CHEMICAL KINETICS & RADIOACTIVITY

CONTENTS

JEE(Advanced) Syllabus

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

JEE(Main) Syllabus

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

Chemical Kinetics & Radioactivity

Introduction :

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

Section (A) : Rate of chemical reaction and Dependence of Rate : Basic

Rate/Velocity of chemical reaction :

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

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

For gaseous reactions, when concentration of gases is expressed in terms of their partial pressure, then units of rate equation will be $atms^{-1}$.

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

Types of Rates of chemical reaction :
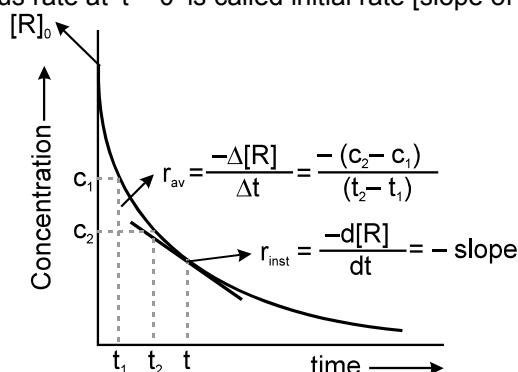
For a reaction R $\longrightarrow$ P

Average rate = $\dfrac{\text{Total change in concentration}}{\text{Total time taken}} = \dfrac{\Delta c}{\Delta t} = -\dfrac{\Delta[R]}{\Delta t} = \dfrac{\Delta[P]}{\Delta t}$

Instantaneous rate : rate of reaction at a particular instant.

$R_{instantaneous} = \lim\limits_{t \to 0}\left[\dfrac{\Delta c}{\Delta t}\right] = \dfrac{dc}{dt} = -\dfrac{d[R]}{dt} = \dfrac{d[P]}{dt}$

Instantaneous rate can be determined by drawing a tangent at time t on curve drawn for concentration versus time.

Initial Rate : Instantaneous rate at 't = 0' is called initial rate [slope of tangent at t = 0].

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

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

$\quad$ Rate of reaction of $N_2 = -\dfrac{d[N_2]}{dt}$; $\qquad$ Rate of reaction of $H_2 = -\dfrac{d[H_2]}{dt}$

$\quad$ Rate of reaction of $NH_3 = \dfrac{d[NH_3]}{dt}$

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

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

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

Solved Examples

Ex-1. From the concentrations of R at different times given below, calculate the average rate of the reaction:
R → P during different intervals of time.

t/s	0	5	10	20	30
$10^3 \times$ [R]/mol L^{-1}	160	80	40	10	2.5

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

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

Factors affecting rate of chemical reaction :

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

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

1. **Effect of concentration :** We known from law of mass action that Rate is proportional to concentration of reactants. "So rate of reaction decreases with passage of time, since concentration of reactants decreases.

2. **Effect of temperature :** Most of the chemical reactions are accelerated by increases in T. This will be discussed in detail further.
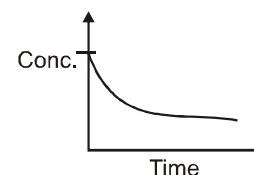
3. **Effect of nature of reactants and Products :**
(a) Physical state of reactants :
Gaseous state > Liquid state > Solid state
Decreasing order of rate of reaction.
Because collisions in homogeneous system are more effective than heterogenous system.
(b) Physical size of reactants : As we decreases 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 bond strength is more, rate of reaction will be slow.

4. **Effect of Catalyst :**
❍   Presence of positive catalyst lower down the activation energy hence increases the rate of reaction.
❍   Presence of negative catalyst increases activation energy hence decreases the rate of reaction.

5. **Effect of pH of solution :** Few reactions take place only in a particular medium.

Ex. $Fe(CN)_6^{4-} \xrightarrow{\ (Tl^{3+})\ } [Fe(CN)_6]^{3-}$
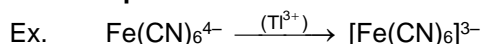
This reaction takes place with appreciable rate in acidic medium, but does not take place in basic medium.

6. **Effect of dielectric constant of the medium :** More is the dielectric constant of the medium greater will be the rate of ionic reactions.

7. **Effect of radiations/light :** Radiation are useful for photochemical reaction.

8. **Effect of pressure :** Pressure is important factor for gaseous reaction.

9. **Effect of electrical & Magnetic field :** Electric and magnetic fields are rate determining factors if a reaction involves polar species.

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

The representation of rate of reaction in terms of the concentration of the reactants is called the rate law.

It can only be established by experiments.

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

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

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

Rate = K (conc.)^{order} This is the differential rate equation or rate expression/Rate law.

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

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

K depend on temperature only and not on concentration.

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

Order of reaction :

Let there be a reaction, $m_1A + m_2B \longrightarrow$ products.

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

$R \propto [A]^p [B]^q$ where p may or may not be equal to m_1 and similarly 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' or any whole number, it can be a fractional number and it can even be negative with respect to a particular reactant. But overall order is not found to be negative for any reaction till observed.

Examples showing different values of order of reactions :

	Reaction	Rate law	Order
(i)	$2N_2O_5\,(g) \longrightarrow 4NO_2\,(g) + O_2\,(g)$	$R = K[N_2O_5]^1$	1
(ii)	$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(\ell) + 3H_2O(\ell)$	$R = K[Br^-]\,[BrO_3^-]\,[H^+]^2$	1 + 1 + 2 = 4
(iii)	$H_2\,(Para) \longrightarrow H_2\,(ortho)$	$R = K[H_{2(Para)}]^{3/2}$	3/2
(iv)	$NO_2\,(g) + CO(g) \longrightarrow NO\,(g) + CO_2\,(g)$	$R = K[NO_2]^2[CO]^0$	2 + 0 = 2
(v)	$2O_3(g) \longrightarrow 3O_2\,(g)$	$R = K[O_3]^2\,[O_2]^{-1}$	2 − 1 = 1
(vi)	$H_2 + Cl_2 \xrightarrow{\;h\nu\;} 2\,HCl$	$R = K[H_2]^0[Cl_2]^0$	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 = order of the reactions. But for complex reactions order is to be experimentally calculated.

Solved Examples

Ex-2. The rate of a certain reaction depends on concentration according to the equation : $\dfrac{-dC}{dt} = \dfrac{K_1C}{1+K_2C}$

What will be the order of reaction, when concentration (C) is : (a) very-very high, (b) very-very low.

Sol. (a) $\dfrac{-dC}{dt} = \dfrac{K_1C}{1+K_2C} = \dfrac{K_1}{\dfrac{1}{C}+K_2}$

if C is very-very high then $\dfrac{1}{C}$ being small may be neglected.

$\therefore$ $\dfrac{-dC}{dt} = \dfrac{K_1}{K_2}$ = constant, i.e., zero order reaction.

(b)   If C is very-very low $1 + K_2C \approx K'$

$\therefore$ $\dfrac{-dC}{dt} = \dfrac{K_1C}{K'} = \left(\dfrac{K_1}{K'}\right) \times$ concentration   i.e., I order reaction.

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Section (B) : Integrated rate law : Zero and First Order Reaction

(a) Zero order reactions :

For a zero order reaction
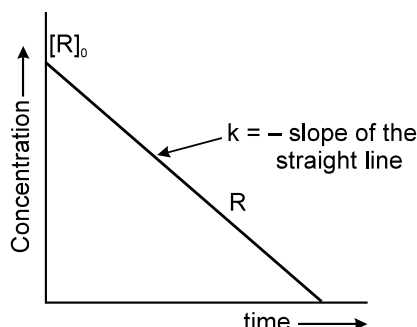
General rate law is, Rate = k [conc.]^0 = constant

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

Rate = k = $\dfrac{C_0 - C_t}{'t'}$ or $kt = C_0 - C_t$ or $C_t = C_0 - kt$

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

Time for completion = $\dfrac{C_0}{k}$

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

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

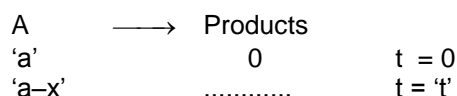### Examples of zero order reactions :

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

$2PH_3 \text{ (g)} \xrightarrow{\text{Ni}} 2P + 3H_2$ Rate = K [PH$_3$]^0

$2HI \text{ (g)} \xrightarrow{\text{Au}} H_2 + I_2$

$2NH_3 \text{(g)} \xrightarrow{\text{Pt}} N_2 + 3H_2$

$H_2 + Cl_2 \xrightarrow{\text{hv}} 2HCl$ Rate = R [H$_2$]^0 [Cl$_2$]^0
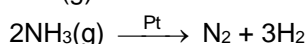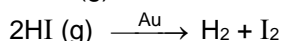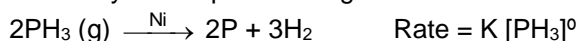
(b)   First Order Reactions :

(i) Let a 1st order reaction is

A	$\longrightarrow$ Products	
'a'	0	t = 0
'a–x'	....	t = 't'

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

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

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

$$k = \dfrac{2.303}{t} \log \dfrac{C_0}{C_t}$$

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

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

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

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

Graphical representation :

$$t = -\dfrac{2.303}{k} \log C_t + \dfrac{2.303}{k} \log C_0$$

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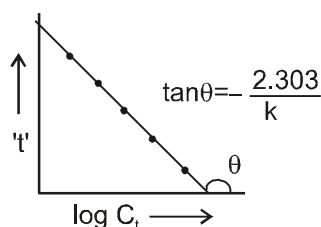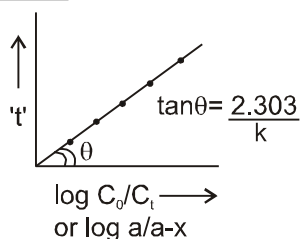
First order growth reaction :

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

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

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

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

Generation time :

At $\quad$ t = generation time, x = a $\qquad \therefore \qquad t = \dfrac{0.693}{K}$
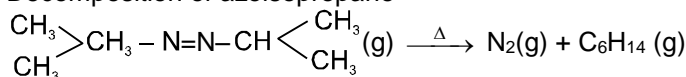
Examples of 1ˢᵗ order reactions :

1. Decomposition of azoisopropane

$$\begin{array}{c}CH_3 \\ \diagdown \\ CH_3 \end{array}\!\!CH_3 - N\!\!=\!\!N - CH\!\!\begin{array}{c} CH_3 \\ \diagup \\ CH_3 \end{array}\!\!(g) \xrightarrow{\;\Delta\;} N_2(g) + C_6H_{14}\,(g)$$

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

3. $H_2O_2 \longrightarrow H_2O + \dfrac{1}{2} O_2$ (g)

4. $NH_4\,NO_2 \longrightarrow 2H_2O + N_2$ (g)
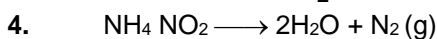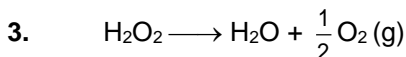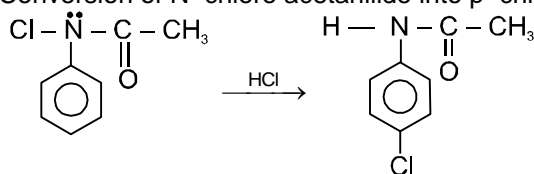
5. Radioactive decay

All radioactive decays are always first order kinetics.

$$^{226}_{88}Ra \longrightarrow \;^{222}_{86}Ra \; + \;_2H^4$$
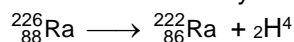
Solved Examples

Ex-3. Calculate $\dfrac{t_{0.75}}{t_{0.50}}$ for a 1ˢᵗ order reaction :

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

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

    (A) 4   (B) 5   (C) 6   (D) 7

Sol.   **(B)** $100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25 \xrightarrow{t_{1/2}} 12.5 \xrightarrow{t_{1/2}} 6.25 \xrightarrow{t_{1/2}} 3.125$

                    0%   50%   75%   87.5%   93.75%   96.875%

Section (C) : Integrated Rate law : Second Order & Pseudo first order reaction

(a)   **Second Order reaction :**

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2nd order Reactions
Two types

</div>

A + A ⟶ products	A + B ⟶ products.
a a	a b 0
(a – x) (a –x)	a – x b – x
$\therefore \dfrac{dx}{dt} = k(a-x)^2$	Rate law
	$\dfrac{dx}{dt} = k(a-x)(b-x)$
$\Rightarrow \displaystyle\int_0^x \dfrac{dx}{(a-x)^2} = \int k\,dt$	$\displaystyle\int_0^x \dfrac{dx}{(a-x)(b-x)} = \int_0^t k\,dt$
$\Rightarrow \left(\dfrac{1}{(a-x)}\right)_0^x = kt$	$\boxed{k = \dfrac{2.303}{t(b-a)} \log \dfrac{a(b-x)}{b(a-x)}}$
$\Rightarrow \dfrac{1}{(a-x)} - \dfrac{1}{a} = kt$ or $\dfrac{1}{C_t} - \dfrac{1}{C_0} = kt$	

(b)   **Pseudo first order reaction :**

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

$\therefore$ For A + B ⟶ Products   [Rate = K [A]^1 [B]^1]

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

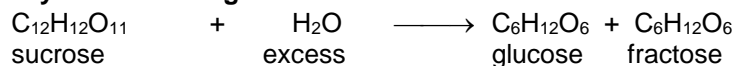Now if 'B' is taken in large excess b >> a.

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

$\because$ 'b' is very large can be taken as constant $\Rightarrow$ $kb = \dfrac{2.303}{t} \log \dfrac{a}{a-x}$ $\Rightarrow$ $k' = \dfrac{2.303}{t} \log \dfrac{a}{a-x}$

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

●   **Examples of Pseudo 1st order reactions :**

    (a) Hydrolysis of canesugar :

        $C_{12}H_{12}O_{11}$ + H_2O ⟶ $C_6H_{12}O_6$ + $C_6H_{12}O_6$

        sucrose   excess   glucose   fractose

    (b) Hydrolysis of esters :

        CH_3COOCH_3 + H_2O $\xrightarrow{H^+}$ $CH_3COOH + CH_3OH$

                           excess

Solved Examples

Ex-5. Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of the ester at different times is given below :

t/min	0	30	60	90
c/M	0.8500	0.8004	0.7538	0.7096.

Show that it follows a pseudo first order reaction as the concentration of H_2O remains nearly constant (51.2 M) during the course of the reaction. What is the value of k in the equation?

        rate = k [CH_3COOCH_3] [H_2O]

Sol. For pseudo first order reaction, the reaction should be first order with respect to the ester when $[H_2O]$ = constant. From the above data we note

t	c	k$\{H_2O\}$ = min^{-1}
0	0.8500	–
30	0.8004	2.004×10^{-3}
60	0.7538	2.002×10^{-3}
90	0.7096	2.005×10^{-3}

It can be seen that k $[H_2O]$ is constant and equal to 2.004×10^{-3} min^{-1} and hence it is pseudo first order reaction. We can now determine k from

$$k\,[H_2O] = 2.004 \times 10^{-3} \text{ min}^{-1}$$
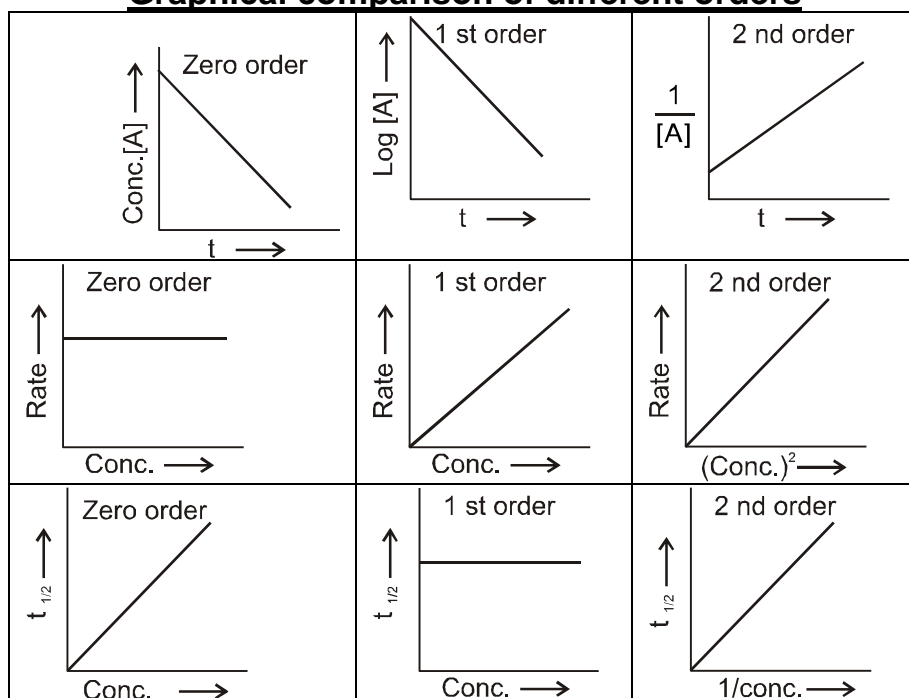$$k\,[51.2 \text{ M}] = 2.004 \times 10^{-3} \text{ min}^{-1}$$
$$k = 3.914 \times 10^{-5} \text{ M}^{-1} \text{ min}^{-1}$$

It has the units of a second order reaction.

Table : Characteristics of Zero, First, Second and nth Order Reactions of the Type A $\longrightarrow$ Products

	Zero Order	**First-Order**	**Second-Order**	**nth order**
Differential Rate law	$\dfrac{-d[A]}{dt} = k[A]^0$	$\dfrac{-d[A]}{dt} = k[A]$	$\dfrac{-d[A]}{dt} = k[A]^2$	$\dfrac{-d[A]}{dt} = k[A]^n$
(Integrated Rate law)	$[A]_t = [A]_0 - kt$	$\ln [A]_t = -kt + \ln [A]_0$	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$	$\dfrac{1}{(A_t)^{n-1}} - \dfrac{1}{(A_0)^{n-1}} = (n-1)kt$
Linear graph	$[A]_t$ v/s t	$\ln [A]$ 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 $[A]_0$)	$t_{1/2} \propto \dfrac{1}{(A_0)^{n-1}}$
Unit	mol L^{-1} s^{-1}	s^{-1}	mol^{-1} Ls^{-1}	$\dfrac{(\text{conc.})^{1-n}}{t}$

Graphical comparison of different orders

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Section (D) : Experimental method to calculate order and rate law of reaction and methods to monitor the progress of reaction

Methods to determine order of a reaction :

(A) Initial rate method :

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

$$r = k [A]^a [B]^b [C]^c \qquad \text{if} \qquad [B] = \text{constant}$$
$$[C] = \text{constant}$$

then for two different initial concentrations of A we have

$$r_{0_1} = k [A_0]_1{}^a \qquad\qquad r_{0_2} = k [A_0]_2{}^a$$

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

Or   in log form we have

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

(B) integrated rate law method :

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

——— *Solved Examples* ———

Ex-6. The rate of decomposition of 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., $\qquad k = \dfrac{\ln(c_0/c)}{t}$

t/min	c/M	$k = \dfrac{\ln(c_0/c)}{t}$ min^{-1}
0	2.08	6.32×10^{-4}
135	1.91	6.30×10^{-4}
342	1.67	6.32×10^{-4}
683	1.35	6.32×10^{-4}
1693	0.57	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 $k = 6.31 \times 10^{-4}$ min^{-1} .

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

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

(C)   Method of half lives :

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

for n^{th} order reaction $\qquad t_{1/2} \propto \dfrac{1}{[C_0]^{n-1}} \qquad\qquad \Rightarrow \qquad \dfrac{t_{1/2}}{t'_{1/2}} = \dfrac{(C'_0)^{n-1}}{(C_0)^{n-1}}$

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Solved Examples

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

Sol. For a nth order reaction (n ≠ 1), $t_{1/2} \propto \dfrac{1}{c_0^{n-1}}$

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

Methods to monitor the progress of the reaction :

(A) **Pressure measurement :**
Progress of gaseous reaction can be monitored by measuring total pressure at a fixed volume & temperature.
This method can applied for those reaction also in which a gas is produced because of decomposition of a solid or liquid. We can get an idea about the concentration of reacting species at a particular time by measuring pressure.
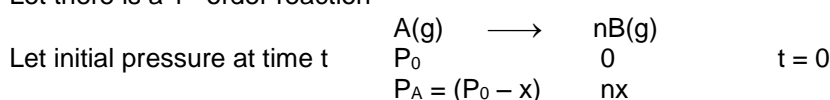
● The pressure data can be given in terms of
(i) Partial pressure of the reactant   (ii) Total pressure of the reaction system

Solved Examples

Ex-8. Find the expression for K in terms of P_0, P_t and n
Sol. Let there is a 1st order reaction

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

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

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

∴ $x = \dfrac{P_t - P_0}{n-1}$

∴ $P_A = P_0 - \dfrac{P_t - P_0}{n-1} = \dfrac{P_0 n - P_t}{n-1}$

∴ $a \propto p_0$ & $a - x \propto P_A = \dfrac{nP_0 - P_t}{n-1}$

∴ $\mathbf{k = \dfrac{2.303}{t} \log \dfrac{P_0(n-1)}{nP_0 - P_t}}$

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

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

(B) **Volume measurement :**
(i) **By measuring the volume of product formed we can monitor the progress of reactions.**

Solved Examples

Ex-9. Study of a reaction whose progress is monitored by measuring the volume of a escaping gas.

$$NH_4NO_2\,(s) \xrightarrow{\Delta} 2H_2O\,(\ell) + N_2\,(g)$$
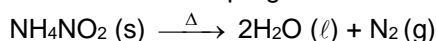
Sol. Let, V_t be the volume of N_2 collected at time 't'
V_∞ = be the volume of N_2, collected at the end of the reaction.
     $a \propto V_\infty$ and $x \propto V_t$
     $(a - x) \propto V_\infty - V_t$
∴ $k = \dfrac{2.303}{t} \log \dfrac{V_\infty}{V_\infty - V_t}$

Section (E) : Method to monitor the progress of Reactions (Titration Method and Optical Activity Method)

(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.

Solved Examples

Ex-10. 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 number of ml of potassium permagnate required to react with a definite volume of hydrogen peroxide solution.

Sol. The equation for a first order reaction is $2H_2O_2 \xrightarrow{\Delta} 2H_2O\,(\ell) + O_2\,(g)$

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

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

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

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

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

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-11. Conversion of N-chloro acetanilide into p-chloroacetanilide

$Cl - N - COCH_3 \qquad H - N - COCH_3$

$\xrightarrow{HCl}$
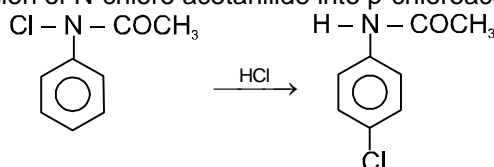
The above reaction is first order reaction and its progress is monitored by iodometric titration in which liberated iodine is titrated against a standard solution of Hypo using starch as indicator. Given that in this reaction KI does not react with the product (p–chloro acetanilide). Calculate the rate constant of the reaction. Given that volume of hypo consumed at $t = 0$ is V_0 and at time 't', V_t

Sol. Let, $\qquad V_0$ = volume of hypo consumed at $t = 0$

Similarly $\qquad V_t$ = volume of hypo consumed at $t = $ 't'

$\therefore$ $a \propto V_0$ {$\because$ KI reacts with the reactant only}

$a - x \propto V_t$

$k = \dfrac{2.303}{t} \log \dfrac{V_0}{V_t}$

Ex-12. Study of acid hydrolysis of an ester.

$CH_3COOCH_3 + H_2O \text{ (excess)} \xrightarrow[\text{(HCl)}]{H^+} CH_3COOH + CH_3OH$
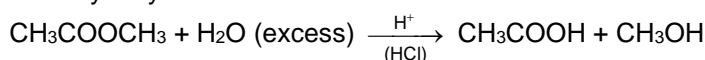
The progress of this reaction is monitored or determined by titrating the reaction mixture at different time intervals against a standard solution of NaOH using phenolphthalein as indicator. Find out rate constant of the reaction in terms of volume of NaOH consumed at $t = 0$, V_0, at $t = \infty$, V_∞ & at time t, V_t.

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

           V_t = vol. of NaOH used at 't'

           V_∞ = vol. of NaOH used at t = ∞

           $a \propto V_\infty - V_0$

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

           $x \propto V_t - V_0$

           $a \propto V_\infty - V_0$; $k = \dfrac{2.303}{t} \log \dfrac{V_\infty - V_0}{V_\infty - V_t}$

(C)   **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.
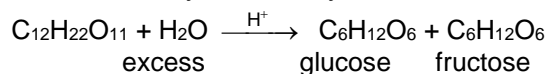
●   The optically active species may be present in reactant or product.

        It is found that $\begin{array}{l}(r_\infty - r_0) \propto a \\ (r_\infty - r_t) \propto (a - x)\end{array}$ (a = initial concentration, x = amount consumed)

        where are r_0, r_t, r_∞ are angle of optical rotation at time   t = 0, t = t and t = ∞

Solved Examples

Ex-13. 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 as fructose obtained becomes laevorotatory. That's why this reaction is also known as inversion of cane sugar.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\;H^+\;} C_6H_{12}O_6 + C_6H_{12}O_6$$

                        excess   glucose   fructose

Sp. rotation $+66.5^0$ $+52.7^0$ -92.4^0

Let the readings in the polarimeter are

     t = 0, θ_0 ; t = 't', θ_t and at t = ∞ , θ_∞

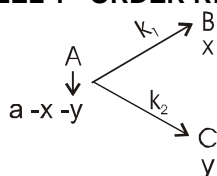Then calculate rate constant 'k' in terms of these readings.

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

     ∴ $a \propto \theta_0 - \theta_\infty$; $a - x \propto \theta_t - \theta_\infty$

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

Section (F) : Complication in 1st Order Reaction

PARALLEL 1st ORDER REACTION OR COMPETING FIRST-ORDER REACTIONS

At   t = 0   [A] = a   [B] = [C] = 0

Calculate effective $t_{1/2}$ for   [A], [B], [C] & [B] / [C]

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

        $\dfrac{-d[A]}{dt} = \dfrac{d[B]}{dt} + \dfrac{d[C]}{dt}$

        $\dfrac{-d[A]}{dt} = (k_1 + k_2) [A] = k_{eff} [A]$

        $k_{eff} = k_1 + k_2$

        $\dfrac{\ell n2}{T_{eff}} = \dfrac{\ell n2}{T_1} + \dfrac{\ell n2}{T_2}$ (where T represent half life)

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$$\boxed{\frac{1}{T_{eff}} = \frac{1}{T_1} + \frac{1}{T_2}}$$ (remember)

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

$\dfrac{d[B]}{dt} = k_1 [A]$

$\dfrac{d[B]}{dt} = k_1 ae^{-(k_1+k_2)t}$

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

similarly $[C] = \dfrac{k_2 a}{k_1 + k_2}(1 - e^{-(k_1+k_2)t})$

$$\boxed{\frac{[B]}{[C]} = \frac{k_1}{k_2}}$$ (remember)

$k_{eff} = k_1 + k_2$

$A_{eff} \cdot e^{-Ea/RT} = A_1 e^{-Ea_1/RT} + A_2 e^{-Ea_2/RT}$

on differentiating

$-\dfrac{E_a}{R}\left(\dfrac{-1}{T^2}\right) A_{eff}.e^{-Ea/RT} = -\dfrac{E_{a_1}}{R}\left(\dfrac{-1}{T^2}\right) A_1 e^{-Ea_1/RT} - \dfrac{E_{a_2}}{R}\left(\dfrac{-1}{T^2}\right) A_2 e^{-Ea_2/RT}$

$\dfrac{Ea}{RT^2} \times \dfrac{Ea_1}{RT^2} k_{eff} = k_1 + \dfrac{Ea_2}{RT^2} k_2$

$E_a \times k_{eff} = E_{a1} k_1 + E_{a2} k_2$

$$\boxed{E_a = \frac{E_{a_1}k_1 + E_{a_2}k_2}{k_1 + k_2}}$$

Section (G) : Temperature dependence of rate
Effect of temperature on rate of reaction :

In early days the effect of temperature on reaction rate was expressed in terms of **temperature coefficient** 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)

$\text{T.C.} = \dfrac{K_t + 10}{K_t} \approx 2 \text{ to } 3$ (for most of the reactions)

Solved Examples

Ex-14. For a reaction T.C. = 2, Calculate $\dfrac{k_{40ºC}}{k_{25ºC}}$ for this reaction.

