

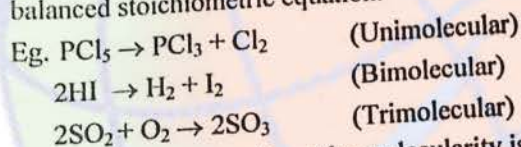α, β & γ are order of reaction w.r.t. A, B & C respectively.

Note :

(i) If $\alpha = a$, $\beta = b$ & $\gamma = c$ then order of reaction = molecularity of reaction. Such reaction will be definitely single step reaction.

(ii) Order is an experimently determined quantity.

(iii) It may be zero, positive, negative, fractional and greater than three.

(iv) Infinite and imaginary values are not possible.

(v) α, β and γ are not stoichiometric coefficients as used in law of mass action. Actually, law of mass action applicable only on elementary chemical reactions, for which order and molecularity are same.
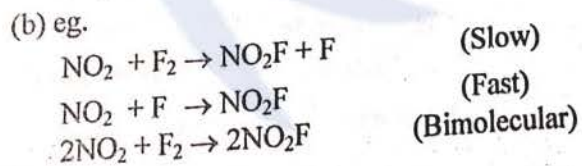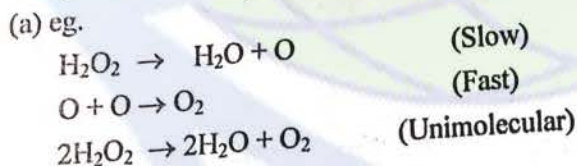
e.g.

(a) $N_2O_5 \longrightarrow N_2O_4 + 1/2 \, O_2$

rate = $k \, [N_2O_5]$ (from experiment)

order is unity or first

(b) $2NO_2 + F_2 \longrightarrow 2NO_2F$

rate = $k \, [NO_2] \, [F_2]$ (from experiment)

order is two or second

6.1 Pseudo unimolecular reactions :

In second order reaction, when one reactant is present in large excess, the second order reaction confirms to the first order and is known as **Pseudo unimolecular reaction.**

e.g.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

molecularity = 2 ; order = 1 (H_2O in excess)
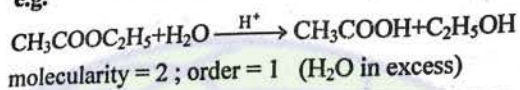
7. Integrated Rate Laws

Differential equation (rate laws) obtained from experimental data or mechanism of reaction can be integrated for certain time period to get the concentrations of reaction components.

7.1 Kinetics of nth order :

Consider the reaction A → product ; which is n^{th} order reaction so

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

or, $\dfrac{dx}{(a-x)^n} = kdt$

integrating both side.

$$\int \frac{dx}{(a-x)^n} = \int kdt \qquad \dots(1)$$

Case 1 :

when $n \neq 1$, on integration of equation (1)

$$\frac{1}{(n-1)} \cdot \frac{1}{(n-1)^{n-1}} = k.t + C$$

at t = 0 x = 0

$$C = \frac{1}{(n-1)} \cdot \frac{1}{(a)^{n-1}}$$

so $k = \dfrac{1}{t}\dfrac{1}{(n-1)}\left[\dfrac{1}{(a-x)^{n-1}} - \dfrac{1}{a^{n-1}}\right]$

or $\boxed{k = \dfrac{1}{t(n-1)}\left[\dfrac{1}{[A]_t^{n-1}} - \dfrac{1}{[A]_0^{n-1}}\right]}$ ...(2)

Case 2 :

when n = 1, on integration of equation (1)

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

at t = 0 ; x = 0 ⇒ c = $-\log_e a$

or $\log_e a - \log_e(a-x) = kt$

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right) \qquad \dots(3)$$

another form of above equation is

$$\boxed{k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}}$$

or $\boxed{[A]_t = [A]_0 e^{-kt}}$ ...(4)

(it is known as **wilhelmy** eq.)
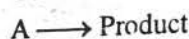
From above equation we conclude

(a) $t_{\frac{1}{2}} \alpha \dfrac{1}{c^{n-1}}$ and

(b) graph between $\dfrac{1}{(a-x)^{n-1}}$ versus t is linear.
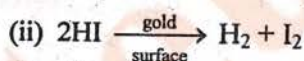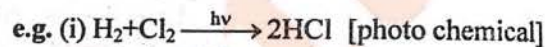
7.2 Zero order reactions :

Reactions whose rate is not affected by concentration of reactants or rate of reaction is proportional to the zeroth power of concentration of the reactants.
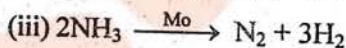
Consider a reaction

