CHEMICAL KINETICS

1. INTRODUCTION

Chemical kinetics deals with the rates of chemical processes. Any chemical process may be broken down into a sequence of one or more single-step processes known either as elementary processes, elementary reactions, or elementary steps. Elementary reactions usually involve either a single reactive collision between two molecules, which we refer to as a bimolecular step, or dissociation/ isomerisation of a single reactant molecule, which we refer to as a unimolecular step. Very rarely, under conditions of extremely high pressure, a termolecular step may occur, which involves simultaneous collision of three reactant molecules. An important point to recognise is that, many reactions that are written as a single reaction equation, in actual fact, consist of a series of elementary steps. This will become extremely important as we learn more about the theory of chemical reaction rates.

As a general rule, elementary processes involve a transition between two atomic or molecular states separated by a potential barrier. The potential barrier constitutes the activation energy of the process, and determines the rate at which it occurs. When the barrier is low, the thermal energy of the reactants will generally be high enough to surmount the barrier and move over to products, and the reaction will be fast. However, when the barrier is high, only a few reactants will have sufficient energy, and the reaction will be much slower. The presence of a potential barrier to reaction is also the source of the temperature dependence of reaction rates.

The huge variety of chemical species, types of reaction, and the accompanying potential energy surfaces involved means that the time scale over which chemical reactions occur covers many orders of magnitude, from very slow reactions, such as iron rusting, to extremely fast reactions, such as the electron transfer processes involved in many biological systems or the combustion reactions occurring in flames.

A study into the kinetics of a chemical reaction is usually carried out with one or both of two main goals in mind :

(i) Analysis of the sequence of elementary steps giving rise to the overall reaction. i.e. the reaction mechanism.

(ii) Determination of the absolute rate of the reaction and/or its individual elementary steps.

2. CLASSIFICATION OF REACTION

(i) There are certain reactions which are too slow. **Ex.** Rusting of Iron, weathering of rocks.

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

(iii) Neither too fast nor too slow. **Ex.** Combination of H_2 and Cl_2 in presence of light, hydrolysis of ethyl acetate catalysed by acid, decomposition of Azomethane.

3. Types of Rates of chemical reaction :

For a reaction R $\longrightarrow$ P ,

- **Average rate** $= \dfrac{\text{Total change in concentration}}{\text{Total time taken}} = \dfrac{|\Delta c|}{\Delta t} = -\dfrac{\Delta[\text{Reactant}]}{\Delta t} = \dfrac{\Delta[\text{Product}]}{\Delta t}$

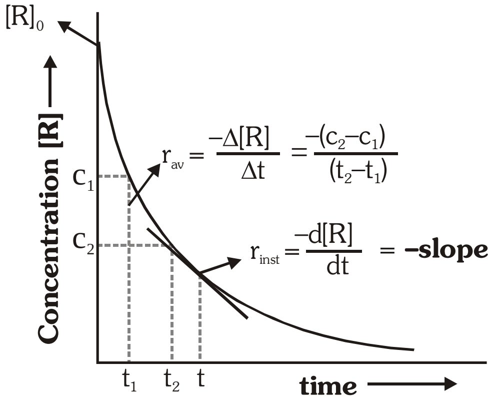
- **Instantaneous rate** : Rate of reaction at a particular instant.

$$\mathbf{R}_{\textbf{instantaneous}} = \lim_{\Delta t \to 0}\left[\frac{|\Delta c|}{\Delta t}\right] = \left|\frac{dc}{dt}\right| = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Instantaneous rate can be determined from slope of a tangent at time t on curve drawn for concentration versus time.

3.1 Initial Rate :

Initial Rate : Instantaneous rate at ‘t = 0’ is called initial rate [Slope of tangent at t = 0].



❖ Reaction rates and stoichiometry :

We have seen that for stoichiometrically simple reactions of the type A → B, the rate can be either expressed in terms of the decrease in reactant concentration with time, –Δ[A]/Δt or the increase in product concentration with time, Δ[B]/Δt. For more complex reactions, we must be careful in writing the rate expressions. Consider for example, the reaction,

$$\mathbf{2\,A \longrightarrow B}$$

Two moles of A disappear for each mole of B that forms – that is, the rate of disappearance of A is twice as fast as the rate of appearance of B. We write the overall rate of reaction as either

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

In general, for the reaction, $\mathbf{aA + bB \longrightarrow cC + dD}$

the rate is given by

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Ex. : **For the reaction in terms : $N_2 + 3H_2 \longrightarrow 2NH_3$**

Rate of reaction in terms of $N_2 = -\frac{d[N_2]}{dt}$ = rate of disappearance of N_2

Rate of reaction in terms of $H_2 = -\frac{d[H_2]}{dt}$ = rate of disappearance of H_2

Rate of reaction in terms of $NH_3 = \frac{d[NH_3]}{dt}$ = rate of appearance of NH_3

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

- **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: The value of rate of reaction is dependent on the stoichiometric coefficients used in the reaction while the rate of increase or decrease in amount of any species will be fixed value under given conditions.

Ex.1 **The following reaction was studied in a closed vessel**

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

It was found that the concentration of NO_2 increases by 2.0×10^{-2} mol L^{-1} in five seconds. Calculate.

(i) **The rate of reaction**

(ii) **The rate of decrease of concentration of N_2O_5**

Sol. **(i)** Rate of reaction $= \frac{1}{4}\frac{d[NO_2]}{dt}$

But $\frac{d[NO_2]}{dt} = \frac{2.0 \times 10^{-2} \text{mol L}^{-1}}{5s} = 4 \times 10^{-3}$ mol L^{-1} s^{-1}

Rate of reaction $\frac{1}{4} \times 4 \times 10^{-3} = 10^{-3}$ mol L^{-1} s^{-1}

(ii) Rate of decrease of conc. of N_2O_5

$= -\frac{d[N_2O_5]}{dt} = -\frac{1}{2} \times$ Rate of formation of $NO_2 = +\frac{1}{2}\frac{d[NO_2]}{dt}$

$= +\frac{1}{2} \times 4 \times 10^{-3} = 2 \times 10^{-3}$ mol L^{-1} s^{-1}

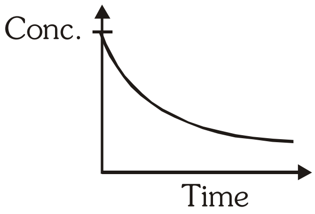
3.3 FACTORS AFFECTING RATE OF CHEMICAL REACTION

(i) Concentration
(ii) Temperature
(iii) Nature of reactants and products
(iv) Catalyst
(v) pH of the solution
(vi) Dielectric constant of the medium.
(vii) Radiations / light
(viii) Pressure
(ix) Electrical and magnetic field.

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

(i) Effect of concentration :

For most of the reactions, rate depends on concentration of reactants. So rate of reaction decreases with passage of time, since concentration of reactants decreases .



(ii) Effect of temperature : Generally rate of reaction increases on increasing temperature.

(iii) Effect of nature of reactants and products :

(a) Physical state of reactants : Gaseous state > Liquid state > Solid state
(Decreasing order of rate of reaction)

Because collisions in gaseous systems are more effective than condensed systems (solid & liquid).

(b) Physical size of reactants : In heterogeneous reactions, as we decreases 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 if bond strength in reactants is more, rate of reaction will be slow.

(iv) Effect of Catalyst :

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

(v) Effect of pH of solution : Ex. $[Fe(CN)_6]^{4-} \xrightarrow{(Tl^{3+})} [Fe(CN)_6]^{3-}$

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

(vi) Effect of dielectric constant of the medium : More is the dielectric constant of the medium greater will be the rate of ionic reactions.

(vii) Effect of radiations / light : Radiations are useful for photochemical reactions.

(viii) Effect of pressure : Pressure is important factor for gaseous reactions.

(ix) Effect of electrical & magnetic field : Electric and magnetic fields are rate determining factors if a reaction involves polar species.

4. 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 :

Rate $\propto$ (conc.)$^{\text{order}}$

Rate = K (conc.)$^{\text{order}}$ **This is the differential rate equation or rate expression.**

Where K = Rate constant = specific reaction rate = rate of reaction when concentration is unity

unit of K = (conc)$^{1-\text{order}}$ time^{-1}

Note: Value of K is a constant for a given reaction, depending only on temperature and catalyst use.

4.1 Order of reaction :

Let there be a reaction , $m_1A + m_2B \longrightarrow$ products.
Now, if on the basis of experiment, we find that

$$\mathbf{R \propto [A]^p\,[B]^q}$$

where p may or may not be equal to m_1 and similarily q 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', any whole number, fractional number or even be negative with respect to a particular reactant.

❖ **Examples showing different values of order of reactions :**

	Reaction	Rate law	Order
(i)	$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$	$R = K[N_2O_5]^1$	1
(ii)	$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq)$ $\rightarrow 3Br_2(\ell) + 3H_2O(\ell)$	$R = K[Br^-][BrO_3^-][H^+]^2$	1 + 1 + 2 = 4
(iii)	H_2 (Para) $\rightarrow H_2$ (ortho)	$R = K[H_{2\,(\text{Para})}]^{3/2}$	3/2
(iv)	$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$	$R = K[NO_2]^2[CO]^o$	2 + 0 = 2
(v)	$2O_3(g) \rightarrow 3O_2(g)$	$R = K[O_3]^2[O_2]^{-1}$	2 – 1 = 1
(vi)	$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$	$R = K[H_2]^o[Cl_2]^o$	0 + 0 = 0

The reaction (ii) 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 places in a sequence of a number of ***Elementary reactions***. For an elementary reaction, the sum of stoichiometric coefficients of reactants = order of the reaction. But for complex reactions, order is to be experimentally calculated.

4.2 Molecularity of reaction :

The number of molecules that react in an elementary step is the molecularity of the elementary reaction. Molecularity is defined only for the elementary reactions and not for complex reactions. No elementary reactions involving more than three molecules are known, because of very low probability of simultaneous collision of more than three molecules.

The rate law for the elementary reaction

$$\mathbf{aA + bB \longrightarrow Products,\ Rate = k[A]^a[B]^b,\quad where\ a + b = 1, 2\ or\ 3}$$

For an elementary reaction, the orders in the rate law equal the coefficients of the reactants. It must be noted that the order is defined for complex as well as elementary reactions and is always experimentally calculated from the mechanism of the reaction, usually by the slowest step of the mechanism known as rate determining step (RDS) of the reaction.

Comparision between molecularity and order of reaction			
	Molecularity of Reaction		***Order of Reaction***
1	It is defined as the no. of molecules of reactant taking part in a chemical reaction. $NH_4NO_2 \rightarrow N_2 + 2H_2O$, molecularity = 1	1	It is defined as the sum of the power of concentration terms that appear in rate law. $NH_4NO_2 \rightarrow N_2 + 2H_2O$. Rate = $k[NH_4NO_2]$, order =1
2	It is always a whole number. It can neither be zero nor fractional.	2	It may be zero, fractional or integer.
3	It is derived from RDS in the mechanism of reaction	3	It is derived from rate expression.
4	It is theoretical value.	4	It is experimental value.
5	Reactions with molecularity > 3 are rare.	5	Reactions with order of reaction > 4 are also rare.
6	Molecularity is independent of pressure and temperature.	6	Order of reaction may depend upon pressure and temperature.

5. INTEGRATED RATE LAW :

For a single reactant reaction where the chemical equation has the form

$$\mathbf{A \rightarrow products}$$

and the rate law is assumed to be of the form

$$\mathbf{Rate = -d[A]/dt = k\,[A]^m}$$

Where m is the order of the reaction with respect to substance A. Three important cases can be treated : m = 0, m = 1, and m = 2. These are called ***zeroth order***, ***first order***, and ***second order***, respectively.

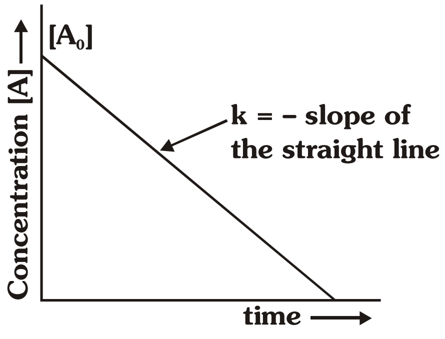
5.1 Zero - order reaction :

For a reaction where the chemical equation has the form

$$\mathbf{A \rightarrow products}$$

and the rate law is assumed to be of the form

$$\mathbf{Rate = -d[A]/dt = k\,[A]^0}$$



$$-\int_{c_0}^{c_t} d[A] = k\int_0^t dt$$

$$k = \frac{C_0 - C_t}{'t'}$$

or $\mathbf{kt = C_0 - C_t}$ or $C_t = C_0 - kt$

- Unit of K is same as that of Rate = mol lit^{-1} sec^{-1}.
- Time for completion = $\frac{C_0}{k}$
- $t_{1/2}$ (half life period)

At $\quad t_{1/2}$, $C_t = \frac{C_0}{2}$,

So $\quad kt_{1/2} = \frac{C_0}{2} \quad \Rightarrow \quad t_{1/2} = \frac{C_0}{2k}$

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

❖ **Examples of Zero order reactions :**

Generally decomposition of gases on metal surfaces at high concentrations follow zero order kinetics as rate depends on surface area of catalyst.

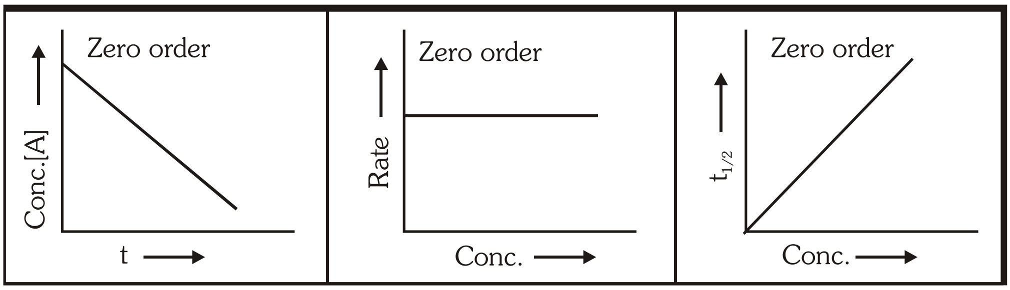
$\boxed{2PH_3\,(g) \xrightarrow{Ni} 2\,P(s) + 3H_2(g)}$ **Rate = K $[PH_3]^0$**

$2HI\,(g) \xrightarrow{Au} H_2(g) + I_2(g)$ **Rate = K $[HI]^0$**

$2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$ **Rate = K $[NH_3]^0$**

$H_2(g) + Cl_2(g) \xrightarrow{hv} 2\,HCl(g)$ **Rate = K $[H_2]^0\,[Cl_2]^0$**

❖ **Graphs :**



Ex.2 For the zero order reaction : A → P , K = 10^{-2} (mol/litre) sec^{-1} If initial concentration of A is 0.3M , then find concentration of A left at 10 sec.

(A) 0 M **(B) 0.2 M** **(C) 0.1 M** **(D) 0.15 M**

Sol. **(B)**

$[A]_t = [A]_0 - Kt = 0.3 - 10^{-2} \times 10 = 0.2$ M

5.2 First order reaction :

Consider a first order reaction with single reactant.

$$\begin{array}{lll} & \textbf{A} \longrightarrow & \textbf{Products} \\ t = 0 & a & 0 \\ t = t & a-x & \end{array}$$

Rate = – d[A]/dt = k $[A]^1$

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

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

$$K = \boxed{\frac{2.303}{t}\log\frac{C_0}{C_t}} \qquad \boxed{\begin{array}{c}\text{Wilhemy formula :}\\ C_t = C_0e^{-kt}\end{array}} \qquad \boxed{\begin{array}{l}\text{Interval formula :}\\ k = \frac{2.303}{(t_2-t_1)}\log\frac{C_1}{C_2}\end{array}}$$

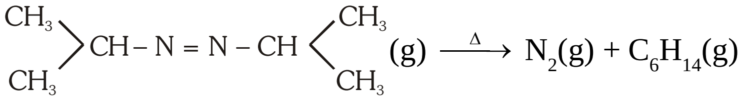
- Unit of k = sec^{-1}, min^{-1}, etc.
- **Half-life time ($t_{1/2}$) :**

$$k = \frac{2.303}{t_{1/2}} \log \frac{2C_0}{C_0} \Rightarrow t_{1/2} = \frac{2.303 \log 2}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

∴ Half-life period for a first order reaction is a constant quantity at given temperature.

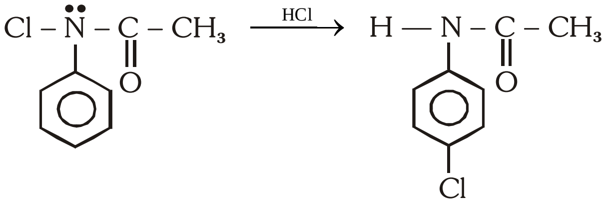
- **Examples of first order reactions :**

(i) Decomposition of azoisopropane



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-N=N-CH<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}(g) \xrightarrow{\Delta} N_2(g) + C_6H_{14}(g)$$

(ii) Conversion of N–chloro acetanilide into p–chloroacetanilide



(iii) $H_2O_2(aq.) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$

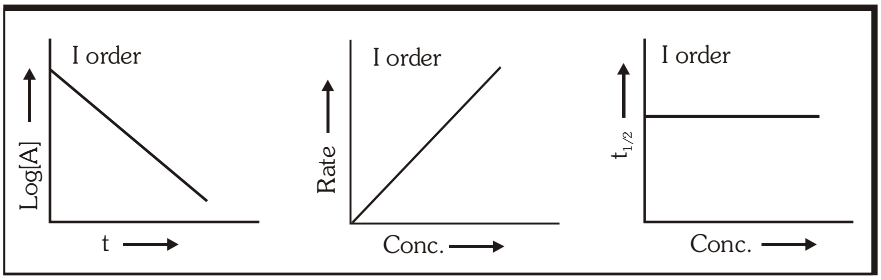
(iv) $NH_4NO_2 \longrightarrow 2H_2O(g) + N_2(g)$

(v) Radioactive decay

All radioactive decays always follow first order kinetics.

$${}^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}_2He^4$$

- **Graphs :**



Ex.3 **Calculate $\frac{t_{0.75}}{t_{0.50}}$ for a first order reaction :**

Sol. $k = \frac{2.303}{t_{3/4}} \log \frac{C_0}{\frac{1}{4}C_0} = \frac{2.303}{t_{1/2}} \log \frac{C_0}{\frac{C_0}{2}} \Rightarrow \frac{t_{3/4}}{t_{1/2}} = \frac{\log\ 4}{\log\ 2} = \frac{2\ \log\ 2}{\log\ 2} = 2$

Ex.4 **90% of a first order reaction was completed in 10 hours. When will 99.9% of the reaction complete ?**

Sol. $K = \frac{2.303}{t} \log \frac{a}{a?\ x}$

a = 100 , x = 90 , t = 10

So $K = \frac{2.303}{10} \log \frac{100}{10}$

$K = 2.303 \times 10^{-1}$ hour^{-1}

Now for 99.9% completion -

a = 100 and x = 99.9

$$t = \frac{2.303}{K} \log \frac{100}{0.1} = \frac{2.303}{2.303 \times 10^{-1}} \times 3 = 30 \text{ hours}$$

Ex.5 **A first order reaction is 90% complete after 40 min. Calculate the half life of reaction.**

Sol. a = 100, x = 90

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

$$= \frac{2.303}{40} \log \frac{100}{10}$$

$$= \frac{2.303}{40} = 5.757 \times 10^{-2} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{K_1} = \frac{0.693}{5.757 \times 10^{-2}} = 12.03 \text{ min.}$$

5.3.1 Second order reaction :

- **Case : 1**

$$\begin{array}{ccccc} A & + & A & \longrightarrow & \text{Products} \\ a & & a & & \\ (a - x) & & (a - x) & & \end{array}$$

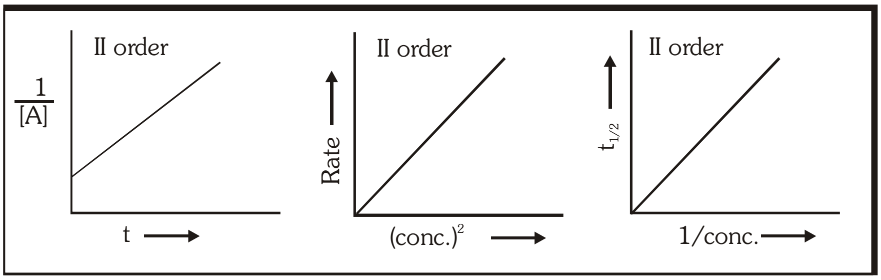
$\therefore \quad \frac{dx}{dt} = k\,(a-x)^2$

$\Rightarrow \quad \frac{1}{(a-x)} - \frac{1}{a} = kt \quad$ or $\quad \frac{1}{C_t} - \frac{1}{C_0} = kt$

- Unit of k = $Lmol^{-1} sec^{-1}$

- Half life, $t_{½} = \dfrac{1}{k.C_o}$

  - **Graphs :**



5.3.2 Case : 2

A + B ⟶ products.
a b 0
a – x b – x
Rate law

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

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

$$\boxed{k = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}}$$ (no need to remember)

where $a \neq b$

Ex.6 For a second order reaction in which both the reactants have equal initial concentration, the time taken for 60% completion of reaction is 3000 second. What will be the time taken for 20% of the reaction?