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

● But the method of temperature coefficient was not exact and to explain the effect of temperature on reaction rate new theory was evolved

Arrhenius theory of reaction rate :
It was developed by Max Trautz and William lewis.
It gives insight in to the energetics and mechanistic aspects of reactions.
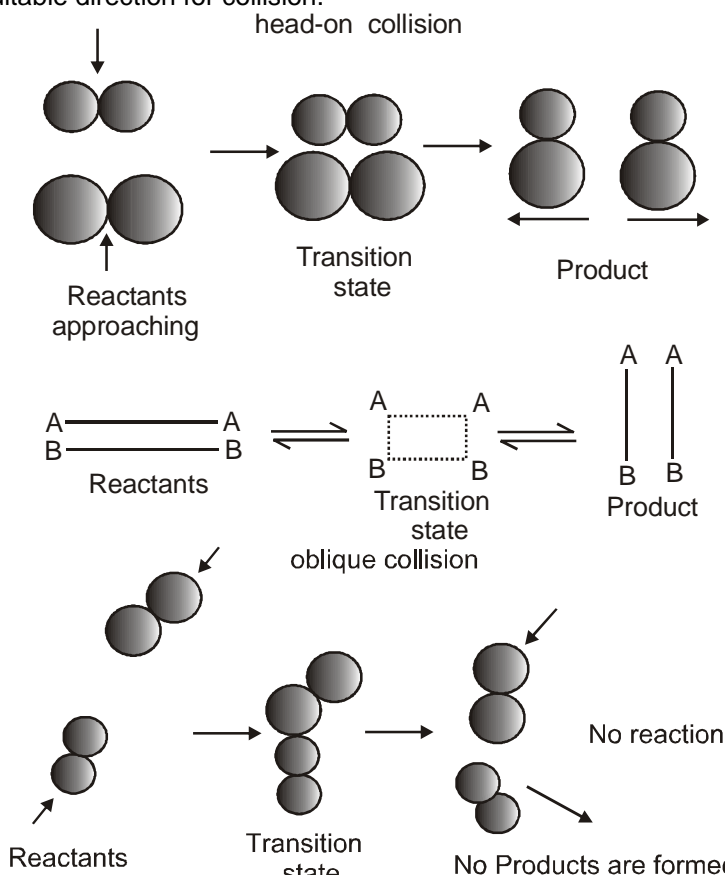It is based upon kinetic theory of gases.
Arrhenius proposed a theory of reaction rate which states as follows :
❍ A chemical reaction takes place due to the collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z).
❍ Every collision does not bring a chemical change. The collision that actually produce the products are effective collision. For a collision to be effective the following two barriers are to be cleared.
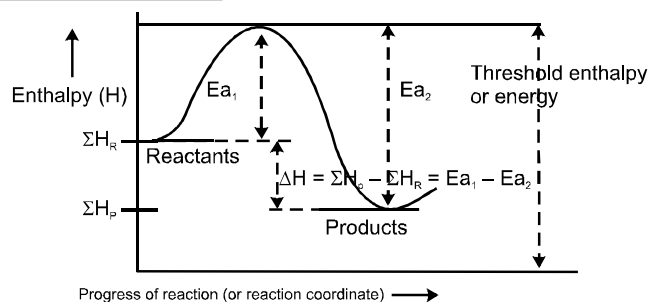
● **Energy barrier :** The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur is known as threshold energy.
"The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy (E_a)"

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

head-on collision

Transition state   Product

Reactants approaching

A————A   ⇌   A┈┈┈A   ⇌   A A
B————B   B┈┈┈B | |
Reactants   Transition   B B
                    state   Product

oblique collision

No reaction

Reactants   Transition state   No Products are formed

○ Collision to be effective the colliding molecules must possess some certain minimum energy called threshold energy of the reaction.

○ Reactant molecules having energy equal or greater than the threshold are called active molecules and those having energy less than the threshold are called passive molecules.

○ At a given temperature there exists a dynamic equilibrium between active and passive molecules. The process of transformation from passive to active molecules being endothermic, increase of temperature increases the number of active molecules and hence the reaction.

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

○ Concept of energy of activation (E_a)

● The 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

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

● The essence of Arrhenius 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.

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ΣH_R = Summation of enthalpies of reactants
ΣH_P = Summation of enthalpies of products
ΔH = Enthalpy change during the reaction
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.
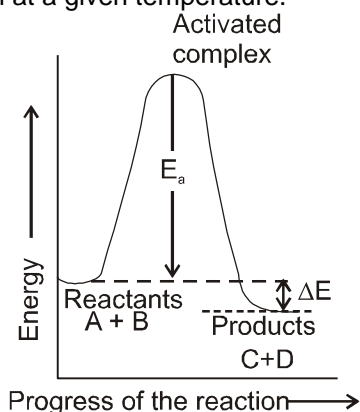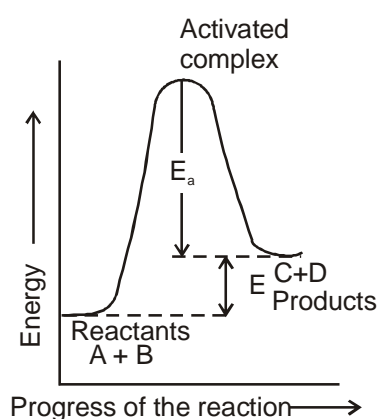

(Exothermic)   **(Endothermic)**

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.

Collision frequency is the number of collisions per unit volume per unit time. It is denoted by the symbol Z. Z is directly proportional to $\sqrt{T}$. By 10⁰C rise in temperature, so it is the fraction of the total number of effective collision that increases markedly resulting into marked increase in the reaction rate.
From maxwellian distribution it is found that fraction of molecules having excess energy greater than threshold energy lead to the formation of product.
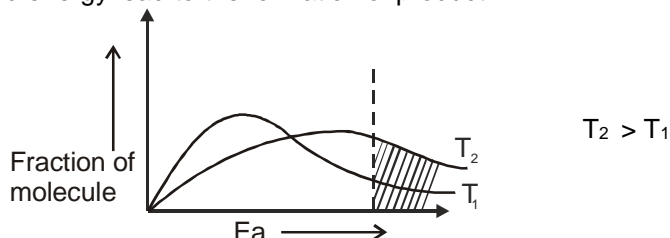
$e^{-E_a/RT}$ → represents fraction of molecules having energy greater E_a

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

dependence of rate on temperature is due to dependence of k on temperature.
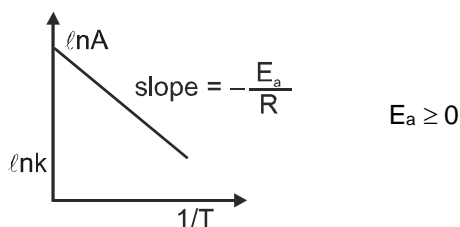
$k \propto e^{-E_a/RT}$
$k = Ae^{-E_a/RT}$ **[Arrhenius equation]**

A is pre exponential factor / frequency factor representing collisions taking place with proper orientation. A and E_a are independent of temperature generally.

E_a = min K. E. that colliding molecules must have to reach transition state.

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

slope $= -\dfrac{E_a}{R}$

$E_a \geq 0$
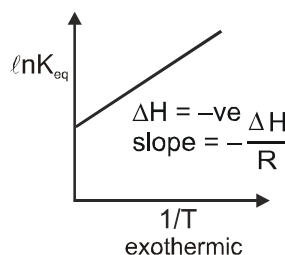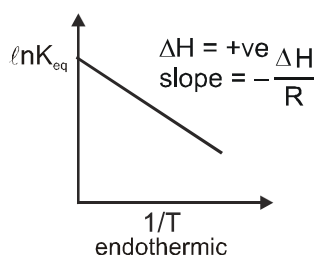
❖ As $T \to \infty$, $K \to A$

REVERSIBLE REACTIONS

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

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

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

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

$\Delta H = +ve$
slope $= -\dfrac{\Delta H}{R}$
endothermic

$\Delta H = -ve$
slope $= -\dfrac{\Delta H}{R}$
exothermic

At temperature T_1, rate constant $= k_1$
At temperature T_2, rate constant $= k_2$

$\ell nk_1 = \ell nA - \dfrac{E_a}{RT_1} \Rightarrow \ell nk_2 = \ell nA - \dfrac{E_a}{RT_2} \Rightarrow \ell n\dfrac{k_2}{k_1} = \dfrac{E_a}{R}\left\{\dfrac{1}{T_1} - \dfrac{1}{T_2}\right\}$ (remember)

Solved Examples

Ex-15. Two Ist order reactions are initially having equal rate at a particular temprature. Temprature of both the reaction is increased by same amount. Calculate rate of which reaction will increase by greater amount (reaction with low E_a or high E_a)

Sol. $\ell n\left(\dfrac{k_2}{k_1}\right) = \dfrac{E_a}{R}\left\{\dfrac{1}{T_1} - \dfrac{1}{T_2}\right\}$ .....(i)

$\ell n\left(\dfrac{k_2{}'}{k_1}\right) = \dfrac{E_a{}'}{R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2{}'}\right]$ .....(ii)

Equation (i) – (ii).

$\ell n\left(\dfrac{k_2}{k_2{}'}\right) = \dfrac{\Delta T}{R}(E_a - E_a{}_,)$ if $E_a > E_a$, $k_2 > k_2{}'$

or $k = A\, e^{-E_a/RT}$ or $\dfrac{dk}{dT} = \dfrac{-E_a}{R}\left(\dfrac{-1}{T^2}\right)A\, e^{-E_a/RT}$

temprature coeff. of rate constant $\dfrac{1}{K}\dfrac{dk}{dT} = \dfrac{E_a}{RT^2}$ or $\dfrac{\Delta k}{k.\Delta T} =$ fractional change / unit temp. rise

Ex-16. Explain on the basis of temprature coeff. of rate const. that equilibrium of endothermic reaction shifts in forward direction on increasing temprature while equilibriums of exothermic shift back.

$\ell n\left(\dfrac{K_{eq_1}}{K_{eq_2}}\right) = \dfrac{\Delta H}{R}\left\{\dfrac{1}{T_1} - \dfrac{1}{T_2}\right\}$

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Sol. $\Delta H = E_{af} - E_{ab} > 0$ (for endothermic)

        $E_{af} > E_{ab}$

on increasing temp. $k_f\uparrow$ more than k_b

equilibrium will shift in forward direction.

Section (H) : Catalyst dependence of rate and type of Reaction and Determination of rate law and order with the help of given mechanism

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**.
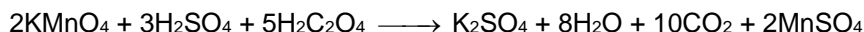
Types of catalyst

Positive Catalyst   Negative catalyst

increases the rate of reaction   decreases the rate of reaction
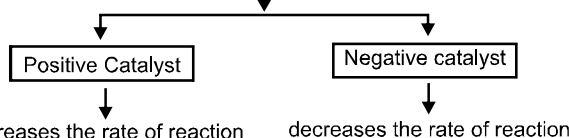
Catalyst are generally foreign substances but sometimes one of the product may act as a catalyst and such catalyst is called **"auto catalyst"** and the phenomena is called **auto catalysis**.

Examples of catalysis

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

$$2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2\uparrow + [MnO_2]$$
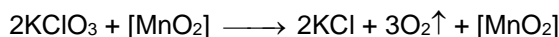
● MnO_2 can be received in the same composition and mass at the end of the reaction.

(b) 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.

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 8H_2O + 10CO_2 + 2MnSO_4$$

General characteristics of catalyst :

●   A catalyst does not initiate the reaction. 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^0. 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 go to 75% of completion before 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 = Energy of activation in presence of catalyst.

    $E_a - E'_a$ = lowering of activation energy by catalyst.
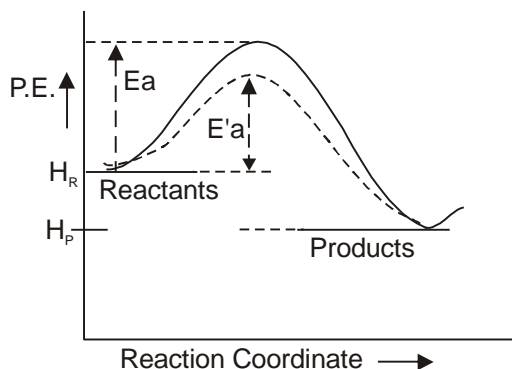
**Comparison of rates of reaction in presence and absence of catalyst :**

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

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

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Since $E_a - E'_a$ is positive so $k_{cat} > k$. the ratio $\dfrac{k_{cat}}{k}$ 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 $\dfrac{E'_a}{T_1} = \dfrac{E_a}{T_2}$

Catalyzed pathway (a)   Uncatalyzed pathway (b)
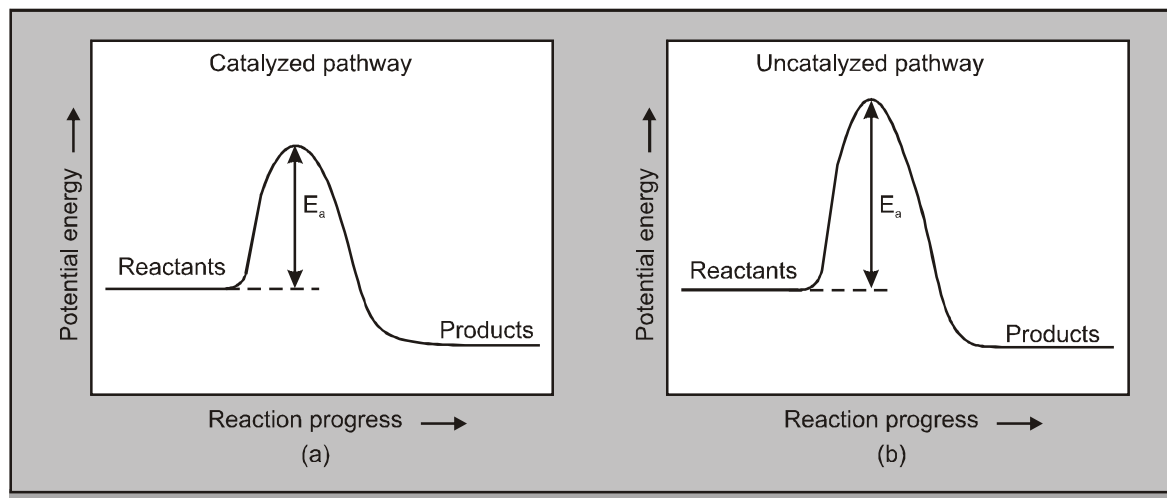
Solved Examples

Ex-17. For the reaction $CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$ under the same concentration conditions of the reactants, the rate of the reaction at 250°C is 1500 times as fast as the same reaction at 150°C. Calculate the activation energy of the reaction. If the frequency factor is 2.0×10^{10} M^{-1} sec^{-1}, calculate the rate constant of the reaction at 150°C.

Sol. $\log \dfrac{k_2}{k_1} = \dfrac{E}{2.303R}\left[\dfrac{T_2 - T_1}{T_1\, T_2}\right]$

$\log 1500 = \dfrac{E}{2.303 \times 2} \times \dfrac{100}{523 \times 423}$

$E = \dfrac{3.1761 \times 2.303 \times 2 \times 523 \times 423}{100} = 32.36$ kcal mol^{-1}

$\log k = \log A - \dfrac{E}{2.303\,RT} = \log(2.0 \times 10^{10}) - \dfrac{32360}{2.303 \times 2 \times 423} = 10.301 - 16.609 = -6.308$

$k = 4.92 \times 10^{-7}$ litres mol^{-1} sec^{-1}

Ex-18. The pyrolysis of an organic ester follows a first order process and its rate constant can be expressed as

$\ln k = 78.09 - \dfrac{42075}{T}$ where k is given in the min^{-1}.

Calculate the time required for 25 percent reaction to complete at 227°C.

Sol. $\ln k = 78.09 - \dfrac{42075}{500} = -6.06$

$\log k = -\dfrac{6.06}{2.303} = -2.63$; $k = 2.344 \times 10^{-3}$ min^{-1}

when $x = 0.25$; $k = \dfrac{2.303}{t_{1/4}} \log \dfrac{a}{0.75a}$

$t_{1/4} = \dfrac{2.303}{2.344 \times 10^{-3}} \log 1.333 = 123.06$ min

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Ex-19. 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 = $\frac{-E}{2.303R}$ = -5.4×10^3

E = $5.4 \times 10^3 \times 2.303 \times 1.987$ = 24.624 cal mol^{-1}

(b) K = $Ae^{-E/RT}$; log 1.155×10^{-2} = log A $- \dfrac{24.624}{2.303 \times 1.987 \times 373}$ or A = 1.764×10^3 sec^{-1}

Molecularity and Order :

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 near-simultaneous collision of more than three molecules.

The rate law for the elementary reaction

$\qquad$ aA + bB $\longrightarrow$ products $\qquad$ rate = $k[A]^a[B]^b$, where a + b = 1, 2 or 3.

For an elementary reaction, the orders in the rate law equal the coefficients of the reactants.

While, the order is defined for complex as well as elementary reactions and is always experimentally calculated by the mechanism of the reaction, usually by the slowest step of the mechanism known as **rate determining step (RDS) of the reaction.**

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

Mechanism of a reaction :

Reactions can be divided into
- Elementary / simple / single step
- Complex / multi-step

- **ELEMENTARY REACTION :**
- These reaction take place in single step without formation of any intermediate
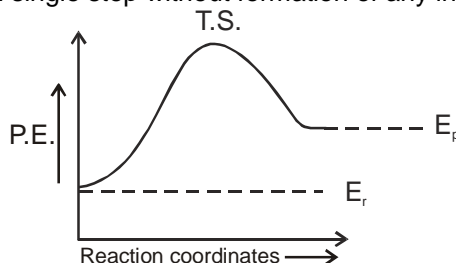
- For elementary reaction we can define molecularity of the reaction which is equal to no of molecules which make transition state or activated complex because of collisions in proper orientation and with sufficient energy
- Molecularity will always be a natural number.
  1 = unimolecular one molecule gets excited (like radioactivity)
  2 = bimolecular
  3 = trimolecular

❍ Molecularly ≤ 3 because the probability of simultaneous collision between 4 or more molecules in proper orientation is very low

❍ For elementary reaction there is only single step and hence it is going to be rate determining step so order of an elementary reaction is its molecularity
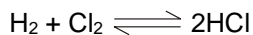
Order of elementary reaction w.r.t. reactant = stoichiometric co-efficient of the reactant

$H_2 + I_2 \rightleftharpoons 2HI$ (Simple reaction)

rate = k $[H_2]$ $[I_2]$

$2H_2 + 2I_2 \rightleftharpoons 4HI$ (not elementary)

reaction obtained by multiplying an elementary reaction with some number will not be of elementary nature

$H_2 + Cl_2 \rightleftharpoons 2HCl$

order = 0

● **COMPLEX REACTION :**

❍ Reaction which proceed in more than two steps or having some mechanism. (Sequence of elementary reaction in which any complex reaction procceds)

❍ For complex reaction each step of mechanism will be having its own molecularity but molecularity of net complex reaction will not be defined.
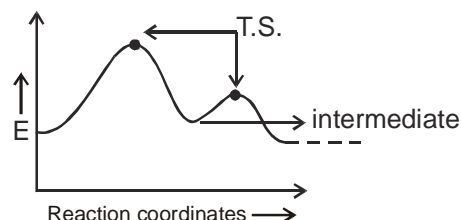
❍ Order of complex reaction can be zero fractions whole no, even negative w.r.t. some species.

❍ Order of reaction or rate law of reaction is calculated with the help of mechanism of the reaction generally using Rate determine step (R.D.S) if given.

❍ Rate law of a reaction is always written in terms of conc. of reactant, products or catalysts but never in terms of conc. of intermediates.

The mechanism of any complex reaction is always written in terms of elementary steps, so molecularity of each of these steps will be defined but net molecularity of complex reaction has no meaning.

The mechanism of most of the reaction will be calculated or predicted by using mainly the following approximations.

CALCULATION OF RATE LAW/ ORDER

(A) MECHANISM IN WHICH R.D.S. GIVEN

(i) If R.D.S. involves only reactant, product or catalyst on reactant side

    rate law of R.D.S. = rate law of reaction

Solved Examples
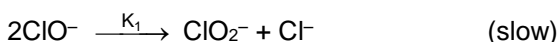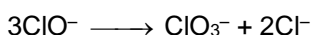
Ex-20. Calculate order and rate law of reaction

    $2NO_2 + F_2 \longrightarrow 2NO_2F$ with help of mechanism

I	$NO_2 + F_2 \xrightarrow{K_1} NO_2F + F$	(slow)	molecularity = 2 for both
II	$NO_2 + F \xrightarrow{K_2} NO_2F$	(fast)	

    According to RDS

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

Ex-21. Calculate rate law

    $3ClO^- \longrightarrow ClO_3^- + 2Cl^-$

    $2ClO^- \xrightarrow{K_1} ClO_2^- + Cl^-$ (slow)

    $ClO_2^- + ClO^- \xrightarrow{K_2} ClO_3^- + Cl^-$ (fast)

    Rate = $k_1[ClO^-]^2$

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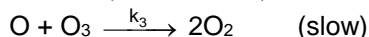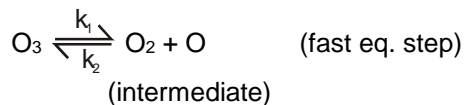**Toll Free :** 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

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(ii) **RDS is having intermediate on reactant side**
To calculate order, we have to specify [intermediate] in expression of rate law in terms of conc. of [R], [P] or catalyst with the help of some equilibrium step given in mechanism.

Solved Examples

Ex-22. $2O_3 \longrightarrow 3O_2$

$O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ (fast eq. step)

(intermediate)

$O + O_3 \xrightarrow{k_3} 2O_2$ (slow)

From R.D.S., rate = $k_3 [O_3] [O]$

According to equilibrium step.

$$K_{eq.} = \frac{k_1}{k_2} = \frac{[O_2][O]}{[O_3]}$$

$$[O] = \left[\frac{k_1[O_3]}{k_2[O_2]} \right]$$

Rate = $k_3[O_3] [O] = k_3[O_3] \left[\dfrac{k_1[O_3]}{k_2[O_2]} \right]$.

Rate = $\dfrac{k_1 k_3}{k_2} \dfrac{[O_3]^2}{[O_2]}$

Ex-23 $H^+ + HNO_2 + C_6H_5NH_2 \xrightarrow{Br^-} C_6H_5N_2^+ + 2H_2O$

intermediate

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

intermediate

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

$NOBr + C_6H_5NH_2 \xrightarrow{k_4} C_6H_5N_2^+ + Br^- + H_2O$ (fast)
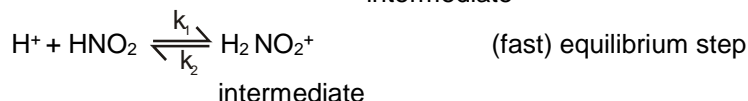
Sol. $r = k_3[Br^-] [H_2NO_2^+]$

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

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

$$r = \frac{k_1 k_3}{k_2} [H^+] [HNO_2] [Br^-].$$

(B) **MECHANISMS IN WHICH RDS NOT SPECIFIED**
STEADY STATE APPROXIMATION

Initially, for most of the cases only reactants are taken and hence the rate of production of intermediate is large in comparison to its rate of consumption but after some time rate of consumption of intermediate will become equal to its rate of production. This is known as steady state of reaction. Finally when reaction is going to get completed, rate of consumption will become more then rate of production. But for most of the times reaction remains at steady state. So rate law of reaction during steady state can be taken to be final or net rate law of reaction.

At steady state $\dfrac{d [intermediate]}{dt} = 0$

Solved Examples

Ex-24 $2O_3 \longrightarrow 3O_2$

$O_3 \xrightarrow{k_1} O_2 + O$

$O_2 + O \xrightarrow{k_2} O_3$

$O_3 + O \xrightarrow{k_3} 2O_2$
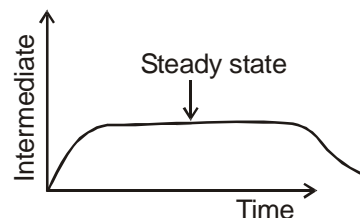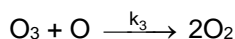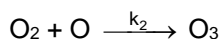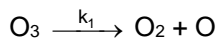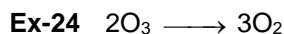
Sol. Rate $= \dfrac{-1}{2}\dfrac{d[O_3]}{dt} = \dfrac{1}{3}\dfrac{d[O_2]}{dt}$

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

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

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

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

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

$\qquad \dfrac{d[O_3]}{dt} = -k_1[O_3] + \dfrac{\{k_2[O_2]\ k_1[O_3]\}}{k_2[O_2]+k_3[O_3]} - \dfrac{k_1k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$

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

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

$\qquad \left[\dfrac{-1}{2}\dfrac{d}{dt}[O_3]\right] = \dfrac{k_1k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$

$\qquad$ Rate $= -\dfrac{1}{2}\dfrac{d}{dt}[O_3]$

So,$\qquad$ Rate (r) $= \dfrac{k_1k_3[O_3]^2}{k_2[O_2]+k_3[O_3]}$

if 3rd step is RDS then $k_1 \gg k_3$

$\qquad\qquad\qquad\qquad k_2 \gg k_3$

$\qquad$ r $= \dfrac{k_1k_3[O_3]^2}{k_2[O_2]}$

Ex-25 $H^+ + HNO_2 + C_6H_5NH_2 \xrightarrow{Br} C_6H_5N_2^+ + 2H_2O$

$H^+ + HNO_2 \xrightarrow{k_1} H_2NO_2^+$

$H_2NO_2^+ \xrightarrow{k_2} H^+ + HNO_2$

$H_2NO_2^+ + Br^- \xrightarrow{k_3} NOBr + H_2O.$

$NOBr + C_6H_5NH_2 \xrightarrow{k_4} C_6H_5N_2^+ + H_2O + Br^-$
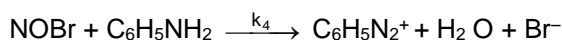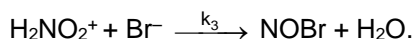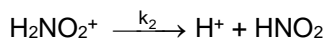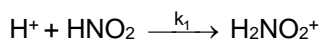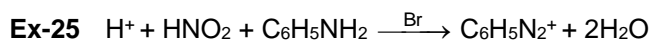
Sol. $\dfrac{d[H_2NO_2^+]}{dt} = k_1 [H^+][HNO_2] - k_2 [H_2NO_2^+] - k_3 [H_2 NO_2^+] [Br^-] = 0$

$[H_2NO_2^+] = k_1 \dfrac{[H^+]HNO_2]}{k_2 + k_3[Br^-]}$

$\text{rate} = \dfrac{d}{dt}[C_6H_5NH_2] = \dfrac{d}{dt}[HNO_2]$

$\dfrac{d}{dt}[C_6H_5NH_2] = k_4 [NOBr] [C_6H_5NH_2]$

$\dfrac{d}{dt} [NOBr] = - k_4 [C_6H_5NH_2][NOBr] + k_3 [Br^-] [H_2NO_2^+] = 0$

$[NOBr] = \dfrac{k_3[Br^-][H_2NO_2^+]}{k_4[C_6H_5NH_2]}$

$r = \dfrac{k_4 k_3[Br^-][H_2NO_2^+]}{k_4[C_6H_5NH_2]} [C_6H_5NH_2]$

$r = \dfrac{k_1 k_3[Br^-][H^+][HNO_2]}{k_2 + k_3[Br^-]}$

Section (I) : Radio Activity

* All radioactive disintegration follow Ist order kinetics.

$$A \longrightarrow B + C$$
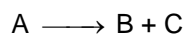
Int. nuclie N_0

At time t.   N

decay constant

$$\boxed{\dfrac{-dN}{dt} = \lambda N} \rightarrow \text{No. of nuclei of A at time } t$$

rate decay(A)
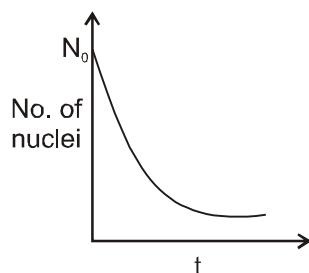
* λ = Not dependent on temperature.