A $\longrightarrow$ Product

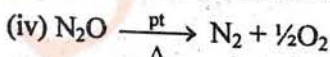$$\frac{dx}{dt} = k[A]^o = k$$

7.2.1 Some photochemical reactions, hetrogeneous reactions and enzyme catalyzed reactions are zero order reactions.

e.g. (i) $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$ [photo chemical]

(ii) $2HI \xrightarrow[\text{surface}]{\text{gold}} H_2 + I_2$

[hetrogeneous adsorption]

(iii) $2NH_3 \xrightarrow{Mo} N_2 + 3H_2$

[hetrogeneous adsorption]

(iv) $N_2O \xrightarrow[\Delta]{pt} N_2 + \frac{1}{2}O_2$

(v) Enzyme catalyzed reactions

eg. substrate $\xrightarrow{\text{enzyme}}$ Product
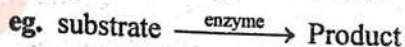
rate = k [enzyme]^1 [substrate]^0

7.2.2 Integrated rate law :

Putting the value n = 0 in equation (2), we get

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

7.2.3 Half life ($t_{\frac{1}{2}}$) :

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

from eq (1)

$$t_{\frac{1}{2}} = \frac{a}{2k} \qquad \text{or} \qquad t_{\frac{1}{2}} \propto a$$

so half life is directly proportional to the initial concentration of the reactant.

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7.2.4 Graphical representation & unit of rate constant
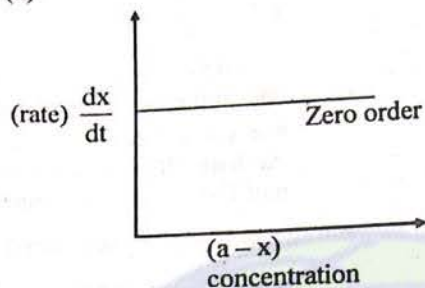
(a)

(b) Unit of rate constant

$$\text{unit of } k = \left(\frac{L}{mole}\right)^{n-1} \times time^{-1}, n = 0$$

so unit of $k = mol\ L^{-1}sec^{-1}$ i.e. unit of rate of reaction.

7.3 First order reactions :

A reaction is called first order if its rate is determined by the change of one concentration term only i.e. rate is proportional to unity power of concentration term.

7.3.1 Example of first order reactions :

(i) $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

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

(iii) $C_6H_5N_2Cl + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$

(iv) $(CH_3)_3COOC(CH_3)_3 \longrightarrow 2CH_3COCH_3 + C_2H_6$
di–tertbutyl peroxide

(v) $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

(vi) $(CH_3)_2CHN_2CH(CH_3)_2 \longrightarrow N_2 + C_6H_{14}$
Azoiso propane

(vii) $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

(viii) Radio active decay, virus or bacteria generation or inactivation.

7.3.2 Integrated rate law :

from equation (3) and (4)

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$$

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

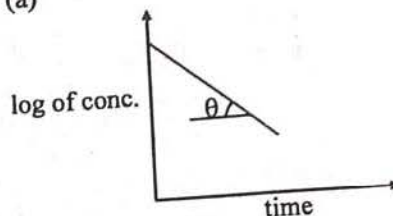### 7.3.3 Half life ($t_{1/2}$) :

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

from eq (1) $k = \dfrac{2.303}{t_{1/2}} \log\left(\dfrac{2a}{2}\right)$

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

i.e. $t_{1/2}$ does not depend on initial concentration of reactant.

7.3.4 Graphical representation & unit of rate constant

(a)

$$\text{slope} = \tan\theta = \frac{2.303}{k}$$

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

$y = mx + C$

here slope $= m = \dfrac{2.303}{k}$

(b) Unit of rate constant $= \left(\dfrac{L}{mol}\right)^{n-1} \times time^{-1}$

$n = 1$

so unit of $k = sec^{-1}$

7.4 Second order reaction (Only for REE aspirants.) :

A reaction is called second order reaction if it is depend on two concentration terms.

7.4.1 Example :

(i) $CH_3COO\ C_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$
(Saponification)

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

(iii) $2\ O_3 \longrightarrow 3O_2$

(iv) $2\ Cl_2O \longrightarrow 2\ Cl_2 + O_2$

(v) $2CH_3CHO \longrightarrow 2CH_4 + 2CO$

(vi) $S_2O_8^{2-} + 2I \longrightarrow 2SO_4^{2-} + I_2$
(Persulphate ion)
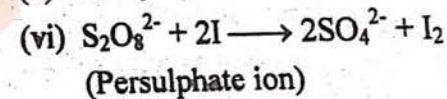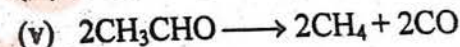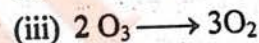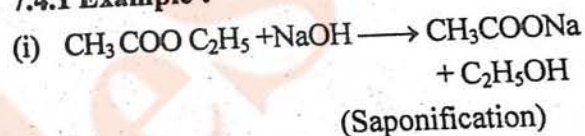
7.4.2 Second order kinetics can be applied on two types of reactions viz.