Sol. $k_2 = \dfrac{1}{t}\dfrac{x}{a(a-x)}$

Let a = 1,

$$k_2 = \frac{1}{t}\frac{x}{(1-x)}$$

$$= \frac{1}{3000}\left(\frac{0.6}{1-0.6}\right)$$

$$= \frac{1}{3000}\times\frac{0.6}{0.4} = \frac{1}{2000}$$

So time for the 20% completion :

$$t = \frac{1}{k_2}\frac{x}{a(a-x)}$$

$$= 2000\times\frac{0.20}{0.80} = 500 \text{ sec.}$$

5.4 Pseudo order reaction :

For, $A + B \longrightarrow$ Products

t=0 $\quad a \qquad b$

t=t $\quad a-x \qquad b-x$

$$\textbf{Rate} = \mathbf{K\,[A]^n\,[B]^m}$$

If $[B] = \text{constant} \Rightarrow [b-x] \approx \text{constant}$

$$\text{Rate} = K'\,[A]^n$$

$$\text{when } K' = K[B]^n$$

- **Case 1 :**
  If concentration of B is much greater than A, then $[B] = \text{Constant} \Rightarrow [b-x] \approx \text{Constant}$.
- **Case 2 :**
  If B is a catalyst , then $[B] = \text{Constant} \Rightarrow [b-x] \approx \text{Constant}$.
- **Case 3 :**
  If B is a solvent , then $[B] = \text{Constant} \Rightarrow [b-x] \approx \text{Constant}$.

5.4.1 PSEUDO FIRST ORDER REACTIONS :

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**.

$\therefore$ For $A + B \longrightarrow$ Products $\quad$ **[Rate] = K [A]^1 [B]^1**

$$K = \frac{2.303}{t\ (a-b)} \log \frac{b(a-x)}{a(b-x)} \qquad \text{(from 5.3.2)}$$

Now if ‘B’ is taken in large excess b > > a.

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

$$\Rightarrow \quad K.b = \frac{2.303}{t} \log \frac{a}{a-x} \quad \Rightarrow \quad K' = \frac{2.303}{t} \log \frac{a}{a-x}$$

K' is pseudo first order rate constant.
K' will have units of first order.
K will have units of second order.

❖ **Table :** Characteristics of Zero, First, Second and nth order reactions of the type **A** ⟶ **Products**

	Zero order	**First order**	**Second order**	**n^{th} order**
Differential Rate law	$-\dfrac{d[A]}{dt} = k[A]^{\circ}$	$-\dfrac{d[A]}{dt} = k[A]$	$-\dfrac{d[A]}{dt} = k[A]^2$	$-\dfrac{d[A]}{dt} = k[A]^n$
Integrated Rate law	$[A]_t = [A]_0 - kt$	$\text{In}[A]_t = -kt + \text{In}[A]_0$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$\dfrac{1}{[A_t]^{n-1}} - \dfrac{1}{[A_0]^{n-1}} = (n-1)\ kt$
Linear graph	$[A]_t$ v/s t	In [A] v/s t	$\dfrac{1}{[A]}$ v/s t	$\dfrac{1}{[A_t]^{n-1}}$ v/s t
Half-life	$t_{1/2} = \dfrac{[A]_0}{2k}$ (depends on $[A]_0$)	$t_{1/2} = \dfrac{0.693}{k}$ (independent of $[A]_0$)	$t_{1/2} = \dfrac{1}{k[A]_0}$ (depends on$[A]_0$)	$t_{1/2} \propto \dfrac{1}{[A_0]^{n-1}}$

6 Methods to determine order of a reaction :

6.1 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.

$r = k\,[A]^a\,[B]^b\,[C]^c$ if [B] = constant and [C] = constant

then for two different initial concentrations of A we have

$$r_{0_1} = k\,[A_0]_1^{\,a} \qquad r_{0_2} = k\,[A_0]_2^{\,a} \qquad \Rightarrow \qquad \frac{r_{0_1}}{r_{0_2}} = \left(\frac{[A_0]_1}{[A_0]_2}\right)^a$$

or in log form we have

$$a = \frac{\log\ \left(r_{0_1}/r_{0_2}\right)}{\log\ \left([A_0]_1/[A_0]_2\right)}$$

6.2 Integrated rate law method :

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

Ex.7 The rate of decomposition of N_2O_5 in CCl_4 solution has been studied at 318 K and the following results have been obtained :

t/min	0	135	342	683	1693
c/M	2.08	1.91	1.67	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 these data will not satisfy the integrated rate law of zero order. 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	6.32×10^{-4}
135	1.91	6.30×10^{-4}
339	1.68	6.32×10^{-4}
683	1.35	6.32×10^{-4}
1680	0.72	6.31×10^{-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 $k = 6.31 \times 10^{-4} \text{ min}^{-1}$.

$$t_{1/2} = \frac{0.693}{6.31 \times 10^{-4} \text{ min}^{-1}} = 1.094 \times 10^{3} \text{ min}^{-1}$$

6.3 Method of half lives :

The half lives of each order is unique so by comparing half lives we can determine order for nth order reaction $t_{1/2} \propto \frac{1}{[A_0]^{n-1}}$ (Remember)

$$\frac{(t_{1/2})_1}{(t'_{1/2})_2} = \frac{[A'_0]_2^{n-1}}{[A_0]_1^{n-1}}$$ (Remember)

Ex.8 In a decomposition reaction, 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 nth order reaction $t_{1/2} \propto \frac{1}{c_0^{n-1}}$

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

6.4 Ostwald's isolation method :

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

$$\textbf{Rate} = k\,[A]^a\,[B]^b\,[C]^c = k_0\,[A]^a$$

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

6.5 Initial rate method :

For reaction : $A + B \longrightarrow$ Products

Initial rate, $r_0 = K.[A_0]^n [B_0]^m$

Now, order with respect to A may be determined by comparing the initial rate of reaction at different initial concentration of A but fixed initial concentration of B.

Ex.9 Consider the following data for the reaction :

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

Run	Initial concentration	Initial concentration	Initial rate (mol s^{-1})
1	0.10 M	1.0 M	2.1×10^{-3}
2.	0.20 M	1.0 M	8.4×10^{-3}
3.	0.20 M	2.0 M	8.4×10^{-3}

Determine the order of reaction with respect to A and with respect B and the over all order of reaction.

Sol. The rate law may be expressed as :

Rate = $k [A]^p [B]^q$

Comparing experiments 2 and 3

$(\text{Rate})_2 = k[0.2]^p [1.0]^q = 8.4 \times 10^{-3}$ (1)

$(\text{Rate})_3 = k[0.2]^p [2.0]^q = 8.4 \times 10^{-3}$ (2)

Dividing equation (2) by (1)

$$\frac{(\text{Rate})_3}{(\text{Rate})_2} = \frac{k[0.2]^p[2.0]^q}{k[0.2]^p[1.0]^q} = \frac{8.4\times10^{-3}}{8.4\times10^{-3}}$$

$[2]^q = [2]^0$

or $q = 0$

Comparing experiments 1 and 2,

$(\text{Rate})_2 = k[0.20]^p [1.0]^q = 8.4 \times 10^{-3}$ (3)

$(\text{Rate})_1 = k[0.10]^p [1.0]^q = 2.1 \times 10^{-3}$ (4)

Dividing equation (3) by (4)

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k[0.20]^p[1.0]^q}{k[0.10]^p[1.0]^q} = \frac{8.4\times10^{-3}}{2.1\times10^{-3}} = 4$$

$[2]^p = [2]^2$ or $p = 2$

so order with respect to A = 2

order with respect to B = 0

overall order = 2

7. APPLICATION OF FIRST ORDER REACTION

(Methods to monitor the progress of the reaction)

7.1 Case : 1

First order gaseous reaction :

Progress of gaseous reactions can be monitored by measuring total pressure at a fixed volume & temperature. This method can be applied for those reactions 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

(i) Partial pressure of the reactant

(ii) Total pressure of the reaction system

(iii) Pressure at only some points of time.

Ex.10 Find the expression for K in terms of P_0, P_t and n. For the reaction

$$A(g) \longrightarrow nB(g)$$

Sol.

$$A(g) \longrightarrow nB(g)$$

P_0

$P_A = (P_0 - x) \qquad nx$

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

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

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

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

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

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

Do not remember the formula but derive it for each question.

7.2 Case : 2

Volume measurement :

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

Ex.11 Study of a reaction whose progress is monitored by measuring the volume of a escaping gas.

$$NH_4NO_2(s) \xrightarrow{\Delta} 2H_2O(\ell) + N_2(g)$$

Sol. Let, V_t be the volume of N_2 collected at time 't'

V_∞ = be the volume of N_2 collected at the end of the reaction.

$$a \propto V_\infty \text{ and } \qquad x \propto V_t$$

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

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

(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 milliequivalent or millimoles are calculated using valence factors.

Ex.12 **From the following data show that the decomposition of hydrogen peroxide in aqueous solution is a first - order reaction. What is the value of the rate constant?**

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

Where V is the volume in mL of standard $KMnO_4$ solution required to react with a definite volume of hydrogen peroxide solution.

Sol. The equation for a first order reaction is,

$$2H_2O_2(\ell) \xrightarrow{\Delta} 2H_2O(\ell) + O_2(g)$$

the volume of $KMnO_4$ used, evidently corresponds to the undecomposed hydrogen peroxide.

Hence the volume of $KMnO_4$ used, at zero time corresponds to the initial concentration a and the volume used after time t, corresponds to (a – x) at that time. Inserting these values in the above equation, we get

$$\text{When } t = 10 \text{ min. } k_1 = \frac{2.303}{10} \log \frac{25}{20.0} = 0.022318 \text{ min}^{-1} = 0.000372 \text{ s}^{-1}$$

$$\text{When } t = 20 \text{ min. } k_1 = \frac{2.303}{20} \log \frac{25}{15.7} = 0.023265 \text{ min}^{-1} = 0.000387 \text{ s}^{-1}$$

$$\text{When } t = 30 \text{ min. } k_1 = \frac{2.303}{30} \log \frac{25}{12.5} = 0.02311 \text{ min}^{-1} = 0.000385 \text{ s}^{-1}$$

$$\text{When } t = 40 \text{ min. } k_1 = \frac{2.303}{40} \log \frac{25}{9.6} = 0.023932 \text{ min}^{-1} = 0.0003983 \text{ s}^{-1}$$

The constancy of k, shows that the decomposition of H_2O_2 in aqueous solution is a **first order** reaction. The average value of the rate constant is 0.0003879 s^{-1} .

Ex.13 Study of acid hydrolysis of an ester.

$$CH_3COOCH_3 + \underset{(excess)}{H_2O} \xrightarrow[(HCl)]{H^+} CH_3COOH + CH_3OH$$

The progress of this reaction is monitored or determined by titrating the fixed volume of 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.

Sol. Let, V_0 = Volume of NaOH used at t = 0 [this is exclusively for HCl.]

V_t = Volume of NaOH used at 't'

V_∞ = Volume of NaOH used at $t = \infty$

$a \propto (V_\infty - V_0)$

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

$x \propto (V_t - V_0)$

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

7.3 Case : 3

Optical rotation measurement :

It is used for optically active sample. It is applicable if there is at least one optically active species involved in chemical reaction.

- The optically active species may be present in reactant or product.

It is found that $(r_\infty - r_0) \propto a$ (a = concentration , x = amount consumed)

$(r_\infty - r_t) \propto (a - x)$

Where are r_0, r_t, r_∞ are angle of optical rotation at time t = 0, t = t and $t = \infty$.

$$k = \frac{2.303}{t} \log \frac{r_\infty - r_0}{r_\infty - r_t} \quad \text{(Remember)}$$

Ex.14 Study of hydrolysis of sucrose, progress of this reaction is monitored with the help of polarimeter because a solution of sucrose is dextrorotatory and on hydrolysis, the mixture of glucose and fructose obtained becomes laevorotatory. That's why this reaction is also known as inversion of cane sugar.

$$\mathbf{C_{12}H_{22}O_{11} + \underset{excess}{H_2O} \xrightarrow{H^+} \underset{glucose}{C_6H_{12}O_6} + \underset{fructose}{C_6H_{12}O_6}}$$

Let the readings in the polarimeter be
$t = 0$, θ_0 ; t = 't', θ_t and at $t = \infty$, θ_∞
Then calculate rate constant 'k' in terms of these readings.

Sol. The principle of the experiment is that change in the rotation is directly proportional to the amount of sugar hydrolysed.

$\therefore \quad a \propto (\theta_0 - \theta_\infty) \quad ; \quad (a - x) \propto (\theta_t - \theta_\infty) \; ; \; x \propto (\theta_0 - \theta_t)$

$$k = \frac{2.303}{t} \log\left(\frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}\right)$$

7.4 Case : 4

First order growth reaction :

For bacteria multiplication or virus growth use following concept

Consider a growth reaction,

Time	**Population (or colony)**
0	a
t	(a + x)

$\frac{dx}{dt} = k\,(a + x) \quad \text{or} \quad \frac{dx}{(a+x)} = kdt$

On integration

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

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

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

❖ **Generation time :**

At t = generation time , x = a $\quad \therefore \quad t = \frac{0.693}{K}$

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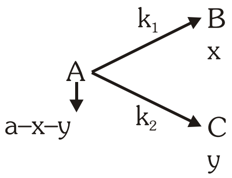
8. SOME SPECIAL CASES :

8.1 FIRST ORDER PARALLEL OR COMPETING OR SIMULTANEOUS REACTIONS



At $\quad t = 0 \quad [A] = a \quad [B] = [C] = 0$

(i) Differential rate law :

$$\frac{d[B]}{dt} = k_1\,[A] \; ; \; \frac{d[C]}{dt} = k_2\,[A]$$

and, $\frac{-d[A]}{dt} = \frac{d[B]}{dt} + \frac{d[C]}{dt} \Rightarrow \frac{-d[A]}{dt} = (k_1 + k_2)\,[A] = k_{eff}\,[A]$

$k_{eff} = k_1 + k_2$ = overall rate constant for the disappearance of 'A'

(ii) Integral rate law :

$[A]_t = ae^{-k_{eff}t} = ae^{-(k_1 + k_2)t}$

$$\frac{d[B]}{dt} = k_1 [A] \Rightarrow \frac{d[B]}{dt} = k_1 a\, e^{-(k_1+k_2)t}$$

$$[B] = \left(\frac{k_1 a}{k_1+k_2}\right)(1 - e^{-(k_1+k_2)t})$$

$$\text{Similarly, } [C] = \left[\frac{k_2 a}{k_1+k_2}\right](1 - e^{-(k_1+k_2)t})$$

(iii) Composition of product :

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$

8.2 FIRST ORDER REVERSIBLE REACTION

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

	A	B
$t = 0$	a	0
$t = t$	$a - x$	x
$t = t_{eq.}$	$a - x_{eq.}$	$x_{eq.}$

$x_{eq.}$ = eq conc. of product

(i) $\dfrac{d[A]}{dt} = \dfrac{d[B]}{dt} = 0$ **($\because$ At equilibrium, conc. will not changed)**

(ii) $\dfrac{d[A]}{dt} = -k_f[A] + k_b[B] \Rightarrow \dfrac{d[B]}{dt} = -k_b[B] + k_f[A]$

$$\frac{d(a-x)}{dt} = -k_f(a-x) + k_b x$$

$$-\frac{dx}{dt} = -k_f a + (k_f + k_b)x$$

$$\text{At eq}^m, \frac{dx}{dt} = 0 = k_f a + (k_f + k_b)x_{eq}$$

$$k_f a = (k_f + k_b)x_{eq}$$

$$-\frac{dx}{dt} = -(k_f + k_b)x_{eq} + (k_f + k_b)x$$

$$\frac{dx}{dt} = (k_f + k_b)(x_{eq} - x)$$

$$\int_0^x \frac{dx}{(x_{eq} - x)} = (k_f + k_b)\int_0^t dt$$

$$\mathbf{k_f + k_b = \frac{1}{t}\ \ell n\left(\frac{x_{eq.}}{x_{eq.} - x}\right)} \quad \text{(No need to remember this equation)}$$

8.3 FIRST ORDER SEQUENTIAL REACTION

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$ **All first order reactions**

$t = 0$	a	0	0
$t = t$	$a - x$	y	z

(i) For 'A'

$$\frac{-d[A]}{dt} = r_1 = k_1 [A]$$

$$\frac{-d[A]}{[A]} = k_1\, dt$$

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

$$a - x = a e^{-k_1 t}$$

$$x = a\left(1 - e^{-k_1 t}\right)$$

(ii) For 'B'

$$\frac{dy}{dt} = k_1 a e^{-kt} - k_2 y$$

$$\frac{dy}{dt} + k_2 y = k_1 a e^{-kt}$$

$$dy + k_2 y dt = k_1\, a e^{-kt}\, dt$$

$$e^{k_2 t} dy + k_2\, y e^{k_2 t} = k_1 a e^{-k_1 t} . e^{k_2 t} \quad dt$$

$$\int_0^t d(k_2 y e^{k_2 t}) = \int_0^t k_1 a e^{(k_2 - k_1)t} dt$$

$$\mathbf{k_2 y}\, e^{k_2 t} \mathbf{=} \left(\frac{\mathbf{k_1 a}}{\mathbf{k_2 - k_1}}\right) \mathbf{e^{(k_2 - k_1)t} + y} \qquad \text{(No need to remember)}$$

(iii) Calculate time at which concentration of B will be maximum.

$$\frac{dy}{dt} = 0$$

$$-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0$$

$$e^{-k_2 t} = \frac{k_1}{k_2} e^{-k_1 t}$$

$$e^{k_1 t} = \frac{k_1}{k_2} e^{k_2 t} \quad \Rightarrow \quad k_1 t = \ell n \frac{k_1}{k_2} + k_2 t$$

$$\mathbf{t_{max.} = \frac{1}{(k_1 - k_2)}\ \ell n \frac{k_1}{k_2}}$$

(iv) $[B]_{max} = a \times \left[\frac{k_2}{k_1}\right]^{\frac{k_2}{k_1-k_2}} = [A_0]\left[\frac{k_2}{k_1}\right]^{\frac{k_2}{k_1-k_2}}$

8.3.1 Case -I

$k_1 >> k_2$

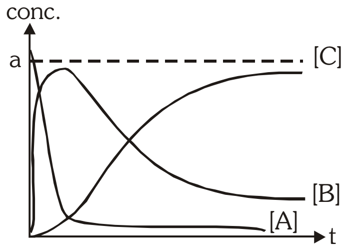
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\begin{array}{ccc} & a & \\ \left[\begin{array}{c}\text{Tends to zero}\\ \text{very fast}\end{array}\right] & a - x & x \end{array}$$

$[A] = ae^{-k_1 t}$

$[B] = ae^{-k_2 t}$

$[C] = a(1 - e^{-k_2 t})$



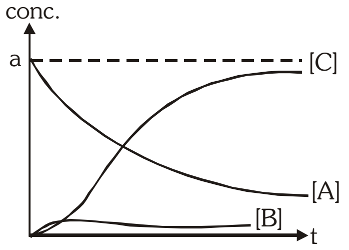
8.3.2 Case -II

$k_2 >> k_1$

$[B]_t \rightarrow 0$

$[A] = ae^{-k_1 t}$

$[C] = a(1 - e^{-k_1 t})$



Note : Both Case (I) and Case (II) show that rate of overall reaction depends on rate of slowest step (RDS.)