$\dfrac{-dN}{dt} = \lambda N$; $\int \dfrac{-dN}{N} = \int \lambda \; dt$

$\boxed{N = N_0 e^{-\lambda t}}$

$\boxed{\lambda = \dfrac{1}{t} \ln\left(\dfrac{N_0}{N}\right)}$; $\boxed{\dfrac{A_0}{A} = \dfrac{N_0}{N} = \dfrac{n_0}{n} = \dfrac{w_0}{w}}$

n_0 = initial moles   ; w_0 = initial weight

$\lambda = \dfrac{1}{t} \ln\left(\dfrac{w_0}{w}\right)$ (w = weight of A remaining after time t)

$$\lambda = \frac{1}{t}\ln\left(\frac{w_0}{w_0 - x}\right)$$

Half life :

$$t = t_{1/2} \quad ; \qquad N = \frac{N_0}{2}$$

$$\lambda = \frac{1}{t_{1/2}}\ln\left(\frac{N_0}{N_0/2}\right)$$

$$\lambda = \frac{\ln 2}{t_{1/2}}$$

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

Average life :

$$T_{avg.} = \frac{1}{\lambda} = 1.44\, t_{1/2}$$

$$T_{avg.} = \frac{\int_0^\infty dN.t}{N_0} = \frac{1}{\lambda} \qquad\qquad \left(\because \frac{-dN}{dt} = \lambda N \text{ and } N = N_0 e^{-\lambda t}, \ \therefore dN = -\lambda N_0 e^{-\lambda t}\, dt\right)$$

Unit of activity :
* Curie (C_i) = 3.7×10^{10} dps
  Millicurie (mC_i) = 3.7×10^7 dps
  Microcurie (μC_i) = 3.7×10^4 dps
* Rutherford (1 Rd) = 1×10^6 dps

Application of radioactivity :

1. **Carbon dating :** (used for wooden object)
In living matter existing in nature : $\qquad {}_6C^{14} \qquad : \quad {}_6C^{12} \qquad = \qquad 1 : 10^{12}$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (radio active) $\quad$ (stable)

In upper atmosphere :

$${}_7N^{14} + {}_0n^1 \longrightarrow {}_6C^{14} + {}_1p^1$$

Ratio of radioactive carbon in dead animals / trees decreases with respect to time.

$$t = \frac{1}{\lambda}\ln\left(\frac{A_0}{A}\right)$$

Half life of ${}_6C^{14}$ = 5770 yrs.
A = activity of old wood piece. $\qquad\qquad ; \qquad\qquad A_0$ = activity of fresh wood piece.

2. **Age of rocks or minerals**

$${}_{92}U^{238} \longrightarrow {}_{82}Pb^{206}$$
$$\text{(radioactive)} \qquad\qquad \text{(stable)}$$

Reaction :

$${}_{92}U^{238} \longrightarrow {}_{82}Pb^{206} + x\, {}_2He^4 + y\, {}_{-1}e^0$$

$${}_zX^A \longrightarrow {}_{z-2}X'^{A-4} + {}_2He^4$$

$${}_zY^A \longrightarrow {}_{z+1}Y'^A + {}_{-1}e^0$$

Number of α-particles = $\dfrac{\text{difference of mass no.}}{4}$ = $\dfrac{238-206}{4}$ = 8

$$238 = 206 + 4x + 0 \qquad .....(1)$$
$$92 = 82 + 2x - y \qquad .....(2)$$

On solving (1) and (2),

$$x = 8 \qquad ; \qquad y = 6$$

$$_{92}U^{238} \longrightarrow \, _{82}Pb^{206} + 8(_2He^4) + 6(_{-1}e^0)$$

At time t   w g   y g

$$t = \frac{1}{\lambda} \ln\left(\frac{w_0}{w}\right)$$

$$t = \frac{1}{\lambda} \ln\left(\frac{w_0}{w_0 - x}\right)$$

$$w = w_0 - x$$

∴ $w_0 = w + x$

1 mole or 238 g U provide 206 g of Pb

∴ $\dfrac{238}{206}$ g U provide 1 g Pb

∴ $\dfrac{238}{206}$ × y g U provide y g Pb

$$x = \frac{238}{206} \times y \qquad ; \qquad w_0 = w + \frac{238}{206} \times y$$

$$_{92}U^{238} \longrightarrow \, _{82}Pb^{206} + 8_2He^4 + 6_{-1}e^-$$

                      V(in mL) collected
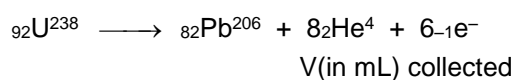
$$n_{He} = \frac{PV}{RT} \qquad .... (1)$$

$$t = \frac{1}{\lambda} \ln\left(\frac{n_0}{n}\right)$$

$$n = \frac{w}{238} \qquad .... (2)$$

$$n_0 = n + \frac{n_{He}}{8}$$

Summary

Chemical kinetics — is concerned with:

- **Reaction mechanism** — consists of **Elementary reaction steps**
  - molecularity can be: **Unimolecular / Bimolecular / Termolecular**
  - slowest step is **Rate-determining step**
  - may involve **Reaction intermediates**
- **Reaction rate** — depends on:
  - **Catalysts**
    - Provides alternate path
    - Reduces E_a
    - Applied for spontaneous Rxns.
    - Does not change ΔG
  - **Temperature** — dependence given by **Arrhenius equation** $K = Ae^{-E_a/RT}$
    - explained by **Collision theory**
    - contains:
      - **Activation energy (E_a)** — depends on **Transition state**
      - **Frequency factor** — depends on **Steric factor** / **Collision frequency**
  - **Concentration** — dependence given by **Rate law**
    - contains **Rate constant**
      - depends on T
      - varies with Rxns.
    - alternative form: **Integrated rate law** — type:
      - n^{th}-order: $\frac{1}{(C_t)^{n-1}} - \frac{1}{(C_0)^{n-1}} = (n-1)Kt$; $t_{1/2} \propto \frac{1}{(C_0)^{n-1}}$
      - First-order: $C_t = C_0 e^{-Kt}$; Constant $t_{1/2} = \frac{.693}{K}$
      - Zeroth-order: $C_t = C_0 - Kt$; $t_{1/2} = \frac{C_0}{2K}$
    - gives **Reaction order**
      - Always experimental
      - Can be (+)ve, (–)ve, or Zero, fractional
      - Varies with conditions

MISCELLANEOUS SOLVED PROBLEMS (MSPS)

Ex-1. For each reaction below, express the rates of change of [product] and [reactant] in the correct relationship to each other.

(a) $2O_3(g) \rightarrow 3O_2(g)$ (b) $2HOF(g) \rightarrow 2HF(g) + O_2(g)$
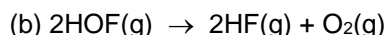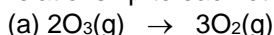
Sol. (a) $-\dfrac{1}{2}\dfrac{d[O_3]}{dt} = +\dfrac{1}{3}\dfrac{d[O_2]}{dt}$ (b) $-\dfrac{1}{2}\dfrac{d[HOF]}{dt} = +\dfrac{1}{2}\dfrac{d[HF]}{dt} = +\dfrac{d[O_2]}{dt}$

$\dfrac{-d[O_3]}{dt} = \dfrac{2}{3}\dfrac{d}{dt}[O_2]$ $\dfrac{-d[HOF]}{dt} = +\dfrac{d[HF]}{dt} = +\dfrac{2d[O_2]}{dt}$

Ex-2. In a catalytic experiment involving the Haber's process, $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of reaction was measured as rate = 2×10^{-4} M.s^{-1}. If there were no side reactions, express the rate of reaction in terms of (a) N_2 (b) H_2?

Sol. Rate of Reaction $= -\dfrac{d[N_2]}{dt} = \dfrac{-1}{3}\dfrac{d[H_2]}{dt} = +\dfrac{1}{2}\dfrac{d[NH_3]}{dt}$

(a) $2 \times 10^{-4} = -\dfrac{d[N_2]}{dt}$

(b) $2 \times 10^{-4} \times 3 = -\dfrac{d[H_2]}{dt} = 6 \times 10^{-4}$ MS^{-1}.

Ex-3. Write the units of the rate constants for a (i) Zeroth order, (ii) half order, (iii) first order, (iv) 3/2 order, (v) second order, (vi) 5/2 order, (vii) third order reactions.

Sol. Unit of Rate Constant = $(Mole)^{1-n}(Litre)^{n-1} Sec^{-1}$ Where n is the order of Reaction

(i) For Zeroth order = $Mole^{(1-0)}(Litre)^{(0-1)} Sec^{-1}$

Unit of K

n = 0 $Mole\, Litre^{(-1)} Sec^{-1}$

Similarly For others

Ex-4. The reaction $CO(g) + NO_2(g) \rightarrow CO_2 + NO$ is second order in NO_2 and zero order in CO at temperatures less than 500K.

(a) Write the rate expression for the reaction.

(b) How will the reaction rate change if the NO_2 concentration is halved?

Sol. (a) $\dfrac{-d}{dt}[CO] = \dfrac{-d}{dt}(NO_2) = K[NO_2]^2$ Order is zero w.r.t. CO but Conc will Still change

(b) Rate of Rxn = $K[NO_2]^2$ of Conc of NO_2 Half The Rate becomes One fourth

Ex-5. For a reaction $A + 3B \rightarrow$ Product, Rate = $\{-d[A]/dt\} = k[A]^2[B]$, the expression for the rate of reaction in terms of change in the concentration of B; $\{-d[B]/dt\}$ will be :

(A) $k[A]^2[B]$ (B) $k[A]^2[3B]$ (C) $3k[A^2][B]$ (D) $(1/3)k[A^2][B]$

Sol. **(C)** For the given reaction

$\dfrac{-d[A]}{dt} = \dfrac{1}{3}\dfrac{-d[B]}{dt} = K[A]^2[B]$

then $\dfrac{-d[B]}{dt} = 3K[A]^2[B]$

Ex-6. Gaseous cyclobutane isomerizes to butadiene in a first order process which has k = 3.3×10^{-4} s^{-1} at 153^{0}C. How many minutes would it take for the isomerization to proceed 40% completion at this temperature.

Sol. For the First order Rxn

$t = \dfrac{2.303}{K}\log\dfrac{a}{(a-x)}$ $t = \dfrac{2.303}{3.3 \times 10^{-4}}\log\left(\dfrac{100}{60}\right)$

$t = 1.54 \times 10^{+3}$ Second.   = 25.80 Minute

Ex-7. Calculate $\dfrac{t_{0.5}}{t_{0.25}}$ for a 1st order reaction

Sol. $\dfrac{t_{0.5}}{t_{0.25}} = \dfrac{\dfrac{2.303}{K}\log\dfrac{a}{(a-\frac{a}{2})}}{\dfrac{2.303}{K}\log\dfrac{a}{(a-\frac{a}{4})}} = \dfrac{\log 2}{(\log\frac{4}{3})}$ = Ans.

Ex-8. For the reaction A + B $\longrightarrow$ products
the following date were obtained :

Initial rate *(mole/liter.sec)*	0.030	0.059	0.060	0.090	0.089
[A] *(mole/liter)*	0.10	0.20	0.20	0.30	0.30
[B] *(mole/liter)*	0.20	0.20	0.30	0.30	0.50

Write the rate equation for this reaction. Be sure to evaluate k.

Sol. Rate = $K[A]^x [B]^y$
From data I. $0.030 = K [0.10]^x [0.20]^y$ (1)
From data II. $0.059 = K [0.20]^x [0.20]^y$ (2)
From III. $0.060 = K [0.20]^x [0.30]^y$ (3)
divide 1 equation by (2)

$\dfrac{0.030}{0.059} = \dfrac{K[0.10]^x[0.20]^y}{K[0.20]^x[0.20]^y}$ $\Rightarrow$ x = 1

Then divide (2) equation by (3)

$\dfrac{0.059}{0.060} = \dfrac{K[0.20]^x[0.20]^y}{K[0.20]^x[0.30]^y}$ $\Rightarrow$ y = 0
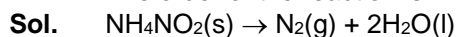
Put the value of x and y in (1) equation
$0.030 = K[0.10]^1 [0.20]^0$
$K = \dfrac{0.030}{0.10}$ = 0.3 sec^{-1}

Ex-9. The following data is for the decomposition of ammonium nitrite in aqueous solution.

Volume of N_2 in cc.	Time (minutes)
6.25	10
9.00	15
11.40	20
13.65	25
35.05	infinity

The order of the reaction is

Sol. $NH_4NO_2(s) \rightarrow N_2(g) + 2H_2O(l)$
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
$a \propto V_\infty$
$(a - x) \propto V_\infty - V_t$
Then from the given data we assume the Rxn is first order Then

$K = \dfrac{2.303}{t}\log\dfrac{a}{(a-x)} = \dfrac{2.303}{t}\log\dfrac{V_\infty}{V_\infty - V_t}$

From Ist data $K = \dfrac{2.303}{10}\log\dfrac{35.05}{(35.05-6.25)}$ = 1.96 × 10^{-2} sec^{-1}

IInd data $K = \dfrac{2.303}{15}\log\dfrac{35.05}{(35.05-9)}$ = 1.96 × 10^{-2} sec^{-1}

IIIrd data $K = \dfrac{2.303}{20}\log\dfrac{35.05}{(35.05-11.40)}$ = 1.96 × 10^{-2} sec^{-1}

From these relation the value of K are same the reaction will be First order

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Ex-10. Decomposition of H_2O_2.

$$H_2O_2 \longrightarrow H_2O\ (\ell) + \frac{1}{2} O_2\ (g)$$
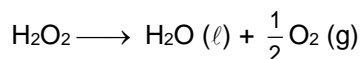
The progress of this reaction is measured by titrating the reaction mixture with $KMnO_4$ at different time intervals. Calculate rate constant of the reaction in terms of volume of $KMnO_4$ consumed at time t = 0, V_0 and at time t, V_t.

Sol. Assume the decomposition of H_2O_2 is a first order reaction

$$H_2O_2 \rightarrow H_2O\ (l) + \frac{1}{2} O_2(g)$$
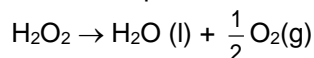
$KMnO_4$ react only with the H_2O_2 them

For I^{st} order reaction $K = \dfrac{2.303}{t} \log \dfrac{a}{(a-x)}$

Then $a\,\alpha\ V_0$ and $(a-x)\alpha\ V_t$

Then $K = \dfrac{2.303}{t} \log\left(\dfrac{V_0}{V_t}\right)$

Ex-11. $A \xrightarrow{\ D\ } B + C$

Time	0	t	∞
Volume of reagent	V_1	V_2	V_3

The reagent reacts with only B, C and D. Find k.

Sol. $A \xrightarrow{\quad D \quad} B + C$

at t = 0	a	0	0
t = t	(a – x)	x	x
t = ∞	o	a	a

at t = 0   only D. React

after t = 0 reagent react with B.C.D.

$2a\ \alpha\ (V_3 - V_1)$

$A\ \alpha\ \dfrac{(V_3 - V_1)}{2}$

$2x\ \alpha\ (V_2 - V_1)$

$2(a - x)\ \alpha\ (V_3 - V_1 - V_2 + V_1)$

$(a - x)\ \alpha\ \dfrac{(V_3 - V_2)}{2}$

Then, $K = \dfrac{1}{t} \ln \dfrac{(V_3 - V_1)}{(V_3 - V_2)}$

Ex-12. $A \rightarrow B + C$

Time	0	t
Volume of reagent	V_1	V_2

The reagent reacts with A, B and C. Find k.

Sol. $A \rightarrow B + C$
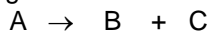
t = 0	a	0	0
t = t	(a – x)	x	x

$a\,\alpha\ V_1$

$(a – x) + x + x\ \alpha\ V_2$

$(a + x)\ \alpha\ V_2$

$(a - x)\ \alpha\ (2V_1 - V_2)$; $K = \dfrac{1}{t} \ln \dfrac{[A]_o}{[A]_t} = \dfrac{1}{t} \ln \dfrac{V_1}{(2V_1 - V_2)}$

Ex-13. $A \rightarrow B + C$

Time	T	∞
Volume of reagent	V_2	V_3

Reagent reacts with all A, B and C and have 'n' factors in the ratio of 1 : 2 : 3 with the reagent. Find k.

Sol.
$$A \rightarrow B + C$$

t = 0	a	0	0
t = t	(a– x)	x	x
t = ∞	0	a	a
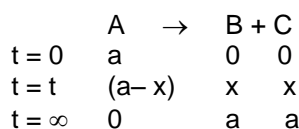
Reagent React with all A, B, C. and have 'n' factor in the Ratio 1 **:** 2 **:** 3

$$(2a + 3a) \, \alpha \, V_3$$

$$a \, \alpha \, \frac{V_3}{5}$$

$$(a - x) \times 1 + 2x + 3x \, \alpha \, V_2$$

$$(a + 4x) \, \alpha \, V_2$$

$$\frac{V_3}{5} + 4x \, \alpha \, V_2$$

$$x \, \alpha \, \frac{1}{4}\left(V_2 - \frac{V_3}{5}\right) \qquad \Rightarrow \qquad (a - x) \, \alpha \, \frac{V_3}{5} - \frac{1}{4}\left(V_2 - \frac{V_3}{5}\right)$$

$$(a-x) \, \alpha \, \frac{5(v_3 - v_2)}{20} \qquad \Rightarrow \qquad K = \frac{1}{t} \, \ln \frac{4V_3}{5(v_3 - v_2)}$$

Ex-14. Now, let us assume that A, B and C are optically active compounds, which rotate the plane polarized light in the clockwise or anticlockwise direction.

$$A(soln.) \longrightarrow B(soln.) + C(soln.)$$
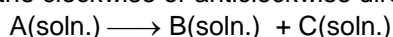
Time	0	t	∞
Total rotation in degrees	R_0	r_t	r_∞

Calculate the expression of rate constant.

Sol. The principle of the experiment is that change in the rotation is directly proportional to concentration.

$$a \, \alpha \, (r_0 - r_\infty)$$
$$(a - x) \, \alpha \, (r_t - r_\infty)$$

Then Expression For rate constant

$$K = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

Ex-15. The hydrolysis of cane sugar was studied using an optical polarimeter and the following readings were taken.

time (min.) :   0   84 min   ∞
observed rotation (degrees) :   50   20   –10

When will the mixture optically inactive? (log 2 = 0.3, log 3 = 0.48)

Sol. From the hydrolysis

$$K = \frac{2.303}{t} \log \frac{(r_0 - r_\infty)}{r_t - r_\infty} = \frac{2.303}{84} \log \frac{50 + 10}{20 + 10}$$

$$K = \frac{2.303}{84} \times 0.3010 = 8.252 \times 10^{-3}$$

The time taken when sample are optically Inactive is t

$$K = \frac{2.303 \times 0.3010}{84} = \frac{2.303}{t} \log \frac{50 + 10}{+10}$$

$$t = 217.14 \text{ minute}$$

Ex-16. The optical rotation of sucrose in 0.5 M HCl at 35^0C at various time intervals are given below. Show that the reaction is first order.

Time (minutes)	0	10	20	30	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	–11.1

Sol. If reaction first order the value of K same in First-Order Expression

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

$$K = \frac{2.303}{10} \log \frac{32.4 + 11.1}{28.8 + 11.1} = \frac{0.03751 \times 2.303}{10} = 8.63 \times 10^{-3}$$

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$$K = \frac{2.303}{20} \log \frac{32.4 + 11.1}{25.5 + 11.1} = 8.63 \times 10^{-3}$$

$$K = \frac{2.303}{30} \log \frac{32.4 + 11.1}{22.4 + 11.1} = 8.63 \times 10^{-3}$$

$$K = \frac{2.303}{40} \log \frac{32.4 + 11.1}{19.6 + 11.1} = 8.63 \times 10^{-3}$$

The reaction show 1st order kinetics

Ex-17. Temperature coefficient of the rate of a reaction is 3. How many times the rate of reaction would increase if temperature is raised by 30 K :
(A) 3   (B) 9   (C) 27   (D) 81

Sol. **(C)** For same concentration $\frac{R_2}{R_1} = \frac{K_2}{K_1} = 3^{\frac{30}{10}} = 27$.

Ex-18. The reaction A + B $\longrightarrow$ products is first order with respect to both A and B has a rate constant of 6.0 L mol^{-1} sec^{-1}. at 27°C. Calculate the initial rate of the reaction at 47°C when equal volumes of A and B of concentration 0.01 moles litre^{-1} in each are mixed. The activation energy of the energy of the reaction is 42 kJ mol^{-1} .

Sol. Reaction A + B $\longrightarrow$ Product

We know $\log \left(\frac{K_2}{K_1} \right) = \frac{\Delta E}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

$$\log \left(\frac{K_2}{K_1} \right) = \frac{\Delta E}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \left(\frac{K_2}{6} \right) = \frac{42 \times 10^3 [320 - 300]}{2.303 \times 8.3 \times 300 \times 320} = \frac{840}{1835.03}$$

$$\log \frac{K_2}{6} = .4577$$

$$\frac{K_2}{6} = \text{anti log } (.4577)$$

$K_2 = 2.863 \times 6 = 17.178$
Rate at 47°C will be
The Rate$_2$ = 17.178 × [0.01] × [0.01]
Rate$_2$ = 17.178 × 10^{-4} = 1.7178 × 10^{-3}

Ex-19. An exothermic reaction A $\rightarrow$ B has an activation energy of 17 KJ per mole of A. The heat of reaction is – 40 KJ/mole. The activation energy for the reverse reaction B $\rightarrow$ A is :
(A) 75 KJ per mole   (B) 67 KJ per mole   (C) 57 KJ per mole   (D) 17 KJ per mole

Sol. **(C)** $\Delta H = E_A - E_B$
$-40 = 17 - E_B$
$E_B = 57$

Ex-20. The rate of decomposition for methyl nitrite and ethyl nitrite can be given in terms of rate constant (in sec^{-1}) K_1 and K_2 respectively. The energy of activations for the two reactions are 152.30 kJ mol^{-1} and 157.7 kJ mol^{-1} as well as frequency factors are 10^{13} and 10^{14} respectively for the decomposition of methyl and ethyl nitrite. Calculate the temperature at which rate constant will be same for the two reactions.

**Sol.** Rate constant will be same.
$K_1 = K_2$

$$A_1 e^{\frac{-Ea_1}{RT}} = A_2 e^{\frac{-Ea_2}{RT}}$$

$$T = \frac{Ea_2 - Ea_1}{2.303 \log \left(\frac{A_2}{A_1} \right) \times R} \quad \Rightarrow \quad T = \frac{157.7 - 152.3}{2.303 \times 8 \times \log \left(\frac{10^4}{10^3} \right)} \quad \Rightarrow \quad T = 282K$$

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Ex-21. Use the diagram below to answer the following questions.

(a) Is the reaction exothermic or endothermic?

(b) What is the approximate value of ΔE for the forward reaction?

(c) What is activation energy in each direction?

(d) A catalyst is found that lowers the activation energy of the reaction by about 10 kJ/mol. How will this catalyst affect the rate of the reverse reaction?

Sol.

Reaction coordinate
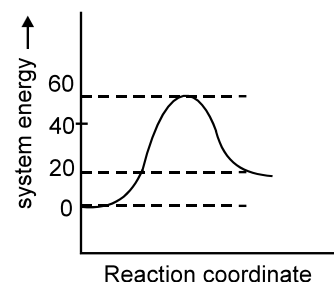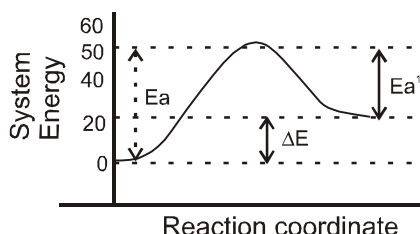
(a) Forward Rxn are endothermic

(b) $\Delta E = (E_a - E_a^1) = (50 - 30) = 20$ KJ / Mole.

(c) $E_{af} = 50$ KJ/Mole, $E_{ab} = 30$ KJ/Mole

(d) Increases

Ex-22. The rate of a first order reaction is 0.05 mole/L/s at 10 minutes and 0.04 mole/L/s at 30 minutes after initiation. Find the half-life of the reaction

Sol. Let the concentrations of the reactant after 10 min and 30 min be C_1 and C_2 respectively.

Rate after 10 min = $KC_1 = 0.05 \times 60$ and Rate after 30 min = $KC_2 = 0.04 \times 60$

$\therefore \quad \dfrac{c_1}{c_2} = \dfrac{5}{4}$.

Supposing the reaction starting after 10 minutes

$$k = \frac{2.303}{20} \log \frac{c_1}{c_2} = \frac{2.303}{20} \log \frac{5}{4} = 0.011159$$

$\therefore \quad t_{1/2} = \dfrac{0.6932}{k} = \dfrac{0.6932}{0.011159} = 62.12$ min.

Ex-23. For a chemical reaction A+B $\rightarrow$ Product, the order is 1 with respect to each of A and B Find x and y from the given data.

Rate (moles/L/s)	[A]	[B]
0.10	0.1 M	0.1M
0.80	x M	0.1M
0.40	0.2 M	y M

Sol. The rate law may be written as

rate = k [A] [B]

Substituting the first set of data in the rate law, we get,

0.10 = k × 0.1 × 0.1 $\Rightarrow$ k = 10

Now substituting the second and third sets of data, we get,

0.8 = 10 × x × 0.1 $\Rightarrow$ x = 0.80 M

and, 0.4 = 10 × 0.2 × y $\Rightarrow$ y = 0.20 M.