(a) $2A \longrightarrow$ product

$t = 0$ a or $[A]_0$ $x/2$

$t = t$ a–x or $[A]_t$

7.7 First order kinetics in terms of volume, pressure and rotation:

(a) If volume of reagent or product is given then use following relation.

consider A $\longrightarrow$ product

at $t = 0$ v_0 (used)

at $t = t$ v_t (used)

at $t = \infty$ v_∞ (used) (i.e. reaction is almost complete)

$$k = \frac{2.303}{t} \log\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

Note :

(i) If v_0 is not given then left v_0 term in formula.

(ii) If v_∞ is not given then left v_∞ term in formula.

(iii) If v_0, v_t or v_∞ is not given directly use stoichiometric equation to get then.

(b) If pressure is given in gaseous reactions then use following formula.

$$k = \frac{2.303}{t} \log_{10}\left(\frac{P_0}{P_0 - x}\right)$$

P_0 = Initial pressure of reagent

$P_0 - x$ = pressure of reactant at time 't'.

Note :

(i) If P_0 and $(P_0 - x)$ is not given directly use stoichiometric realtion to set them.

(ii) If the presence of mixture is given then use following concept.

consider reaction

$$A_{(g)} \longrightarrow B_{(g)} + 2C_{(g)} + D_{(liq.)}$$

at $t = 0$ P_0 –   –   –

at $t = t$ $P_0 - P'$ P' $2P'$ –

at $t = \infty$ – P^0 $2P^0$ –
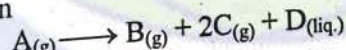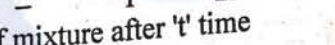
so total press. of mixture after 't' time

$P_{total} = P^0 - P' + P' + 2P'$

and P_{total} after long period or $t = \infty$

$P_{total} = P^0 + 2P^0$

(iii) If vapour pressure of liquid is given then it will remain constant throughout the reaction.

(c) If rotation of optically active species is given then use following formula

$$k = \frac{2.303}{t} \log\left(\frac{r_\infty - r_0}{r_\infty - r_t}\right)$$

r_∞ = angle of rotation at $t = \infty$

r_0 = angle of rotation at $t = 0$

r_t = angle of rotation at $t = 't'$

8. Method of Determination of Order of Reaction

8.1 Method of integration (Hit & Trial) :

In this method we put given data in various order's integrated laws to get rate constant. It should be constant throughout the given set of data.

i.e.

(i) $k = \dfrac{2.303}{t} \cdot \log_{10} \dfrac{a}{a - x}$ for 1st order

(ii) $k = \dfrac{1}{t}\left[\dfrac{1}{(a-x)} - \dfrac{1}{a}\right]$ for 2nd order

(iii) $[A]_t = [A]_0 - kt$ for zero order

8.2 Graphical method :

for a reaction of nth order a graph of $\dfrac{1}{(a-x)^{n-1}}$ versus time must be a straight line.
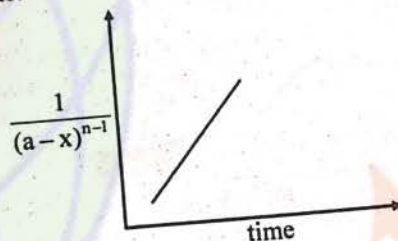
8.3 Half life method :

General expression for half life is $t_{1/2} \propto \dfrac{1}{a^{n-1}}$

where a = initial concentration and n = order of reaction

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

taking log both side

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

8.4 Vant Hoff's differential method :

Consider two reaction having C_1 & C_2 as initial concentration with n^{th} order.

$$-\frac{dC_1}{dt} = kC_1^n \quad \text{and} \quad -\frac{dC_2}{dt} = kC_2^n$$

taking log both side

$$\log\left(\frac{dC_1}{dt}\right) = \log k + n \log C_1 \quad ...(1)$$

$$\log\left(\frac{dC_2}{dt}\right) = \log k + n \log C_2 \quad ..(2)$$

from (1) & (2)

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

$-\dfrac{dC_1}{dt}$ & $-\dfrac{dC_2}{dt}$ are rate of reaction w.r.t. reactants.

9. Collision Theory

9.1 Assumptions :

(i) 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).