9. EFFECT OF TEMPERATURE ON RATE OF REACTION :

In early days the effect of temperature on reaction rate was expressed in terms of ***temperature coefficient*** (μ) which was defined as the ratio of rate of reaction at two different temperature differing by 10ºC (usually these temperatures were taken as 25ºC and 35ºC)

T.C, $\mu = \frac{K_{T+10}}{K_T} \approx 2$ to 3 **(for most of the reactions)**

Exception : For some reactions, temperature coefficient is also found to be less than unity.

For example, $2NO + O_2 \rightarrow 2NO_2$ rate of reaction decreases on increasing temperature.

Note : Rate of reaction increases on increasing temperature (Generally ; T.C > 1)

Ex.15 For a reaction T.C. = 2, Calculate $\frac{k_{40°C}}{k_{25°C}}$ for this reaction. Assuming T.C remains constant.

Sol. $\frac{k_2}{k_1} = (\text{T.C.})^{\frac{\Delta t}{10}} = (2)^{\frac{15}{10}} = (2)^{\frac{3}{2}} = \sqrt{8}$

But the method of temperature coefficient was not exact to explain the effect of temperature on reaction rate. For that a new theory was evolved.

9.1 Collision 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.

According the this theory :

(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).

(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.

❖ **Energy barrier :** The minimum amount of absolute energy which the colliding molecules must possess as to make the chemical reaction to occur is known as **threshold energy**.

- 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.

Passive molecules $\rightleftharpoons$ Active molecules, $\Delta H = +ve$

- "The minimum amount of excess energy required by reactant molecules to participate in a reaction is called **activation energy (E_a)".**

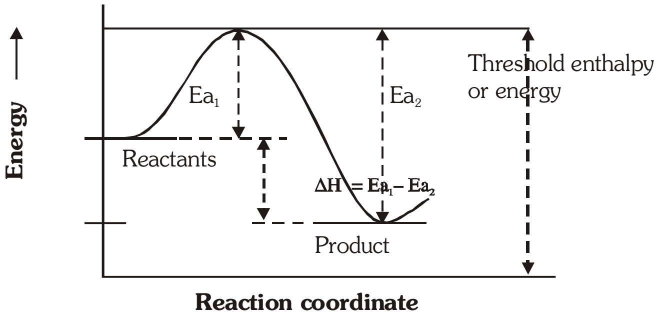
CONCEPT OF ENERGY OF ACTIVATION (E_a) :

- The average extra amount of energy which the reactant molecules (having energy less than the threshold) must acquire so that their mutual collision may lead to the breaking of bond(s) and hence the energy is known as energy of activation of the reaction. It is denoted by the symbol E_a. Thus,

E_a = Threshold energy – Actual average energy of reactants

E_a is expressed in kcal mole^{-1} or kJ mole^{-1}.

- The essence of Collision Theory of reaction rate is that there exists an energy barrier in the reaction path between reactant(s) and product(s) and for reaction to occur, the reactant molecules must climb over the top of the barrier which they do by collision. The existence of energy barrier and concept of E_a can be understood from the following diagram.



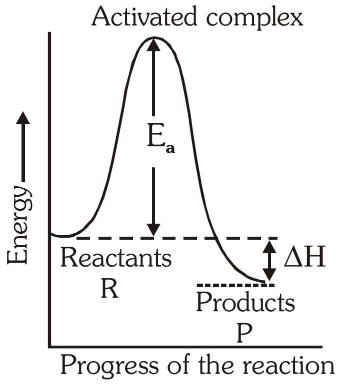
ΔH = Enthalpy change during the reaction ($R \rightarrow P$)

Ea_1 = Energy of activation of the forward reaction

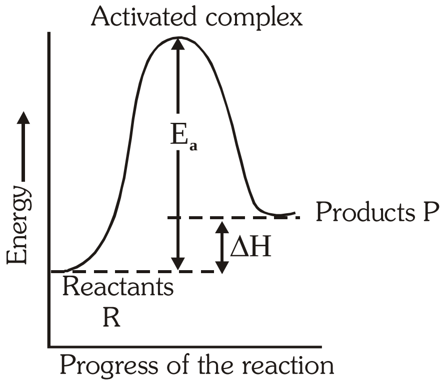
Ea_2 = Energy of activation of the backward reaction

From the figure above it can be concluded that the minimum activation energy of any exothermic reaction will be zero while minimum activation energy for any endothermic reaction will be equal to ΔH.

Greater the height of energy barrier, greater will be the energy of activation and more slower will be the reaction at a given temperature.



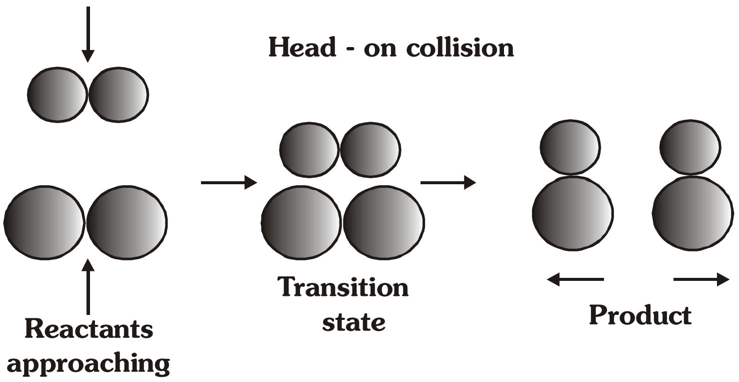
Exothermic

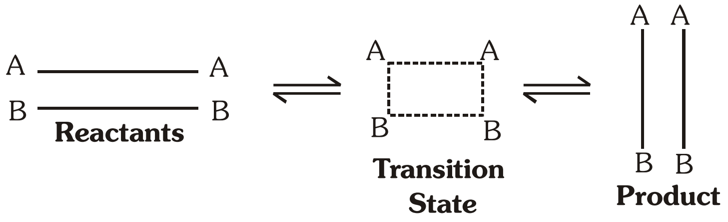


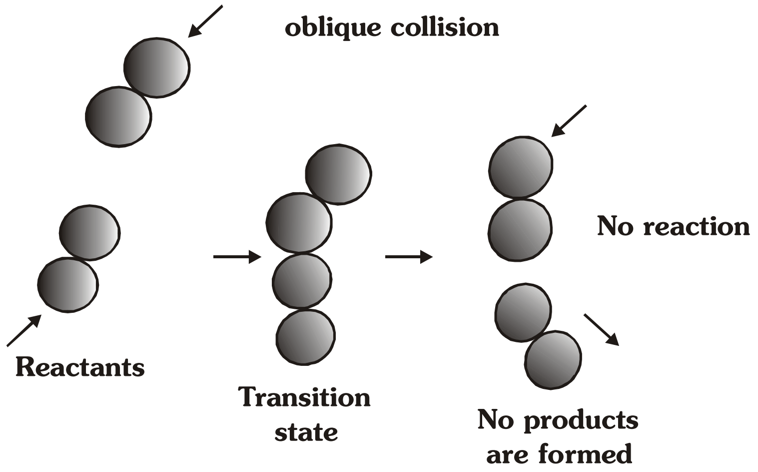
Endothermic

❖ **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.

Consider reaction : $A_2 + B_2 \rightarrow 2AB$



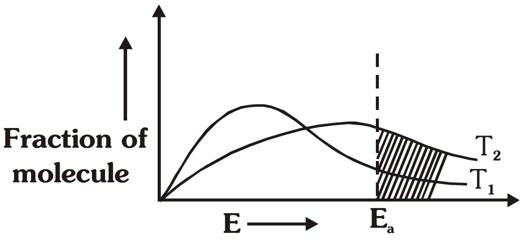




(iii) **Rate of any chemical reaction** = Collision frequency × fraction of the total number of effective collision.

= Collision frequency × fraction of the total number of collision in which K.E. of the colliding molecules equals to E_a or exceeds over it × fraction of collision in proper orientation.

From Maxwellian distribution, it is found that fraction of molecules having excess energy greater than threshold energy lead to the formation of product.



$T_2 > T_1$

$e^{-E_a/RT} \rightarrow$ Represents fraction of molecules having K.E. greater than or equal to E_a.

$$\text{Rate} \propto e^{-E_a/RT}$$

Dependence of rate on temperature is due to dependence of k on temperature.

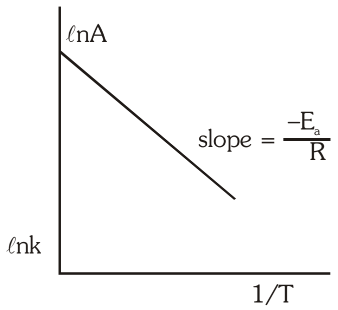
$$k \propto e^{-E_a/RT}$$

$$\mathbf{k = Ae^{-E_a/RT}}$$ **[Arrhenius equation]**

'A' is **pre-exponential** factor or **frequency factor** representing collisions taking place with proper orientation. A and E_a are assumed to be independent of temperature.

$$\ell nk = \ell n\,A - \frac{E_a}{RT}$$

As $T \to \infty$, $K \to A$



At temperature T_1, Rate constant = k_1
At temperature T_2, Rate constant = k_2

$$\ell nk_1 = \ell nA - \frac{E_a}{RT_1} \quad \& \; \ell nk_2 = \ell nA - \frac{E_a}{RT_2} \quad \Rightarrow \quad \ell n\frac{\mathbf{k_2}}{\mathbf{k_1}} = \frac{\mathbf{E_a}}{\mathbf{R}}\left(\frac{1}{\mathbf{T_1}} - \frac{1}{\mathbf{T_2}}\right)$$

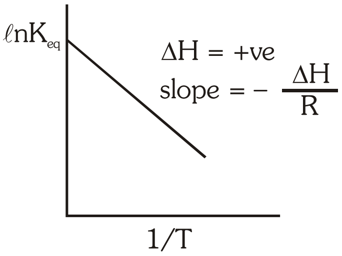
9.2 REVERSIBLE REACTIONS

$$k_f = A_f\; e^{-E_{af}/RT}$$

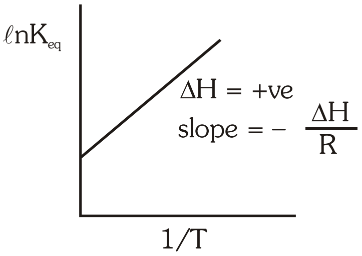
$$k_b = A_b\; e^{-E_{ab}/RT}$$

$$K_{eq} = \frac{k_f}{k_b} = \frac{A_f\;\; e^{-E_{af}/RT}}{A_b\;\; e^{-E_{ab}/RT}} = \left(\frac{A_f}{A_b}\right)\; e^{-(E_{af}-E_{ab})/RT}$$

$$\ell n\,K_{eq} = -\frac{\Delta H}{RT} + \ell n\left(\frac{A_f}{A_b}\right)$$



endothermic



exothermic

Ex.16 For a reaction, temperature coefficient = 2, then calculate the activation energy (in kJ) of the reaction.

Sol. **Given :** Temperature coefficient $= \frac{K_2}{K_1} = 2$

$T_1 = 25 + 273 = 298$ k
$T_2 = 35 + 273 = 308$ k

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \left(\frac{10}{298 \times 308}\right)$$

$E_a = 52.31$ kJ mol^{-1}

Ex.17 **For first order gaseous reaction, log k when plotted against $\frac{1}{T}$, it give a straight the with a slope of –8000. Calculate the activation energy of the reaction.**

Sol. For an arrhenius equation $k = Ae^{-E_a/RT}$

$$\log k = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$

when curve is plotted between log k and $\frac{1}{T}$. A straight line is obtained and a slope of this curve

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

Then, $\frac{E_a}{2.303R} = 8000$

or $E_a = 8000 \times 2.303 \times 2 = 36848$ calories

Ex.18 **The slope of the plot of log k vs $\frac{1}{T}$ for a certain reaction was found to be -5.4×10^3. Calculate the energy of activation of the reaction. If the rate constant of the reaction is 1.155×10^{-2} sec^{-1} at 373 K, what is its frequency factor ?**

Sol. **(a)** Slope $= \frac{-E}{2.303\ \ R} = -5.4 \times 10^3$

$E_a = 5.4 \times 10^3 \times 2.303 \times 1.987$

$= 24.624$ cal mol^{-1}

(b) $K = Ae^{-E/RT}$; $\log 1.155 \times 10^{-2} = \log A - \frac{24.624}{2.303 \times 1.987 \times 373}$

or $A = 1.764 \times 10^3$ sec^{-1}

---

10. CATALYST AND CATALYSIS :

A catalyst is a substance, which increases the rate of a reaction without itself being consumed at the end of the reaction, and the phenomenon is called ***catalysis***.

Thermal decomposition of $KClO_3$ is found to be accelerated by the presence of MnO_2. Here MnO_2 acts as a catalyst.

$$\mathbf{2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2 \uparrow + [MnO_2]}$$

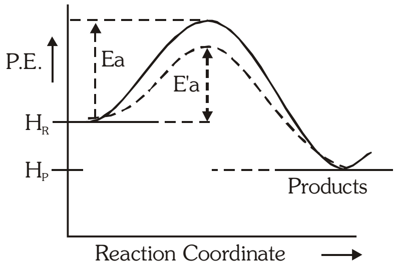
- MnO_2 can be received in the same composition and mass at the end of the reaction.
- The word catalyst should not be used when the added substance reduces the rate of reaction. The substance is then called **inhibitor**.
- Catalyst are generally foreign substances but sometimes one of the product may act as a catalyst and such catalyst is called ***"auto catalyst"*** and the phenomena is called ***auto catalysis***.

In the permanganate titration of oxalic acid initially there is slow discharge of the colour of permanganate solution but afterwards the discharge of the colour become faster. This is due to the formation of $MnSO_4$ during the reaction which acts as a catalyst for the same reaction. Thus, $MnSO_4$ is an ***"auto catalyst"*** for this reaction. This is an example of auto catalyst.

$$\mathbf{2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_2 \longrightarrow K_2SO_4 + 8H_2O + 10CO_2 + MnSO_4}$$

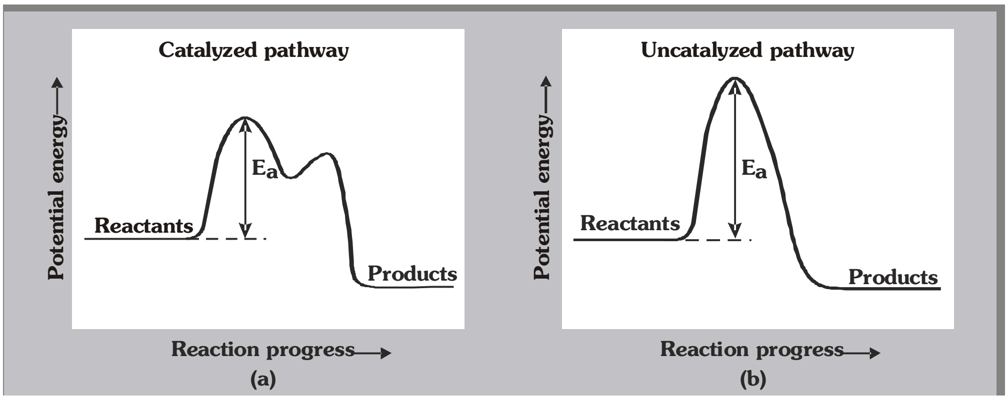
10.1 General characteristics of catalyst :

- A catalyst does not initiate the reaction normally. It simply fastens it.
- Only a small amount of catalyst can catalyse the reaction.
- A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant and hence ΔG°. It simply lowers the time needed to attain equilibrium. This means if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst, the reaction will still go to 75% of completion on the attainment of equilibrium but the time needed for this will be less than 20 minutes.



A catalyst drives the reaction through a low energy path and hence E_a is less. That is, the function of the catalyst is to lower down the activation energy.

E_a = Energy of activation in absence of catalyst.
E_a' = Overall Energy of activation in presence of catalyst.
$E_a - E_a'$ = Lowering of activation energy by catalyst.



(a) (b)

10.2 Comparison of rates of reaction in presence and absence of catalyst :

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

$$\frac{k_{cat}}{k} = \frac{Ae^{-E'a/RT}}{Ae^{-Ea/RT}} = Ae^{(E_a - E'_a)/RT}$$

Since $E_a - E'_a$ is positive so $k_{cat} > k$. the ratio $\frac{k_{cat}}{k}$ gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature.