Ex-24. In the decomposition of H_2O_2 at 300 K, the energy of activation was found to be 16 kcal/ mole, while it decreased to 10 kcal/ mole when the decomposition was carried out in the presence of a catalyst at 300 K, How many times is the catalysed reaction faster than the uncatalysed one?

Sol. Suppose E_1 and E_2 are the energies of activation when the reaction is carried out in the absence and presence of a catalyst respectively.

Thus, $k_1 = Ae^{-E_1/RT}$, $\qquad k_2 = Ae^{-E_2/RT}$

Taking log, $\ln k_1 = \ln A - \dfrac{E_1}{RT}$

$\ln k_2 = \ln A - \dfrac{E_2}{RT}$

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$$\therefore \quad \ln k_2 - \ln k_1 = -\frac{E_2}{RT} + \frac{E_1}{RT} \qquad \text{or} \qquad \ln\frac{k_2}{k_1} = \frac{1}{0.002\times300}(16-10) = \frac{6}{0.002\times300}$$

$$2.303 \log\frac{k_2}{k_1} = 10$$

$$\log\frac{k_2}{k_1} = \frac{10}{2.303} = 4.342$$

Taking antilog $\frac{k_2}{k_1} = 2.190 \times 10^4$

Ex-25. In Arrhenius`s equation for a certain Reaction, the value of A and E (activation energy) are 6×10^{13} s^{-1} and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half-life period be 20 minutes ?

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

$$\ln k = \ln A - \frac{E}{RT}$$

$$2.303 \log k = 2.303 \log A - \frac{E}{RT} \qquad \text{or} \qquad \log k = \log A - \frac{E}{2.303 RT} . \qquad .....(1)$$

Given that $\qquad A = 6 \times 10^{13}$ s^{-1}, E = 98.6 kJ mol^{-1}
$$t_{1/2} = 20 \times 60 \text{ s.}$$

For first-order reaction $k = \dfrac{0.6932}{t_{1/2}} = \dfrac{0.6932}{1200}$ s^{-1}

Thus (1) becomes,
$$\log\frac{0.6932}{1200} = \log(6\times10^{13}) - \frac{98.6}{2.303\times8.314\times10^{-3}\times T} \qquad [\text{R} = 8.314 \times 10^{-3} \text{ kJ/K/mol}]$$
$$T = 302.26 \text{ K.}$$

Ex-26. The decomposition of N_2O_5 according to the equation, $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$
is a first-order reaction. After 30 minutes from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction.

Sol.
$$\qquad\qquad\qquad 2N_2O_5 \rightarrow 4NO_2 + O_2$$
at t = 0 $\qquad\qquad$ a
After 30 min: $\qquad$ a – x $\qquad$ 2x $\qquad$ x/2

$$\therefore \quad (a-x) + 2x + \frac{x}{2} = 284.5 \qquad \text{or} \qquad a + \frac{3x}{2} = 284.5 \qquad ....(1)$$

After complete decomposition of N_2O_5.
$$\qquad\qquad\qquad 2N_2O_5 \rightarrow 4NO_2 + O_2$$
$$\qquad\qquad\qquad 0 \qquad\quad 2a \quad\quad a/2$$
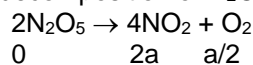
$$\therefore \quad 2a + \frac{a}{2} = 584.5 \qquad \text{or} \qquad \frac{5a}{2} = 584.5 \qquad ....(2)$$

From (1) and (2), we get,
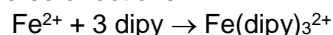$$a = 233.5, \ x = 34$$
Thus, for a first-order reaction of the type 2A $\rightarrow$ products

$$k = \frac{1}{2t}\log\frac{a}{a-x}$$

$$k = \frac{2.303}{2\times30}\log\frac{233.5}{233.5-34} = 2.625 \times 10^{-3} \text{ min}^{-1}$$

Ex-27. The complexation of Fe^{2+} with the chelating agent dipyridyl has been studied kinetically in both forward and reverse directions.
$$Fe^{2+} + 3 \text{ dipy} \rightarrow Fe(dipy)_3^{2+}$$
Rate (forward) = (1.80×10^{13}) [Fe^{2+}] [dipy]^3
and rate (reverse) = (1.20×10^{-4}) [Fe (dipy)$_3^{2+}$]
Find the stability constant for the complex.

Sol. At dynamic equilibrium,
rate of formation of complex = rate of its decomposition
$$(1.8 \times 10^{13}) \, [Fe^{2+}] \, [dipy]^3 = (1.20 \times 10^{-4}) \, [Fe(dipy)_3^{2+}]$$
$$K_s = \frac{[Fe(dipy)_3^{2+}]}{[Fe^{2+}][dipy]^3} = \frac{1.8 \times 10^{13}}{12 \times 10^{-4}} = 1.5 \times 10^{17}$$

**Ex-28.** The approach to the following equilibrium was observed kinetically from both directions.
$$PtCl_4^{2-} + H_2O \rightleftharpoons Pt(H_2O)Cl_3^- + Cl^- \text{ at } 25^oC \text{ It was found that}$$
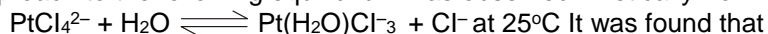
$$-\frac{d[PtCl]^{2-}}{dt} = (4.8 \times 10^{-5}) \, [PtCl_4]^{2-} - (2.4 \times 10^{-3}) \, [Pt(H_2O)Cl_3^-] \, [Cl^-]$$

Calculate the equilibrium constant for the complexation of Cl^- with Pt(II).

Sol. At equilibrium, $\dfrac{d[PtCl_4]^{2-}}{dt} = 0$

Hence, $4.8 \times 10^{-5} \, [PtCl^{2-}_4] = 2.4 \times 10^{-3} \, [Pt(H_2O)Cl_3^-] \, [Cl^-]$

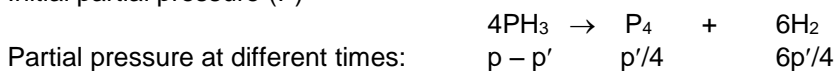or $\quad K = \dfrac{[PtCl_4]^{2-}}{[Pt(H_2O)Cl_3^-][Cl^-]} = \dfrac{2.4 \times 10^{-3}}{4.8 \times 10^{-5}} = 50.$

Ex-29. Some $PH_3(g)$ is introduced into a flask at 600^oC containing an inert gas PH_3 proceeds to decompose into $P_4(g)$ and $H_2(g)$ and the reaction goes to completion. The total pressure is given below as a function of time. Find the order of the reaction and calculate the rate constant for the reaction:

Time (s)	0	60	120	∞
p mm (Hg)	262.40	272.90	275.51	276.40

$$4PH_3 \rightarrow P_4 + 6H_2$$
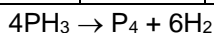
Sol. Let the initial Partial pressures of PH_3 and the inert gas be p and p' mm respectively and p' mm of PH_3 decomposes at different time intervals.
Initial partial pressure (P)

$$\qquad\qquad\qquad 4PH_3 \;\rightarrow\; P_4 \;+\; 6H_2$$
Partial pressure at different times: $\quad p - p' \qquad p'/4 \qquad 6p'/4$
As given, at t = 0 seconds.
$$p + p' = 262.40 \qquad\qquad\qquad ...(1)$$
and, t = 60 second $\quad p - p' + \dfrac{p'}{4} + \dfrac{6p'}{4} + p' = 272.90 \qquad ...(2)$

At t = ∞: $\quad \dfrac{p}{4} + \dfrac{6p}{4} + p' = 276.40. \qquad ...(3)$

Solving, equations (1), (2) and (3), we get,
$$p = 18.67 \text{ and } p' = 14.$$
Similarly, at t = 120 seconds
$$p - p' + \dfrac{p'}{4} + \dfrac{6p'}{4} + p' = 275.51. \qquad ...(4)$$
Solving, equations (1), (4) and (3), we get
$$p = 18.67 \text{ and } p' = 17.48.$$
As the given reaction is of the type $nA \rightarrow$ products, where n = 4, we have the following equation for first-order kinetics
$$k_1 = \frac{2.303}{4t} \log\frac{a}{a-x} = \frac{2.303}{4t} \log\frac{p}{p-p'}.$$

Thus, at t = 60s; $\quad k_1 = \dfrac{2.303}{4 \times 60} \log \dfrac{18.67}{18.67-14} = 5.8 \times 10^{-3} \, s^{-1}$

$\qquad$ t = 120s; $\quad k_1 = \dfrac{2.303}{4 \times 120} \log \dfrac{18.67}{18.67-17.48} = 5.8 \times 10^{-3} \, s^{-1.}$

As the values of k_1 are constant, the given reaction following the first order kinetics.

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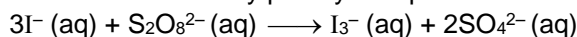ADVCHK - 33

Exercise-1

✎ **Marked questions are recommended for Revision.**

PART - I : SUBJECTIVE QUESTIONS

CHEMICAL KINETICS-I

Section (A) : Rate of chemical reaction and Dependence of Rate : Basic

A-1. The oxidation of iodide ion by peroxy disulphate ion is described by the equation :

$$3I^- (aq) + S_2O_8^{2-} (aq) \longrightarrow I_3^- (aq) + 2SO_4^{2-} (aq)$$

(a) If $-\dfrac{\Delta[S_2O_8^{2-}]}{\Delta t} = 1.5 \times 10^{-3}$ Ms^{-1} for a particular time interval, what is the value of $-\dfrac{\Delta[I^-]}{\Delta t}$ for the same time interval ?

(b) What is the average rate of formation of SO_4^{2-} during that time interval ?

A-2. ✎ In the following reaction $2H_2O_2$ (aq) $\longrightarrow 2H_2O(\ell) + O_2$ (g) rate of formation of O_2 is 36 g min^{-1},

(a) What is rate of formation of H_2O? (b) What is rate of disappearance of H_2O_2?

A-3. Hydrogenation of vegetable ghee at 25ºC reduces the pressure of H_2 from 2 atm to 1.2 atm in 50 minute. Calculate the rate of reaction in terms of change :

(a) In pressure per minute. (b) In molarity per second.

A-4. The stoichiometric equation for the oxidation of bromide ions by hydrogen peroxide in acid solution is

$$2Br^- (aq) + H_2O_2 (aq) + 2H^+ (aq) \longrightarrow Br_2 (\ell) + 2H_2O (\ell)$$
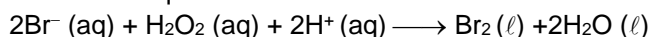
Since the reaction does not occur in one stage, the rate equation does not correspond to this stoichiometric equation but is rate = $k[H_2O_2] [H^+] [Br^-]$.

(a) If the concentration of H_2O_2 is increased by a factor of 3, by what factor is the rate of consumption of Br^- ions increased.

(b) If, under certain conditions, the rate of consumption of Br^- ions is 7.2×10^{-3} mole dm^{-3} s^{-1}, what is the rate of consumption of hydrogen peroxide. What is the rate of production of bromine.

(c) What is the effect on the rate constant k of increasing the concentration of bromide ions.

(d) If by the addition of water to the reaction mixture the total volume were doubled, what would be the effect on the rate of change of the concentration of Br^-. What would be the effect on the rate constant k.

Section (B) : Integrated rate law : Zero and First Order Reaction

B-1. For the zero order reaction A $\longrightarrow$ 2B, the rate constant is 2×10^{-6} M min^{-1}. The reaction is started with 10 M of A.

(i) What will be the concentration of A after 2 days? (ii) What is the initial half-life of the reaction ?

(iii) In what time, the reaction will complete?

B-2. ✎ Substance A reacts according to a first order rate law with k = 5×10^{-5} s^{-1}.

(a) If the initial concentration of A is 1.0 M, what is initial rate.

(b) What is the rate after 1.0 hour. (Given $e^{-0.18} = 0.84$)

B-3. ✎ A and B are two different chemical species undergoing 1st order decomposition with half lives equal to 5 sec. and 7.5 sec. respectively. If the initial concentration of A and B are in the ratio 3 : 2. Calculate $\dfrac{C_{A_t}}{C_{B_t}}$ after three half lives of A. Report your answer after multiplying it with 100.

B-4. ✎ In the biological processes, the time taken by certain virus or bacteria to double its population, is called generation time. In milk, at 37ºC, lactobacillus acidophilus has a generation time of about 75 min. Calculate the population relative to the initial value at 60 min.

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Section (C) : Integrated Rate law : Second Order & Pseudo first order reaction

C-1. The rate constant for a certain second order reaction is 8×10^{-5} M^{-1} min^{-1} . How long will it take a 1 M solution to be reduced to 0.5 M in reactant ? How long will it take from that point until the solution is 0.25 M in reactant.

C-2. Compound A and B react to form C and D in a reaction that was found to be second-order over all and second-order in A . The rate constant –at 30ºC is 0.622 L mol^{-1} min^{-1}. What is the half-life of A when 4.10×10^{-2} M of A is mixed with excess B ?

C-3. The reaction $CH_3-CH_2-NO_2 + OH^- \longrightarrow CH_3-\overset{\ominus}{CH}-NO_2 + H_2O$ obeys the rate law for pseudo first order kinetics in the presence of a large excess of hydroxide ion. If 1% of nitro ethane undergoes reaction in half a minute when the reactant concentration is 0.002 M. What is the pseudo first order rate constant ? (log 99 = 1.996)

Section (D) : Experimental method to calculate order and rate law of reaction and methods to monitor the progress of reaction

D-1. The following data are for the reaction A + B $\rightarrow$ products :

conc. A (M)	conc. B (M)	Initial Rate (mol L^{-1} s^{-1})
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	2.0×10^{-3}
0.5	0.5	1.0×10^{-2}

(i) What is the order with respect to A and B for the reaction?
(ii) Calculate the rate constant.
(iii) Determine the reaction rate when the concentrations of A and B are 0.20 M and 0.35 M, respectively.

D-2. **(a)** The half life period and initial concentration for a reaction are as follows. What is order of reaction?

Initial concentration	350	540	158
$t_{1/2}$	425	275	941

(b) The half-life period for the thermal decomposition of PH_3 at three different pressures are given below

Initial pressure (mm Hg)	707	79	37.5
Half--life (seconds)	84	84	83

What is the order of the reaction ?

D-3. For the reaction A $\longrightarrow$ products, the following data is given for a particular run.

time (min.) : 0 5 15 35

$\dfrac{1}{[A]}$ (M^{-1}) : 1 2 4 8

Determine the order of the reaction.

Section (E) : Method to monitor the progress of Reactions (Titration Method and Optical Activity Method)

E-1. The kinetic of hydrolysis of methyl acetate in excess dilute HCl at 25°C were followed by withdrawing 2 mL of the reaction mixture at intervals of (t), adding 50 mL water and titrating with baryta water. Determine the velocity constant of hydrolysis.

t (in minute)	0	75	119	259	∞
Titre value (in mL)	19.24	24.20	26.60	32.23	42.03

$[\ln \dfrac{22.79}{17.83} = 0.2454, \ln \dfrac{22.79}{15.43} = 0.39, \ln \dfrac{22.79}{9.8} = 0.8439]$

E-2. The decomposition of hydrogen peroxide in an aqueous solution is a first order reaction. It can be studied by titrating quickly 10 mL portions of reactions mixture at various times from the t = 0 of reaction against a standard solution of $KMnO_4$. Volume of $KMnO_4$ solution used in each case is proportional to the remaining concentration of H_2O_2.

From the following data calculate the rate constant of the reaction,

Time (seconds)	0	600	1200
$KMnO_4$ solution used (mL)	22.8	13.8	8.2

E-3. For a first order reaction A $\longrightarrow$ 2B + C. It was found that at the end of 10 minutes from the start, the total optical rotation of the system was 60° and when the reaction is complete, it was 180°. The B and C are only optically active and intially only A was taken.

(i) What is the rate constant of the above reaction (in hour^{-1}) ?

(ii) At what time (in minute) from the start, total optical rotation will be 90°.

(Take log2 = 0.3, log3 = 0.48, log7 = 0.85, ln10 = 2.3)

Section (F) : Complication in 1st Order Reaction

F-1. For a first order reaction

$$A \underset{K_2}{\overset{K_1}{\big\langle}} \begin{matrix} 2B \\ 3C \end{matrix}$$
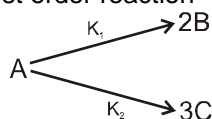
Percentage of B in the product is 30%.Calculate the value of k_1 and k_2. (($t_{1/2})_{over\ all}$ = 100 hr))

F-2. An organic compound dissociates into n parallel first order reactions simultaneously and produces n different products P_1, P_2, P_3, ..., P_n having rate constants k, 2k, 3k, ..., nk and activation energies E, 2E, 3E ...., nE respectively. Calculate the overall energy of activation of the compound P.

CHEMICAL KINETICS-II

Section (G) : Temperature dependence of rate

**G-1.** From the following data for the reaction between A and B.

	[A] (mole dm^{-3})	[B] (mole dm^{-3})	Initial rate (mole dm^{-3} min^{-1}) 300 k	Initial rate (mole dm^{-3} min^{-1}) 320 k
(i)	2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	
(ii)	5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	2.0×10^{-3}
(iii)	1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	

Calculate the following

(i) The order w.r.t. A and w.r.t. B   (ii) The rate constant at 300 K

(iii) The energy of activation   (iv) The pre-exponential factor

[$e^{-22.18}$ = 2.3283 × 10^{-10} , ln2 = 0.693]

**G-2.** Find out the percentage of the reactant molecules crossing over the activation energy barrier at 325 K, given that ΔH_{325} = 0.12 kcal, $E_{a(b)}$ = + 0.02 kcal.

G-3. Consider the following figure for the reaction :

$$A + B \longrightarrow M + N$$
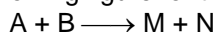
Answer the following :

(A) Energy level of (A + B)

(B) Energy lelvel of (M + N)

(C) Threshold energy level for the reaction

(D) Energy of activation for the forward reaction.

(E) Energy of activation for the backward reaction.

(F) ΔH or heat of reaction.
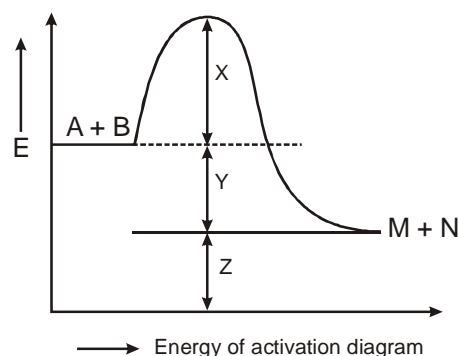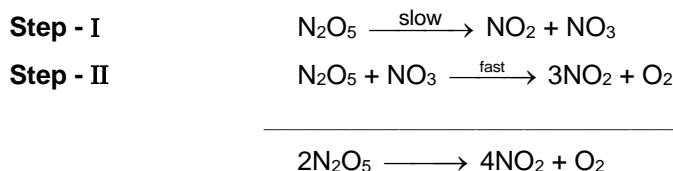

Energy of activation diagram

Section (H) : Catalyst dependence of rate and type of Reaction and Determination of rate law and order with the help of given mechanism
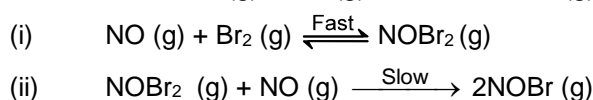
H-1. On introducing a catalyst at 500 K, the rate of a first order increase to 1.718 times. The activation energy in the presence of a catalyst is 6.05 KJ/mole. The slope of the plot of lnk (sec^{-1}) against 1/T in the absence of catalyst is.

**H-2.** The thermal decomposition of N_2O_5 occurs in the following steps.

Step - I $\qquad$ $N_2O_5 \xrightarrow{\text{slow}} NO_2 + NO_3$

Step - II $\qquad$ $N_2O_5 + NO_3 \xrightarrow{\text{fast}} 3NO_2 + O_2$

_____

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

suggest the rate expression.

H-3. The reaction $2NO\ (g) + Br_2\ (g) \longrightarrow 2NOBr\ (g)$, obeys the following mechanism.

(i) $\qquad NO\ (g) + Br_2\ (g) \underset{}{\overset{\text{Fast}}{\rightleftharpoons}} NOBr_2\ (g)$

(ii) $\qquad NOBr_2\ (g) + NO\ (g) \xrightarrow{\text{Slow}} 2NOBr\ (g)$

Suggest the rate expression.

H-4. Given the following steps in the mechanism for a chemical reaction :

$\qquad A + B \longrightarrow C \qquad$ (fast)

$\qquad B + C \longrightarrow D + E \qquad$ (slow)

$\qquad D + F \longrightarrow A + E \qquad$ (fast)
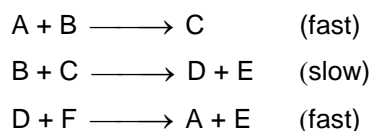
At any time [C] is directly proportional to [A].

(a) What is the stoichiometric equation for the reaction ?

(b) Which species, if any, are catalysts in this reaction ?

(c) Which species, if any, are intermediates in this reaction?

(d) Write the rate law for the rate-determining step.

(e) Write the rate law for this reaction.

(f) What is overall order of the reaction ?

Section (I) : Radio Activity

I-1. The activity of a radio-isotope falls to 12.5% in 90 days. Compute the half life and decay constant of the radio-isotope.

I-2. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half life of 5770 years. What is the rate constant (in years $^{-1}$) for the decay? What fraction would remain after 11540 years.

I-3. 1 gram of $_{79}Au^{198}$ ($t_{1/2}$ = 65 hrs) decays by beta emission and produces stable mercury. How much mercury will be present after 260 hours.

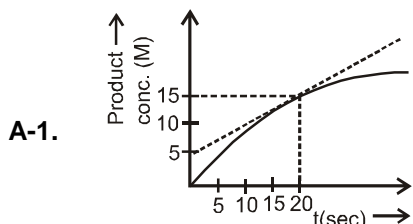**I-4.** A sample of U^{238} (half life = 4.5×10^9 year) ore is found to contain 23.8 g of U^{238} and 20.6 g of Pb^{206}. Calculate the age of the ore.

PART - II : ONLY ONE OPTION CORRECT TYPE

CHEMICAL KINETICS-I

Section (A) : Rate of chemical reaction and Dependence of Rate : Basic

A-1.

Rate of formation of product at t = 20 seconds is

(A) $0.5 \, MS^{-1}$ (B) $1 \, M \, S^{-1}$ (C) $1.5 \, M \, S^{-1}$ (D) $2MS^{-1}$

A-2. In the following reaction : $xA \longrightarrow yB$

$$\log \left[-\frac{d[A]}{dt} \right] = \log \left[\frac{d[B]}{dt} \right] + 0.3$$

where –ve sign indicates rate of disappearance of the reactant. Thus, x : y is :
(A) 1 : 2   (B) 2 : 1   (C) 3 : 1   (D) 3 : 10

A-3. Rate of formation of SO_3 in the following reaction $2SO_2 + O_2 \rightarrow 2SO_3$ is 100 g min^{-1}. Hence rate of disappearance of O_2 is :
(A) 50 g min^{-1} (B) 40 g min^{-1} (C) 200 g min^{-1} (D) 20 g min^{-1}

A-4. $aA + bB \longrightarrow$ Product, $dx/dt = k \, [A]^a \, [B]^b$. If concentration of A is doubled, rate is four times. If concentration of B is made four times, rate is doubled. What is relation between rate of disappearance of A and that of B ?
(A) $-\{d[A] / dt\} = -\{d[B] / dt\}$ (B) $-\{d[A] / dt\} = -\{4 \, d[B] / dt\}$
(C) $-\{4 \, d[A] / dt\} = -\{d[B] / dt\}$ (D) None of these

A-5. For the reaction, $2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$ the rate expression can be written in the following ways:

$\{d[N_2] / dt\} = k_1 [NO][H_2]$; $\{d[H_2O] / dt\} = k[NO][H_2]$; $\{- d[NO] / dt\} = k'_1 [NO] [H_2]$; $\{-d[H_2] / dt\} = k''_1 [NO][H_2]$

The relationship between k, k_1 , k'_1 and k''_1. is :

(A) $k = k_1 = k'_1 = k''_1$ (B) $k = 2k_1 = k'_1 = k''_1$ (C) $k = 2k'_1 = k_1 = k''_1$ (D) $k = k_1 = k'_1 = 2 \, k''_1$

A-6. For a reaction $pA + qB \rightarrow$ products, the rate law expression is $r = k[A]^1 [B]^m$, then :
(A) $(p+1) < (1+ m)$ (B) $(p + q) > (1 + m)$
(C) $(p + q)$ may or may not be equal to $(1+ m)$ (D) $(p + q) = (1 + m)$

A-7. For the irreversible process, $A + B \longrightarrow$ products, the rate is first–order w.r.t. A and second–order w.r.t. B. If 1.0 mol each of A and B introduced into a 1.0 L vessel, and the initial rate was 1.0×10^{-2} mol $L^{-1} \, s^{-1}$, rate when half reactants have been turned into products is :
(A) 1.25×10^{-3} mol $L^{-1} \, s^{-1}$ (B) 1.0×10^{-2} mol $L^{-1} \, s^{-1}$
(C) 2.50×10^{-3} mol $L^{-1} \, s^{-1}$ (D) 2.0×10^{-2} mol $L^{-1} \, s^{-1}$

A-8. If rate constant is numerically the same for the three reactions of first, second and third order respectively. Assume all the reactions of the kind A $\rightarrow$ products. Which of the following is correct :
(A) if $[A] = 1$ then $r_1 = r_2 = r_3$ (B) if $[A] < 1$ then $r_1 > r_2 > r_3$
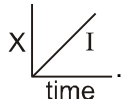(C) if $[A] > 1$ then $r_3 > r_2 > r_1$ (D) All

Section (B) : Integrated rate law : Zero and First Order Reaction

B-1. The rate constant of the reaction $A \rightarrow 2B$ is 1.0×10^{-3} mol lit^{-1} min^{-1}, if the initial concentration of A is 1.0 mole lit^{-1} what would be the concentration of B after 100 minutes.
(A) 0.1 mol lit^{-1} (B) 0.2 mol lit^{-1} (C) 0.9 mol lit^{-1} (D) 1.8 mol lit^{-1}

B-2. A drop of solution (volume 0.05 mL) contains 3.0×10^{-6} moles of H^+. If the rate constant of disappearance of H^+ is 1.0×10^7 mole litre^{-1} sec^{-1}. How long would it take for H^+ in drop to disappear :
(A) 6×10^{-8} sec (B) 6×10^{-7} sec (C) 6×10^{-9} sec (D) 6×10^{-10} sec

B-3. Graph between concentration of the product and time of the reaction $A \rightarrow B$ is of the type .
Hence graph between $- d[A]/dt$ and time will be of the type :

(A) (B) (C) (D)
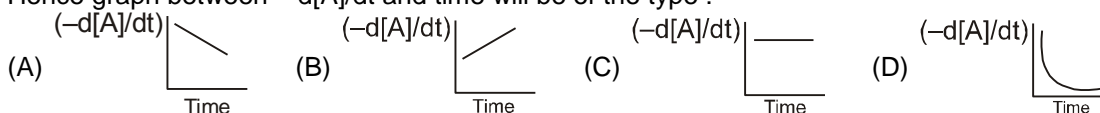
B-4. What will be the order of reaction and rate constant for a chemical change having log $t_{50\%}$ vs log concentration of (A) curves as :
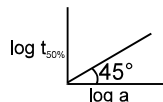
(A) 0, 1/2 (B) 1, 1 (C) 2, 2 (D) 3, 1