E = Threshold energy

Fraction of molecules capable or bringing effective collision
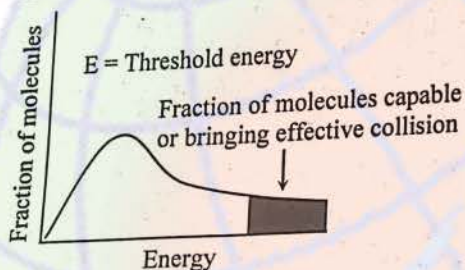
(ii) Every collision does not bring a chemical change. The collision that actually produce the products are effective collision. For a collision to be effective the following two barriers are to be cleared.

9.2 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.
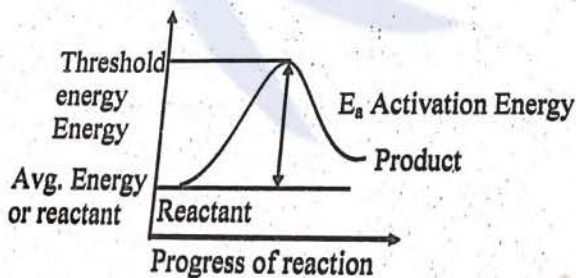
From the given diagram we can conclude that " The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy (E_a) ".

9.3 Orientation

Energy alone does the collision. The reacting effectiveness of the collision in proper direction to molecules must collide in proper direction to make collision effective. Following diagrams can explain importance of suitable direction for collision.
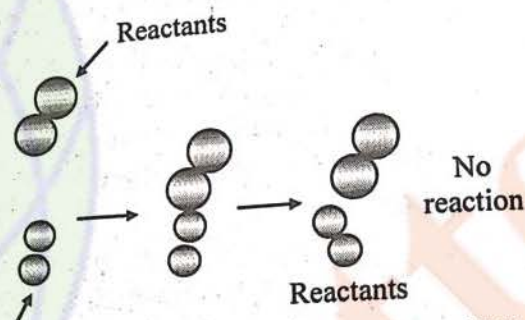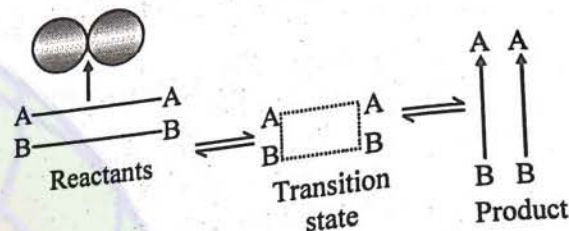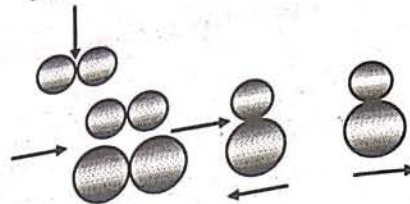
So one can conclude that the colliding molecules must be in the direction of maximum overlapping.

Hence, rate of reaction may be given by

Rate = collision frequency x fraction of effective collision   **R = Z × f**

10. Factor Affecting Rate of Reaction

10.1 Nature of Reactants :

(a) **Physical state of reactants** - This has considerable effect over rate of reaction. We have following relation between state of reactant & rate of reaction.

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

Because collisions in homogeneous system are more effective than heterogenous system.

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

(c) Chemical nature of reactants – Number of bonds to be broken and bond strength of reacting molecules also affect the rate of reaction.

   (i) If more bonds are to be broken, the rate of reaction will be slow.

   (ii) Similarly bond strength is more, rate of reaction will be slow.

10.2 Concentration of Reactants :
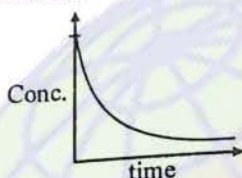
We know from law of mass action that " Rate is proportional to concentration of reactants." So rate of reaction decreases with passage of time, since concentration of reactants decreases. The curve show decrease in the slope with time and slope is the measure of rate.

10.3 Effect of temperature :

(i) Rate of reaction increases with increase in temperature. In general for every 10°C rise in temperature rate of reaction increases 2 to 3 times.

(ii) The temperature coefficient (μ) of a chemical reaction is defined as the ratio of the specific rates of a reaction at two temperature differing by 10°C (25°C to 35°C).

$$\mu = \frac{k(t+10)}{k(t)} = 2 \text{ to } 3 \quad \text{or} \quad \frac{k_{T_2}}{k_{T_1}} = \mu^{\frac{(T_2-T_1)}{10}}$$

Arrhenious suggested an equation which describes k as a function of temperature.