The rate of reaction in the presence of catalyst at any temperature T_1 may be made equal to the rate of reaction in absence of catalyst but for this sake we will have to raise the temperature. Let this temperature be $T_2 = e^{-E'_a/RT_1} = e^{-E_a/RT_2}$ or $\frac{E'_a}{T_1} = \frac{E_a}{T_2}$

11 CALCULATION OF RATE LAW / ORDER

11.1 When first step is rate determining step.

Ex.19 Calculate order and rate law of reaction -

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

with help of mechanism

I. $NO_2 + F_2 \xrightarrow{K_1} NO_2F + F$ **(slow)**

II. $NO_2 + F \xrightarrow{K_2} NO_2F$ **(fast)**

Sol. According to RDS

Rate = $k_1\,[NO_2]\,[F_2]$

11.2 Equilibrium approach :

Ex.20 For the reaction , $H^+ + HNO_2 + C_6H_5NH_2 \xrightarrow{Br^-} C_6H_5N_2^{\;+} + 2H_2O$, the mechanism is ,

$H^+ + HNO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\text{intermediate}}{H_2NO_2^{\;+}}$ **(fast equilibrium step)**

$H_2NO_2^{\;+} + Br^- \xrightarrow{k_3} NOBr + H_2O$ **(slow)**

$NOBr^- + C_6H_5NH_2 \xrightarrow{k_4} C_6H_5N_2^{\;+} + Br^- + H_2O$ **(fast)**

Derive the rate law expression for the reaction

Sol. $r = k_3\,[Br^-]\,[H_2NO_2^{\;+}]$

$$K_{eq} = \frac{k_1}{k_2} = \frac{[H_2NO_2^{\;+}]}{[H^+][HNO_2]}$$

$$[H_2NO_2^{\;+}] = \left[\frac{k_1}{k_2}\right][H^+]\,[HNO_2]$$

$$r = \frac{k_1k_3}{k_2}[H^+]\,[HNO_2]\,[Br^-].$$

Note : Rate law can have reactant product or catalyst concentration terms but not any intermediate terms.

11.3 CASE-III : STEADY STATE APPROXIMATION :

Ex.21 **For the reaction , $2O_3 \rightarrow 3O_2$, the mechanism is**

$$O_3 \xrightarrow{k_1} O_2 + O$$

$$O_2 + O \xrightarrow{k_2} O_3$$

$$O_3 + O \xrightarrow{k_3} 2O_2$$

Derive the rate law expression for the reaction

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

$$\frac{d[O_3]}{dt} = -k_1[O_3] + k_2[O_2][O] - k_3[O_3][O]$$

$$\frac{d[O_2]}{dt} = k_1[O_3] - k_2[O_2][O] + k_3[O_3][O]$$

At steady state $\frac{d[O]}{dt} = 0$

$$\frac{d[O]}{dt} = k_1[O_3] - k_2[O_2][O] - k_3[O_3][O] = 0$$

$$[O] = \frac{k_1[O_3]}{k_2[O_2]+k_3[O_3]}$$

$$\frac{d[O_3]}{dt} = -k_1[O_3] + \frac{\{k_2[O_2]\;\;k_1[O_3]\}}{k_2[O_2]+k_3[O_3]} - \frac{k_1\;\;k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$$

$$= -k_1[O_3] + \frac{k_1k_2[O_2]\;\;[O_3] - k_1k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$$

$$= \frac{k_1k_2[O_2][O_3] - k_1k_3[O_3]^2 + k_1k_2[O_2][O_3] - k_1k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$$

$$= \frac{-2k_1\;\;k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$$

$$\left[\frac{-1}{2}\;\;\frac{d}{dt}[O_3]\right] = \frac{k_1\;\;k_3\;\;[O_3]^2}{k_2[O_2]+k_3[O_3]}$$

$$\text{Rate} = -\frac{1}{2}\frac{d}{dt}[O_3]$$

So, Rate (r) $= \frac{k_1\;\;k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$

if 3rd step is RDS then $k_1 >> k_3$

$k_2 >> k_3$

Rate (r) $= \frac{k_1k_3}{k_2}[O_3]^2[O_2]^{-1}$ (ie. first order)

MISSLENIOUS PREVIOUS YEARS QUESTION

1. Which of the following statement(s) is (are) correct **[JEE 1999]**

(A) A plot of log K_p versus 1/T is linear

(B) A plot of log [X] versus time is linear for a first order reaction, $X \longrightarrow P$

(C) A plot of log P versus 1/T is linear at constant volume.

(D) A plot of P versus 1/V is linear at constant temperature.

Ans. **(A,B,D)**

2. The rate constant for an isomerisation reaction $A \rightarrow B$ is 4.5×10^{-3} min^{-1}. If the initial concentration of A is 1 M. Calculate the rate of the reaction after 1 h. **[JEE 1999]**

Ans. **3.435×10^{-3} M/min**

Sol. $r = k[A]$

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

$r = (4.5 \times 10^{-3})\ e^{-4.5 \times 10^{-3} \times 60}$ M/min.

3. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 $kJmol^{-1}$. **[JEE 2000]**

Ans. **100 $kJmol^{-1}$**

Sol.

$$\ln\left(\frac{r_2}{r_2}\right) = -\frac{1}{R}\left(\frac{Ea_2}{T_2} - \frac{Ea_1}{T_1}\right)$$

$$\ln(1) = -\frac{1}{R}\left(\frac{Ea_1 - 20}{40} - \frac{Ea_1}{500}\right)$$

$Ea_1 = 100$

4. The rate constant for the reaction **[JEE SCR 2000]**

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

is 3.0×10^{-5} sec^{-1}. if the rate is 2.4×10^{-5} mol $litre^{-1}$ sec^{-1}, then the concentration of N_2O_5 (in mol $litre^{-1}$) is

(A) 1.4 (B) 1.2 (C) 0.004 (D) 0.8

Ans. **(D)**

Sol. $r = k[N_2O_5]^2$

$2.4 \times 10^{-5} = 3 \times 10^{-5}[N_2O_5]^2$

5. If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process : $AB + h\nu \longrightarrow AB$, the rate of formation of AB is directly proportional to **[JEE SCR 2001]**

(A) C (B) I (C) I^2 (D) CI

Ans. **(B)**

Sol. For phot chemical reaction

$r \propto I$

6. The rate of a first order reaction is 0.04 mole $litre^{-1}$ s^{-1} at 10 minutes and 0.03 mol $litre^{-1}$ s^{-1} at 20 minutes after initiation. Find the half life of the reaction. **[JEE 2001]**

Ans. **$t_{1/2}$ = 24.14 min**

Sol.

$$\left(\frac{\ln 2}{t_{1/2}}\right)(20 - 10) = \ln\left(\frac{0.04}{0.03}\right)$$

7. Consider the chemical reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. The rate of this reaction can be expressed in term of time derivative of concentration of $N_2(g)$, $H_2(g)$ or NH_3 (g). Identify the correct relationship amongst the rate expressions. **[JEE SCR 2002]**

(A) Rate $= -d[N_2]/dt = -1/3\ d[H_2]/dt = 1/2d[NH_3]/dt$

(B) Rate $= -d[N_2]/dt = -3\ d[H_2]/dt = 2d[NH_3]/dt$

(C) Rate $= d[N_2]/dt = 1/3\ d[H_2]/dt = 1/2d[NH_3]/dt$

(D) Rate $= -d[N_2]/dt = -d[H_2]/dt = d[NH_3]/dt$

Ans. **(A)**

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

8. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant of reaction in sec^{-1} is **[JEE SCR 2003]**

(A) 2×10^4 (B) 3.45×10^{-5}

(C) 1.3486×10^{-4} (D) 2×10^{-4}

Ans. **(C)**

Sol. $$K(2 \times 10^4) = \ln\left(\frac{800}{50}\right)$$

9. The reaction, $X \longrightarrow$ Product follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M. Then the rate of reaction when concentration of X is 0.01 M

(A) 1.73×10^{-4} M min^{-1} (B) 3.47×10^{-5} M min^{-1}

(C) 3.47×10^{-4} M min^{-1} (D) 1.73×10^{-5} M min^{-1} **[JEE SCR 2004]**

Ans. **(C)**

Sol. $$K(40) = \ln\left(\frac{0.1}{0.25}\right)$$

$$K = \frac{\ln 2}{20}$$

$$r = K[X]$$

$$= \frac{\ln 2}{20} \times 0.1$$

10. $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

Time (in Min)	0	100	200
Partial pressure of X (in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate

(a) Order of reaction

(b) Rate constant (K_X)

(c) Time taken for 75% completion of reaction

(d) Total pressure when $P_X = 700$ mm. **[JEE 2005]**

Ans. **(a) 1, (b) 6.93 × 10^{-3} min^{-1} , (c) 200, (d) 950 mm**

Sol. (a) As half life is constant so it will be of first order.

(b) $K_x(100) = \ln\left(\frac{800}{400}\right)$

(c) $t = 75\% = 2t_{50\%} = 2\left(\frac{\ln 2}{K_x}\right)$

(d) $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

$800 - x \qquad \frac{3x}{2} \qquad x$

Here x = 100

So $P_T = 800 + \frac{3x}{2} = 950$

11. Which of the following statement is incorrect about order of reaction? **[JEE 2005]**

(A) Order of reaction is determined experimentally

(B) It is the sum of power of concentration terms in the rate law expression

(C) It does not necessarily depend on stoichiometric coefficients

(D) Order of the reaction can not have fractional value.

Ans. **(D)**

12. Consider a reaction aG + bH → Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is :

[JEE 2006]

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

Ans. **(D)**

Sol. $\frac{r_2}{r_1}\left(\frac{[G\ ]_2}{[G\ ]_1}\right)^{\alpha}\left(\frac{[H]_2}{[H]_1}\right)^{\alpha}$

$8 = 2^{\alpha} . 2^{\beta}$ ....(1)

$2 = 2^{\alpha}$ ....(2)

$\alpha = 1, \beta = 2$

13. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constants for first order (k_1) and zero order (k_0) of the reactions is **[JEE 2008]**

(A) 0.5 mol^{-1} dm^3 (B) 1.0 mol dm^{-3}

(C) 1.5 mol dm^{-3} (D) 2.0 mol^{-1} dm^3

Ans. **(A)**

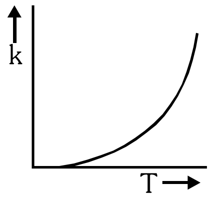
Sol. $K_1 = \dfrac{\ln 2}{40}$

$K_0 = \dfrac{1.386}{2 \times 20}$

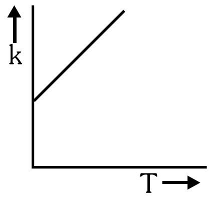
$\dfrac{K_1}{K_0} = 0.5$

14. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is – **[JEE 2010]**

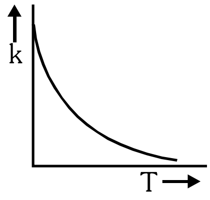
(A)



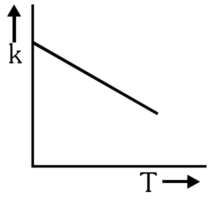
(B)



(C)

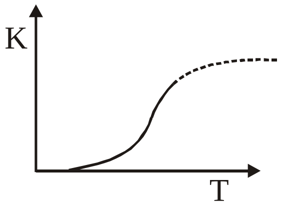


(D)



Ans. **(A)**

Sol.



15. The concentration of R in the reaction R → P was measured as a function of time and the following data is obtained :

[R] (molar)	1.0	0.75	0.40	0.10
t(min.)	0.0	0.05	0.12	0.18

The order of the reaction is. **[JEE 2010]**

Ans. **Zero**

Sol. By hit and trial method het reaction is zero order.

$K_1 = \dfrac{[A]_0 - [A]_1}{t_1}$

$K_1 = \dfrac{1 - 0.75}{0.05} = 5$

$K_2 = \dfrac{[A]_0 - [A]t_2}{t_2}$

$K_2 = \dfrac{1 - 0.4}{0.12} = 5$

As $K_1 \approx K_1$ so reaction will be zero order reaction.

EXERCISE # (S-1)

RATE OF REACTION

1. Ammonia and oxygen reacts at higher temperatures as

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

In an experiment, the concentration of NO increases by 1.08×10^{-2} mol litre^{-1} in 3 seconds. Calculate.

(i) rate of reaction

(ii) rate of disappearance of ammonia

(iii) rate of formation of water

2. The reaction $2A + B + C \rightarrow D + E$ is found to be first order in A, second order in B and zero order in C.

(i) Give the rate law for the reaction in the form of differential equation.

(ii) What is the effect in rate of increasing concentrations of A, B, and C two times?

3. At 27°C, it was observed during a reaction of hydrogenation that the pressure of hydrogen gas decreases from 2 atmosphere to 1.1 atmosphere in 75 minutes. Calculate the rate of disappearance reaction in M sec^{-1} and in terms of atm min^{-1}. [Use : R = 0.08 atm-L/K-mole]

4. For the elementary reaction $2A + B_2 \longrightarrow 2AB$. Calculate how much the rate of reaction will change if the volume of the vessel is suddenly reduced to one third of its original volume?

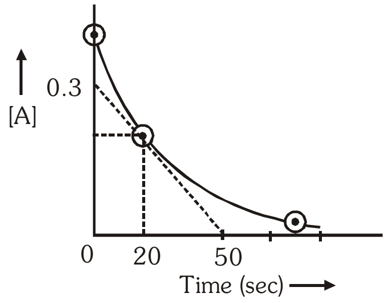
5. For the reaction $3BrO^- \rightarrow BrO_3^- + 2Br^-$ in an alkaline aqueous solution, the value of the second order (in BrO^-) rate constant at 80°C in the rate law for $-\dfrac{d[BrO^-]}{dt}$ was found to be 0.057 L mol^{-1} s^{-1}. What is the rate constant when the rate law is written for :

(a) $\dfrac{d[BrO_3^-]}{dt}$, (b) $\dfrac{d[Br^-]}{dt}$?

6. $xA + yB \rightarrow zC$. If $-\dfrac{d[A]}{dt} = -\dfrac{d[B]}{dt} = 1.5\dfrac{d[C]}{dt}$, then (x + y + z) is. (x, y & z are the lowest integral value.)

7. For the reaction : $3A(g) \rightarrow 2B(g)$, the rate of formation of 'B' at 298 K, is represented as $ln\left(\dfrac{d[B]}{dt}\right) = -0.04 + 2 \times ln[A]$. The order of reaction is-

8. A certain reaction **A → B** follows the given concentration (Molarity) – time graph. Calculate the rate for this reaction at 20 second.



9. The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.6$ and $P_B = 0.8$ atm. Calculate the ratio of rate of reaction relative to initial rate when P_C becomes 0.2 atm.

ZERO ORDER REACTIONS

10. In the reaction ($A \longrightarrow B$) rate constant is 1.2×10^{-2} M s^{-1} . What is concentration of B after 10 and 20 min., if we start with 10 M of A.

11. From the following data for the zero order reaction : $A \longrightarrow$ products. Calculate the value of k.

Time (min.)	**[A]**
0.0	0.10 M
1.0	0.09 M
2.0	0.08 M

12. A drop of solution (volume 0.10 ml) contains 6×10^{-6} mole of H^+. If the rate constant of disappearance of H^+ is 1×10^7 mole litre^{-1} sec^{-1}, how long would it take for H^+ in drop to disappear?

13. A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given: order of reaction is zero for both A & B.)

14. For a zero order chemical reaction,

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

rate of reaction = 0.1 atm/sec. Initially only NH_3 is present & its pressure = 3 atm. Calculate total pressure at t = 10 sec.

FIRST ORDER REACTIONS

15. A first order reaction is 75% completed in 72 min. How long time will it take for

(i) 50% completion (ii) 87.5% completion

16. A first order reaction is 20% complete in 10 min. Calculate (i) the specific rate constant , (ii) the time taken for the reactions to go to 75% completion. [ln 10 = 2.3, ln2 = 0.7]

17. Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place is ten times that required for half of the reaction.

18. A drug is known to be ineffective after it has decomposed 75%. The original concentration of a sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 250 units/ml. Assuming that decomposition is of I order, what will be the expiry time of the drug?

19. A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment, 2.0 % of the virus was found to be inactivated per minute . Evaluate k for inactivation process. [ln 10 = 2.3, ln 98 = 4.58]

20. The reaction $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$ is a first order gas reaction with $k = \left(\frac{35}{9}\right) \times 10^{-4}$ sec^{-1} at 320°C. What % of SO_2Cl_2 is decomposed on heating this gas for 90 min. (ln2 = 0.7)

21. The decomposition of a compound A in solution follow first order kinetics. If 10% w/v solution of A is 10% decomposed in 10 minutes at 10°C, then 20% w/v solution of A is .... % decomposed in 20 minutes at 10°C.

22. Calculate the half-life of the first-order reaction

$$C_2H_4O(g) \longrightarrow CH_4(g) + CO(g)$$

if the initial pressure of $C_2H_4O(g)$ is 80 mm of Hg and the total pressure at the end of 20 minutes is 120 mm of Hg

SECOND ORDER REACTIONS

23. In the II order reaction : $2A \rightarrow A_2$. The rate of formation of A_2 is 10^{-5} M sec^{-1} at 0.01M concentration of A. Calculate the rate constant in the rate of disappearance of 'A'.

24. If $t_{1/2}$ of a second order reaction is 1.0 hr. After what time, the amount of reactant will be 25% of the intial amount?

25. Reaction : $A + B \rightarrow C + D$, follows the rate law : $r = (2 \times 10^{-3} M^{-1} s^{-1})$ [A] [B]. The reaction is started with 1.0 mole each of 'A' and 'B', in constant volume of 5 litre. In what time, the moles of 'A' become 0.25 ?

DETERMINATION OF ORDER OF REACTION & RATE LAW

26. At 800° C, the rate of reaction

$$2\,NO(g) + H_2(g) \longrightarrow N_2(g) + H_2O(g)$$

changes with the concentration of NO(g) and $H_2(g)$ as-

Exp.no.	**[NO] in M**	**[H_2] in M**	$-\frac{1}{2}\frac{d[NO]}{dt}$ **in M sec^{-1}**
(i)	1.5×10^{-3}	4×10^{-3}	4.50×10^{-9}
(ii)	1.5×10^{-3}	2×10^{-3}	2.25×10^{-9}
(iii)	3.0×10^{-3}	2×10^{-3}	9.00×10^{-9}

(a) What is the order of reaction?

(b) What is the rate equation for the reaction?

(c) What is the rate of reaction when $[H_2] = 1.5 \times 10^{-3}$ M and $[NO] = 1.0 \times 10^{-3}$M?

27. The catalytic decomposition of $N_2O(g)$ by gold at 900°C and at an initial pressure of 200 mm is 50% complete in 53 minutes and 73% complete in 100 minutes.

(i) What is the order of the reaction?

(ii) Calculate the velocity constant.

(iii) How much of percentage $N_2O(g)$ will decompose in 100 min. at the same temperature but at initial pressure of 600 mm of Hg ?

28. The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different time and the results are given below

t (sec)	0	100	200	300
Pr. (Pascal)	4×10^3	3.5×10^3	3×10^3	2.5×10^3

Determine the order of reaction and its rate constant.

29. The half life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction?

30. For a chemical reaction $A + B \rightarrow$ products, the order is one with respect to each A and B. The sum of x and y from the following data is.