B-5. For a reaction $2A + B \rightarrow$ product, rate law is $-\dfrac{d[A]}{dt} = k[A]$. At a time when t = $\dfrac{1}{k}$, concentration of the reactant is : (C_0 = initial concentration)

(A) $\dfrac{C_0}{e}$ (B) $C_0 e$ (C) $\dfrac{C_0}{e^2}$ (D) $\dfrac{1}{C_0}$

B-6. Two substances A ($t_{1/2}$ = 5 min) and B ($t_{1/2}$ = 15 min) are taken in such a way that initially [A] = 4[B]. The time after which both the concentration will be equal is : (Assume that reaction is first order)
(A) 5 min (B) 15 min
(C) 20 min (D) concentration can never be equal

B-7. A reaction follows the given concentration (M)–time graph. The rate for this reaction at 20 seconds will be :
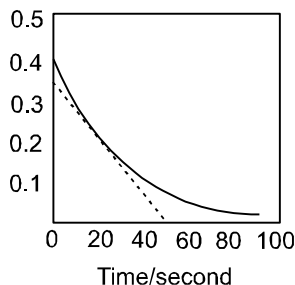
(A) 4×10^{-3} M s^{-1} (B) 8×10^{-2} M s^{-1} (C) 2×10^{-2} M s^{-1} (D) 7×10^{-3} M s^{-1}

B-8. In a first order reaction the reacting substance has half-life period of ten minutes. What fraction of the substance will be left after an hour the reaction has occurred ?
(A) 1/6 of initial concentration (B) 1/64 of initial concentration
(C) 1/12 of initial concentration (D) 1/32 of initial concentration

B-9. A certain zero order reaction has k = 0.025 M s^{-1} for the disappearance of A. What will be the concentration of A after 15 seconds if the initial concentration is 0.50 M ?
(A) 0.50 M (B) 0.375 M (C) 0.125 M (D) 0.060 M

Section (C) : Integrated Rate law : Second Order & Pseudo first order reaction

C-1. A reaction, which is second order, has a rate constant of 0.002 L mol^{-1} s^{-1}. If the initial conc. of the reactant is 0.2 M. how long will it take for the concentration to become 0.0400 M ?
(A) 1000 sec
(B) 400 sec
(C) 200 sec
(D) 10, 000 sec

C-2. Which is not true for a second order reaction ?
(A) It can have rate constant 1×10^{-2} L mol^{-1} s^{-1}
(B) Its half-life is inversely proportional to its initial concentration
(C) Time to complete 75% reaction is twice of half-life
(D) $T_{50} = \dfrac{1}{K \times \text{Initial conc.}}$

C-3. For the reaction $2NO_2 \longrightarrow N_2O_2 + O_2$, rate expression is as follows :
$-\dfrac{d[NO_2]}{dt} = k \,[NO_2]^n$, where $k = 3 \times 10^{-3}$ mol^{-1} L sec^{-1}. If the rate of formation of oxygen is 1.5×10^{-4}
mol L^{-1} sec^{-1}, then the molar concentration of NO_2 in mole L^{-1} is
(A) 1.5×10^{-4}
(B) 0.0151
(C) 0.214
(D) 0.316

C-4. At the point of intersection of the two curves shown, the conc. of B is given by.......for, $A \rightarrow nB$:
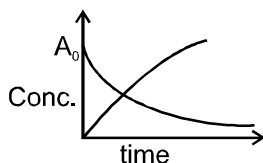
(A) $\dfrac{nA_0}{2}$
(B) $\dfrac{A_0}{n-1}$
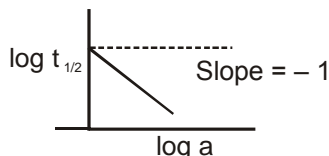(C) $\dfrac{nA_0}{n+1}$
(D) $\left(\dfrac{n-1}{n+1}\right)A_0$

C-5. A graph between log $t_{1/2}$ and log a (abscissa) a being the initial concentration of A in the reaction
For reaction $A \rightarrow$ Product, the rate law is

(A) $\dfrac{-d[A]}{dt} = k$
(B) $\dfrac{-d[A]}{dt} = k\,[A]$
(C) $\dfrac{-d[A]}{dt} = k\,[A]^2$
(D) $\dfrac{-d[A]}{dt} = k\,[A]^3$

Section (D) : Experimental Method to calculate order and rate law of reaction and Methods to Monitor the progress of Reaction

D-1. The data for the reaction $A + B \rightarrow C$ is

Exp.	$[A]_0$	$[B]_0$	initial rate
1	0.012	0.035	0.10
2	0.024	0.035	0.80
3	0.012	0.070	0.10
4	0.024	0.070	0.80

The rate law is
(A) $r = k\,[B]^3$
(B) $r = k\,[A]^3$
(C) $r = k\,[A]\,[B]^4$
(D) $r = k\,[A]^2\,[B]^2$.

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D-2. The kinetic data for the given reaction A(g) + 2B(g) $\longrightarrow$ C(g) is provided in the following table for three experiments at 300 K.

Ex. No.	[A/M]	[B/M]	[Initial rate (M sec⁻¹)]
1	0.01	0.01	6.930×10^{-6}
2	0.02	0.01	1.386×10^{-5}
3	0.02	0.02	1.386×10^{-5}

In another experiment starting with intitial concentration of 0.5 and 1 M respectively for A and B at 300 K. Find the rate of reaction after 50 minutes from start of experiment (in m/sec) ?

(A) 6.93×10^{-4} (B) 0.25×10^{-7} (C) 4.33×10^{-5} (D) 3.46×10^{-9}

D-3. In three different reactions, involving a single reactant in each case, a plot of rate of the reaction on the y−axis, versus concentration of the reactant on the x−axis, yields three different curves shown below.

(i) $-\dfrac{dC}{dt}$ C   (ii) $-\dfrac{dC}{dt}$ C $\longrightarrow$ (iii) $-\dfrac{dC}{dt}$ C
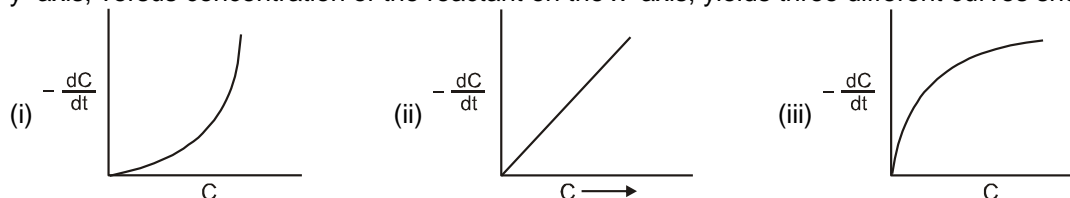
What are the possible orders of the reactions (i), (ii), (iii).

(A) 1, 2, 3   (B) 2, 1, 1/2   (C) 0, 1, 2   (D) 0, 1, ½

D-4. At 373 K, a gaseous reaction A → 2B + C is found to be of first order. Starting with pure A, the total pressure at the end of 10 min was 176 mm of Hg and after a long time when A was completely dissociated, it was 270 mm of Hg. The pressure of A at the end of 10 minutes was :

(A) 94 mm of Hg   (B) 47 mm of Hg   (C) 43 mm of Hg   (D) 90 mm of Hg

D-5. The reaction A(s) → 2 B(g) + C(g) is first order. The pressure after 20 min and after very long time are 150 mm Hg and 225 mm Hg. The value of rate constant and pressure after 40 min are :

(A) 0.05 ln 1.5 min⁻¹ ,200 mm   (B) 0.5 ln 2 min⁻¹ ,300 mm
(C) 0.05 ln 3 min⁻¹, 300 mm   (D) 0.05 ln 3 min⁻¹ , 200 mm

D-6. Which integrated equation is correct for the following Iˢᵗ order reaction started with only A(g) in a closed rigid vessel.

A (g) $\longrightarrow$ B (g) + C (g) + D (g)
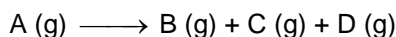
P_i = initial pressure   ; P_t = total pressure at time t

(A) $K = \dfrac{2.303}{t} \log_{10} \left[\dfrac{P_i}{P_t} \right]$ (B) $K = \dfrac{2.303}{t} \log_{10} \left[\dfrac{P_t}{P_i} \right]$

(C) $K = \dfrac{2.303}{t} \log_{10} \left[\dfrac{2P_i}{3P_i - P_t} \right]$ (D) $K = \dfrac{2.303}{t} \log_{10} \left[\dfrac{3P_i}{2P_i - 3P_t} \right]$

D-7. The decompostion NH₃ gas on a heated tungsten surface gave the following results :

Initial pressure (mm of Hg)   65   105   y   185
Half-life (sec)   290   x   670   820

Calculate approximately the values of x and y.

(A) x = 410 sec, y = 115 mm of Hg   (B) x = 467 sec , y = 150 mm of Hg
(C) x = 490 sec, y = 120 mm of Hg   (D) x = 430 sec, y = 105 mm of Hg

D-8. In the reaction NH₄NO₂ (aq.) → N₂ (g) + 2 H₂O (l) the volume of N₂ after 20 min and after a long time is 40 ml and 70 ml respectively. The value of rate constant is :

(A) (1/20) log (7/4) min⁻¹   (B) (2.303 /1200) log (7/3) sec⁻¹
(C) (1/20) log (7/3) min⁻¹   (D) (2.303 / 20) log (11/7) min⁻¹

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D-9.^ If no catalyst (H^+) is present in acid hydrolysis of ester then rate constant k is : (Where V_0, V_t and V_∞ are volumes of NaOH used to titrate reaction mixture at t = 0, t = t and t = ∞)

(A) $\dfrac{2.303}{t} \log \dfrac{V_0}{(V_t - V_\infty)}$

(B) $\dfrac{2.303}{t} \log \dfrac{V_\infty}{(V_\infty - V_t)}$

(C) $\dfrac{2.303}{t} \log \dfrac{V_0}{V_t}$

(D) $\dfrac{2.303}{t} \log \dfrac{V_\infty}{(V_t - V_\infty)}$

Section (E) : Method to monitor the progress of Reactions (Titration Method and Optical Activity Method)

E-1. For a reaction A $\longrightarrow$ B + C, it was found that at the end of 10 minutes from the start the total optical rotation of the system was 50° and when the reaction is complete, it was 100°. Assuming that only B and C are optically active and dextrorotatory. Calculate the rate constant of this first order reaction.

(A) 0.693 min^{-1} (B) 0.0693 sec^{-1} (C) 0.0693 min^{-1} (D) 0.00693 sec^{-1}

E-2. The following data were obtained in an experiment on inversion of cane sugar (a first order kinetics)

Time (min)   0   10   After a long time
Total angle of rotation (degree)   +40   +15   – 10

The rate constant (in second^{-1}) is [ln 2 = 0.693]

(A) 0.0693 (B) 1.15×10^{-3} (C) 0.693 (D) 1.15×10^{-2}

E-3. Half life of reaction : $H_2O_2(aq) \longrightarrow H_2O(l) + \dfrac{1}{2} O_2(g)$ is independent of initial concentration of H_2O_2 volume of O_2 gas after 20 minute is 5L at 1 atm and 27°C and after completion of reaction 50L. The rate constant is

(A) $\dfrac{1}{20} \log 10 \, \text{min}^{-1}$

(B) $\dfrac{2.303}{20} \log 10 \, \text{min}^{-1}$

(C) $\dfrac{2.303}{20} \log \dfrac{50}{45} \, \text{min}^{-1}$

(D) $\dfrac{2.303}{20} \log \dfrac{45}{50} \, \text{min}^{-1}$

E-4. The decomposition of N_2O_5 in chloroform was followed by measuring the volume of O_2 gas evolved : $2N_2O_5(CCl_4) \rightarrow 2N_2O_4(CCl_4) + O_2(g)$. The maximum volume of O_2 gas obtained was 100 cm^3. In 500 minutes, 90 cm^3 of O_2 were evolved. The first order rate constant (in min^{-1}) for the disappearance of N_2O_5 is :

(A) $\dfrac{2.303}{500}$ (B) $\dfrac{2.303}{500} \log \dfrac{100}{90}$ (C) $\dfrac{2.303}{500} \log \dfrac{90}{100}$ (D) $\dfrac{100}{10 \times 500}$

Section (F) : Complication in 1st Order Reaction

F-1. The substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as :

$$A \underset{K_2}{\overset{K_1}{<}} \begin{matrix} B \\ C \end{matrix}$$
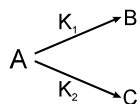
$K_1 = 1.26 \times 10^{-4}$ sec^{-1} and $K_2 = 3.8 \times 10^{-5}$ sec^{-1}

The percentage distribution of B and C

(A) 80% B and 20% C (B) 76.83% B and 23.17%C

(C) 90% B and 10% C (D) 60% B and 40% C

F-2. The rate constant for two parallel reactions were found to be 1.0×10^{-2} dm^3 mol^{-1} s^{-1} and 3.0×10^{-2} dm^{3}mol^{-1}s^{-1}. If the corresponding energies of activation of the parallel reactions are 60.0 kJ mol^{-1} and 70.0 kJ mol^{-1} respectively, what is the apparent overall energy of activation ?

(A) 130.0 kJ mol^{-1} (B) 67.5 kJ mol^{-1} (C) 100.0 kJ mol^{-1} (D) 65.0 kJ mol^{-1}

F-3. For a hypothetical elementary reaction.

$$A \underset{k_2}{\overset{k_1}{<}} \begin{array}{l} 2B \\ 2C \end{array}$$

where $\dfrac{k_1}{k_2} = \dfrac{1}{2}$

Initially only 2 moles of A are present. The total number of moles of A, B and C at the end of 75% of reaction are :

(A) 2   (B) 3   (C) 4   (D) 3.5

F-4. For the follwing parallel chain reaction

$$A \underset{k_2 = 3 \times 10^{-4} \, s^{-1}}{\overset{k_1 = 2 \times 10^{-4} \, s^{-1}}{<}} \begin{array}{l} 2B \\ 3C \end{array}$$

if the sum of the concentration of B and C at any time is 2M then what will be $[B]_t$ and $[C]_t$ respectively ?
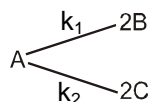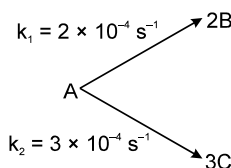
(A) $\dfrac{11}{12}M$, $\dfrac{13}{12}M$ (B) $\dfrac{3}{4}M, \dfrac{5}{4}M$ (C) $\dfrac{4}{5}M, \dfrac{6}{5}M$ (D) $\dfrac{8}{13}M, \dfrac{18}{13}M$

CHEMICAL KINETICS-II

Section (G) : Temperature dependence of rate

G-1. The rate constant, the activation energy and the frequency factor 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 as $T \to \infty$ is :

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

G-2. The rate constant K_1 of a reaction is found to be double that of rate constant K_2 of another reaction. The relationship between corresponding activation energies of the two reactions at same temperature (E_1 and E_2) can be represented as :

(A) $E_1 > E_2$ (B) $E_1 < E_2$ (C) $E_1 = E_2$ (D) None of these

G-3. When a graph between log K and 1/T is drawn a straight line is obtained. The point at which line cuts y-axis and x-axis respectively correspond to the temp :

(A) 0, E_a / 2.303 R log A   (B) ∞, Ea / (R In A)
(C) 0, log A   (D) None of these.

G-4. How much faster would a reaction proceed at 25°C than at 0°C if the activation energy is 65 kJ?

(A) 2 times   (B) 5 times   (C) 11 times   (D) 16 times

G-5. For a reaction A → B, $E_a = 10$ kJ mol^{-1} , $\Delta H = 5$ kJ mol^{-1} . Thus, potential energy profile for this reaction is :
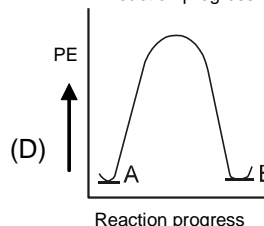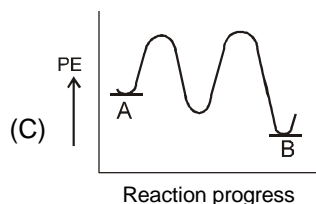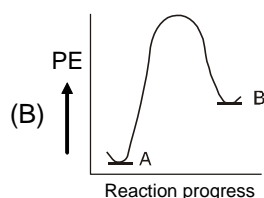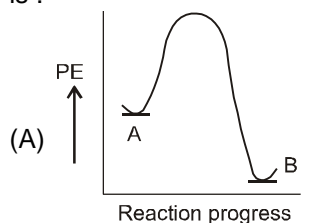
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Section (H) : Catalyst dependence of rate and type of Reaction and Determination of rate law and order with the help of given mechanism

H-1. The E_a of a reaction in presence of a catalyst is 4.15 kJ mol^{-1} and in absence of a catalyst is 8.3 kJ mol^{-1}. What is slope of the plot of ln k vs $\dfrac{1}{T}$ in the absence of catalyst

(A) + 1   (B) –1   (C) + 1000   (D) –1000

H-2. For the decomposition of HI the following logarithmic plot is shown : [R = 1.98 cal/mol-K]

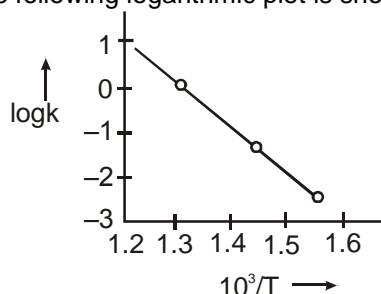The activation energy of the reaction is about
(A) 45600 cal   (B) 13500 cal   (C) 24600 cal   (D) 32300 cal

H-3. For the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ the experiment data suggested that $r = k[H_2][Br_2]^{1/2}$
The molecularity and order of the reaction are respectively :
(A) 2, 3/ 2   (B) 3/2 , 3/2   (C) Not defined, 3/2   (D) 1,1/2

H-4. The reaction of NO_2 (g) and O_3 (g) is first-order in NO_2 (g) and O_3 (g)
$$2 NO_2 (g) + O_3 (g) \longrightarrow N_2O_5 (g) + O_2 (g)$$
The reaction can take place by mechanism :
I : $NO_2 + O_3 \xrightarrow{\text{slow}} NO_3 + O_2$
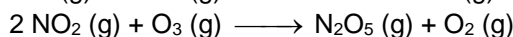
    $NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$

II : $O_3 \underset{k_b}{\overset{k_a \text{ fast}}{\rightleftharpoons}} O_2 + [O]$

    $NO_2 + O \xrightarrow{\text{slow}} NO_3$

    $NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$
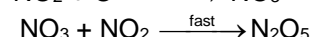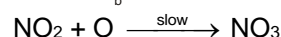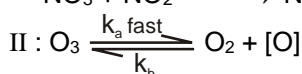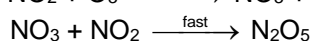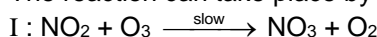
Select correct mechanism.
(A) I only   (B) II only   (C) both I and II   (D) None of I and II

H-5. A hypothetical reaction $X_2 + Y_2 \longrightarrow 2XY$ follows the mechanism given below.
    $X_2 \rightleftharpoons X + X$ [Fast]
    $X + Y_2 \longrightarrow XY + Y$ [Slow]
    $X + Y \longrightarrow XY$ [Fast]
The order of overall reaction is
(A) 2   (B) 1   (C) 1.5   (D) Zero
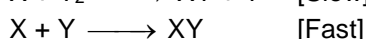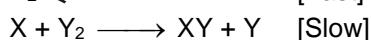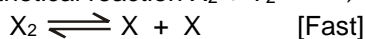
H-6. The reaction of hydrogen, and iodine monochloride is represented by the equation :
$$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$$
This reaction is first–order in $H_2(g)$ and also first–order in ICl(g). Which of these proposed mechanism can be consistent with the given information about this reaction ?
    Mechanism I : $H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$
    Mechanism II : $H_2(g) + ICl(g) \xrightarrow{\text{Slow}} HCl(g) + HI(g)$
        $HI(g) + ICl(g) \xrightarrow{\text{fast}} HCl(g) + I_2(g)$
(A) I only   (B) II only   (C) both I and II   (D) neither I nor II
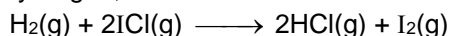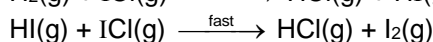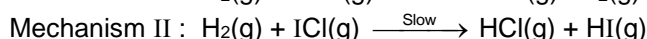
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H-7. Reaction A + B ⟶ D + E take place as

A + B $\xrightarrow{K_1}$ 2C

C + B $\xrightarrow{K_2}$ 2D

C + A $\xrightarrow{K_3}$ 2E
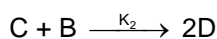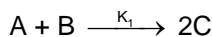
The rate of disapperance of C is given by

(A) $-\dfrac{d[C]}{dt} = K_2[B][C] + K_3[A][C] - 2K_1[A][B]$ (B) $-\dfrac{d[C]}{dt} = K_2[B][C] + K_3[E] - K_1[C]$

(C) $-\dfrac{d[C]}{dt} = K_2[D]O + K_3[E] - K_1[C]$ (D) $-\dfrac{d}{dt}[C] = 2K_1[A][B] - K_2[B][C] - K_3[A][C]$

RADIO ACTIVITY

Section (I) : Radio Activity

I-1. Radioactivity is affected by :
(A) temperature
(B) Pressure
(C) electric and magnetic field
(D) none of these

I-2. Half life period of 10 gm radioactive element is 20 days. Then half life period of 100 gm of this element is :
(A) 20 days   (B) 200 days   (C) 100 days   (D) 10 days

I-3. Determine the average life of U^{238} having $t_{0.5}$ = 138.5 day.
(A) 138.5 day   (B) 199.86 day   (C) 238 day   (D) None of these

I-4. A radioactive element has a half life of one day. After three days the amount of the element left will be :
(A) 1/2 of the original amount
(B) 1/4 of the original amount
(C) 1/8 of the original amount
(D) 1/16 of the original amount

I-5. The activity per mL of a solution of radioactive substance is x. How much water be added to 200 mL of this solution so that the acitivity falls to x/20 per mL after 4 half-lives ?
(A) 100 mL   (B) 150 mL   (C) 80 mL   (D) 50 mL

I-6. A sample of rock from moon contains equal number of atoms of uranium and lead ($t_{1/2}$ for U = 4.5×10^9 years). The age of the rock would be :
(A) 9.0×10^9 years   (B) 4.5×10^9 years   (C) 13.5×10^9 years   (D) 2.25×10^9 years

I-7. The half-life of ^{99}Tc is 6.0 h. The total residual activity in a patient after receiving an injection containing ^{99}Tc must not be more than 0.01 μCi , after 36.0 hours. What is the maximum activity (in μCi) that the sample injected can have ?
(A) 0.06   (B) 0.16   (C) 0.32   (D) 0.64

I-8. The radioactive decay is first order reaction. Its rate, on increasing 10^oC temperature
(A) increases 2-3 times
(B) decreases 2-3 times
(C) does not change
(D) increases 10 times

I-9. The half − life of a radioactive isotope is 3 hours . If the initial mass of the isotope were 256 gm , the mass of it remaining undecayed after 18 hours would be :
(A) 4 gm   (B) 8 gm   (C) 12 gm   (D) 16 gm

I-10. A radioactive isotope X with half - life of 6.93×10^9 years decay to Y which is stable. A sample of rock from the moon was found to contain both the element X and Y in the mole ratio 1 : 7.What is the age of the rock?
(A) 2.079×10^{10} years   (B) 1.94×10^{10} years   (C) 1.33×10^9 years   (D) 10^{10} years

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PART - III : MATCH THE COLUMN

1. Match the following :

	Column-I		Column -II
	(Graph)		**(Slope)**
(A)	c vs t (abscissa) for zero order	(p)	unity
(B)	log c vs t (abscissa) for first order	(q)	zero
(C)	$\left(\dfrac{-dc}{dt}\right)$ vs c for zero order	(r)	– k
(D)	$\ln\left(\dfrac{-dc}{dt}\right)$ vs ln c for first order	(s)	$-\dfrac{k}{2.303}$

2. Match the following :

	Column–I		Column–II
(A)	$A + B \longrightarrow C + D$ $r = k_1 [A][B]$	(p)	Unit of rate constant possess concentration unit
(B)	$A + B \longrightarrow C + D$ $r = k_2 [A][B]^0$	(q)	Rate constant for the reaction of both the reactants are equal
(C)	$A + B \longrightarrow C + D$ $r = k_3 [A]^0 [B]^0$	(r)	Rate of consumption of at least one of the reactants is equal to rate of production of at least one of the products
(D)	$2A + B \longrightarrow 2C + 3D$ (s) $r = k_3 [A]^0 [B]^0$	(s)	If both reactants are taken in stoichiometric ratio, half life for both reactants are equal.