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

where

E_a = activation energy

A = Frequency factor or pre exponential factor

Taking log $\quad \log(k) = \log(A) - \dfrac{E_a}{2.303RT}$

$$\text{Slope} = \tan\theta = \frac{E}{2.303R}$$

$$\text{Intercept} = \log A$$

If $T_2 > T_1$ and corresponding rate constant are k_2 and k_1 then

$$\log\left(\frac{k_2}{k_1}\right)\frac{E_a}{2.303} = \left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

10.4 Presence of catalyst :

(a) Presence of positive catalyst lower down the activation energy hence increases the rate of reaction.

(b) Presence of negative catalyst increases activation energy hence decreases the rate of reaction.

11. Kinetics of Simultaneous Reactions

11.1 Parallel reactions :

Consider following first order reaction proceeding through two parallel paths one leading to product B and other leading to product C.
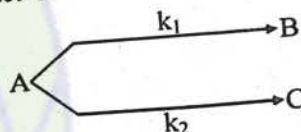
where k_1 and k_2 are respective rate constants.

so overall rate constant

$k = k_1 + k_2$

fractional yield of B $= \dfrac{k_1}{k_1 + k_2}$

fractional yield of C $= \dfrac{k_2}{k_1 + k_2}$

11.2 Successive reactions :

Consider A converted into B according to first order kinetics and simultaneously B converted into C following first order kinetics

$A \xrightarrow{k_1} B \xrightarrow{k_2} C \quad$ where $[A]_0$ is the

$t_{1/2}(A) \quad t_{1/2}(B) \quad$ initial conc. of A

$[A]_0$
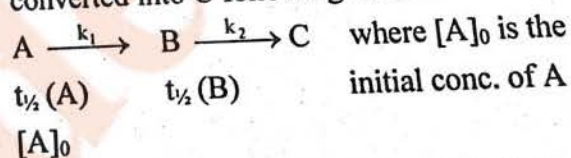
Let after time 't' concentration of A & B are $[A]_t$ and $[B]_t$ respectively.

$[A]_t = [A]_0 \, e^{-k_1 t}$

$[B]_t = \dfrac{k_1[A]_0}{(k_2 - k_1)}[e^{-k_1 t} - e^{-k_2 t}]$

from the above equation following cases of equilibrium may be considered.

(i) **Transient equilibrium**

when $(t_{1/2})_A > (t_{1/2})_B$ or $k_1 < k_2$

$$\frac{[A]_t}{[B]_t} = \frac{k_2 - k_1}{k_1}$$

(ii) **Secular equilibrium**

if $(t_{1/2})_A \gg (t_{1/2})_B$ or $k_1 \ll k_2$

$$\frac{[A]_t}{[B]_t} = \frac{k_2}{k_1}$$

(iii) **Disequilibrium**

if $(t_{1/2})_A < (t_{1/2})_B$ or $k_1 > k_2$
then calculation is beyond our scope.

(iv) Maximum concentration of B can be achieved in time (t) which can be calculated as

$$t = \frac{2.303(\log k_1 - \log k_2)}{k_1 - k_2}$$

SOLVED EXAMPLES

Ex.1 Chemical kinetics, a branch of physical chemistry, deals with–
(A) Heat change in a reaction
(B) Physical change in a reaction
(C) Rates of reaction
(D) Structure of molecules

Sol.[C] (definition of chemical kinetics)

Ex.2 Which of the following rate laws has an overall order of 0.5 for the reaction A+B+C → Product –
(A) $R = k[A].[B].[C]$
(B) $R = k[A]^{.5} [B]^{.5} [C]^{.5}$
(C) $R = k[A]^{1.5} [B]^{-1}[C]^0$
(D) $R = k[A] [B]^0 [C]^{.5}$

Sol. [C]
Order = 1.5 + (–1) + 0 = 0.5

Ex.3 In a reaction, the rate = $k [A] [B]^{2/3}$ the order of reaction is
(A) 1   (B) 2
(C) 5/3   (D) zero

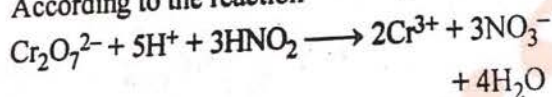**Sol.** Order of reaction = $1 + \dfrac{2}{3} = \dfrac{5}{3}$

so correct answer is (C)

Ex.4 For the reaction, $2NO \longrightarrow N_2 + O_2$, the expression $-\dfrac{1}{2}\dfrac{d[NO]}{dt}$ represents–
(A) The rate of formation of NO
(B) The average rate of the reaction
(C) The instantaneous rate of reaction
(D) All the above

Sol. [C]

Ex.5 According to the reaction
$Cr_2O_7^{2-} + 5H^+ + 3HNO_2 \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$

The rate of disappearance of $Cr_2O_7^{2-}$ is found to be 2.4×10^{-4} mole $L^{-1}s^{-1}$. Find the rate of appearance of Cr^{3+} during given time interval.