Rate (mol l^{-1}s^{-1})	**[A](mol l^{-1})**	**[B](mol l^{-1})**
0.10	0.20	0.05
0.40	x	0.05
0.80	0.40	y

CALCULATION OF RATE CONSTANT USING DIFFERENT PARAMETERS

31. For the Ist order reaction,

$$A \longrightarrow B + C$$

Time	t	∞
Total pressure of (A + B + C)	P_2	P_3

Find k in term of P_2, P_3 and t

32. For the Ist order reaction $S \longrightarrow G + F$

Time	t	∞
Rotation of (G + F)	r_t	r_∞

Find k in term of r_t, r_∞ and t

33. The thermal decomposition of dimethyl ether was measured by finding the increase in pressure at 500°C in the reaction

$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

Time (sec.)	200	400	∞
Pressure increase (mm Hg)	540	594	600

The initial pressure of ether was 300 mm Hg. Determine the rate constant of reaction.

34. From the following data, show that decomposition of H_2O_2 in aqueous solution is first order.

Time (in minutes)	0	10	20
Volume (in c.c. of $KMnO_4$)	22.8	11.4	5.7

35. The following data were obtained in experiment of inversion of cane sugar.

Time (minutes)	0	60	120	180	∞
Angle of rotation (degree)	+15	+ 7	+ 3	+1	–1

Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter?

36. The decomposition of N_2O_5 according to the equation $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ is a first order reaction. After 60 min. from start of decomposition in a closed rigid vessel, the total pressure developed is found to be 350 mm Hg. On complete decomposition, the total pressure is 500 mm Hg. Calculate the rate constant for disappearance of $N_2O_5(k_{N_2O_5})$ for the reaction.

37. The reaction given below, rate constant for disappearance of A is 8×10^{-3} sec^{-1}. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm and also find the total pressure after 100 sec. [ln7 = 1.9 , ln 10 = 2.3].

$$2A(g) \longrightarrow 4B(g) + C(g)$$

38. The reaction $A(aq) \longrightarrow B(aq) + C(aq)$ is monitered by measuring optical rotation of reaction mixture at different time interval. The species A, B and C are optically active with specific rotations 20°, 30° and – 40° per mole respectively. Starting with pure A, if the value of optical rotation was found to be 2.5° after 6.93 minutes and optical rotation was –5° after infinite time. Find the rate constant for first order conversion of A into B and C.

39. For the hydrolysis of ethyl acetate in presence of H^+ as catalyst.

$$CH_3COOC_2H_5(aq.) + H_2O \xrightarrow{H^+} CH_3COOH(aq) + C_2H_5OH(aq.)$$

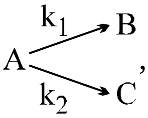
the experimentally observed rate law is

$$\text{rate} = k\ [\text{ester}]\ [H_2O]\ [H^+].$$

If the value of rate constant is $1.386 \times 10^{-3}\ M^{-2}\ min^{-1}$ and concentration of $[H^+]$ ion is 1.8 M, how many seconds will it take for concentration of ester to become half of initial value ?

40. If 0.01 % of a substance undergoing decomposition is consumed in 1 milli seconds when the concentration is 0.02M and in 0.25 milli seconds when the concentration is 0.04M. The order of reaction is.

PARALLEL , SEQUENTIAL REACTIONS AND REVERSIBLE

41. 

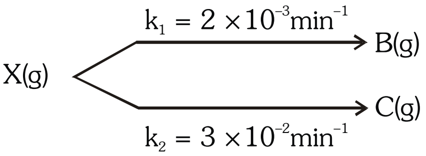
, $k_1 = x\ hr^{-1}$; $k_1 : k_2 = 1 : 10$. Calculate $\frac{[C]}{[A]}$ after one hour from the start of the reaction.

Assuming only A was present in the beginning.

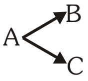
42. How much time would be required for the B to reach maximum concentration for the reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C.\ \text{Given } k_1 = \frac{\ln 2}{4}\ min^{-1},\ k_2 = \frac{\ln 2}{2} min^{-1}$$

43. A gaseous reactant **X** decompose to produce gaseous product B & C in a parallel reaction, both by first order, as follows :



If the decomposition is carried out in a sealed flask, partial pressure of B after very long time was found to be 100 mm Hg. Determine the time when pressure of **X**(g) was 100 mm Hg.
[ln2 = 0.693]

44. The reaction A proceeds in parallel channels 

. Suppose the half life values for the two branches are 60 minutes and 90 minutes, what is the overall half-life value?

45. For the given sequential reaction

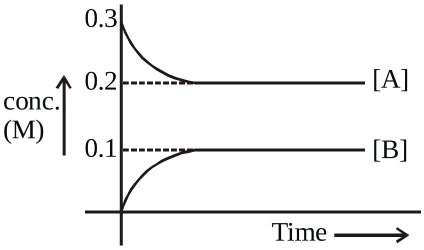
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Initial concentration of A is 20M. Calculate the approximate concentration of C after 10 min, if $k_1 = 2 \times 10^8\ min^{-1}$ & $k_2 = 0.0693 min^{-1}$

46. Consider a reversible reaction :

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

Which is a first order in both the direction ($k_1 = \frac{1.38}{3} \times 10^{-2}\ \text{min}^{-1}$). The variation in concentration is plotted with time as shown below.



Calculate the time (in minute) at which 25% of A would be exhausted. [$\ell n2 = 0.69$]

47. 3 mole mixture of two different substances A & B (mole fraction of A = 2/3) undergoes parallel first order reaction to form product 'C' as follow at 300 K.

$$A \xrightarrow{k_1} C \qquad t_{1/2} = 2\text{hr}$$

$$B \xrightarrow{k_2} C \qquad t_{1/2} = 4\text{hr}$$

The time at which there will be 2 mole of 'C' is

48. For the series of competitive reactions :

$$H + HO_2 \xrightarrow{K_1} H_2 + O_2$$

$$H + HO_2 \xrightarrow{K_2} 2OH$$

$$H + HO_2 \xrightarrow{K_3} H_2O + O$$

It has been found that $K_1 : K_2 : K_3 = 0.60 : 0.30 : 0.10$. The molar ratio of the product, H_2, O_2, OH, H_2O and O, at time t, is -

49. In the parallel reactions : $A \xrightarrow{K_1 = \ln 3\,\text{min}^{-1}} B$ and $A \xrightarrow{K_2 = \ln 3\,\text{min}^{-1}} C$, the time when the concentration of A, B and C becomes equal is -

50. For the sequential reactions :

$A \xrightarrow{K_1 = 0.02\,\text{min}^{-1}} B \xrightarrow{K_2 = 0.02\,\text{min}^{-1}} C$, the initial concentration of 'A' was 0.2M and initially 'B' and 'C' were absent. The time at which the concentration of 'B' becomes maximum and the maximum concentration of 'B' are respectively.

TEMPERATURE DEPENDENCE OF RATE

51. In gaseous reactions important for understanding the upper atmosphere, H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and E_a=77 kJ mol^{-1}, then calculate E_a for the bimolecular recombination of 2OH radicals to form H_2O & O at 500 K

52. The specific rate constant for a reaction increases by a factor of 4, if the temperature is changed from 27°C to 47°C. Find the activation energy (in kcal) for the reaction (Use ln 2 = 0.7)

53. Given that the temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate activation energy for the saponification of ethyl acetate. Let initial temperature is 298K.
[**Use :** ln (1.75) = 0.56]

54. The energy of activation for a reaction is at 27ºC 10 kJ/mol. The presence of catalyst lowers the energy of activation by 75%. Find the factor by which rate of reaction increases at 27ºC due to catalyst. **(Take R = 25/3 J/mol-k)**

55. At 380°C, the half–life period for the first order decomposition of H_2O_2 is 360 min.The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450°C.

Use : $\left[\frac{1}{653}-\frac{1}{723}\right]=1.5\times10^{-4}$, $e^{3.6} = 36$, $R = \frac{25}{3}\,J/k-mol$

56. The rate constant for decomposition of $COCl_2$ (g) according to following reaction $COCl_2(g) \rightarrow CO(g) + Cl_2(g)$; $\Delta H = 19$ kcal/mol, is expressed as

$$ln\,k = 15 - \frac{5000}{T}$$

Calculate activation energy for given reaction (in Kcal/mol.)

57. At 300 K, 50% of molecule collide with energy greater than or equal to E_a. At what temperature, 25% molecule will have energy greater than or equal to E_a.

58. For a zero order reaction at 200K reaction complete in 5 minutes while at 300K, same reaction completetes in 2.5 minutes. What will be the activation energy in calorie.
(R = 2 Cal/mol-k; *l*n 2 = 0.7)

59. For a first order reaction : $A \rightarrow P$, the temperature (T) dependent rate constant (k) was found to follow the equation $\log_{10}k = -(2000)\,\frac{1}{T} + 6$. Then activation energy equation of reaction will be (ln x = 2.3 × log x)

60. A reaction takes place in three steps. The rate constants are k_1 , k_2 , k_3. The overall rate constant $k = \frac{k_1\sqrt{k_3}}{k_2}$. If energy of activation is 40 , 30 and 20 kJ respectively, the overall energy of activation is :

MECHANISM OF REACTION

61. The reaction $2NO + Br_2 \longrightarrow 2NOBr$, is supposed to follow the following mechanism

(i) $NO + Br_2 \xrightleftharpoons{\text{fast}} NOBr_2$

(ii) $NOBr_2 + NO \xrightarrow{\text{slow}} 2NOBr$

Suggest the rate law expression.

62. For the reaction $2H_2 + 2NO \longrightarrow N_2 + 2H_2O$, the following mechanism has been suggested :

$2NO \rightleftharpoons N_2O_2$ equilibrium constant = K_1 (fast)

$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$ (slow)

$N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O$ (fast)

Establish the rate law for given reaction.

63. For the reaction : $2O_3(g) \longrightarrow 3O_2(g)$

Mechanism :

Step - I $O_3(g) \overset{\text{fast}}{\rightleftharpoons} O_2(g) + O(g)$

Step - II $O(g) + O_3(g) \xrightarrow{\text{slow}} 2O_2(g)$

Overall order of reaction based on mechanism is

64. A complex reaction : $2X + Y \rightarrow Z$, takes place in two steps :

$X + Y \xrightarrow{K_1} 2W$

$X + 2W \xrightarrow{K_2} Z$

If $K_1 << K_2$, order of reaction will be -

65. The suggested mechanism for the reaction : $CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$, is -

$Cl_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2\dot{C}l(\text{fast})$

$CHCl_3 + \dot{C}l \xrightarrow{K_3} HCl + \dot{C}Cl_3\ (\text{slow})$

$\dot{C}Cl_3 + \dot{C}l \xrightarrow{K_4} CCl_4(\text{fast})$

The experimental rate law consistent with the mehanism.

EXERCISE # (S-2)

1. The decomposition of a compound P, at temperature T according to the equation

$$2P_{(g)} \longrightarrow 4Q_{(g)} + R_{(g)} + S_{(l)}$$

is the first order reaction. After 30 minutes from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 minutes, if volume of liquid S is supposed to be negligible. Also calculate the time fraction $t_{7/8}$.

Given : Vapour pressure of S (l) at temperature T = 32.5 mm Hg.

[ln = 1.169) = 0.156, ln2 = 0.7, $e^{0.39} = 1.5$]

2. For the reaction : $A + B \longrightarrow$ Product, rate law is : rate = k $[A]^2$ [B], where $k = 5 \times 10^{-5}$ $(mol/L)^{-2}$ min^{-1} . Determine the **time (in minutes)** in which concentration of 'A' becomes half of its initial concentration, if initial concentration of A and B are 0.2 M and 2×10^3 M respectively.

3. An optically active compound A upon acid catalysed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was 5° while after completion of the reaction it was – 20°. If optical rotation per mole of A, B & C are 60°, 40° & – 80°. Calculate half life of the reaction.

4. The reaction

$$cis\text{–}Cr(en)_2(OH)^+_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} trans\text{–}Cr(en)_2(OH)^+_2$$

is first order in both directions. At 25°C, the equilibrium constant is 0.1 and the rate constant k_1 is $2 \times 10^{-4} s^{-1}$. In an experiment starting with the pure *cis* form, how long would it take for half the equilibrium amount of the *trans* isomer to be formed ? [ln2 = 0.693]

5. For the two parallel first order reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, show that the activation energy E′ for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by

$$E' = \frac{k_1E_1 + k_2E_2}{k_1 + k_2}$$

6. At room temperature (27°C), orange juice gets spoilt in about 64 hours. In a refrigerator at 7°C, juice can be stored three times as long before it gets spoilt. Estimate

(a) the activation energy of the reaction that causes the spoiling of juice.

(b) How long should it take for juice to get spoilt at 47°C?

[$e^{0.9625} = 2.5$, ln3 = 1.1 , R = 2 cal/mol-K]

7. Two reactions (i) A → products (ii) B → products, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310K. The half life for this reaction at 310K is 30 minutes. At 310K temperature and same concentration of reactant in both reaciton B, decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300K.

8. The reaction of formation of phosgene from CO and Cl_2 is $CO + Cl_2 \longrightarrow COCl_2$

The proposed mechanism is

(i) $Cl_2 \underset{K-1}{\overset{K_1}{\rightleftharpoons}} 2Cl$ (fast equilibrium)

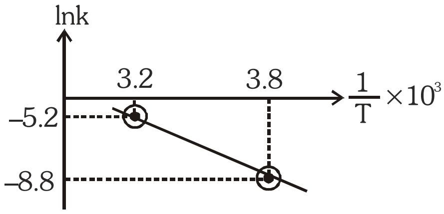
(ii) $Cl + CO \underset{K-2}{\overset{K_2}{\rightleftharpoons}} COCl$ (fast equilibrium)

(iii) $COCl + Cl_2 \xrightarrow{K_3} COCl_2 + Cl$ (slow)

Show that the above mechanism leads to the following rate law $\frac{d[COCl_2]}{dt} = K[CO][Cl_2]^{3/2}$,

where $K = k_3 . \frac{k_2}{k_{-2}} \left(\frac{k_1}{k_{-1}}\right)^{1/2}$.

9. For any elementary reaction, following observation is made :



If the above reaction is carried out in the presence of catalyst at 300K, the reaction proceeds with same rate as without catalyst at 400K. By what amount (in kcal) catalyst has decreased E_a.

10. Milk is pasteurised if it is heated at 67°C for 4 hours. If $\frac{E_a}{2.303}$ for the process is 23.8 kcal / mol then minimum how much seconds will be required for the the process at 77°C ? [R = 2cal /K-mol]

11. When CrI_3 reacts with H_2O_2 in presence of NaOH forming Na_2CrO_4, $NaIO_4$ & H_2O then find how many times will be rate of disappearance of NaOH compared to CrI_3.

12. Conversion of A into B and C follows first order kinetics. A, B and C all are optically active, initially A is present in 500 ml solution and 100 minutes after the start of reaction, the resulting solution becomes optically inactive. If angle of rotation of A is +50 degree per molar, B is –20 degree per molar and C is +10 degree per molar, then find the time for completion of $\left(\frac{875}{9}\right)\%$ of the chemical reaction in minutes.

$A(aq.) \rightarrow B(aq.) + C(aq.)$

13. A gas phase reaction is,

$A(g) + 2B(g) \rightarrow C(g)$

The reaction was carried out with stoichiometric proportions of A and B and the following data is obtained

Half life (min)	**10**	**160**
Initial pressure of A(atm)	**40 atm**	**10 atm**

What is overall order of reaction

14. For the reaction

$$A \longrightarrow P$$

If ratio of $t_{7/8} : t_{1/4}$ is 7 : 2 what is order of reaction.
$t_{7/8}$ = time in which 7/8 part of reactant is reacted
$t_{1/4}$ = time in which 1/4 part of reactant is reacted

15. A certain reactant A^{n+} is getting converted to $A^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with A^{n+} and $A^{(n+4)+}$. In this process, it converts A^{n+} to $A^{(n-2)+}$ and $A^{(n+4)+}$ to $A^{(n-1)+}$.

Time	0	10 min
Volume of reagent consumed	30 ml	45 ml

Calculate the rate constant (in min^{-1}) of the conversion of A^{n+} to $A^{(n+4)+}$ assuming it to be first order reaction.

[n-factor of reagent remain same when it reacts with A^{n+} & $A^{(n+4)+}$]

[Given: *l*n 3/2 = 0.4]

16. Consider two I^{st} order reactions at 25°C with same initial concentrations of 1M

I. $A \xrightarrow{t_{1/2} = 40\,min}$ product (temperature coefficient = 2)

II. $B \xrightarrow{t_{1/2} = 30\,min}$ product (temperature coefficient = 3)

If both reactions are carried out at 35°C. Find ratio of concentrations of A & B after one hour.

17. Consider two reactions at 27°C

(I). $A \longrightarrow B$; (First order kinetics)

(II). $X \longrightarrow Y$; (Zero order kinetics)

If both A & X each having initial concentration 0.1M & same half life period. Then find simplest ratio of rate constants for I & II reactions. [ln2 = 0.7]

18. The rate of first-order reaction is 0.04 mol $litre^{-1}s^{-1}$ at 10 minutes and 0.03 mol $litre^{-1}s^{-1}$ at 22 minutes after initiation. The half life of the reaction (in seconds) is (ln2 = 0.7, ln3 = 1 .1).

19. In order to determine the order of reaction : $A(g) \rightarrow 2B(g)$, vapour density of the system is determined at different stages of reaction, at constant temperature. The reaction is started with pure A(g). From the following data, the order of reaction is -

Time (min)	0	10	20
Vapour density	42	35	30

20. In the reaction : $A \rightarrow P$, the rate is doubled when the concentration of 'A' is quadrupled. If 50% of the reaction occurs in $8\sqrt{2}$ hr, how long (in hours) would it take for the completion of next 50% reaction.