3. **Match the following :**

	Column-I		Column-II
(A)	If the activation energy is 65 kJ then how much time faster a reaction proceed at 25ºC than at 0ºC	(p)	2
(B)	Rate constant of a first-order reaction is 0.0693 min^{-1}. If we start with 20 mol L^{-1}, it is reduced to 2.5 mol L^{-1} in how many minutes.	(q)	Zero
(C)	Half-lives of first-order and zero order reactions are same. Ratio of rates at the start of reaction is how many times of 0.693. Assume initial concentration to be same for the both.	(r)	11
(D)	The half-life periods are given , [A]$_0$ (M) 0.0677 0.136 0.272 t$_{1/2}$ (sec) 240 480 960 order of the reaction is	(s)	30

▮ **Exercise-2** ▦

✎ **Marked questions are recommended for Revision.**

PART - I : ONLY ONE OPTION CORRECT TYPE

1. For a chemical reaction A $\rightarrow$ products, the rate of disappearance of A is given by :

$\dfrac{-dC_A}{dt} = \dfrac{K_1 C_A}{1 + K_2 C_A}$ At low C_A the reaction is of the ..... order with rate constant.....(Assume K_1, K_2 are lesser than 1)

(A) I, $\dfrac{K_1}{K_2}$ (B) I, K_1 (C) II, K_1/K_2 (D) II, $\dfrac{K_1}{K_1 + K_2}$

2. In the following graphical representation for the reaction

  A $\longrightarrow$ B   there are two types of regions :
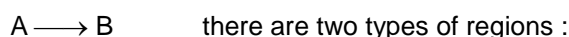
(A) I and II both represent kinetic region at different interval

(B) I and II both represent equilibrium regions at different time interval

(C) I represents kinetic while II represents equilibrium region

(D) I represents equilibrium while II represents kinetic region
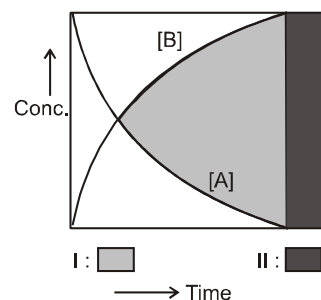
3. If for a reaction in which A(g) converts to B(g) the reaction carried out at const. V & T results into the following graph.
(A) then the reaction must be A(g) $\rightarrow$ 3B(g) and is a first order reaction.
(B) then the reaction must be A(g) $\rightarrow$ 3B(g) and is a second order reaction.
(C) then the reaction must be A(g) $\rightarrow$ 3B(g) and is a zero order reaction.
(D) then the reaction must be A(g) $\leftrightarrow$ 3B(g) and is a first order reaction.
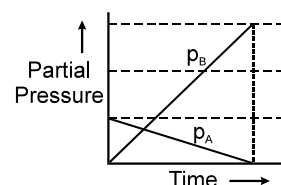
4. Concentration of the reactant in first-order is reduced to $\dfrac{1}{e^2}$ of initial concentration after :

(Natural life = $\dfrac{1}{K}$)
(A) one natural life-time   (B) two-natural life-time
(C) three natural life-time   (D) four natural life-time

5. In a reaction involving one single reactant, the fraction of the reactant consumed may be defined as f = $\left(1 - \dfrac{C}{C_0}\right)$ where C_0 and C are the concentrations of the reactant at the start and after time, t. For a first order reaction

(A) $\dfrac{df}{dt} = k(1 - f)$ (B) $-\dfrac{df}{dt} = kf$ (C) $-\dfrac{df}{dt} = k(1 - f)$ (D) $\dfrac{df}{dt} = kf$

6. A $\rightarrow$ Product and $\left(\dfrac{dx}{dt}\right) = k[A]^2$. If log $\left(\dfrac{dx}{dt}\right)$ is plotted against log [A], then graph is of the type :

(A)   (B)   (C)   (D)
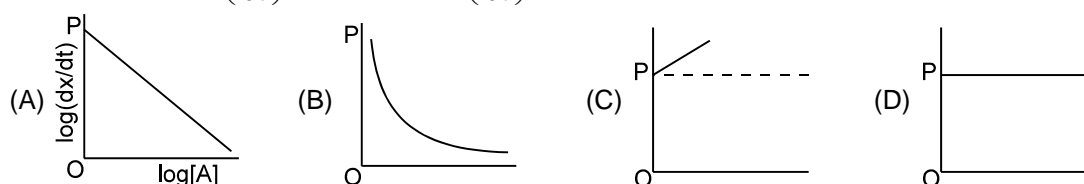
7. For a first order reaction, nA $\longrightarrow$ B whose concentration vs time curve is as shown in the figure. If half life for the reaction is 24 minutes . Find out the value of n.
(A) 1
(B) 2
(C) 3
(D) 4
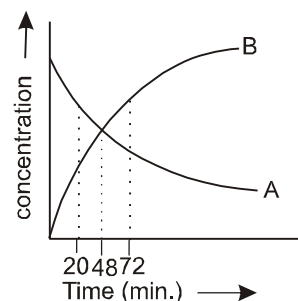
8. The inversion of cane sugar proceeds with half life of 50 minute at pH = 5 for any concentration of sugar. However if pH = 6, the half life changes to 500 minute of any concentration of sugar. The rate law expression for the inversion of cane sugar is written as : r = K [sugar]^1 [H$^+$]^y. Determine the value of y.
(A) r = K [sugar]^1 [H$^+$]$^{-1}$ (B) r = K [sugar]^1 [H$^+$]^2 (C) r = K [sugar]^1 [H$^+$]^1 (D) r = K [sugar]^1 [H$^+$]^0.

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9. The following data is for the decomposition of ammonium nitrite in aqeous solution.

Volume of N_2 in cc.	Time (minutes)
6.25	10
9	15
11.4	20
13.65	25
35.05	infinity

The order of the reaction is
(A) zero (B) one (C) – one (D) – two

10. For the first-order reaction T_{av} (average life), T_{50} and T_{75} in the increasing order are :
(A) $T_{50} < T_{av} < T_{75}$ (B) $T_{50} < T_{75} < T_{av}$ (C) $T_{av} < T_{50} < T_{75}$ (D) $T_{av} = T_{50} < T_{75}$

11. Formation of NO_2F from NO_2 and F_2 as per the reaction $2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$ is a second order reaction, first order with respect to NO_2 and first order with respect to F_2. If NO_2 and F_2 are present in a closed vessel in ratio 2 :1 maintained at a constant temperature with an initial total pressure of 3 atm, what will be the total pressure in the vessel after the reaction is complete?
(A) 1atm (B) 2 atm (C) 2.5 atm (D) 3 atm

12. In a hypothetical reaction, $A(aq) \rightleftharpoons 2B(aq) + C(aq)$ (1st order decomposition)
'A' is optically active (dextro-rototory) while 'B' and 'C' are optically inactive but 'B' takes part in a titration reaction (fast reaction) with H_2O_2. Hence, the progress of reaction can be monitored by measuring rotation of plane polarised light or by measuring volume of H_2O_2 consumed in titration.
In an experiment the optical rotation was found to be $\theta = 40°$ at t = 20 min and $\theta = 10°$ at t = 50 min. from start of the reaction. If the progress would have been monitored by titration method, volume of H_2O_2 consumed at t = 15 min. (from start) is 40 ml then volume of H_2O_2 consumed at t = 60 min will be:
(A) 60 ml (B) 75 ml (C) 52.5 ml (D) 90 ml

13. Inversion of sucrose ($C_{12}H_{22}O_{11}$) is first-order reaction and is studied by measuring angle of rotation at different instant of time

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
$$\underset{d}{\text{Sucrose}} \qquad \underset{d}{\text{Glucose}} \quad \underset{l}{\text{Fructose}}$$
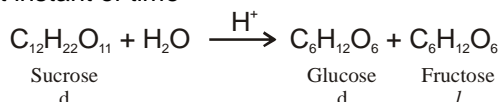
If $(r_\infty - r_0) = a$ and $(r_\infty - r_t) = (a - x)$ (where r_0, r_t and r_∞ are the angle of rotation at the start, at the time t and at the end of the reaction respectively), then there is 50% inversion when :
(A) $r_0 = 2r_t - r_\infty$ (B) $r_0 = r_t - r_\infty$ (C) $r_0 = r_t - 2r_\infty$ (D) $r_0 = r_t + r_\infty$

14. A.G.M. counter is used to study the radioactive process of first-order. In absence of radioactive substance A, it counts 3 disintegration per second (dps). When A is placed in the G.M. counter, it records 23 dps at the start and 13 dps after 10 minutes. It records x dps after next 10 minutes and A has half-life period y minutes. x and y are :
(A) 8 dps, 10 min (B) 5 dps, 10 min (C) 5 dps, 20 min (D) 5 dps, 5 min

15. For the following parallel chain reaction what will be that value of overall half-life of A in minutes? $\left[\text{Given that } \dfrac{[B]_t}{[C]_t} = \dfrac{16}{9}\right]$

(A) 3.3 (B) 6.3
(C) 3.6 (D) None of these

16. For the follwing parallel chain reaction $A \big\langle \substack{B \\ C}$ the overall half life of A is 12 hours If rate of formation of C is 60% of a rate of decomposition of A then what will be half life of A while it is converting into B ?
(A) 40 hours (B) 60 hours (C) 50 hours (D) 30 hours

17. The Arrhenius relationship of two different reactions is shown below. Which reaction is faster at a lower temperature and which is more sensitive to changes of temperature ?

(A) B faster, A more sensitive   (B) B in both cases
(C) A in both cases   (D) A faster, B more sensitive
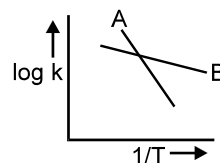
18. For the same mechanism as Problem refer to the given Fig. and choose the correct set of identifications.

$$E + S \rightleftharpoons ES$$
(enzyme)   (reactant)   (intermediate-1)

$$ES \rightleftharpoons EP$$
(intermediate-1)   (intermediate-2)

$$EP \rightleftharpoons E + P$$
(intermediate-2)   (enzyme)   (product)

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

19. The potential energy diagram for a reaction $R \longrightarrow P$ is given below :

ΔH^o of the reaction corresponds to the energy –

(A) x
(B) y
(C) z
(D) (x + y)
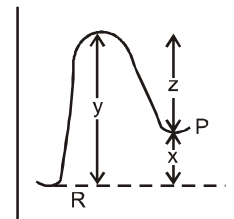
20. In gaseous reactions important for the understanding of the upper atmosphere H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and E_a is 77 kJ mol^{-1}, then E_a for the bimolecular recombination of two OH radicals to form H_2O and O is :

(A) 3 kJ mol^{-1} (B) 4 kJ mol^{-1} (C) 5 kJ mol^{-1} (D) 7 kJ mol^{-1}

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. In a catalyst experiment involving the Haber process $N_2 + 3H_2 \longrightarrow 2NH_3$, the rate of reaction was measured.

Rate = $\dfrac{\Delta[NH_3]}{\Delta t}$ = 2.0 × 10^{-4} mol L^{-1} S^{-1}.

The rate of reaction of N_2 is p ×10^{-4}. Then find the value of p.

2. The acid catalysed hydrolysis of an organic compound A at 30°C has a time for half change of 100 minutes, when carried out in a buffer solution at pH 5 and of 10 minutes, when carried out at pH 4. Both times of half change are independent of the initial concentration of A. If the rate of reaction is given by

$\dfrac{-d[A]}{dt}$ = k[A]^a[H$^+$]^b, what are the values of (a + b) ?

3. For a first order reaction, time required for 99.0% completion is x times for the time required for the completion of 90% of the reaction x is :

4. The rate of decomposition of a substance increases by a factor 2.25 for 1.5 times increase in concentration of substance at same temperature. Find out order of reaction.

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5. Half-life period for decomposition of NH_3 over tungsten wire are given below :

Initial Pressure in min	50	100	200
$T_{1/2}$	3.52	1.82	0.93

Calculate order of reaction.

6. A substance A is mixed with equal quantities of the substance B and C. At the end of 1000 second, half of the amount of A has reacted. What fraction of A will be left unreacted at the end of 2000 second. If the reaction is zero order with respect to A ?

7. At 80% of a radioactive element undergoing decay is left over after a certain period of time t from pure start, how many such periods should elapse from the start for just over 50% of the element to be left over.

8. The rate constant for the II order neutralization of 2-nitropropane by aqueous alkali obeys the equation

$$\log_{10} K = \frac{3163}{T} + 12 \qquad \text{T is temperature in Kelvin.}$$

Time and concentration were in minute and mol litre^{-1} respectively. If half life at 43.3°C and for an initial concentration of 0.001 mol litre^{-1} for each of the reactant is. Expresed as 10^{-x}, then x is :

9. In a II order reaction, when the concentration of both the reactants are equal, the reaction is completed 20% in 500 sec. How long it would take for the reaction to go to 60% completion ? (Report your answer terms of minutes).

10. A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 54.0 min for A and 18.0 min for B. If the concentrations of A and B are equal initially, how long (in minute) will it take for the concentration of A to be four times that of B ?

11. The ratio of activities of two radio nuclides X and Y in a mixture at time t = 0 was found to be 4 : 1. After two hours, the ratio of activities become 1 : 1. If the $t_{1/2}$ of radio nuclide X is 20 min then $t_{1/2}$ [in minutes] of radio nuclide Y is :

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Which of the following are true about rate of a reaction?
(A) Rate of a reaction cannot be negative
(B) Rate of a reaction of a reactant is change in concentration of the reactant per unit time.
(C) Average rate and instantaneous rate can never be equal.
(D) Rate depends upon surface area of the reactants.

2. Which of the following statement is/are correct?
(A) A second order reaction must be a bimolecular elementary reaction
(B) A bimolecular elementary reaction must be a second order reaction
(C) Order of reaction can't be predicted by stoichiometry of reaction.
(D) First order reaction may be complex or elementary reaction

3. For the reaction $2A + B \longrightarrow C$ with the rate law $\dfrac{d[C]}{dt} = k[A]^1 [B]^{-1}$ and started with A and B in stoichiometric proportion. Which is/are true?
(A) unit of k is Ms^{-1} 　　　　　　　　(B) [A], [B] and [C] all will be linear functions of time
(C) [C] = 2kt 　　　　　　　　　　　　(D) [C] = kt

4. Decomposition of $3A(g) \longrightarrow 2B(g) + 2C(g)$ follows first order kinetics. Initially only A is present in the container. Pressure developed after 20 min. and infinite time are 3.5 and 4 atm respectively. Which of the following is true.
(A) $t_{50\%}$ = 20 min 　　　(B) $t_{75\%}$ = 40 min 　　　(C) $t_{99\%}$ = 64/3 min 　　　(D) $t_{87.5\%}$ = 60 min

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5. For a second order reaction plots are made for $\dfrac{1}{[A]}$ vs time for the reaction, $2A \longrightarrow$ Product. Pick up the correct sentences. [K = Rate constant of A]

(A) the graph will show straight line with slope K

(B) the graph will show straight line with intercept $[A]_0$

(C) the graph will show straight line with slope $[A]_0$

(D) the graph will show straight line with intercept $\dfrac{1}{[A]_0}$

6. Taking the reaction, $A + 2B \longrightarrow$ Products, to be of second order, which of the following is/are the correct rate law expression(s) ?

(A) $\dfrac{dx}{dt} = k[A]^2$ (B) $\dfrac{dx}{dt} = k[A][B]^2$ (C) $\dfrac{dx}{dt} = k[A][B]$ (D) $\dfrac{dx}{dt} = k_1[A] + k_2[B]^2$

7. In the following gaseous phase first order reaction, $A(g) \longrightarrow 2B(g) + C(g)$

initial pressure was found to be 400 mm and it changed to 1000 mm after 20 min. Then :

(A) Half life for A is 10 min   (B) Rate constant is 0.0693 min^{-1}

(C) Partial pressure of C at 30 min is 350 mm   (D) Total pressure after 30 min is 1100 mm

8. For the reaction $CH_4 + Br_2 \longrightarrow CH_3Br + HBr$ the experimental data require the following rate equation :

$$\dfrac{d}{dt}[CH_3Br] = \dfrac{k_1[CH_4][Br_2]}{1 + k_2[HBr]/[Br_2]}$$

Which of the following is/are true regarding this ?

(A) The reaction is a single step reaction

(B) The reaction is 2nd order in the initial stages $\{[HBr] \approx 0\}$

(C) The reaction is 2nd order in the final stages $\{[Br_2] \approx 0\}$

(D) The molecularity of the reaction is two

9. 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) the increase in the number of activated molecules

(C) The shortening of mean free path   (D) the lowering of activation energy

10. Which of the following statements about the arrhenius equation are correct ?

(A) The pre exponential factor become equal to the rate constant of the reaction at temperature $T \rightarrow \infty$

(B) When the activation energy of the reaction $\rightarrow$ zero, the rate becomes independent of temperature.

(C) The term $e^{-E_a/Rt}$ represents the fractions of the molecules having energy is excess of the threshold value.

(D) On raising temperature , rate constant of the reaction of greater activation energy increases less rapidly than that of the reaction of smaller activation energy.

11. Rate constant k varies with temperature by equation , $\log k(min^{-1}) = 5 - \dfrac{2000}{T(K)}$. We can conclude :

(A) pre-exponential factor A is 5   (B) E_a is 2000 k cal

(C) pre-exponential factor A is 10^5 (D) E_a is 9.212 k cal

12. Activation energy of a chemical reaction can be determined by :

(A) evaluating rate constant at standard temperature

(B) evaluating velocities of reaction at two different temperatures

(C) evaluating rate constant at two different temperatures

(D) changing concentration of reactants

13. Select the correct statements :

(A) the molecularity of an elementary reaction indicates how many reactant molecules take part in the step.

(B) the rate law of an elementary reaction can be predicted by simply seeing the stoichiometry of reaction.

(C) the slowest elementary step in sequence of the reactions governs the overall rate of formation of product.

(D) a rate law is often derived from a proposed mechanism by imposing the steady state approximation or assuming that there is a pre-equilibrium.

14. Which of the following statement are true regarding the log K vs. 1/T plot shown in the given diagram ?

(A) Plot P shows that the energy of activation is independent of temperature.

(B) Plot Q describes the behaviour of temperature dependence of energy of activation.

(C) Arrhenius behaviour is described by P.

(D) The slope of curve P gives the value $-\dfrac{E_a}{R}$.

$K = Ae^{-E_a/RT}$

15. If the rate of reaction, $2SO_2(g) + O_2(g) \xrightarrow{\;Pt\;} 2SO_3(g)$ is given by :

$$\text{Rate} = K\frac{[SO_2]}{[SO_3]^{1/2}}$$

which statements are correct :

(A) The overall order of reaction is $-1/2$

(B) The overall order of reaction is $+1/2$

(C) The reaction slows down as the product SO_3 is build up

(D) The rate of reaction does not depend upon concentration of SO_3 formed

16. Rate of radioactive disintegration $(-dN/dt)$ is also known as :

(A) Activity   (B) Radioactivity   (C) Half-life period   (D) Average life period
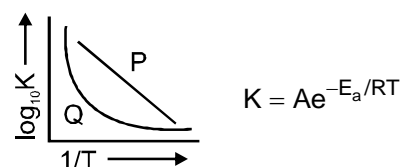
PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

$$A(g) \longrightarrow 2B(g) + C(g)$$
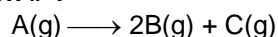
Initially at t = 0 gas A was present along with some amount of gas C. At t = 0 mole fraction of gas C is 1/3. After some time $t = t_1$, total pressure is half of the final total pressure at $t = t_x$ (a very long time). Assume this decomposition is a first order, at a constant temperature. It is also given at $t = t_x$, final total pressure is 35 bar.

1. At $t = t_1$ pressure of gas B is :

(A) 2.5 bar   (B) 1.25 bar   (C) 5.0 bar   (D) data is insufficient

2. Rate constant $(k) = (\log 64 - \log 49)$ s^{-1}. Value of t_1 in seconds is :

(A) 2.15 s   (B) 1.5 s   (C) 2.3 s   (D) 1.15 s

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3. Ratio of rate constant at $t = 0$ to $t = t_1$ to $t = t_x$ is :
(A) 2 : 3 : 4   (B) 1 : 1 : 1   (C) 1 : 3 : 5   (D) 1 : 3 : 5

Comprehension # 2

Set-I (Without catalyst)			
Reaction	**Temperature**	**E (activation)**	**k**
$A \rightarrow B$	$T_1 K$	Ea_1	k_1
$A \rightarrow B$	$T_2 K$	Ea_2	k_2

Set-II (With catalyst) (Consider catalyst being positive only)			
Reaction	**Temperature**	**E (activation)**	**k**
$A \rightarrow B$	$T_1 K$	Ea_3	k_3
$A \rightarrow B$	$T_2 K$	Ea_4	k_4

4. For the (Set-1) :
(A) if $T_1 > T_2$, $k_1 > k_2$ always   (B) if $T_1 > T_2$, $k_1 > k_2$ (for exothermic reaction)
(C) if $T_1 > T_2$, $k_1 < k_2$ (for endothermic reaction)   (D) $Ea_1 \neq Ea_2$

5. For the (Set-1) :
(A) $Ea_1 > Ea_2$ if $T_1 > T_2$ (B) $Ea_1 < Ea_2$ if $T_1 > T_2$
(C) $Ea_1 = Ea_2$ (D) $Ea_1 = 0.5 \, Ea_2$

6. Comparing set-I and II :
(A) $k_4 > k_3$ & $k_2 > k_1$, if $T_2 > T_1$ (endothermic)   (B) $k_4 < k_3$ & $k_2 > k_1$, if $T_2 < T_1$ (endothermic)
(C) $k_4 > k_3$ & $k_2 > k_1$, if $T_2 < T_1$ (exothermic)   (D) $k_4 < k_3$ & $k_2 < k_1$, if $T_2 > T_1$ (exothermic)

Comprehension # 3

Competing first-order reactions :

Frequently a species can react in different ways to give a variety of products. For example, toluene can be nitrated at the ortho, meta, or para positions, We shall consider the simplest case, that of two competing irreversible first-order reactions :

$$A \xrightarrow{\;k_1\;} C \text{ and } A \xrightarrow{\;k_2\;} D$$
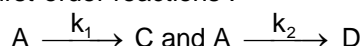
where the stoichiometric coefficients are taken as unity for simplicity. The rate law is

$$\left(\frac{d[A]}{dt}\right) = -k_1[A] - k_2[A] = -(k_1 + k_2)[A] \qquad \Rightarrow \qquad [A] = [A]_0 \, e^{-(k_1+k_2)t} .$$

For C, we have $\left(\dfrac{d[C]}{dt}\right) = k_1[A] = k_1[A]_0 \, e^{-(k_1+k_2)t}$. Multiplication by dt and integration from time 0

(where $[C]_0 = 0$) to an arbitary time t gives $\qquad [C] = \dfrac{k_1[A]_0}{k_1 + k_2}(1 - e^{-(k_1+k_2)t})$

Similarly, integration of $\left(\dfrac{d[D]}{dt}\right)$ gives $\qquad [D] \dfrac{k_2[A]_0}{k_1 + k_2} = (1 - e^{-(k_1+k_2)t})$

The sum of the rate constants $k_1 + k_2$ appears in the exponentials for both [C] and [D].

At any time we also have $\qquad \dfrac{[C]}{[D]} = \dfrac{k_1}{k_2}$

7. $A \begin{array}{c} \nearrow^{k_1} 2B \\[4pt] \searrow_{k_2} 3C \end{array}$ starting initially with only A Which of the following is correct at time t

(A) $[A]_0 = [A]_t + [B]_t + [C]_t$ (B) $[A]_0 = [A]_t + 2[B]_t + 3[C]_t$

(C) $[A]_0 = [A]_t + \dfrac{[B]_t}{2} + \dfrac{[C]_t}{3}$ (D) $[A]_0 = \dfrac{2}{3}[A]_t + [B]_t + [C]_t$

8. $X \overset{k_1}{\underset{k_2}{\diagup\diagdown}} \overset{Y}{\underset{Z}{}}$ starting with only 'X', ratio $\dfrac{[X]_t}{[Y]_t + [Z]_t}$

(A) Independent of time

(B) $\dfrac{1}{(e^{kt} - 1)}$

(C) Depends upon initial concentration of X

(D) $[A]_0 (e^{kt} - 1)$

9.   At high temperature acetic acid decomposes into CO_2 & CH_4 and simultaneously into CH_2CO (ketene) and H_2O

(i) $CH_3COOH \xrightarrow{\;k_1 = 3s^{-1}\;} CH_4 + CO_2$

(ii) $CH_3COOH \xrightarrow{\;k_2 = 4s^{-1}\;} CH_2CO + H_2O$

What is the fraction of acetic acid reacting as per reaction (i) ?

(A) $\dfrac{3}{4}$ (B) $\dfrac{3}{7}$ (C) $\dfrac{4}{7}$ (D) none of these

10. For $A \overset{k_1}{\underset{k_2}{\diagup\diagdown}} \overset{3B}{\underset{4C}{}}$ starting with pure A ratio of rate of production of B to C is

(A) Independent of time

(B) Independent of temperature

(C) Depends upon initial concentration of A

(D) Independent of mechanism of reaction

Comprehension # 4

Answer Q.11, Q.12 and Q.13 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2 and 3 contain the Order of the reaction, value of K and half-life respectively.		
Column-1	**Column-2**	**Column-3**
(I) First order reaction	(i) $k = \dfrac{1}{2t}\left[\dfrac{1}{(a-x)^2} - \dfrac{1}{a^2}\right]$	(P) Half life $\propto \dfrac{1}{a^2}$
(II) Second order reaction	(ii) $k = \dfrac{1}{t}\left[\dfrac{1}{a-x} - \dfrac{1}{a}\right]$	(Q) Half life $\propto \dfrac{1}{a}$
(III) Third order reaction	(iii) $k = \dfrac{x}{t}$	(R) Half life is doubled on doubling the initial concentration
(IV) Zero order reaction	(iv) $k = \dfrac{1}{t}\log_e\left(\dfrac{a}{a-x}\right)$	(S) 50% reaction takes same time even if concentration is halved or doubled.

11. The correct combination for reaction $A \xrightarrow{\;2\times10^{-3}\,min^{-1}\;} B$ is :

(A) (II) (ii) (Q)   (B) (IV) (iv) (S)   (C) (I) (iv) (S)   (D) (I) (iii) (R)

12. The incorrect combination among the following is :

(A) (I) (iii) (S)   (B) (II) (ii) (Q)   (C) (III) (i) (P)   (D) (IV) (iii) (R)

13. For an elementary reaction $2A \longrightarrow B$, correct combination is :

(A) (I) (iv) (Q)   (B) (I) (iv) (S)   (C) (II) (ii) (Q)   (D) (II) (ii) (R)

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Exercise-3

* **Marked Questions may have more than one correct option.**

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. The rate constant for the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$, is 3×10^{-5} s^{-1}. If the rate is 2.4×10^{-5} mol L^{-1} s^{-1}, then the concentration of N_2O_5 (in mol L^{-1}) is : **[JEE-2000(S), 1/35]**
   (A) 1.4   (B) 1.2   (C) 0.04   (D) 0.8

2. $^{238}_{92}U$ is radioactive and it emits α and β particles to form $^{206}_{82}Pb$. Calculate the number of α and β particles emitted in this conversion. An ore of $^{238}_{92}U$ is found to contain $^{238}_{92}U$ and $^{206}_{82}Pb$ in the weight ratio of 1 : 0.9 the half life period of $^{238}_{92}U$ is 4.5×10^9 years. Calculate the age of the ore. **[JEE-2000(M)]**

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 kJ mol^{-1}. **[JEE-2000(M), 3/100]**

4. If 'I' is the intensity of absorbed light and 'C' is the concentration of AB for the photochemical process, $AB + h\nu \rightarrow AB^*$, the rate of formation of AB^* is directly proportional to **[JEE-2001(S), 1/35]**
   (A) C   (B) I   (C) I^2 (D) C.I

5. 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(M), 5/100]**

6. Consider the chemical reaction,
   $$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$
   The rate of this reaction can be expressed in terms of time derivatives of conc. of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst rate expressions : **[JEE-2002(S), 3/90]**

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

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

   (C) Rate = $\dfrac{d[N_2]}{dt} = -\dfrac{1}{3}\dfrac{d[H_2]}{dt} = \dfrac{1}{2}\dfrac{d[NH_3]}{dt}$

   (D) Rate = $-\dfrac{d[N_2]}{dt} = -\dfrac{d[H_2]}{dt} = \dfrac{d[NH_3]}{dt}$

7. ^{64}Cu (half life = 12.8 hours) decays by β^- emission(38%), β^+ emission(19%) and electron capture(43%). Write the decay products and calculate partial half lives for each of the decay processes.
   [JEE-2002(M), 5/60]

8. In the biologically-catalysed oxidation of ethanol, the concentration of ethanol decreases in a first order reaction from 800 mol dm^{-3} to 50 mol dm^{-3} in 2×10^4 s. The rate constant (s^{-1}) of the reaction is :
   [JEE-2003(S), 3/84]
   (A) 3.45×10^{-5} (B) 1.38×10^{-4} (C) 1.00×10^{-4} (D) 5.00×10^{-5}

9. Given   X $\longrightarrow$ product (Taking 1st order reaction)
   conc   0.01   0.0025
   (mol/lit)
   time (min)   0   40
   Initial rate of reaction is in mol /ℓ/min. **[JEE-2004(S), 3/84]**
   (A) 3.43×10^{-4} (B) 1.73×10^{-4} (C) 3.43×10^{-5} (D) 1.73×10^{-5}

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10. Initial rates, r_0, of the $A + B \rightarrow P$ at different initial concentrations of A and B ($[A]_0$ and $[B]_0$) are given below:

$[A]_0$ (mol L^{-1})	$[B]_0$ (mol L^{-1})	r_0 (mol $L^{-1} s^{-1}$)
0.1	0.1	0.05
0.2	0.1	0.10
0.1	0.2	0.05

(a) Write the rate equation.   (b) Calculate the rate constant of the reaction.   **[JEE-2004(M), 2/60]**

11. For a reaction $2X(g) \longrightarrow 3Y(g) + 2Z(g)$ the following data is obtained.

Time (min)	Px (mm of Hg) (Partial pressure of X)
0	800
100	400
200	200

Find order with respect to X, rate constant of the reaction, time taken for 75% completion and find the total pressure when partial pressure of X, Px = 700 mm of Hg.   **[JEE-2005(M), 2/60]**

Comprehension #

Carbon–14 is used to determine the age of organic material. The procedure is based on the formation of ^{14}C by neutron capture in the upper atmosphere.

$$^{14}_{7}N + {}_{0}n^1 \longrightarrow {}^{14}_{6}C + {}_{1}p^1$$
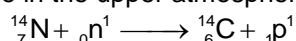
^{14}C is absorbed by living organisms during photosynthesis. The ^{14}C content is constant in living organism, once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ^{14}C in the dead being, falls due to the decay which C^{14} undergoes

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + \beta^-$$
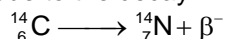
The half life period of ^{14}C is 5770 years. The decay constant (λ) can be calculated by using the following formula $\lambda = \dfrac{0.693}{t_{1/2}}$

The comparison of the β^- activity of the dead matter with that of the carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 years. The proportion of ^{14}C to ^{12}C in living matter is $1 : 10^{12}$.