Sol. rate expression

$$-\frac{d[Cr_2O_7^{2-}]}{dt} = \frac{1}{2}\frac{d[Cr^{3+}]}{dt}$$

it is given that

$$\frac{d[Cr_2O_7^{2-}]}{dt} = 2.4 \times 10^{-4} \text{ mole } L^{-1}s^{-1}$$

so $\dfrac{d[Cr^{3+}]}{dt} = 2 \times 2.4 \times 10^{-4}$ mole $L^{-1}s^{-1}$

$= 4.8 \times 10^{-4}$ mole $L^{-1}s^{-1}$

Ex.6 A zero order reaction is one –
(A) In which reactants to not react
(B) In which one of the reactants is in large excess
(C) Whose rate does not change with time
(D) Whose rate increase with time

Sol. [C]

Ex.7 For a given reaction the concentration of the reactant plotted against time gave a straight line with negative slope. The order of the reaction is-
(A) 3   (B) 2
(C) 1   (D) 0

Sol.[D] Rate law is $[A_0] - [A] = K t$

or $[A] = [A_0] - K t$

Hence, graph is straight line with negative slope.

Ex.8 Which of the following curves represents a Ist order reaction -
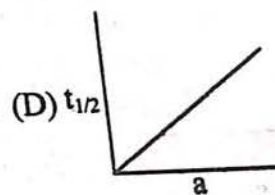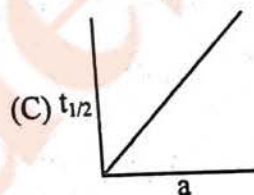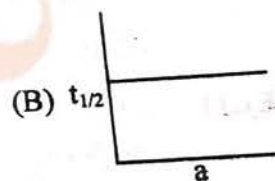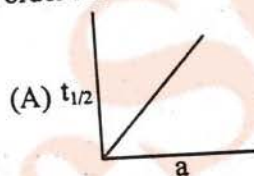
Sol.[B] Half life is independent to the initial concentration of the reactant.

Ex.9 If 'a' is the initial concentration of a substance which reacts according to zero order kinetic and k is rate constant, the time for the reaction to go to completion is
(A) a/k   (B) 2/ka
(C) k/a   (D) infinite

Sol. For zero order reaction
$[A]_t = [A]_0 - kt$
for completion of reaction $[A]_t = 0$ and
$t = \dfrac{[A]_0}{k}$ & $A_0 = a$
$t = \dfrac{a}{k}$ Correct answer is (A)

Ex.10 The rate for the reactio $2Cl_2O \rightarrow 2Cl_2 + O_2$ at 200°C is found to be rate = k $[Cl_2O]^2$
(a) How would the rate change is $[Cl_2O]$ is reduced to one third of its original value?
(b) How should the $[Cl_2O]$ be changed in order to double the rate?

Sol. (a) $r = k [Cl_2O]^2$ ...(1)
let new rate is r'
so $r' = k\left[\dfrac{Cl_2O}{3}\right]^2 = \dfrac{r}{9}$
so new rate is 1/9 of initial rate
(b) In order to have rate = 2r
let $[Cl_2O] = x$
so $2r = k (x)^2$ ...(2)
from (1) & (2)
$x^2 = 2 [Cl_2O]^2$
$x = \sqrt{2}\ [Cl_2O]$
so concentration of Cl_2O must be increases to $\sqrt{2}$ times of its initial value.

Ex.11 For the chemical reaction between mercuric chloride and potassium oxalate the mass of Hg_2Cl_2 precipited from different situation in a given time at 100°C is given in following table.

Exp. No.	HgCl₂ (mol L⁻¹)	K₂Cr₂O₇ (mol L⁻¹)	Time (min.)	Hg₂Cl₂ (mol L⁻¹)
1.	0.0836	0.404	65	0.0068
2.	0.0836	0.0202	120	0.0031
3.	0.0418	0.0404	60	0.0032

from these data calculate order of reaction.

Sol. let rate = k $[HgCl_2]^a [K_2Cr_2O_7]^b$
so from exp. (1)
$\dfrac{0.0068}{65} = k [0.0836]^a [0.404]^b$ ...(1)
from exp. (2)
$\dfrac{0.0031}{120} = k [0.0418]^a [0.404]^b$ ...(2)
from exp. (3)
$\dfrac{0.0032}{60} = k [0.0418]^a [0.404]^b$ ...(3)
from (1) & (2)
$4 = 2^b$ or $(2)^2 = (2)^b$
$\Rightarrow b = 2$
from (1) & (3)
$2 = 2^b$ or $a = 1$
so overall order = 2 + 1 = 3
rate = k $[HgCl_2]^2 [K_2C_2O_4]$

Ex.12 The decomposition of H_2O_2 in aqueous solution is a reaction of first order. How can it be justified from the following data.