EXERCISE # (O-1)

SINGLE CORRECT

RATE OF REACTION

1. The rate of a reaction is expressed in different ways as follows :

$$+\frac{1}{2}\frac{d[C]}{dt}=-\frac{1}{3}\frac{d[D]}{dt}=+\frac{1}{4}\frac{d[A]}{dt}=-\frac{d[B]}{dt}$$

The reaction is:

(A) $4A + B \longrightarrow 2C + 3D$ (B) $B + 3D \longrightarrow 4A + 2C$

(C) $A + B \longrightarrow C + D$ (D) $B + D \longrightarrow A + C$

2. For the reaction $2A + 3B \rightarrow 4C$
the rate of reaction may be represented as :–

(A) $r = -2\frac{d(A)}{dt} = -3\frac{d(B)}{dt} = 4\frac{d(C)}{dt}$ (B) $r = -2\frac{d(A)}{dt} = -4\frac{d(B)}{dt} = 3\frac{d(C)}{dt}$

(C) $r = -\frac{1}{2}\frac{d(A)}{dt} = \frac{1}{3}\frac{d(B)}{dt} = \frac{1}{4}\frac{d(C)}{dt}$ (D) $r = -\frac{1}{2}\frac{d(A)}{dt} = -\frac{1}{3}\frac{d(B)}{dt} = \frac{1}{4}\frac{d(C)}{dt}$

3. In a reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, the rate of appearance of NH_3 is 2.5×10^{-4} $molL^{-1}sec^{-1}$. The rate of reaction & rate of disappearance of H_2 will be (In $molL^{-1}sec^{-1}$)

(A) 3.75×10^{-4}, 1.25×10^{-4} (B) 1.25×10^{-4}, 2.5×10^{-4}

(C) 1.25×10^{-4}, 3.75×10^{-4} (D) 5.0×10^{-4}, 3.75×10^{-4}

4. For the reaction $4A + B \rightarrow 2C + 2D$, the incorrect statement is :–

(A) The rate of disappearance of B is one fourth the rate of disappearance of A

(B) The rate of appearance of C is half the rate of disappearance of B

(C) The rate of formation of D is half the rate of consumption of A

(D) The rates of formation of C and D are equal

5. Which of the following rate law has an overall order of 0.5 for reaction involving substances x,y and z ?

(A) Rate = $k\,[C_x]\,[C_y]\,[C_z]$ (B) Rate = $k\,[C_x]^{0.5}[C_y]^{0.5}[C_z]^{0.5}$

(C) Rate = $k\,[C_x]^{1.5}\,[C_y]^{-1}[C_z]^{\circ}$ (D) Rate = $k\,[C_x][C_z]^{\circ}\,/\,[C_y]^{2}$

6. For a reaction $A + B \rightarrow$ products, the rate of the reaction was doubled when the concentration of A was doubled, the rate was again doubled when the conc. of A & B were doubled. The order of the reaction with respect to A & B are:–

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

7. If the rate of the reaction is equal to the rate constant, the order of the reaction is:-

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

8. If the first order reaction involves gaseous reactants and gaseous products the units of its rate may be –

(A) atm. (B) atm - sec. (C) atm – sec^{-1} (D) atm^2 sec^2

9. If concentration of reactants is increased by 'x', then the rate constant (k) becomes :-

(A) $\ln\frac{k}{x}$ (B) $\frac{k}{x}$ (C) k + x (D) k

10. The rate constant of n^{th} order reaction has units

(A) $litre^{1-n}\ mol^{1-n}\ sec^{-1}$ (B) $mol^{n-1}\ litre^{1-n}\ sec^{-1}$

(C) $mol^{1-n}\ litre^{n-1}\ sec^{-1}$ (D) None

11. A reaction is found to have the rate constant x sec^{-1}. By what factor the rate is increased if initial conc. of A is tripled ?

(A) 3 (B) 9 (C) x (D) Remains same

12. Consider following two reactions

$$A \longrightarrow \text{Product} ; -\frac{d[A]}{dt} = k_1 [A]^0$$

$$B \longrightarrow \text{Product} ; -\frac{d[B]}{dt} = k_2 [B]$$

k_1 and k_2 are expressed in terms of molarity (mol L^{-1}) and time (sec) as

(A) sec^{-1}, M sec^{-1} (B) M sec^{-1}, M sec^{-1} (C) sec^{-1}, M^{-1} sec^{-1} (D) M sec^{-1}, sec^{-1}

13. $A(g) \longrightarrow B(g) + 3C(g)$

In a closed container at a given temperature, pressure increases from 100 mm Hg to 160 mm Hg in 10 sec. for reaction.

Then the average rate of reaction in first 10 sec. will be -

(A) 2 mm/sec. (B) 4 mm/sec. (C) 6 mm/sec. (D) 3 mm/sec.

ZERO ORDER REACTION

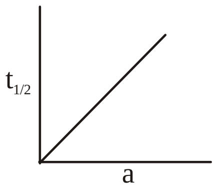
14. H_2 gas is adsorbed on the metal surface like tungsten. This follows .... order reaction -

(A) Third (B) Second (C) Zero (D) First

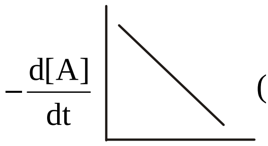
15. The rate constant of a zero order reaction is 0.2 mol $dm^{-3}h^{-1}$. If the concentration of the reactant after 30 minutes is 0.05 mol dm^{-3}. Then its initial concentration would be :

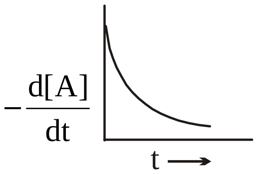
(A) 0.15 mol dm^{-3} (B) 1.05 mol dm^{-3} (C) 0.25 mol dm^{-3} (D) 4.00 mol dm^{-3}

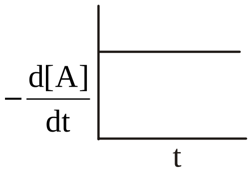
16. Consider the reaction $A \longrightarrow B$, graph between half life ($t_{1/2}$) and initial concentration (a) of the reactant is

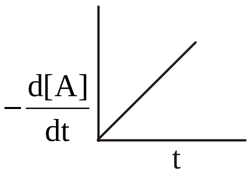


Hence graph between $-\frac{d[A]}{dt}$ and time will be

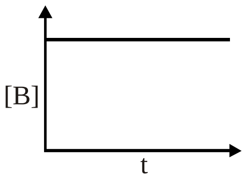
(A) 

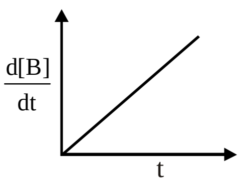
(B) 

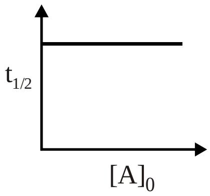
(C) 

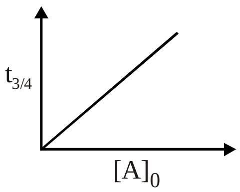
(D) 

17. Which graph represents zero order reaction $[A(g) \rightarrow B(g)]$:

(A) 

(B) 

(C) 

(D) 

18. K for a zero order reaction is 2×10^{-2} molL^{-1} sec^{-1}. If the concentration of the reactant after 25 sec is 0.5 M, then concentration after 50 sec. must have been.

(A) 0.5 M (B) 0.25 M (C) 0.125 M (D) 0.0 M

FIRST ORDER REACTION

19. The rate constant of a first order reaction is 4×10^{-3} sec^{-1}. At a reactant concentration of 0.02 M, the rate of reaction would be –

(A) 8×10^{-5} M sec^{-1} (B) 4×10^{-3} M sec^{-1}

(C) 2×10^{-1} M sec^{-1} (D) 4×10^{-1} M sec^{-1}

20. In a first order reaction the concentration of the reactant is decreased from 1.0 M to 0.25 M in 20 min. The rate constant of the reaction would be –

(A) 10 min^{-1} (B) 6.931 min^{-1} (C) 0.6931 min^{-1} (D) 0.06931 min^{-1}

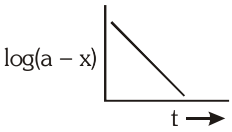
21. A first order reaction has a half life period of 69.3 sec. At 0.10 mol lit^{-1} reactant concentration rate will be –

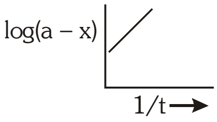
(A) 10^{-4} M sec^{-1} (B) 10^{-3} M sec^{-1} (C) 10^{-1} M sec^{-1} (D) 6.93×10^{-1}Msec^{-1}

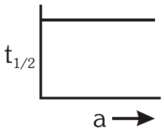
22. What fraction of a reactant (in first order reaction) is left after 40 minute if $t_{½}$ is 20 minute

(A) 1/4 (B) 1/2 (C) 1/8 (D) 1/6

23. Which of the following curve represents a Ist order reaction :–

(A)


(B)


(C)


(D) 1 & 3 both

24. After how many seconds will the conc. of the reactant in a first order reaction be halved, if the rate constant is 1.155×10^{-3} sec^{-1} :-

(A) 600 (B) 100 (C) 60 (D) 10

25. Correct statement about first order reaction is:-

(A) $t_{completion}$ = finite (B) $t_{1/2} \propto \frac{1}{a}$

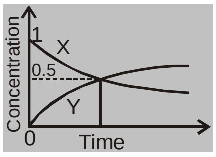
(C) Unit of k is mole lit^{-1} sec^{-1} (D) $t_{1/2} \times k$ = const.

26. For a given reaction of first order, it takes 20 minute for the concentration to drop from 1 M to 0.6 M. The time required for the concentration to drop from 0.6 M to 0.36 M will be :

(A) More than 20 min (B) Less than 20 min

(C) Equal to 20 min (D) Infinity

27. The accompanying figure depicts the change in concentration of species X and Y for the reaction X → Y as a function of time. The point of intersection of the two curves represents.



(A) $t_{1/2}$

(B) $t_{3/4}$

(C) $t_{2/3}$

(D) Data insufficient to predict

28. A reaction is of first order. After 100 minutes, 75 g of the reactant A are decomposed when 100g are taken initially. Calculate the time required when 150g of the reactant A are decomposed, the initial weight taken is 200g.

(A) 100 minutes (B) 200 minutes (C) 150 minutes (D) 175 minutes

29. Consider the reaction :

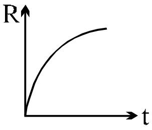
$A \longrightarrow B + C$

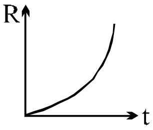
Initial concentration of A is 1 M. 20 minutes time is required for completion of 80 % reaction.

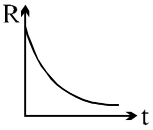
If $\frac{d[B]}{dt} = k[A]$, then half life ($t_{1/2}$) is (Use : ln 5 = 1.6, ln2 = 0.7)

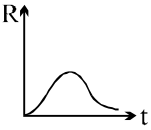
(A) 55.44 min. (B) 50 min (C) 8.75 min (D) 12.5 min

30. If decomposition reaction A (g) $\longrightarrow$ B (g) follows first order kinetics, then the graph of rate of formation (R) of B against time t will be

(A) 

(B) 

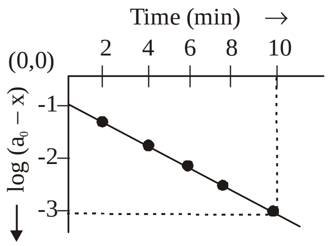
(C) 

(D) 

31. For the first order decomposition of $SO_2Cl_2(g)$,

$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$

a graph of log ($a_0 - x$) vs t is shown in figure. What is the rate constant (sec^{-1})?



(A) 0.2 (B) 4.6×10^{-1} (C) 7.7×10^{-3} (D) 1.15×10^{-2}

32. The rate constant for a second order reaction is 8×10^{-5} M^{-1} min^{-1}. How long will it take a 1M solution to be reduced to 0.5 M ?

(A) 8.665×10^{3} min (B) 8×10^{-3} min (C) 1.25×10^{4} min (D) 4×10^{-5} min

33. The rate law of the reaction : A + 2B $\rightarrow$ product(P) is given by $\frac{d[P]}{dt} = K[A]^2[B]$. If A is taken in large excess, the order of the reaction will be –

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

CALCULATION OF ORDER OF REACTION

34. Time required to complete a half fraction of a reaction varies inversely to the concentration of reactant then the order of reaction is –

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

35. The reaction L $\rightarrow$ M is started with 10 g of L. After 30 and 90 minute, 5 g and 1.25 g of L are left respectively. The order of reaction is –

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

36. From different sets of data of $t_{1/2}$ at different initial concentrations say 'a' for a given reaction, [$t_{1/2} \propto a$] is found. The order of reaction is :–

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

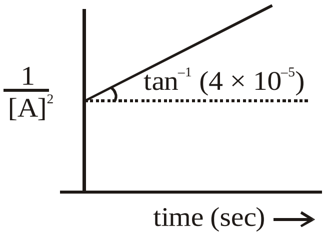
37. At certain temperature, the half life period for the thermal decomposition of a gaseous substance depends on the initial partial pressure of the substance as follows

P(mmHg)	500	250
$t_{1/2}$(in min.)	235	950

Find the order of reaction [Given log (23.5) = 1.37 ; log (95) = 1.97; log 2 = 0.30]

(A) 1 (B) 2 (C) 2.5 (D) 3

38. For a reaction A $\longrightarrow$ Product



What is the value of k for the given reaction-

(A) $4\times10^{-5}\ M^{-1}s^{-1}$ (B) $\frac{4}{3}\times10^{-5}\ M^{-2}s^{-1}$ (C) $2\times10^{-5}\ M^{-2}s^{-1}$ (D) $\frac{2}{3}\times10^{-5}\ M^{-2}s^{-1}$

39. Azo isopropane decomposes according to the equation :–

$(CH_3)_2CHN{=}NCH(CH_3)_2(g)\xrightarrow{250-290^0C}N_2(g)+C_6H_{14}(g)$

It is found to be a first order reaction. If initial pressure is P_o and pressure of the mixture at time t is (P_t) then rate constant K would be :–

(A) $k=\frac{2.303}{t}\log\frac{P_o}{2P_o-P_t}$ (B) $k=\frac{2.303}{t}\log\frac{P_o-P_t}{P_o}$

(C) $k=\frac{2.303}{t}\log\frac{P_o}{P_o-P_t}$ (D) $k=\frac{2.303}{t}\log\frac{2P_o}{2P_o-P_t}$

40. For a 1st order homogeneous gaseous reaction

$A\rightarrow 2B + C$,

if the pressure after time t was P_t and after long time was P_∞, then rate constant (k) in terms of P_t & P_∞ and t is -

(A) $k=\frac{2.303}{t}\log\left(\frac{P_\infty}{P_\infty-P_t}\right)$ (B) $k=\frac{2.303}{t}\log\left(\frac{2P_\infty}{P_\infty-P_t}\right)$

(C) $k=\frac{2.303}{t}\log\left(\frac{2P_\infty}{3(P_\infty-P_t)}\right)$ (D) None of these

41. The first order reaction

$A(g)\rightarrow B(g)+C(g)+D(s)$

taking place at constant pressure and temperature condition. Initially volume of the container containing only A was found to be V_0 and after time 't' it was V_t. Rate constant for the reaction is.

(A) $\frac{1}{t}\ln\frac{V_0}{2V_0-V_t}$ (B) $\frac{1}{t}\ln\frac{V_0}{V_0-V_t}$ (C) $\frac{1}{t}\ln\frac{2V_0}{2V_0-V_t}$ (D) $\frac{1}{t}\ln\frac{2V_0}{V_0+V_t}$

42. For the inversion of cane sugar ($C_{12}H_{22}O_{11}$) obeying I order following data were obtained

Time (min.)	0	10	∞
Angle of rotation of solution (degree)	+20	–2.5	–10

What will be rate constant in min^{-1} **(ln 2 = 0.7)**

(A) 0.7 (B) 0.14 (C) 0.21 (D) 0.07

COLLISION THEORY AND ARRHENIUS EQUATION

43. The rate constant for the forward reaction $A(g) \rightleftharpoons 2B(g)$ is $1.5 \times 10^{-3}\ s^{-1}$ at 100 K. If 10^{-5} moles of A and 100 moles of B are present in a 10 litre vessel at equilibrium then rate constant for the backward reaction at this temperature is

(A) 1.50×10^{4} L mol^{-1} s^{-1} (B) 1.5×10^{11} L mol^{-1} s^{-1}

(C) 1.5×10^{10} L mol^{-1} s^{-1} (D) 1.5×10^{-11}L mol^{-1} s^{-1}

44. According to collision theory of reaction –

(A) Every collision between reactant leads to chemical reaction

(B) Rate of reaction is proportional to velocity of molecules

(C) All reactions which occur in gaseous phase are zero order reaction

(D) Rate of reaction is directly proportional to collision frequency.

45. Activation energy of a reaction is –

(A) The energy released during the reaction

(B) The energy evolved when activated complex is formed

(C) Minimum amount of energy needed to overcome the potential barrier of reaction

(D) The energy needed to form one mole of the product

46. The minimum energy for molecules to enter into chemical reaction is called

(A) Kinetic energy (B) Potential energy (C) Threshold energy (D) Activation energy

47. For producing the effective collisions, the colliding molecules must possess:-

(A) A certain minimum amount of energy

(B) Energy equal to or greater than threshold energy

(C) Proper orientation

(D) Threshold energy as well as proper orientation of collision

48. A large increase in the rate of a reaction for a rise in temperature is due to –

(A) Increase in the number of collisions (B) Increase in the number of activated molecules

(C) Lowering of activation energy (D) Shortening of the mean free path

49. Slope of which plot can give the value of activation energy

(A) k versus T (B) $\frac{1}{k}$ versus T (C) Log k versus 1/T (D) C versus T

50. Given that K is the rate constant for any order reaction at temperature T, then the value of $\lim\limits_{T\to\infty} \log k$ ________.

(A) $\frac{A}{2.303}$ (B) A (C) 2.303 A (D) log A

51. For a certain gaseous reaction a 10° C rise of temperature from 25° C to 35° C doubles the rate of reaction. What is the value of activation energy :–

(A) $\frac{10}{2.303R \times 298 \times 308}$ (B) $\frac{2.303 \times 10}{298 \times 308R}$

(C) $\frac{0.693R \times 10}{290 \times 308}$ (D) $\frac{0.693R \times 298 \times 308}{10}$

52. From the following data, the activation energy (cal/mol) for the reaction $H_2 + I_2 \rightarrow 2HI$, is about

T (in k)	1/T, (in, k^{-1})	$\log_{10} k$
769	1.3×10^{-3}	2.9
667	1.5×10^{-3}	1.1

(A) 4×10^4 (B) 2×10^4 (C) 8×10^4 (D) 3×10^4

53. The rate constant, the activation energy and the Arrhenius parameter (A) of a chemical reaction at 25°C are $3.0 \times 10^{-4}\ s^{-1}$, 104.4 kJ mol^{-1} and $6.0 \times 10^{14} s^{-1}$ respectively. The value of the rate constant at $T \rightarrow \infty$ is

(A) $2.0 \times 10^{18}\ s^{-1}$ (B) $6.0 \times 10^{14}\ s^{-1}$ (C) infinity (D) $3.6 \times 10^{30}\ s^{-1}$

54. A first order reaction is 50% completed in 20 minutes at 27°C and in 5 min at 47°C. The energy of activation of the reaction is

(A) 100 kJ/mol (B) 55.14 kJ/mol (C) 11.97 kJ/mol (D) 6.65 kJ/mol

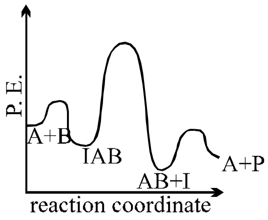
55. For the first order reaction $A \longrightarrow B + C$, carried out at 27 °C if 3.8×10^{-16} % of the reactant molecules can overcome energy barrier, the E_a (activation energy) of the reaction is [log 3.8 = 0.58, 2.303 × 8.314 × 17.42 = 333.33]

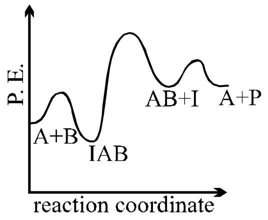
(A) 12 kJ/mole (B) 831.4 kJ/mole (C) 100 kJ/mole (D) 111.11 J/mole

56. The following mechanism has been proposed for the exothermic catalyzed complex reaction.

$$A + B \underset{}{\overset{\text{fast}}{\rightleftharpoons}} I\,AB \xrightarrow{k_1} AB + I \xrightarrow{k_2} P + A$$

If k_1 is much smaller than k_2. The most suitable qualitative plot of potential energy (P.E.) versus reaction coordinate for the above reaction.