12. Which of the following option is correct?   **[JEE-2006, 5/184]**
(A) Rate of exchange of carbon between atmosphere and living is slower than decay of ^{14}C.
(B) Carbon dating can be used to find out the age of earth crust and rocks
(C) Rate of exchange of ^{14}C between atmosphere and living organism is so fast that an equilibrium is set up between the intake of ^{14}C by organism and its exponential decay.
(D) Carbon dating can not be used to determine concentration of ^{14}C in dead beings.

13. What should be the age of fossil for meaningful determination of its age?   **[JEE-2006, 5/184]**
(A) 6 years   (B) 6000 years
(C) 60,000 years   (D) It can be used to calculate any age

14. A nuclear explosion has taken place leading to increase in concentration of ^{14}C in nearby areas. ^{14}C concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be T_1 and T_2 at the places respectively then   **[JEE-2006, 5/184]**
(A) The age of the fossil will increase at the place where explosion has taken place and
$T_1 - T_2 = \dfrac{1}{\lambda} \ln \dfrac{C_1}{C_2}$
(B) The age of the fossil will decrease at the place where explosion has taken place and
$T_1 - T_2 = \dfrac{1}{\lambda} \ln \dfrac{C_1}{C_2}$

(C) The age of fossil will be determined to be same   (D) $\dfrac{T_1}{T_2} = \dfrac{C_1}{C_2}$

15. 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-2007, 3/162]**
(A) 0   (B) 1   (C) 2   (D) 3

16. 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 $\left(\dfrac{k_1}{k_0}\right)$ of the rate constant for first order (k_1) and zero order (k_0) of the reaction is. **[JEE-2008, 3/162]**
(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

17. For a first order reaction A → P, the temperature (T) dependent rate constant (k) was found to follow the equation log k = – (2000) $\dfrac{1}{T}$ + 6.0. The pre-exponential factor A and the activation energy E_a, respectively, are : **[JEE-2009, 3/160]**
(A) 1.0×10^6 s^{-1} and 9.2 kJ mol^{-1} (B) 6.0 s^{-1} and 16.6 kJ mol^{-1}
(C) 1.0×10^6 s^{-1} and 16.6 kJ mol^{-1} (D) 1.0×10^6 s^{-1} and 38.3 kJ mol^{-1}

18. 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, 3/163]**

19. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is : **[JEE-2010, 3/163]**
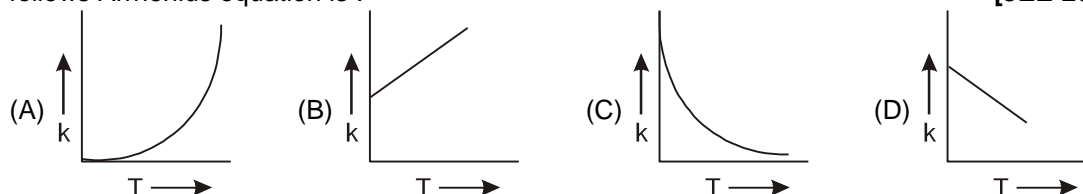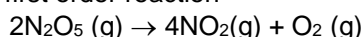
20.* For the first order reaction
      $2N_2O_5$ (g) → $4NO_2$(g) + O_2 (g)   **[JEE-2011, 4/160]**
(A) The concentration of the reactant decreases exponentially with time
(B) The half-life of the reaction decreases with increasing temperature
(C) The half-life of the reaction depends on the initial concentration of the reactant
(D) The reaction proceeds to 99.6% completion in eight half-life duration

21. 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 $\dfrac{[t_{1/8}]}{[t_{1/10}]} \times 10$?
($\log_{10} 2$ = 0.3) **[JEE-2012, 4/136]**

22. In the reaction, P + Q ⟶ 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 : **[JEE(Advanced) 2013, 2/120]**
(A) 2   (B) 3
(C) 0   (D) 1

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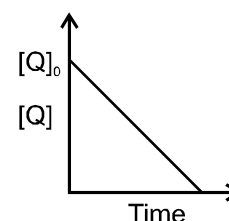
23. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25°C. The K_a of HA is : **[JEE(Advanced)-2013, 4/120]**

(A) 1×10^{-4} (B) 1×10^{-5} (C) 1×10^{-6} (D) 1×10^{-3}

24. For the elementary reaction **M** $\rightarrow$ **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 :

[JEE(Advanced) 2014, 3/120]

(A) 4   (B) 3   (C) 2   (D) 1

25. The % yield of ammonia as a function of time in the reaction :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \ \Delta H < 0$$

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 : **[JEE(Advanced) 2015, 3/168]**

(A)   (B)

(C)   (D)
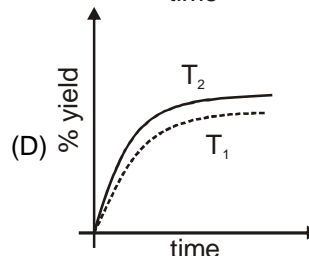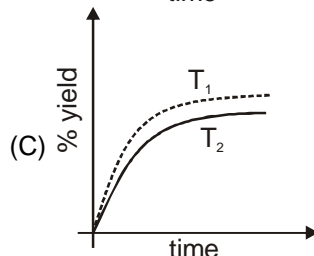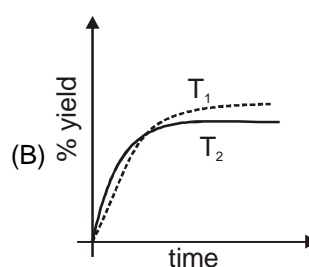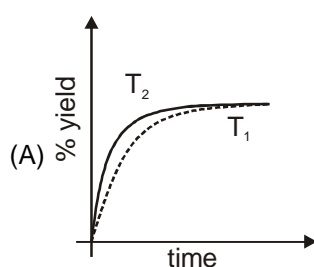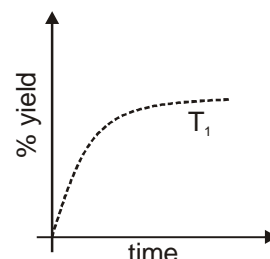
26. In dilute aqueous H_2SO_4, the complex diaquodioxalatoferrate(II) is oxidized by MnO_4^-. For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is : **[JEE(Advanced)-2015, 4/168]**

27. According to the Arrhenius equation, **[JEE(Advanced)-2016, 4/124]**
(A) a high activation energy usually implies a fast reaction.
(B) rate constant increases 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.

28. 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(Advanced)-2017, 4/122]**
(A) The activation energy of the reaction is unaffected by the value of the steric factor.
(B) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation.
(C) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally.
(D) Since P = 4.5, the reaction will not proceed unless an effective catalyst is used.

29.* For a first order reaction $A(g) \rightarrow 2B(g) + C(g)$ at constant volume and 300 K, the total pressure at the beginning (t = 0) and at time t are P_0 and P_t, respectively. Initially, only A is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of A to reach $1/3^{rd}$ of its initial value. The correct option(s) is (are)

(Assume that all these gases behave as ideal gases) **[JEE(Advanced)-2018, 4/120]**

(A) plot of $\ln(3p_0 - P_t)$ vs Time

(B) plot of $t_{1/3}$ vs $[A]_0$

(C) plot of $\ln(p_0 - P_t)$ vs Time

(D) plot of Rate constant vs $[A]_0$
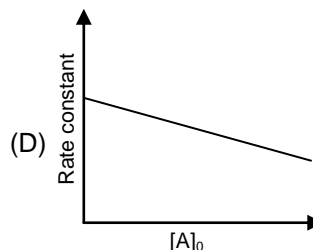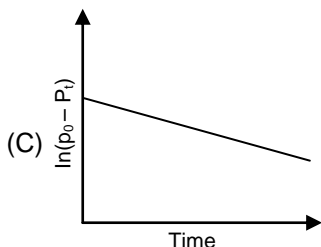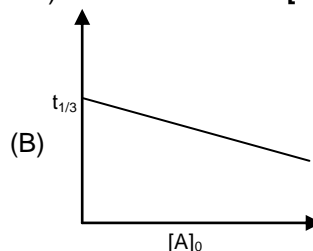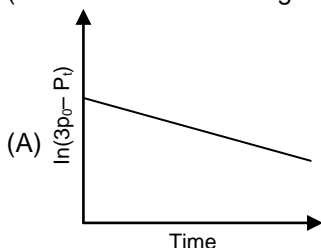
30. Consider the following reversible reaction,

$$A(g) + B(g) \rightleftharpoons AB(g)$$
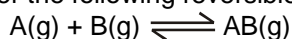
The activation energy of the backward reaction exceeds that of the forward reaction by 2 RT (in J mol⁻¹). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG^{θ} (in J mole⁻¹) for the reaction at 300 K is _____.

(Given : ln(2) = 0.7, RT = 2500 J mol⁻¹ at 300 K and G is the Gibbs energy)

[JEE(Advanced)-2018, 3/120]

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. Units of rate constant of first and zero order reactions in terms of molarity M unit are respectively

[AIEEE-2002, 3/225]

(1) sec⁻¹, M sec⁻¹   (2) sec⁻¹, M   (3) M.sec⁻¹, sec⁻¹   (4) M, sec⁻¹

2. For the reaction $A + 2B \rightarrow C$, rate is given by $R = [A] [B]^2$ then the order of the reaction is :

[AIEEE-2002, 3/225]

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

3. The differential rate law for the reaction $H_2 + I_2 \rightarrow 2HI$ is : **[AIEEE-2002, 3/225]**

(1) $-\dfrac{d[H_2]}{dt} = -\dfrac{d[I_2]}{dt} = -\dfrac{d[HI]}{dt}$ (2) $\dfrac{d[H_2]}{dt} = \dfrac{d[I_2]}{dt} = \dfrac{1}{2}\dfrac{d[HI]}{dt}$

(3) $\dfrac{1}{2}\dfrac{d[H_2]}{dt} = \dfrac{1}{2}\dfrac{d[I_2]}{dt} = -\dfrac{d[HI]}{dt}$ (4) $-2\dfrac{d[H_2]}{dt} = -2\dfrac{d[I_2]}{dt} = +\dfrac{d[HI]}{dt}$

4. The rate law for a reaction between the substances A and B is given by rate = $k [A]^n [B]^m$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as **[AIEEE-2003, 3/225]**

(1) $\dfrac{1}{2^{m+n}}$ (2) (m + n)   (3) (n – m)   (4) $2^{(n-m)}$.

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5. For the reaction system: $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$, volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO, the rate of reaction will : **[AIEEE-2003, 3/225]**
(1) diminish to one-fourth of its initial value
(2) diminish to one-eighth of its initial value
(3) increase to eight times of its initial value
(4) increase to four times of its initial value.

6. In the respect of the equation $k = Ae^{-Ea/RT}$ in chemical kinetics, which one of the following statements is correct : **[AIEEE-2003, 3/225]**
(1) k is equilibrium constant (2) A is adsorption factor
(3) E_a is energy of activation (4) R is Rydberg constant.

7. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is : **[AIEEE-2004, 3/225]**
(1) 30 minutes (2) 15 minutes (3) 7.5 minutes (4) 60 minutes

8. The rate equation for the reaction $2A + B \longrightarrow C$ is found to be : rate = k[A] [B]. The correct statement in relation to this reaction is that the : **[AIEEE-2004, 3/225]**
(1) unit of k must be sec^{-1}
(2) $t_{1/2}$ is a constant
(3) rate of formation of C is twice the rate of disappearance of A
(4) value of k is independent of initial concentrations of A and B.

9. The half - life of a radioisotope is four hours. If the initial mass of the isotope was 200 g, the mass remaining after 24 hours undecayed is : **[AIEEE-2004, 3/225]**
(1) 1.042 g (2) 2.084 g (3) 3.125 g (4) 4.167 g.

10. Consider an endothermic reaction $X \longrightarrow Y$ with the activation energies E_b and E_f for the backward and forward reaction, respectively. In general **[AIEEE-2005, 3/225]**
(1) $E_b < E_f$ (2) $\Delta H = \Delta U$ (3) $\Delta H < \Delta U$ (4) $\Delta H > \Delta U$

11. A reaction involving two different reactants can never be : **[AIEEE-2005, 3/225]**
(1) unimolecular reaction (2) first order reaction
(3) second order reaction (4) bimolecular reaction

12. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will be : **[AIEEE-2006, 3/165]**
(1) remain unchanged (2) tripled
(3) increased by a factor of 4 (4) doubled

13. The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr.
$NO (g) + Br_2 (g) \rightleftharpoons NOBr_2 (g)$; $NOBr_2 (g) + NO (g) \longrightarrow 2NOBr (g)$ (slow step)

If the second step is the rate determining step, the order of the reaction with respect to NO(g) is
[AIEEE- 2007, 3/120]
(1) 1 (2) 0 (3) 3 (4) 2

14. 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}). **[AIEEE- 2007, 3/120]**
(1) 280 (2) 20 (3) 300 (4) 120

15. A radioactive element gets spilled over the floor of a room. Its half-life period is 30days. If the initial activity is ten times the permissible value, after how many days will it be safe to enter the room :
[AIEEE- 2007, 3/120]
(1) 10 days (2) 100 days (3) 1000 days (4) 300 days

16. For a reaction $\frac{1}{2}$ A $\longrightarrow$ 2B, rate of disappearance of 'A' related to the rate of appearance of 'B' by the expression. **[AIEEE- 2008, 3/105]**

(1) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$ (2) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (3) $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$ (4) $-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$

17. The half life period of a first order chemical reaction is 6.93 minutes. Time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301) : **[AIEEE - 2009, 8/144]**
(1) 23.03 minutes   (2) 46.06 minutes   (3) 460.6 minutes   (4) 230.3 minutes

18. The time for half life period of a certain reaction A $\longrightarrow$ Products is 1 hour. When the initial concentration of the reactant 'A', is 2.0 mol L^{-1} , how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1}. If it is a zero order reaction ? **[AIEEE - 2010, 8/144]**
(1) 4 h   (2) 0.5 h   (3) 0.25 h   (4) 1 h

19. Consider the reaction, Cl_2 (aq) + H_2S(aq) $\longrightarrow$ S(s) + $2H^+$ (aq) + $2Cl^-$ (aq)
The rate equation for this reaction is
       rate = k $[Cl_2][H_2S]$
Which of these mechanisms is/are consistent with this rate equation? **[AIEEE - 2010, 4/144]**
A. $Cl_2 + H_2S \longrightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow)
       $Cl^+ + HS^- \longrightarrow H^+ + Cl^- + S$ (fast)
B. $H_2S \Leftrightarrow H^+ + HS^-$ (fast equilibrium)
       $Cl_2 + HS^- \longrightarrow 2Cl^- + H^+ + S$ (slow)
(1) B only   (2) Both A and B   (3) Neither A nor B   (4) A only

20. The rate of a chemical reaction doubles for every 10ºC rise of temperature. If the temperature is raised by 50ºC, the rate of the reaction increases by about : **[AIEEE - 2011, 4/120]**
(1) 10 times   (2) 24 times   (3) 32 times   (4) 64 times

21. A reactant (A) forms two products :
       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 : **[AIEEE - 2011, 4/120]**
(1) $k_2 = k_1 e^{Ea_1/RT}$ (2) $k_2 = k_1 e^{Ea_2/RT}$ (3) $k_1 = A k_2 e^{Ea_1/RT}$ (4) $k_1 = 2k_2 e^{Ea_2/RT}$

22. For a first order reaction (A) $\rightarrow$ products the concentration of A changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of A is 0.01 M is : **[AIEEE - 2012, 4/120]**
(1) 1.73×10^{-5} M/min   (2) 3.47×10^{-4} M/min   (3) 3.47×10^{-5} M/min   (4) 1.73×10^{-4} M/min

23. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be : (R = 8.314 JK^{-1} mol^{-1} and log 2 = 0.301) **[JEE(Main) - 2013, 4/120]**
(1) 53.6 kJ mol^{-1} (2) 48.6 kJ mol^{-1} (3) 58.5 kJ mol^{-1} (4) 60.5 kJ mol^{-1}

24. For the non-stoichiometre reaction 2A + B $\rightarrow$ C + D, the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial concentration (A)	Initial concentration (B)	Initial rate of formation of C (mol L^- S^-)
0.1 M	0.1 M	1.2×10^{-3}
0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is : **[JEE(Main) - 2014, 4/120]**

(1) $\frac{dc}{dt} = k[A] [B]$ (2) $\frac{dc}{dt} = k[A]^2[B]$ (3) $\frac{dc}{dt} = k[A] [B]^2$ (4) $\frac{dc}{dt} = k[A]$

25. Higher order (>3) reactions are rare due to : **[JEE(Main)-2015, 4/120]**
(1) low probability of simultaneous collision of all the reacting species
(2) increase in entropy and activation energy as more molecules are involved
(3) shifting of equilibrium towards reactants due to elastic collisions
(4) loss of active species on collision

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26. 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)-2016, 4/120]**
(1) 6.93×10^{-4} mol min^{-1}
(2) 2.66 L min^{-1} at STP
(3) 1.34×10^{-2} mol min^{-1}
(4) 6.93×10^{-2} mol min^{-1}

27. Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 10kJ 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 : (R = 8.314 J mol^{-1} K^{-1}) **[JEE(Main)-2017, 4/120]**
(1) 12 (2) 6 (3) 4 (4) 8

28. 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(Main)-2018, 4/120]**
(1) 1 (2) 0 (3) 2 (4) 3

JEE(MAIN) ONLINE PROBLEMS

1. The half-life period of a first order reaction is 15 minutes. The amount of substance left after one hour will be : **[JEE(Main) 2014 Online (09-04-14), 4/120]**
(1) 1/4 of the original amount
(2) 1/8 of the original amount
(3) 1/16 of the original amount
(4) 1/32 of the original amount

2. In the reaction of formation of sulphur trioxide by contact process $2SO_2 + O_2 \rightleftharpoons 2SO_3$ the rate of reaction was measured as $\dfrac{d[O_2]}{dt} = -2.5 \times 10^{-4}$ mol L^{-1} s^{-1}. The rate of reaction in terms of $[SO_2]$ in mol L^{-1} s^{-1} will be : **[JEE(Main) 2014 Online (11-04-14), 4/120]**
(1) -1.25×10^{-4} (2) -2.50×10^{-4} (3) -3.75×10^{-4} (4) -5.00×10^{-4}

3. For the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$, the rate equation can be expressed in two ways $-\dfrac{d\ [N_2O_5]}{dt} = k[N_2O_5]$ and $+\dfrac{d\ [NO_2]}{dt} = k'[N_2O_5]$ k and k' related as P: **[JEE(Main) 2014 Online (11-04-14), 4/120]**
(1) k = k' (2) 2k = k' (3) k = 2k' (4) k = 4k'

4. The rate coefficient (k) for a particular reactions is 1.3×10^{-4} M^{-1}s^{-1} at 100°C, and 1.3×10^{-3} M^{-1}s^{-1} at 150°C. What is the energy of activation (E_A) (in kJ) for this reaction ? (R = molar gas constant = 8.314 JK^{-1} mol^{-1}) **[JEE(Main) 2014 Online (12-04-14), 4/120]**
(1) 16 (2) 60 (3) 99 (4) 132

5. For the reaction, $3A + 2B \rightarrow C + D$, the differential rate law can be written as : **[JEE(Main) 2014 Online (19-04-14), 4/120]**
(1) $\dfrac{1}{3}\dfrac{d[A]}{dt} = \dfrac{d[C]}{dt} = k[A]^n[B]^m$
(2) $-\dfrac{d[A]}{dt} = \dfrac{d[C]}{dt} = k[A]^n[B]^m$
(3) $+\dfrac{1}{3}\dfrac{d[A]}{dt} = \dfrac{d[C]}{dt} = k[A]^n[B]^m$
(4) $-\dfrac{1}{3}\dfrac{d[A]}{dt} = \dfrac{d[C]}{dt} = k[A]^n[B]^m$

6. 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 mmHg to 87.5 mm Hg in 30 min. The pressure exerted by the gases after 60 min. wil be (Assume temperature remains constant) : **[JEE(Main) 2015 Online (10-04-15), 4/120]**
(1) 125 mm Hg (2) 106.25 mm Hg (3) 116.25 mm Hg (4) 150 mm Hg

7. $A + 2B \rightarrow C$, the rate equation for this reaction is given as
        Rate = K[A][B]
If the concentration of A is kept the same but that of B is doubled what will happen to the rate itself ? **[JEE(Main) 2015 Online (11-04-15), 4/120]**
(1) halved (2) the same (3) doubled (4) quadrupled

8. 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 $\dfrac{2}{3}$ then : **[JEE(Main) 2015 Online (11-04-15), 4/120]**

(1) E_f = 80 kJ/mol; E_b = 120 kJ/mol
(2) E_f = 60 kJ/mol; E_b = 100 kJ/mol
(3) E_f = 30 kJ/mol; E_b = 70 kJ/mol
(4) E_f = 70 kJ/mol; E_b = 30 kJ/mol

9. A + 2B $\rightarrow$ C, the rate equation for this reaction is given as
        Rate = K[A][B].
If the concentration of A is kept the same but that of B is doubled what will happen to the rate itself ?
[JEE(Main) 2015 Online (11-04-15), 4/120]
(1) halved   (2) the same   (3) doubled   (4) quadrupled

10. The reaction of ozone with oxygen atoms in the presence of chlorine atoms can occur by a two step process show below:
$O_3(g) + Cl^\bullet(g) \rightarrow O_2(g) + ClO^\bullet(g)$ ...(i)
        $k_i = 5.2 \times 10^9$ L mol^{-1} s^{-1}
$ClO^\bullet(g) + O^\bullet(g) \rightarrow O_2(g) + Cl^\bullet(g)$ ...(ii)
        $k_{ii} = 2.6 \times 10^{10}$ L mol^{-1} s^{-1}
The closest rate constant for the overall reaction $O_3(g) + O^\bullet(g) \rightarrow 2O_2(g)$ is:
[JEE(Main) 2016 Online (09-04-16), 4/120]
(1) 1.4×10^{20} L mol^{-1} s^{-1} (2) 5.2×10^9 L mol^{-1} s^{-1}
(3) 3.1×10^{10} L mol^{-1} s^{-1} (4) 2.6×10^{10} L mol^{-1} s^{-1}

11. The rate law for the reaction below is given by the expression k [A][B]
A + B $\rightarrow$ Product
If the concentration of B is increased from 0.1 to 0.3 mole, keeping the value of A at 0.1 mole, the rate constant will be : **[JEE(Main) 2016 Online (10-04-16), 4/120]**
(1) 9 k   (2) 3 k   (3) k/3   (4) k

12. 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. **[JEE(Main) 2017 Online (08-04-17), 4/120]**
(1) 9.84 K   (2) 19.67 K   (3) 2.45 K   (4) 4.92 K

13. 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; ln2 = 0.693; R = 8.314 J mol^{-1} K^{-1}) **[JEE(Main) 2017 Online (09-04-17), 4/120]**
(1) 53.6 kJ mol^{-1} (2) 26.8 kJ mol^{-1} (3) 107.2 kJ mol^{-1} (4) 214.4 kJ mol^{-1}

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 mm Hg to 87.5 mm Hg. The pressure of the gaseous mixture after 100 minute at constant temperature will be : **[JEE(Main) 2018 Online (15-04-18), 4/120]**
(1) 136.25 mm Hg   (2) 106.25 mm Hg   (3) 175.0 mm Hg   (4) 116.25 mm Hg

15. For a first order reaction, A $\rightarrow$ P, $t_{\frac{1}{2}}$ (half-life) is 10 days. The time required for $\dfrac{1}{4}$th conversion of A (in days) is : (ln 2 = 0.693, ln 3 = 1.1) **[JEE(Main) 2018 Online (15-04-18), 4/120]**
(1) 5   (2) 3.2   (3) 4.1   (4) 2.5

16. If 50 % of a reaction occurs in 100 second and 75 % of the reaction occurs in 200 second, the order of this reaction is : **[JEE(Main) 2018 Online (16-04-18), 4/120]**
(1) 2   (2) 3   (3) Zero   (4) 1

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17. The following results were obtained during kinetic studies of the reaction;

2A + B → Products
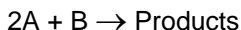
Experiment	[A] (in mol L⁻¹)	[B] (in mol L⁻¹)	Initial Rate of reaction (in mol L⁻¹ min⁻¹)
I	0.10	0.20	6.93×10^{-3}
II	0.10	0.25	6.93×10^{-3}
III	0.20	0.30	1.386×10^{-2}

Time time (in minutes) required to consume half of A is :   **[JEE(Main) 2019 Online (09-01-19), 4/120]**
(1) 1   (2) 5   (3) 10   (4) 100

18. For the reaction, 2A + B → products, when the concentration of A and B both were doubled, the rate of the reaction increased from 0.3 mol L⁻¹s⁻¹ to 2.4 mol L⁻¹s⁻¹. When the concentration of A alone is doubled, the rate increased from 0.3 mol L⁻¹s⁻¹ to 0.6 mol L⁻¹s⁻¹ .
Which one of the following statements is correct?   **[JEE(Main) 2019 Online (09-01-19), 4/120]**
(1) Order of the reaction with respect to B is 1
(2) Order of the reaction with respect to B is 2
(3) Total order of the reaction is 4
(4) Order of the reaction with respect to A is 2

19. 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)
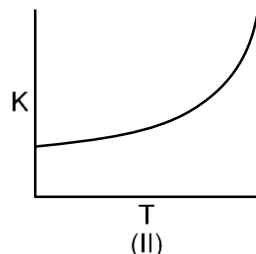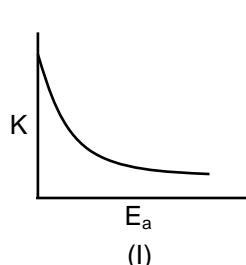
Choose the correct option :   **[JEE(Main) 2019 Online (10-01-19), 4/120]**
(1) I is right but II is wrong   (2) Both I and II are wrong
(3) I is wrong but II is right   (4) Both I and II are correct

20. For an elementary chemical reaction,

$A_2 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2A$ the expression for $\dfrac{d[A]}{dt}$ **[JEE(Main) 2019 Online (10-01-19), 4/120]**
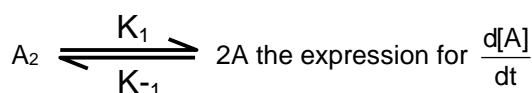
(1) $2k_1[A_2] - k_{-1}[A]^2$ (2) $k_1[A_2] + k_{-1}[A]^2$
(3) $k_1[A_2] - k_{-1}[A]^2$ (4) $2k_1[A_2] - 2k_{-1}[A]^2$

21. If a reaction follows the Arrhenius equation the plot lnk vs 1/(RT) gives straight line with a gradient (−y) unit . The energy required to activate the reactant is :   **[JEE(Main) 2019 Online (11-01-19), 4/120]**
(1) −y unit   (2) y unit   (3) y/R unit   (4) yR unit

22. The reaction 2X → B is a zeroth order reaction. If the intial 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 :   **[JEE(Main) 2019 Online (11-01-19), 4/120]**
(1) 18.0 h   (2) 12.0 h   (3) 7.2 h   (4) 9.0 h

23. 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 ?   **[JEE(Main) 2019 Online (12-01-19), 4/120]**
(1) 40   (2) 25   (3) 20   (4) 50

24. 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: **[JEE(Main) 2019 Online (12-01-19), 4/120]**
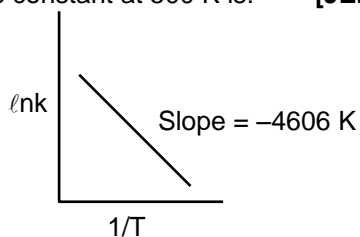
(1) 10^{-4} s^{-1} (2) 4×10^{-4} s^{-1} (3) 2×10^{-4} s^{-1} (4) 10^{-6} s^{-1}

Answers

EXERCISE - 1

PART – I

A-1. (a) 4.5×10^{-3} M sec^{-1} (b) 3.0×10^{-3} M sec^{-1}

A-2. (a) 40.5 g min^{-1} (b) 76.5 g min^{-1}

A-3. (a) 1.6×10^{-2} atm min^{-1} (b) 1.09×10^{-5} mol liter^{-1} sec^{-1}

A-4. (a) 3; (b) Both rates are 3.6×10^{-3} mole dm^{-3}s^{-1}; (c) No effect; (d) Decreased by a factor of 8; No effect

B-1. (i) 9.994 M   (ii) $\dfrac{10}{2 \times (2 \times 10^{-6})}$ (iii) 5×10^6 min

B-2. (a) 5×10^{-5} M/s   (b) 4.2×10^{-5} M/s   **B-3.**   0075.