Time (min.)	0	10	20	30
x	25	20	15.7	12.5

Where x in the volume (mL) of $KMnO_4$ required to titrate a definite volume of H_2O_2?

Sol. $H_2O_2 \longrightarrow H_2O + \frac{1}{2} O_2$
$t = 0$ a
$t = t$ $a - x$
here (a − x) corresponds to the under decomposed H_2O
for t = 10 min
$k_1 = \dfrac{2.303}{10} \log \dfrac{25}{20} = 0.022$ min⁻¹
for t = 20 min
$k_1 = \dfrac{2.303}{10} \log \dfrac{25}{15.7} = 0.023$ min⁻¹
for t = 30 min
$k_1 = \dfrac{2.303}{10} \log \dfrac{25}{12.5} = 0.023$ min⁻¹
The constant value of k_1 shows that the given reaction is of first order.

Ex.13 The optical rotation of conc. sugar in 0.5N lactic acid at 25°C at various time intervals are given below.

Time (min.)	0	1435	11360	∞
rotation(degree)	34.5°	31.1°	13.98°	−10.77°

show that the reaction is of first order.

Sol. Applying formula

$$k = \frac{2.303}{t} \log\left(\frac{r_\infty - r_0}{r_\infty - r_t}\right)$$

at t = 1435 min.

$$k = \frac{2.303}{1435} \log\left(\frac{45.27}{41.87}\right) = 5.44 \times 10^{-5}$$

at t = 11360 min.

$$k = \frac{2.303}{11360} \log\left(\frac{45.27}{24.75}\right) = 5.311 \times 10^{-5}$$

value of k is fairly constant hence reaction is of 1st order.

Ex.14 If for any reaction, the rate constant is equal to the rate of the reaction at all concentration, the order is–

(A) 0   (B) 2
(C) 1   (D) 3

Sol.[A]

Ex.15 For a certain reaction involving a single reactant, it is found that $C_0 \sqrt{T}$ is constant where C_0 is the initial concentration of the reactant and T is the half-life. What is the order of the reaction ?

(A) 1   (B) zero
(C) 2   (D) 3

Sol.[D] ∴ $T \propto (C_0)^{1-n}$

or $T = \text{const.} \times (C_0)^{1-n}$

or $T \times (C_0)^{n-1} = \text{const.}$

or $\sqrt{T \times (C_0)^{n-1}} = \text{const.}$

or $\sqrt{T} \times (C_0)^{\frac{n-1}{2}} = \text{const}$

But from question $\frac{n-1}{2} = 1$

∴ n = 3

Ex.16 For the irreversible unimolecular type reaction $A \xrightarrow{k} $ products in a batch reactor, 80% reactant $A(C_{A0} = 1 \text{ mole/lit.})$ is converted in a 480 second run and conversion is 90% after 18 minute. The order of this reaction is -

(A) 1   (B) 2
(C) 1/2   (D) 3/2

Sol.[B] Let the reaction is of 1st order.

$$K = \frac{2.303}{t} \log\frac{[A_0]}{[A]}$$

from 1st data, $K = \frac{2.303}{480} \log\frac{100}{100-80} = 3.35 \times 10^{-3}$

2nd data $K = \frac{2.303}{18 \times 60} \log\frac{100}{100-90} = 2.132 \times 10^{-3}$

Hence it is not of 1st order

Now try for 2nd order.

$$K = \frac{1}{t}\left[\frac{1}{[A]} - \frac{1}{[A_0]}\right]$$

from 1st data,

$$K = \frac{1}{480}\left[\frac{1}{1 \times \frac{20}{100}} - \frac{1}{1}\right] = 8.33 \times 10^{-3}$$

2nd data

$$K = \frac{1}{18 \times 60}\left[\frac{1}{1 \times \frac{90}{100}} - \frac{1}{1}\right] = 8.33 \times 10^{-3}$$

Since, data is following 2nd order kinetics reaction is of 2nd order.