(A)


(B)


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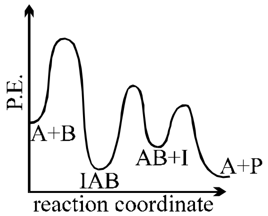

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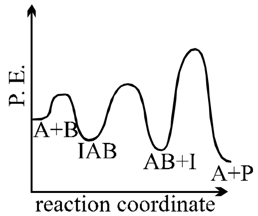


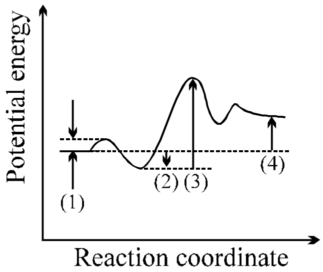
57. Choose the correct set of identifications for the reaction .

Substrate(S) $\xrightarrow{\text{Enzyme(E)}}$ Product (P)

whose mechanism is $E + S \rightleftharpoons ES$

$ES \rightleftharpoons EP$

$EP \rightleftharpoons E + P$



	(1)	(2)	(3)	(4)
(A)	ΔE for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$	E_a for $EP \rightarrow E + P$
(B)	E_a for $E + S \rightarrow ES$	ΔE for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$
(C)	E_a for $ES \rightarrow EP$	E_a for $EP \rightarrow E + P$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$	ΔE for $EP \rightarrow E + P$
(D)	E_a for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	E_a for $EP \rightarrow E + P$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$
(E)	ΔE for $E + S \rightarrow ES$	$\Delta E_{\text{overall}}$ for $S \rightarrow P$	ΔE for$_1$ $EP \rightarrow E + P$	E_a for $EP \rightarrow E + P$

RATE LAW OF MECHANISM OF REACTION

58. Following mechanism has been proposed for a reaction : $2A + B \rightarrow D + E$

Step - I : $A + B \rightarrow C + D$ (slow) **Step - II :** $A + C \rightarrow E$ (fast)

The rate law expression for the reaction is –

(A) $r = k[A]^2 [B]$ (B) $r = k[A] [B]$ (C) $r = k[A]^2$ (D) $r = k[A][C]$

59. The reaction mechanism for the reaction $P \rightarrow R$ is as follows :

$$P \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2Q \text{ (fast) ; } 2Q + P \xrightarrow{K_3} R \text{ (slow)}$$

the rate law for the main reaction ($P \rightarrow R$) is :

(A) $k_1[P]\,[Q]$ (B) $k_1k_2[P]$ (C) $\frac{k_1k_3[P]^2}{k_2}$ (D) $k_1k_2[a]$

60. The energies of activation for forward and reverse reactions for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction ($A_2 + B_2 \rightarrow 2AB$) in the presence of catalyst will be (in kJ mol^{-1}) -

(A) 300 (B) 120 (C) 280 (D) –20

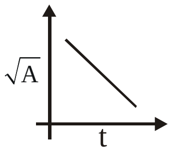
EXERCISE # (O-2)

MORE THAN ONE MAY BE CORRECT

1. For the reaction $A \rightarrow B$, the rate law expression is $-\frac{d[A]}{dt} = k[A]^{1/2}$. If initial concentration of [A] is $[A]_0$, then

(A) The integerated rate expression is $k = \frac{2}{t}(A_0^{1/2} - A^{1/2})$

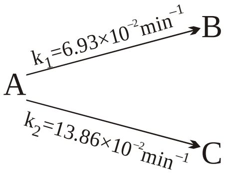
(B) The graph of $\sqrt{A}$ vs t will be



(C) The half life period, $t_{1/2} = \frac{K}{2[A]_0^{1/2}}$

(D) The time taken for 75% completion of reaction $t_{3/4} = \frac{\sqrt{[A]_0}}{k}$

2. Consider the reaction,



A, B and C all are optically active compound . If optical rotation per unit concentration of A, B and C are 60°, –72°, 42° and initial concentration of A is 2 M then select correct statement(s).

(A) Solution will be optically active and dextrorotatory after very long time

(B) Solution will be optically active and levorotatory after very long time

(C) Half life of reaction is 15 min

(D) After 75% conversion of A into B and C angle of rotation of solution will be 36°.

3. Select **incorrect** statement(s):

(A) Unit of pre-exponential factor (A) for second order reaction is mol L^{-1} s^{-1}.

(B) A zero order reaction must be a complex reaction.

(C) Molecularity is defined only for RDS in a complex reaction.

(D) Rate constant (k) remain unaffected on changing temperature.

4. Which of the following is/are **correct** statement?

(A) Stoichiometry of a reaction tells about the order of the elementary reactions.

(B) For a zero order reaction, rate and the rate constant are identical.

(C) A zero order reaction is controlled by factors other than concentration of reactants.

(D) A zero order reaction is always elementary reaction.

5. For the gas phase reaction : $R-H + X_2 \rightarrow R-X + HX$, following mechanism has been proposed

(i) $X_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2X^{\bullet}$ (ii) $X^{\bullet} + R-H \xrightarrow{k_3} R^{\bullet} + H-X$ (slowest)

(iii) $R^{\bullet} + X_2 \xrightarrow{k_4} R-X + X^{\bullet}$

Based on this, select the correct option(s) :-

(A) Effective rate constant for the formation of RX is $k_3k_4\sqrt{\frac{k_1}{k_2}}$ (B) $\frac{d[RX]}{dt} \propto [X_2]$

(C) Overall order of the reaction is 3/2 (D) $\frac{d[RX]}{dt} \propto [RH]^1$

6. For a first order reaction : $A(g) \rightarrow 2B(g)$

Time(in second)	0	20	40	∞
Total pressure of system (in mm.of Hg)	64	112	124	128

(A) Half life of reaction is 10 sec

(B) Value of rate constant for reaction is $6.93 \times 10^{-3} sec^{-1}$

(C) Total pressure at t = 50 sec will be 126 mm of Hg

(D) Reaction must be a complex reaction

7. Which of the following is **INCORRECT** for first order reaction ?

(A) On introducing catalyst, both rate constant and rate of reaction increases.

(B) On increasing temperature both rate constant & rate of reaction increases.

(C) On decreasing volume both rate constant & rate of gaseous reaction increases.

(D) On increasing concentration of gaseous reactant at constant volume & constant temperature both total pressure and rate of the reaction increases.

8. 2X (g) + Y(g) + 3Z (g) → Products. The rate equation of above reaction is given by :

Rate = $K[X]^1[Y]^0[Z]^2$. Choose the correct statements

(A) If [z] >> [x] and 75% of X undergoes reaction in 20 sec, then 50% of X will react in 10 sec. (B) Rate of reaction decreases by reducing the concentration of Y to half of the original value

(C) The half life of Z increases by increasing its concentration if [x] >> [z]

(D) On incresing the concentration of X,Y & Z double, rate of reaction becomes 8 times

9. Select the correct statement -

(A) In a mixture of $KMnO_4$ & $H_2C_2O_4$, $KMnO_4$ decolorises faster at higher temperature than lower temperature

(B) A catalyst participate in a chemical reaction by forming temporary bonds with the reactant resulting in an intermediate complex

(C) In collision theory only activation energy determine the criteria for effective collision

(D) Collision theory assumes molecules to be soft spheres & consider their structural aspects.

10. For the reaction $A + 3B \rightarrow C$, select the correct statement (s)-

(A) $\frac{d[C]}{dt} = \frac{-d[A]}{dt}$ (B) $\frac{3d[C]}{dt} = -\frac{d[B]}{dt}$

(C) Rate law must be $r = k\,[A][B]^3$ (D) Units for rate of reaction are independent of order of reaction

11. Choose the incorrect statement(s) -

(A) Activation energy of reaction always decreases on decreasing temperature

(B) Order of reaction may change with change in temperature

(C) When slowest step is the first step in a mechanism, then the rate law of overall reaction is the same as the rate law for this step

(D) Rate of photochemical reaction is directly proportional to intensity of absorbed photons.

12. The forward rate constant of a reaction increases by 7% when its temperature is raised from 300K to 301K while its equilibrium constant increases by 3%. Which of the following is/are correct -

(A) Activation energy of forward reaction $(Ea)_F$ is $= 300 \times 301 \times R \times \ln(1.03)$

(B) Standard heat of reaction (ΔH°) is $= 300 \times 301 \times R \times \ln(1.07)$

(C) Activation energy of backward reaction $(Ea)_B$ is $= 300 \times 301 \times R \times \ln\left(\frac{1.07}{1.03}\right)$

(D) Activation energy of backward reaction $(Ea)_B$ is $= 300 \times 301 \times R \times \ln\left(\frac{1.03}{1.07}\right)$

13. Which statement(s) is/are false ?

(A) Every reaction has defined overall order

(B) All rate constant have same dimension.

(C) Every chemical species that appears in the rate law of reaction must be reactant or product in that reaction.

(D) Rate constant is never negative.

ASSERTION & REASONING TYPE QUESTIONS

14. **Statement-1** : A fractional order reaction must be a complex reaction.

Statement-2 : Fractional order of RDS equals to overall order of a complex reaction.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

15. **Statement-1** : The time of completion of reactions of type $A \rightarrow$ product (order <1) may be determined.

Statement-2 : Reactions with order ≥ 1 are either too slow or too fast and hence the time of completion can not be determined.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

16. **Statement-1** : In a reversible endothermic reaction, (E_{act}) of forward reaction is higher than that of backward reaction

Statement-2 : The threshold energy of forward reaction is more than that of backward reaction

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

17. **Statement-1** : A catalyst provides an alternative path to the reaction in which conversion of reactants into products takes place quickly

Statement-2 : The catalyst forms an activated complex of lower potential energy, with the reactants by which more number of molecules are able to cross the barrier per unit of time.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

COMPREHENSION

Paragraph for Question Nos. 18 & 19

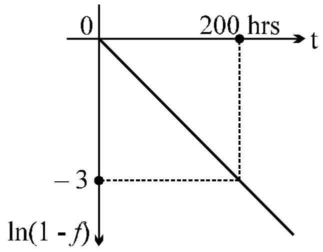
When metal surface is exposed to air if gets oxidised by first order kinetics if **(1– *f*)** is fraction of unoxidised. metal surface thickness and T is total thickness after very long time then it's rate can be represented as.

Rate law : $\frac{df}{dt} = k(1 - f)$**, where** $f = x/T$**,**

x = thickness of oxide film at time 't'

& T = thickness of oxide film at t = ∞

A graph of $\ln(1 - f)$ vs t is shown in the adjacent figure.



18. The time taken for thickness to grow 50% of 'T' is

(A) 23.1 hrs (B) 46.2 hrs (C) 100 hrs (D) 92.4 hrs

19. The exponential variation of '*f*' with t(hrs) is given by

(A) $1 - e^{-3t/200}$ (B) $e^{-3t/200} - 1$ (C) $e^{-3t/200}$ (D) $e^{3t/200}$

Paragraph for Question Nos. 20 & 21

For a hypothetical elementary reaction : $A \begin{array}{l} \xrightarrow{k_1} 2B \\ \xrightarrow[k_2]{} 2C \end{array}$ where $\frac{k_1}{k_2} = \frac{1}{2}$

Initially only 2 moles of A are present.

20. The total number of moles of A, B & C at the end of 50% reaction are

(A) 2 (B) 3 (C) 4 (D) 5

21. Number of moles of B are

(A) 2 (B) 1.333 (C) 0.667 (D) 0.333

Paragraph for Question Nos. 22 & 23

A reaction is said to be first order if it's rate is proportional to the concentration of reactant. Let us consider a reaction

	A(g)	⟶	B(g)	+	C(g)
At t = 0	a		0		0
At time t	a – x		x		x

The rate of reaction is given by the expression $\frac{dx}{dt} = k(a - x)$ and integrated rate equation for a given reaction is represented as $k = \frac{1}{t} \ln\left(\frac{a}{a - x}\right)$ where a = initial concentration and (a – x) = concentration of A after time t.

22. Thermal decomposition of compound X is a first order reaction. If 75% of X is decomposed in 100 min. How long will it take for 90% of the compound to decompose?

Given : log 2 = 0.30

(A) 190 min (B) 176.66 min (C) 166.66 min (D) 156.66 min

23. Consider a reaction $A(g) \longrightarrow 3B(g) + 2C(g)$ with rate constant 1.386×10^{-2} min^{-1}. Starting with 2 moles of A in 12.5 litre a closed vessel initially, if reaction is allowed to takes place at constant pressure & at 298K then find the concentration of B after 100 min.

(A) 0.04 M (B) 0.36 M (C) 0.09 M (D) None of these

Paragraph for Question Nos. 24 & 25

For the given sequential reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

the concentration of A, B & C at any time 't' is given by

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

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

$$[C]_t = [A_0] - ([A]_t + [B]_t)$$

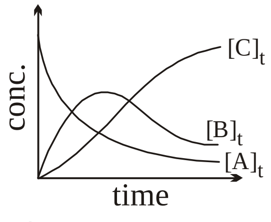
24. The time at which concentration of B is maximum is

(A) $\frac{k_1}{k_2 - k_1}$ (B) $\frac{1}{k_2 - k_1}\ln\frac{k_1}{k_2}$

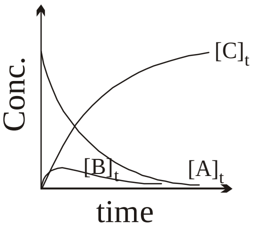
(C) $\frac{1}{k_1 - k_2}\ln\frac{k_1}{k_2}$ (D) $\frac{k_2}{k_2 - k_1}$

25. Select the correct graph if $k_1 = 1000$ s^{-1} and $k_2 = 20$ s^{-1}.

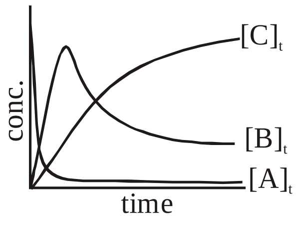
(A)



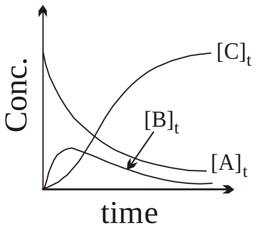
(B)



(C)



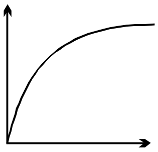
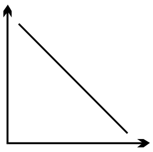
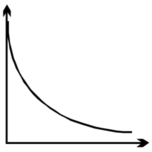
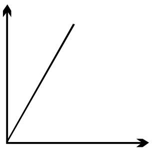
(D)



MATCH THE COLUMN

26. For the reaction of type $A(g) \longrightarrow 2B(g)$

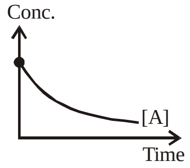
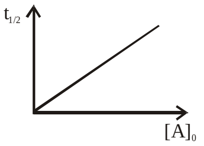
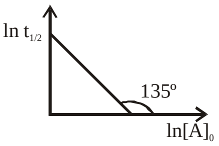
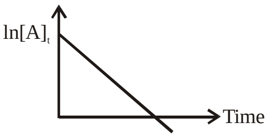
Column-I contains four entries and **column-II** contains four entries. Entry of column-I are to be matched with **<u>ONLY ONE ENTRY</u>** of column-II

Column I	**Column II**
(A) $\frac{d[B]}{dt}$ vs $\frac{-d[A]}{dt}$ for first order	(P) 
(B) [A] vs t for first order	(Q) 
(C) [B] vs t for first order	(R) 
(D) [A] vs t for zero order	(S) 

27. **Match the column :**

	Column-I		**Column-II**
(A)	Inversion of cane sugar in excess water.	(P)	not 100% complete
(B)	saponification reaction with 1M NaOH	(Q)	pseudo-first order
(C)	decomposition of HI on gold	(R)	zero order
(D)	radioactive decay	(S)	second order

28. For the reaction A + B → product, Given : $[A]_0 = [B]_0$

List-I (Observed Rate Law) is -		**List-II (Graph)**	
(P)	$r = k[A]$	(1)	
(Q)	$r = k[A]^{1/2}[B]^{1/2}$	(2)	
(R)	$r = k[A]\,[B]$	(3)	
(S)	$r = k[A]^0\,[B]^0$	(4)	

Code:

	P	**Q**	**R**	**S**
(A)	4	1	3	2
(B)	2	3	1	4
(C)	1	2	3	4
(D)	4	3	2	1

☐ Match the Columns for Reaction A → P

Column - I	**Column - II**	**Column - III**
(I) First Order	(i) Reaction complete in finite time	(P) Rate depends on concentration
(II) Second Order	(ii) Reaction complete in infinite time	(Q) After equal interval of time concentration of reactant left are in G.P.
(III) Third Order	(iii) Half life is independent of concentration of reactant	(R) After equal interval of time concentration of reactant left are in A.P.
(IV) Zero Order	(iv) Half life decreases when concentration of reactant increases	(S) Half life depends on temperature

29. Select only incorrect option :-

(A) (II), (ii), (P)
(B) (IV), (iii), (R)
(C) (III), (ii), (P)
(D) (I), (ii), (Q)

30. Select only incorrect option :-

(A) (IV), (i), (S)
(B) (III), (iv), (P)
(C) (I), (iv), (Q)
(D) (II), (iv), (S)

EXERCISE # (J-MAIN)

1. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about :- **[AIEEE-2011]**

(1) 32 times (2) 64 times (3) 10 times (4) 24 times

2. A reactant (1) forms two products : **[AIEEE-2011]**

$A \xrightarrow{k_1} B$, Activation Energy Ea_1

$A \xrightarrow{k_2} C$, Activation Energy Ea_2

If $Ea_2 = 2\ Ea_1$, then k_1 and k_2 are related as :-

(1) $k_1 = 2k_2e^{Ea_2/RT}$ (2) $k_1 = k_2e^{Ea_1/RT}$ (3) $k_2 = k_1e^{Ea_2/RT}$ (4) $k_1 = [A]\,k_2e^{Ea_1/RT}$

3. For the non-stoichiometric reaction $2A + B \rightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K. **[J-MAIN 2014]**

Initial Concentration (A)	Initial Concentration (B)	Initial rate of formation of C (mol L⁻S⁻)
0.1M	0.1M	1.2×10^{-3}
0.1M	0.2M	1.2×10^{-3}
0.2M	0.1M	2.4×10^{-3}

(1) $\frac{dc}{dt} = k[A][B]^2$ (2) $\frac{dc}{dt} = k[A]$ (3) $\frac{dc}{dt} = k[A][B]$ (4) $\frac{dc}{dt} = k[A]^2[B]$

4. Higher order (>3) reactions are rare due to :- **[JEE-MAIN-(Offline)2015]**

(1) shifting of equilibrium towards reactants due to elastic collision

(2) loss of active species on collision

(3) low probability of simultaneous collision of all the reacting species

(4) increase in entropy and activation energy as more molecules are involved.

5. The reaction : $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$, follows first order kinetics. The pressure of a vessel containing only N_2O_5 was found to increase from 50 mm Hg to 87.5 mm Hg in 30 min. The pressure exerted by the gases after 60 min. will be (Assume temperature remains constant)

(1) 106.25 nm Hg (2) 116.25 nm Hg **[JEE-MAIN-(Online)2015]**

(3) 125 mm Hg (4) 150 mm Hg

6. For the equilibrium, $A(g) \rightleftharpoons B(g)$, ΔH is –40 kJ/mol. If the ratio of the activation energies of the forward (E_f) and reverse (E_b) reactions is $\frac{2}{3}$ then :- **[JEE-MAIN-(Online)2015]**

(1) $E_f = 60$ kJ/mol; $E_b = 100$ kJ/mol (2) $E_f = 30$ kJ/mol; $E_b = 70$ kJ/mol

(3) $E_f = 80$ kJ/mol; $E_b = 120$ kJ/mol (4) $E_f = 70$kJ/mol; $E_b = 30$ kJ/mol

7. Decomposition of H_2O_2 follows a first order reaction. In fifty minutes the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be :- **[JEE-MAIN-(Offline)2016]**

(1) 1.34×10^{-2} mol min^{-1} (2) 6.93×10^{-2} mol min^{-1}

(3) 6.93×10^{-4} mol min^{-1} (4) 2.66 L min^{-1} at STP

8. The reaction of ozone with oxygen atoms in the presence of chlorine atoms can occur by a two step process shown below : **[JEE-MAIN-(Online)2016]**

$O_3(g) + Cl^{\cdot}(g) \rightarrow O_2(g) + ClO^{\cdot}(g)$ ......(i)

$k_i = 5.2 \times 10^9$ L mol^{-1}s^{-1}

$ClO^{\cdot}(g) + O^{\cdot}(g) \rightarrow O_2(g) + Cl^{\cdot}(g)$

$k_{ii} = 2.6 \times 10^{10}$ L mol^{-1}s^{-1} .....(ii)

The closest rate constant for the overall reaction $O_3(g) + O^{\cdot}(g) \rightarrow 2O_2(g)$ is :

(1) 3.1×10^{10} L mol^{-1}s^{-1} (2) 2.6×10^{10} L mol^{-1}s^{-1}

(3) 5.2×10^{9} L mol^{-1}s^{-1} (4) 1.4×10^{20} L mol^{-1}s^{-1}

9. Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 10 kJ mol^{-1}. If k_1 and k_2 are rate constants for reactions R_1 and R_2 respectively at 300 K, then $\ln(k_2/k_1)$ is equal to : **[JEE-MAINS-2017]**
(R = 8.314 J mol^{-1}K^{-1})

(1) 8 (2) 12 (3) 6 (4) 4

10. The rate of a reaction quadruples when the temperature changes from 300 to 310 K. The activation energy of this reaction is (Assume activation energy and pre-exponential factor are independent of temperature ; ln 2 = 0.693, R = 8.314 J mol^{-1}K^{-1}) : **[MAINS-2017(online)]**

(1) 107.2 kJ mol^{-1}K^{-1} (2) 53.6 kJ mol^{-1}K^{-1} (3) 214.4 kJ mol^{-1}K^{-1} (4) 26.8 kJ mol^{-1}K^{-1}

11. The rate of a reaction A doubles on increasing the temperature from 300 to 310 K. By how much, the temperature of reaction B should be increased from 300 K so that rate doubles if activation energy of the reaction B is twice to that of reaction A : **[MAINS-2017(online)]**

(1) 2.45 K (2) 4.92 K (3) 9.84 K (4) 19.67 K

12. At 518° C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr, was 1.00 Torr s^{-1} when 5% had reacted and 0.5 Torr s^{-1} when 33% had reacted. The order of the reaction is : **[JEE-MAINS-2018]**

(1) 3 (2) 1 (3) 0 (4) 2

13 For a first order reaction, $A \rightarrow P$, $t_{1/2}$ (half life) is 10 days. The time required for $\frac{1}{4}^{th}$ conversion of A (in days) is :-**(ln 2 = 0.693, ln 3 = 1.1)** **[MAINS-2018(online)]**

(1) 5 (2) 4.1 (3) 3.2 (4) 2.5

14. N_2O_5 decomposes to NO_2 and O_2 and follows first order kinetics. After 50 minutes, the pressure inside the vessel increases from 50 mmHg to 87.5 mmHg. The pressure of the gaseous mixture after 100 minute at constant temperature will be: **[MAINS-2018(online)]**

(1) 116.25 mmHg (2) 175.0 mmHg (3) 106.25 mmHg (4) 136.25 mmHg

15. The following results were obtained during kinetic studies of the reaction :
$2A + B \rightarrow$ Products

[MAINS-2019(online)]

Experment	**[A] (in mol L^{-1})**	**[B] (in mol L^{-1})**	**Initial Rate of reaction (in mol L^{-1} min^{-1})**
(I)	0.10	0.20	6.93×10^{-3}
(II)	0.10	0.25	6.93×10^{-3}
(III)	0.20	0.30	1.386×10^{-2}

The time (in minutes) required to consume half of A is :
(1) 10 (2) 5 (3) 100 (4) 1

16. For the reaction, $2A + B \rightarrow$ products, when the concentrations of A and B both wrere doubled, the rate of the reaction increased from 0.3 mol $L^{-1}s^{-1}$ to 2.4 mol L^{-1} s^{-1}. When the concentration of A alone is doubled, the rate increased from 0.3 mol $L^{-1}s^{-1}$ to0.6 mol $L^{-1}s^{-1}$**[MAINS-2019(online)]**

Which one of the following statements is correct ?

(1) Order of the reaction with respect to Bis2

(2) Order of the reaction with respect to Ais2

(3) Total order of the reaction is 4

(4) Order of the reaction with respect to B is 1

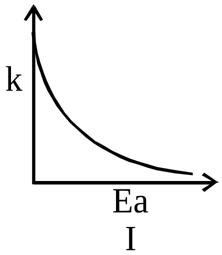
17. For an elementary chemical reaction, **[MAINS-2019(online)]**

$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A$, the expression for $\frac{d[A]}{dt}$ is :

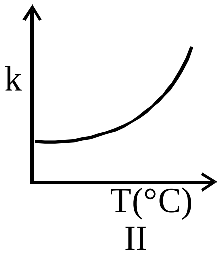
(1) $2k_1[A_2]-k_{-1}[A]^2$ (2) $k_1[A_2]-k_{-1}[A]^2$

(3) $2k_1[A_2]-2k_{-1}[A]^2$ (4) $k_1[A_2]+k_{-1}[A]^2$

18. Consider the given plots for a reaction obeying Arrhenius equation (0°C < T < 300°C) : (k and E_a are rate constant and activation energy, respectively) **[MAINS-2019(online)]**



I



II

Choose the correct option :

(1) Both I and II are wrong

(2) I is wrong but II is right

(3) Both I and II are correct

(4) I is right but II is wrong

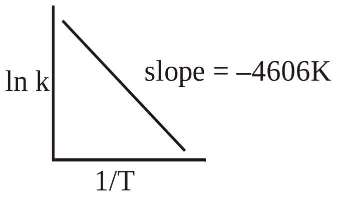
19. The reaction $2X \rightarrow B$ is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be :-

(1) 18.0 h (2) 7.2 h (3) 9.0 h (4) 12.0 h

20. If a reaction follows the Arrhenius equation, the plot lnk vs $\frac{1}{(RT)}$ gives straight line with a gradient (–y) unit. The energy required to activate the reactant is : **[MAINS-2019(online)]**

(1) y unit (2) –y unit (3) yR unit (4) y/R unit

21. For a reaction, consider the plot of ln k versus 1/T given in the figure. If the rate constant of this reaction at 400 K is 10^{-5} s^{-1}, then the rate constant at 500 K is : **[MAINS-2019(online)]**



(1) 2×10^{-4} s^{-1} (2) 10^{-4} s^{-1} (3) 10^{-6} s^{-1} (4) 4×10^{-4} s^{-1}

22. Decomposition of X exhibits a rate constant of 0.05 μg/year. How many years are required for the decomposition of 5 μg of X into 2.5 μg ? **[MAINS-2019(online)]**

(1) 50 (2) 25 (3) 20 (4) 40

EXERCISE # (J-ADVANCED)

1. For the first order reaction, **[JEE 2011]**

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

(A) the concentration of the reactant decreases exponentially with time

(B) the half-life of the reaction decreases with increasing temperature.

(C) the half-life of the reaction depends on the initial concentration of the reactant.

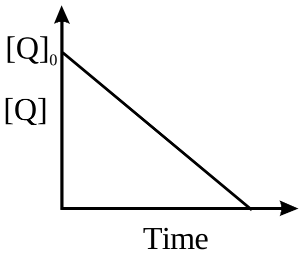
(D) the reaction proceeds to 99.6% completion in eight half-life duration.

2. An organic compound undergoes first-order decomposition . The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{t_{1/10}} \times 10$?

(take $\log_{10}2 = 0.3$) **[JEE 2012]**

3. In the reaction : **[JEE 2013]**

$$P + Q \longrightarrow R + S$$



the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is -

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

4. For the elementary reaction **M** → **N**, the rate of disappearance of **M** increases by a factor of 8 upon doubling the concentration of **M**. The order of the reaction with respect to **M** is

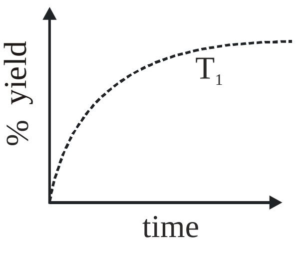
(A) 4 (B) 3 (C) 2 (D) 1 **[JEE 2014]**

5. In dilute aqueous H_2SO_4, the complex diaquodioxalatoferrate(II) is oxidized by MnO_4^-. For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is. **[JEE 2015]**

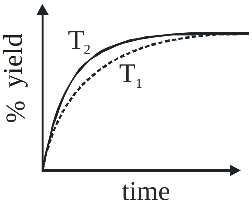
6. The % yield of ammonia as a function of time in the reaction **[JEE 2015]**

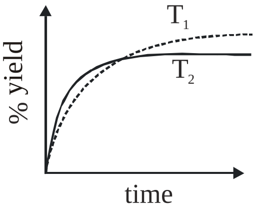
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g),\ \Delta H < 0$$

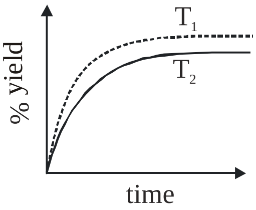
at (P , T_1) is given below -

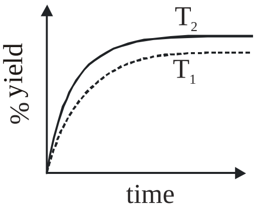


If this reaction is conducted at (P ,T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by -

(A) 

(B) 

(C) 

(D) 

7. According to the Arrhenius equation, **[JEE 2016]**

(A) A high activation energy usually implies a fast reaction

(B) Rate constant increase with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy

(C) Higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant

(D) The pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.

8. In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is(are) : **[JEE 2017]**

(A) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally

(B) The activation energy of the reaction is unaffected by the value of the steric factor

(C) Since P = 4.5, the reaction will not proceed unless an effective catalyst is used.

(D) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation.

ANSWER-KEY

EXERCISE # S-I

1. Ans.(i) $r = \frac{1}{4}\frac{d[NO]}{dt} = 9 \times 10^{-4}$ mol litre^{-1} sec^{-1}, (ii) 3.6×10^{-3} mol litre^{-1}sec^{-1},
(iii) 5.4×10^{-3} mol litre^{-1}sec^{-1}

$$\text{ROR} = \frac{\text{ROA of NO}}{\text{sto.coeff.of NO}} = \frac{(1.08\times10^{-2})/3}{4} = 9 \times 10^{-4}\ \text{M sec}^{-1}$$

2. Ans. (i) $\frac{dx}{dt} = k[A][B]^2$, (ii) rate increases by 8 times
3. Ans.8.33×10^{-6} Ms^{-1}, 0.012 atm min^{-1}
4. Ans.rate increase by 27 times
5. Ans.(a) 0.019 L mol^{-1} s^{-1}, (b) 0.038 L mol^{-1} s^{-1}
6. Ans.(8)
7. Ans. (2)
8. Ans.6×10^{-3} Ms^{-1}
9. Ans. 1/6
10. Ans. (i) 7.2 M, (ii) 10 M
11. Ans. k = 0.01 M min^{-1}
12. Ans. 6×10^{-9} sec
13. Ans. 1.2 hr
14. Ans.(5 atm)
15. Ans. (i) 36 min. (ii) 108 min.
16. Ans. (i) 0.02min^{-1}, (ii) 70 min
17. Ans. $t = 10 \times t_{1/2}$
18. Ans.40 month
19. Ans. 0.02 min^{-1}
20. Ans.87.5 %
21. Ans. (19)
22. Ans.(20 min)
23. Ans. (2×10^{-1}M^{-1}s^{-1})
24. Ans.3 hr
25. Ans.7500 second
26. Ans. (a) Third order, (b) $r = k[NO]^2[H_2]$, (c) 7.5×10^{-10} M sec^{-1}.
27. Ans. (i) first order (ii) $k = 1.308 \times 10^{-2}$ min^{-1} (iii) 73%
28. Ans. (i) Zero order, (ii) K = 5 Pa/s
29. Ans. Zero order
30. Ans. (1)
31. Ans. $k = \frac{1}{t} ln \frac{P_3}{2(P_3 - P_2)}$
32. Ans.$k = \frac{1}{t} ln \frac{r_\infty}{(r_\infty - r_t)}$
33. Ans. 1.15×10^{-2} sec^{-1}
34. Ans. First order
35. Ans. 240 min.
36. Ans. $k_1 = 1.55 \times 10^{-2}$ min^{-1}
37. Ans. 50 sec. , 0.1765 atm
38. Ans. 0.1 min^{-1}
39. Ans. (300 sec.)
40. Ans. (3)
41 Ans. $\frac{[C]}{[A]} = \frac{10}{11}(e^{11x} - 1)$
42. Ans. t = 4 min
43. Ans. 86.625 min
44. Ans. $t_{1/2}$ = 36 min.
45. Ans. 10 M
46. Ans. 100 min.
47. Ans.(4 hour)
48. Ans. (6 : 6 : 6 : 1 : 1)
49. Ans. 30 sec.

50.	Ans. 50 min, $\left(\frac{0.2}{e}\right)$M	51.	Ans. 5 kJ mol^{-1}
52.	Ans. 13.44 kcal/mole	53.	Ans. 10.28 k cal mol^{-1}
54.	Ans. (3)		
55.	Ans. 20 minutes	56.	Ans. (10)
57.	Ans. (150 K)		
58.	Ans. (840)	59.	Ans. (38.3 kJ mol^{-1})
60.	Ans. (20)	61.	Ans. $r = K' [NO]^2[Br_2]$
62.	Ans. $r = K [NO]^2 [H_2]$, where $K = k_2 \times K_1$	63.	Ans. (1)
64.	Ans. (2)	65.	Ans. (rate = $K_3 K_1 / K_2 [CHCl_3][Cl_2]^{1/2}$)

EXERCISE S-II

1.	Ans. 383.2 mm Hg , 403.8 min.	2.	Ans. (50)
3.	Ans. 20 min	4.	Ans. 315 sec.
6.	Ans. (a) 9.24 kcal/mole, (b) 25.6 hour	7.	Ans. k = 0.0327 min^{-1}
9.	Ans. (3)	10.	Ans. (1440 sec)
11.	Ans. (5)	12.	Ans. (200 min)
13.	Ans. (3)	14.	Ans. (0)
15.	Ans. (0.04)	16.	Ans. (8)
17.	Ans. (14)	18.	Ans. (1680)
19.	Ans. (0)	20.	Ans. (8)

EXERCISE (O-1)

1.	Ans.(B)	2.	Ans.(D)	3.	Ans.(C)	4.	Ans.(B)
5.	Ans.(C)	6.	Ans.(C)	7.	Ans.(A)	8.	Ans.(C)
9.	Ans.(D)	10.	Ans.(C)	11.	Ans.(A)	12.	Ans(D)
13.	Ans(A)	14.	Ans.(C)	15.	Ans.(A)	16.	Ans.(C)
17.	Ans.(D)	18.	Ans.(D)	19.	Ans.(A)	20.	Ans.(D)
21.	Ans.(B)	22.	Ans.(A)	23.	Ans.(D)	24.	Ans.(A)
25.	Ans.(D)	26	Ans.(C)	27.	Ans.(A)	28.	Ans.(A)
29.	Ans.(C)	30.	Ans.(C)	31.	Ans.(C)	32.	Ans.(C)
33.	Ans.(B)	34.	Ans.(C)	35.	Ans.(C)	36.	Ans.(A)
37.	Ans.(D)	38.	Ans (C)	39.	Ans.(A)	40.	Ans.(C)
41.	Ans.(A)	42.	Ans (B)	43.	Ans.(D)	44.	Ans.(D)
45.	Ans.(C)	46.	Ans.(C)	47.	Ans.(D)	48.	Ans.(B)
49.	Ans.(C)	50.	Ans.(D)	51.	Ans.(D)	52.	Ans.(A)
53.	Ans.(B)	54.	Ans.(B)	55.	Ans.(C)	56.	Ans.(A)
57.	Ans.(B)	58.	Ans.(B)	59.	Ans. (C)	60.	Ans.(D)

EXERCISE # (O-2)

1.	Ans.(A,B,D)	2	Ans.(A,D)	3	Ans.(A,C, D)	4.	Ans.(A,B,C)
5.	Ans.(C,D)	6.	Ans.(A,C)	7.	Ans. (C)	8.	Ans.(A,D)
9.	Ans.(A, B)	10.	Ans.(A,B,D)	11.	Ans. (A)	12.	Ans.(C)
13.	Ans. (A ,B, C)	14	Ans.(C)	15.	Ans.(C)	16.	Ans.Ans.(C)
17.	Ans.(A)	18.	Ans.(B)	19.	Ans. (A)	20.	Ans.(B)
21.	Ans.(C)	22	Ans.(C)	23.	Ans.(C)	24	Ans.(C)
25.	Ans.(C)						
26.	Ans. (A)→(S) ; (B)→(R) ; (C)→(P), (D)→(Q)						
27.	Ans. (A)→(P,Q) ; (B)→(S,P) ; (C)→(R) ; (D)→(P)						
28.	Ans.(A)	29.	Ans.(B)	30.	Ans.(C)		

EXERCISE # (J-MAIN)

1.	Ans.(1)	2.	Ans.(2)	3.	Ans.(2)	4.	Ans.(3)
5.	Ans.(1)	6.	Ans.(3)	7.	Ans.(3)	8.	Ans.(3)
9.	Ans.(4)	10.	Ans.(1)	11.	Ans.(2)	12.	Ans.(4)
13.	Ans.(2)	14.	Ans.(3)	15.	Ans.(2)	16.	Ans.(1)
17.	Ans.(3)	18.	Ans.(4)	19.	Ans.(1)	20.	Ans.(1)
21.	Ans.(2)	22.	Ans.(1)				

EXERCISE # (J-ADVANCED)

1.	Ans.(A,B,D)	2.	Ans.(9)	3.	Ans.(D)	4.	Ans.(B)
5.	Ans.(8)	6.	Ans.(B)	7.	Ans.(B,C,D)	8.	Ans.(B,D)