Ex.17 For the first order reaction $t_{99\%} = x \times t_{90\%}$ the value of 'x' will be -

(A) 10   (B) 6
(C) 3   (D) 2

Sol.[D] $t_{99\%} = x \times t_{90\%}$

or $\frac{2.303}{K} \log\frac{100}{100-99}$

$= x \times \frac{2.303}{K} \log\frac{100}{100-90}$

or x = 2

Ex.18 The gas phase decomposition $2N_2O_5 \rightarrow 4NO_2 + O_2$ follows the first order rate law. $K = 7.5 \times 10^{-3}$ sec-1. The initial pressure of N_2O_5 is 0.1 atm. The time of decomposition of N_2O_5 so that the total pressure becomes 0.15 atm will be

(A) 54 sec   (B) 5.4 sec
(C) 3.45 sec   (D) 34.55 sec

Sol.[A]

$$2 N_2O_5 \rightarrow 4 NO_2 + O_2$$

Initial pressure   0.1 atm   0   0
pressure at time, t $(0.1 - x)$ atm   2x atm   x/2 atm
Total pressure $= (0.1 - x) + 2x + x/2 = 0.1 + 3x/2 = 0.15$ (from Question)

$\therefore x = 0.1/3$

Now, from Ist order kinetics,

$$t = \frac{2.303}{K} \log \frac{P_0}{P} = \frac{2.303}{7.5 \times 10^{-3}} \log \frac{0.1}{0.1-x} = 54 \text{sec}.$$

Ex.19 If in the fermentation of sugar in an enzymatic solution that is 0.12M, the concentration of the sugar is reduced to 0.06M in 10h and to 0.03M in 20h, what is the order of the reaction--

(A) 1   (B) 2
(C) 3   (D) 0

Sol.[A] Half life is independent to the initial concentration of the reactant.

Ex.20 In a Ist order reaction A $\longrightarrow$ products, the concentration of the reactant decreases to 6.25% of its initial value in 80 minutes. What is (i) the rate constant and (ii) the rate of the reaction. 100 minutes after the starts, if the initial concentration is 0.2 mole/litre ?

(A) 2.17×10^{-2} min^{-1}, 3.47×10^{-4} mol. litre^{-1} min^{-1}
(B) 3.465×10^{-2} min^{-1}, 2.166×10^{-4} mol. litre^{-1} min^{-1}
(C) 3.465×10^{-3} min^{-1}, 2.17×10^{-3} mol. litre^{-1} min ^{1}
(D) 2.166×10^{-3} min^{-1}, 2.667×10^{-4} mol. litre^{-1} min^{-1}

Sol.[B] (i) Given $[A_0] = 0.2$ M & $[A] = 0.2 \times \frac{6.25}{100}$

$= 0.0125$

$$K = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$= \frac{2.303}{80} \log \frac{0.2}{0.0125} = 0.0346 \text{ min}^{-1}$$

Ex.21 At 25°C the second of reaction $I^- + ClO^- \rightarrow IO^-_3 + Cl^-$ is 0.0606 M-^{l}sec-^{1}. If a solution is initially 3.5×10^{-3} M with respect to each reactants, what will be the concentration of each species present after 300 sec—

Sol. $k = 0.0606$ M^{-1}sec^{-1}
$[B_0] = [A_0] = 3.5 \times 10^{-1}$M

$$\frac{1}{[A]} - \frac{1}{[A_0]} = kt$$

$$\frac{1}{[A]} - \frac{1}{[3.5 \times 10^{-3}]} = 0.0606 \times 300 = 18.18$$

or $[A] = 3.29 \times 10^{-3}$ M = [B]

Ex.22 Sucrose decompose in acid solution into glucose and fructose according to a first order rate law, with a half life of 3.33 hour at ?? what fraction of a sample of sucrose remains after 9.00 hour.

Sol.

$$2.303 \log \frac{[A]}{[A_0]} = -kt = -\frac{0.693}{3.3} \times 9$$

$$\log \frac{[A]}{[A_0]} = -0.814$$

$$\frac{[A]}{[A_0]} = 0.153$$

so fraction remaining = 0.153.

Ex.23 Mechanism for the reaction $2A \rightarrow C$ is given as follows.

(i) $A + A \xrightarrow{k_1} A^* + A$ (Activation)

(ii) $A^* + A \xrightarrow{k_2} A + A$ (Deactivation)

(iii) $A^* \xrightarrow{k_3} C$ (Reaction)

deduce general rate law for the reaction, using steady state approximation.

Sol. According to steady state approximation, since A* is an intermediate,
rate of production of A* = rate of destruction of A*

$$k_1[A]^2 = k_2[A^*][A] + k_3[A^*]$$

$$[A^*] = \frac{k_1[A]^2}{k_2[A]+k_3}$$

rate of reaction $= \frac{dc}{dt} = k_3[A^*] = \frac{k_1 k_3 [A]^2}{k_3[A] + k_3}$

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