B-4. 1.73 time   **C-1.** 1.25×10^4 min ; 2.5×10^4 min

C-2. 39.2 minutes   **C-3.** 1.84×10^{-2} min^{-1}

D-1. (i) rate = [A] [B] (ii) k = 4×10^{-2}M^{-1}s^{-1} (iii) rate = 2.8×10^{-3}M·s^{-1}

D-2. **(a)**   n = 2,   **(b)**   First Order   **D-3.**   2

E-1. 3.27×10^{-3} min^{-1}

E-2. Here a = 22.8, a – x = Vol. of KMnO$_4$ used at various times t.

At time 600 seconds :   K = $\dfrac{2.303}{600}$ log $\dfrac{22.8}{13.8}$ = 0.000837

At time 1200 seconds :   K = $\dfrac{2.303}{1200}$ log $\dfrac{22.8}{8.2}$ = 0.000852

Average value of K = $\dfrac{0.000837 + 0.000852}{2}$ = 0.000844 $\times 10^{-4}$ sec^{-1}

E-3. (i) 2.484 hr^{-1} (ii) $\dfrac{50}{3}$ min.   **F-1.** $k_1 = \dfrac{9 \ln 2}{2300}$; $k_2 = \dfrac{14}{2300}$ ln 2

F-2. E$_{overall}$ = E/3(2n+1)

G-1. (i) 2, 1   (ii) 2.67×10^8 mol^{-2} litre^2 sec^{-1} (iii) 55.13 kJ mol^{-1} (iv) 1.147×10^{18} mol^{-2} litre^2 sec^{-1}

G-2. 80.65%.

G-3. (A) y + z   (B) z   (C) x + y + z   (D) x   (E) x + y   (F) – y

H-1. – 1000   **H-2.**   k [N$_2$O$_5$]   **H-3.**   Rate = k [NO]^2 [Br$_2$]

H-4. (a) 2 B+F $\rightarrow$ 2E; (b) A; (c) C,D; (d) rate = k [B][C]; (e) rate = k'[A][B] (f) 2.

I-1. (30 days, 0.0231 per day)   **I-2.**   (12.01×10^{-5} years $^{-1}$, 1/4)

I-3. 0.9375 gram.   **I-4.**   t = 4.5×10^9 year.

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PART – II

A-1.	(A)	**A-2.**	(B)	**A-3.**	(D)	**A-4.**	(B)	**A-5.**	(B)
A-6.	(C)	**A-7.**	(A)	**A-8.**	(D)	**B-1.**	(B)	**B-2.**	(C)
B-3.	(C)	**B-4.**	(A)	**B-5.**	(A)	**B-6.**	(B)	**B-7.**	(D)
B-8.	(B)	**B-9.**	(C)	**C-1.**	(D)	**C-2.**	(C)	**C-3.**	(D)
C-4.	(C)	**C-5.**	(C)	**D-1.**	(B)	**D-2.**	(C)	**D-3.**	(B)
D-4.	(B)	**D-5.**	(D)	**D-6.**	(C)	**D-7.**	(B)	**D-8.**	(B)
D-9.	(B)	**E-1.**	(C)	**E-2.**	(B)	**E-3.**	(C)	**E-4.**	(A)
F-1.	(B)	**F-2.**	(B)	**F-3.**	(D)	**F-4.**	(D)	**G-1.**	(B)
G-2.	(D)	**G-3.**	(B)	**G-4.**	(C)	**G-5.**	(B)	**H-1.**	(D)
H-2.	(A)	**H-3.**	(C)	**H-4.**	(C)	**H-5.**	(C)	**H-6.**	(B)
H-7.	(A)	**I-1.**	(D)	**I-2.**	(A)	**I-3.**	(B)	**I-4.**	(C)
I-5.	(D)	**I-6.**	(B)	**I-7.**	(D)	**I-8.**	(C)	**I-9.**	(A)
I-10.	(A)								

PART – III

1.	(A → r) ; (B → s) ; (C → q) ; (D → p)	**2.**	(A) p, q, r, s ; (B) q, r, s ; (C) p, q, r, s ; (D) p, r, s
3.	(A – r ; B – s ; C – p ; D – q)		

EXERCISE – 2

PART – I

1.	(B)	**2.**	(C)	**3.**	(C)	**4.**	(B)	**5.**	(A)
6.	(C)	**7.**	(C)	**8.**	(C)	**9.**	(B)	**10.**	(A)
11.	(B)	**12.**	(B)	**13.**	(A)	**14.**	(A)	**15.**	(A)
16.	(D)	**17.**	(A)	**18.**	(B)	**19.**	(A)	**20.**	(C)

PART – II

1.	1	**2.**	2	**3.**	2	**4.**	2	**5.**	2
6.	Zero	**7.**	3	**8.**	10^{-19} minute	**9.**	50	**10.**	54
11.	30								

PART – III

1.	(ABD)	**2.**	(BCD)	**3.**	(ABC)	**4.**	(ABD)	**5.**	(AD)
6.	(AC)	**7.**	(ABCD)	**8.**	(BC)	**9.**	(AB)	**10.**	(ABC)
11.	(CD)	**12.**	(BC)	**13.**	(ABCD)	**14.**	(ABC)	**15.**	(BC)
16.	(AB)								

PART – IV

1.	(A)	**2.**	(D)	**3.**	(B)	**4.**	(A)	**5.**	(C)
6.	(A)	**7.**	(C)	**8.**	(B)	**9.**	(B)	**10.**	(A)
11.	(C)	**12.**	(A)	**13.**	(C)					

EXERCISE – 3

PART – I

1.	(D)	**2.**	$t = 4.62 \times 10^9$ years.	**3.**	$E_A = 100$ KJ/mol
4.	(B)	**5.**	$t_{1/2} = 24$ min.	**6.**	(A)
7.	$(t_{1/2})_1 = 36.1$ hr^{-1}, $(t_{1/2})_2 = 72.2$ hr^{-1}, $(t_{1/2})_3 = 27.44$ hr^{-1}.	**8.**	(B)		
9.	(A)	**10.**	(a) $R_0 = k[A_0]$, (b) 0.5 sec^{-1}.		

11.

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

t = 0   800   –   **–**

t   800 – 2x   3x   2x   = (800 + 3x)

from given data in time 100 min the partial pressure of X decreases from 800 to 400 so $t_{1/2}$ 100 min. Also in next 100 min Px decreases from 400 to 200 to again $t_{1/2}$ = 100 min. Since half left is independent of initial concentration so reaction must Ist order with respect to X.

Rate constant $K = \dfrac{\ell n2}{t_{1/2}} = 6.93 \times 10^{-3}$ min^{-1}.

Time taken for 75% completion = 2 × $t_{1/2}$ = 200 min.

Now when Px **=** 700 = 800 – 2x   so x = 50 mm of Hg

so total pressure = 800 + 3x = 950 mm of Hg

12.	(C)	**13.**	(B)	**14.**	(A)	**15.**	(D)	**16.**	(A)
17.	(D)	**18.**	0	**19.**	(A)	**20.**	(ABD)	**21.**	9
22.	(D)	**23.**	(A)	**24.**	(B)	**25.**	(B)	**26.**	8
27.	(BCD)	**28.**	(AB)	**29.**	(AD)	**30.**	8500 J/mole		

PART – II

JEE(MAIN) OFFLINE PROBLEMS

1.	(1)	**2.**	(1)	**3.**	(4)	**4.**	(4)	**5.**	(3)
6.	(3)	**7.**	(1)	**8.**	(4)	**9.**	(3)	**10.**	(1)
11.	(1)	**12.**	(3)	**13.**	(4)	**14.**	(2)	**15.**	(2)
16.	(1)	**17.**	(2)	**18.**	(3)	**19.**	(4)	**20.**	(3)
21.	(3)	**22.**	(2)	**23.**	(1)	**24.**	(4)	**25.**	(1)
26.	(1)	**27.**	(3)	**28.**	(3)				

JEE(MAIN) ONLINE PROBLEMS

1.	(3)	**2.**	(4)	**3.**	(2)	**4.**	(2)	**5.**	(4)
6.	(2)	**7.**	(3)	**8.**	(1)	**9.**	(3)	**10.**	(2)
11.	(4)	**12.**	(4)	**13.**	(3)	**14.**	(2)	**15.**	(3)
16.	(4)	**17.**	(2)	**18.**	(2)	**19.**	(4)	**20.**	(4)
21.	(2)	**22.**	(1)	**23.**	(4)	**24.**	(1)		

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Additional Problems For Self Practice (APSP)

✎ **Marked Questions may have for Revision Questions.**

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time : 1 Hr.   Max. Marks : 120

Important Instructions
1. The test is of **1 hour** duration.
2. The Test Booklet consists of **30** questions. The maximum marks are **120.**
3. Each question is allotted **4 (four)** marks for correct response.
4. Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question. **¼ (one fourth)** marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
5. There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

1. The reaction $A(g) + 2B(g) \rightarrow C(g)$ is an elementary reaction. In an experiment involving this reaction, the initial partial pressures of A and B are $P_A = 0.40$ atm and $P_B = 1.0$ atm respectively. When pressure of C becomes 0.3 atm in the reaction the rate of the reaction relative to the initial rate is :

    (1) $\dfrac{1}{12}$ (2) $\dfrac{1}{50}$ (3) $\dfrac{1}{25}$ (4) none of these

2. The rate law for the dimerisation of NO_2 is

    $$-\frac{d[NO_2]}{dt} = k\,[NO_2]^2$$

    which of the following changes will change the value of the specific rate constant , k :
    (1) Doubling the total pressure on the system   (2) Doubling the temperature
    (3) Both of (1) and (2)   (4) None of the above

3. Which of the following statement is incorrect?
    (1) unit of rate of disapperarance is Ms^{-1} (2) Unit of rate of reaction is Ms^{-1}
    (3) Unit of rate constant k is depend on order   (4) Unit of k for first order reaction is Ms^{-1}

4. Which of the following relation is correct for k_f and k_b in an equilibrium process that contains equal moles of reactants and products.
    (1) $k_f = k_b$ (2) $k_f > k_b$ (3) $k_f < k_b$ (4) we cannot predict

5. ✎ A graph plotted between $\log t_{50\%}$ vs. log concentration is a straight line. What conclusion can you draw from this graph.
    (1) $n = 1$; $t_{1/2} \propto a$ (2) $n = 2$, $t_{1/2} \propto 1/a$
    (3) $n = 1$; $t_{1/2} = (0.693 / k)$ (4) None of these

6. Which of the following statement is incorrect?
    (1) A second order reaction must be a biomolecular elementary reaction
    (2) A bimolecular elementary reaction must be a second order reaction
    (3) Zero order reaction must be a complex reaction
    (4) First order reaction may be complex or elementary reaction

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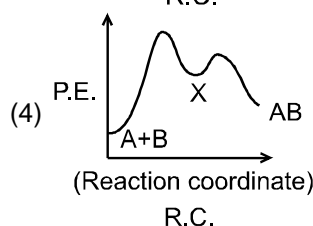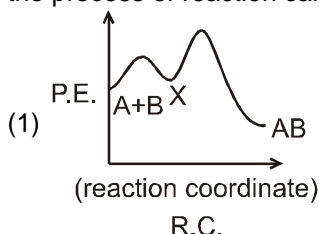**Toll Free :** 1800 258 5555 | **CIN:** U80302RJ2007PLC024029

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7. $A_2 + B_2 \longrightarrow 2AB$; Rate of reaction = $k[A]^a [B]^b$

Initial [A₂]	Initial [Br₂]	Rate of reaction (r) Ms⁻¹
0.2	0.2	0.04
0.1	0.4	0.04
0.2	0.4	0.08

Order of reaction with respect to A_2 and B_2 are respectively :
(1) a = 1, b = 1   (2) a = 2, b = 0   (3) a = 2, b = 1   (4) None of these

8. For a reaction $A(s) + B(s) \rightarrow C(s)$ is rate = $k[A]^{1/2} [B]^2$. What changes in rate if intial concentration of A and B increase by factor 4 and 2 respectively.
(1) 4   (2) 6   (3) 8   (4) None of these

9. Reaction $A \rightarrow B$ follows second order kinetics. Doubling the concetration of A will increase the rate of formation of B by factor of :
(1) 1/4   (2) 1/2   (3) 2   (4) 4

10. The forward rate constant for the elementary reversible gaseous reaction
$C_2H_6 \ \square \ 2CH_3$ is 1.57×10^{-3} s⁻¹ at 100 K
What is the rate constant for the backward reaction at this temperature if 10^{-4} mole of CH_3 and 10 moles of C_2H_6 are present in a 10 litre vessel at equilibrium.
(1) 1.57×10^9 L mol⁻¹ s⁻¹   (2) 1.57×10^{10} L mol⁻¹ s⁻¹
(3) 1.57×10^{11} L mol⁻¹ s⁻¹   (4) 1.57×10^7 L mol⁻¹ s⁻¹

11. Rate constant k is 2.303 min⁻¹ for a particular reaction. The initial concentration of the reaction is 1 mole/litre then rate of reaction after 1 minutes is :
(1) 2.303 M min⁻¹   (2) 0.2303 M min⁻¹   (3) 0.1 M min⁻¹   (4) none of these

12. For an elementary reaction $2A + B \longrightarrow A_2B$ if the volume of vessel is quickly reduced to half of it's original volume then rate of reaction will -
(1) unchange   (2) increase four times
(3) increase eight times   (4) decrease eight time

13. For a first order reaction $A \rightarrow B + 2C + 3D$ (A is optically inactive and B, C and D are dextrorotary), the optical rotation at time t and ∞ are r_t and r_∞ respectively, the expression for rate constant is
(1) $K = \dfrac{1}{t} \ln \dfrac{r_t}{r_\infty - r_t}$ (2) $k = \dfrac{1}{t} \ln \dfrac{r_\infty}{r_\infty - r_t}$ (3) $k = \dfrac{1}{t} \ln \dfrac{r_\infty - r_t}{r_t}$ (4) none of these

14. In the presence of acid, the initial concentration, of cane-sugar was reduced from 0.2 M to 0.1 M in 5 hr and to 0.05 M in 10 hr. The reaction must be of
(1) Zero order   (2) First order   (3) Second order   (4) Fractional order

15. For an exothermic chemical process occurring in two steps as follows
(i) $A + B \longrightarrow X$ (slow)   (ii) $X \longrightarrow AB$ (fast)
the process of reaction can be best describe by :

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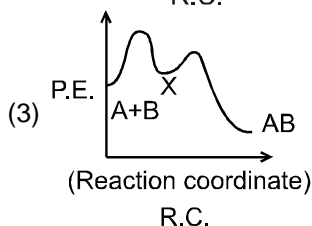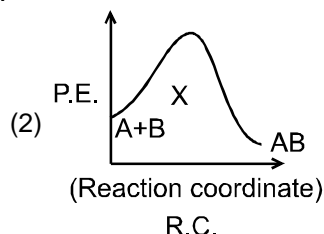
16. The temperature coefficient of a reaction is :
(1) The rate constant
(2) The rate of constant at a fixed temperature
(3) The ratio of rate constant at two temperature
(4) The ratio of rate constant differing by 10°C preferably k_{308}/k_{298}

17. The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A and B are $P_A = 0.60$ and $P_B = 0.80$ atm. When $P_C = 0.2$ atm, the rate of reaction relative to the initial rate is :
(1) 1/48   (2) 1/24   (3) 9/16   (4) 1/6

18. In the following reaction, how is the rate of appearance of the underlined product related to rate of disappearance of the underlined reactant :

$$BrO_3^-(aq) + 5\underline{Br}^-(aq) + 6H^+(aq) \longrightarrow 3\underline{Br_2}(\ell) + 3H_2O(\ell)$$

(1) $\dfrac{d[Br_2]}{dt} = -\dfrac{5}{3}\dfrac{d[Br^-]}{dt}$ (2) $\dfrac{d[Br_2]}{dt} = \dfrac{d[Br^-]}{dt}$

(3) $\dfrac{d[Br_2]}{dt} = -\dfrac{d[Br^-]}{dt}$ (4) $\dfrac{d[Br_2]}{dt} = -\dfrac{3}{5}\dfrac{d[Br^-]}{dt}$

19. $3A \longrightarrow B + C$
It would be a zero order reaction when :
(1) the rate of reaction is proportional to square of concentration of A
(2) the rate of reaction remains same at any concentration of A
(3) the rate remains unchanged at any concentration of B and C
(4) the rate of reaction doubles if concentration of B is increased to double

20. At room temperature, the reaction between NO and O_2 to give NO_2 is fast, while that between CO and O_2 is slow. It is due to :
(1) CO is smaller in size that of NO
(2) CO is poisonous
(3) The activation energy for the reaction, $2NO + O_2 \rightarrow 2NO_2$ is less then $2CO + O_2 \rightarrow 2CO_2$.
(4) None of the above

21. The time of decay for a nuclear reaction is given by $t = 4t_{1/2}$. The relation between the mean life (T) and time of decay (t) is given by :
(1) $2T \ln 2$ (2) $4T \ln 2$ (3) $2T^4 \ln 2$ (4) $\dfrac{1}{T^2} \ln 2$

22. Atoms $_7X^A$, $_8Y^B$ and $_9Z^{17}$ are such that $_8Y$ is an isobar of $_7X$ and atom $_9Z^{17}$ is isotone of $_8Y$. Mass no. of X and no. of neutrons in Y are respectively :
(1) 8, 8   (2) 17, 7   (3) 9, 8   (4) 16, 8

23. The mechanism of the reaction, $2NO + O_2 \longrightarrow 2NO_2$ is

$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ (fast) ;

$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$ (slow) ;

The rate constant of the reaction is :
(1) k_2 (2) $k_2 k_1 (k_{-1})$ (3) $k_2 k_1$ (4) $k_2 \left(\dfrac{k_1}{k_{-1}}\right)$

24. $t_{1/2} = $ constant confirms the first order of the reaction as one $a^2 t_{1/2} = $ constant confirms that the reaction is of :
(1) Zero order   (2) First order   (3) Second order   (4) Third order

25. For which of the following reactions, the units of rate constant and rate of reaction are same ?
(1) First order reaction   (2) Second order reaction
(3) Third order reaction   (4) Zero order reaction

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26. The half-life period of a second order reaction is :
(1) Proportional to the initial concentration of reactants
(2) Independent of the initial concentration of reactants
(3) Inversely proportional to the initial concentration of reactants
(4) Inversely proportional to the square of initial concentration of reactants

27. If the initial concentration of reactants in certain reaction is double, the half-life period of the reaction doubles, the order of a reaction is :
(1) Zero   (2) First   (3) Second   (4) Third

28. Ac^{227} has a half-life of 22 years. The decays folows two parallel paths

$$Ac^{227} \xrightarrow{\lambda_1} Th^{227} \text{ (\% yield = 2)}$$
$$Ac^{227} \xrightarrow{\lambda_2} Fr^{223} \text{ (\% yield = 98)}$$
(λ)
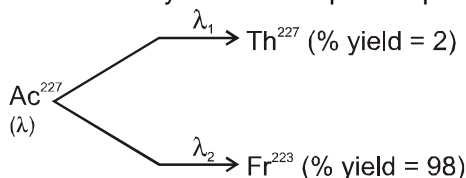
What are the decay constants (λ) for Th and Fr respectively ?
(1) 0.03087, 0.00063   (2) 0.00063, 0.03087   (3) 0.02, 0.98   (4) None of these

29. There are two radio nuclei A and B. A is a α-emitter and B is β-emitter, their disintegration constant are in the ratio of 1 : 2. What should be the number of atoms of two at time t = 0, so that probability of getting of α and β-particles are same at time t = 0
(1) 2 : 1   (2) 4 : 1   (3) 1 : 2   (4) 1 : 4

30. $_{84}Po^{218}$ ($t_{1/2}$ = 183 sec) decay to $_{82}Pb^{214}$($t_{1/2}$ = 161 sec) by α-emission, while Pb^{214} is a β-emitter. In an experiment starting with 1 mole of pure Po^{218}, how much time would be required for the number of nuclei of $_{82}Pb^{214}$ to reach maximum ?
(1) 147.5   (2) 247.5   (3) 182   (4) 304

Practice Test-1 (IIT-JEE (Main Pattern))
OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										
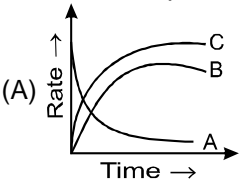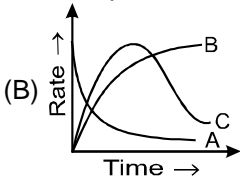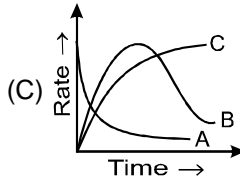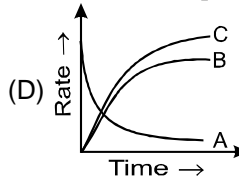
PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. One microcurie of radiation is the quantity of radioactive substance which produces :   **[NSEC-2000]**
(A) 3.7×10^{10} disintegrations per second.   (B) 6.022×10^{10} disintegrations per second
(C) 3.7×10^4 disintegrations per second.   (D) 3.7×10^7 disintegrations per second.

2. The inversion of cane sugar using excess water in the presence of acid catalyst is a reaction of :
    [NSEC-2000]
(A) third order   (B) second order
(C) first order with respect to cane sugar   (D) zero order with respect to cane sugar

3. The reaction, $2A \rightarrow B + C$ follows zero order kinetics. Its rate equation is represented by:**[NSEC-2000]**
(A) dx/dt = k. [A]$^-$ (B) dx/dt = k.[A]   (C) dx/dt = k.[A]^o (D) dx/dt = k.[2A]

4. The radioactive decay of $^{226}_{88}Ra$ is a reaction belonging to : **[NSEC-2000]**

(A) fraction order kinetics   (B) first order kinetics
(C) zero order kinetics   (D) second order kinetics

5. A radioactive element has a half life of 4 minutes. After 20 minutes, 1 gram of the element will reduce to
[NSEC-2000]

(A) 0.0625 g   (B) 0.125 g   (C) 0.25 g   (D) 0.03125 g

6. Decomposition of H_2O is a first order reaction. A 16 volume solution of H_2O_2 of half-life period 30 minutes is present at start. When will the solution become one volume ? **[NSEC-2001]**
(A) after 120 minutes   (B) after 90 minutes   (C) after 60 minutes   (D) after 150 minutes

7. According to Arrhenius equation, the rate of constant k and energy of activation (E) of a reaction are related by : **[NSEC-2001]**
(A) $A = k.e^{-E/RT}$ (B) $k = A.e^{E/RT}$ (C) $k = A.e^{-E/RT}$ (D) $k = - A.e^{E/RT}$

8. For a gaseous reaction, the following data was recorded. **[NSEC-2001]**

Concentration in mol. dm^{-3}	0.1	0.05	0.025	0.0125
Half time in s	30	29.9	30.1	30

The order of reaction is
(A) second   (B) first   (C) zero   (D) fractional order

9. The cell potential (E) and the free energy change (ΔG) accompanying an electrochemical reaction are related by : **[NSEC-2001]**
(A) $\Delta G = nF \log E$ (B) $\Delta G = nFE$ (C) $- \Delta G = nFE$ (D) $-\Delta G = nF \log E$

10. The half time of a second order reaction is : **[NSEC-2001]**
(A) inversely proportional to the square of the initial concentration of the reactants
(B) inversely proportional to the initital cocentration of the reactants
(C) proportional to the initial concentration of reactants
(D) independent of the initial concentration of reactants

11. For a third order reaction, the time for half reaction is related to the initial concentration of the reactants (a) by **[NSEC-2002]**
(A) $t_{1/2}$ is proportional to 1/a   (B) $t_{1/2}$ is proportional to a
(C) $t_{1/2}$ is proportional to $1/a^2$ (D) $t_{1/2}$ is proportional to $1/a^3$.

12. The half-life of a radionuclide is 2.0×10^5 s. Its decay constant will be : **[NSEC-2002]**
(A) 3.465×10^{-6} s^{-1} (B) 2.89×10^5 s^{-1} (C) 5.0×10^{-6} s^{-1} (D) 3.465 s^{-1}

13. 75% of a radioactive element disintegrate 2 hours. Its half life period is : **[NSEC-2002]**
(A) half hour   (B) one hour   (C) two hour   (D) three hour.

14. In an experiment, lead from drinking water is adsorbed onto activated carbon. This adsorption is a first order process with rate constant 1.8×10^{-5} s^{-1}. If the initial concentration of lead in water is 0.3 M, the time required to remove 90% of the initial lead is : **[NSEC-2003]**
(A) 1.3×10^5s   (B) 2.4×10^4s   (C) 1.8×10^7s   (D) 2.7×10^6s.

15. An isotope of a radioactive element is produced with the emission of **[NSEC-2003]**
(A) one α- and one β-particle   (B) one α- and two β-particles
(C) two α- and one β-particle   (C) two α- and two β-particles

16. Gadolinium (^{153} Gd), which has a half- life of 242 days, is used to detect osteoporosis. The percentage of ^{153} Gd left in a patient`s system after 23 years will be **[NSEC-2003]**
(A) 33.0   (B) 25.0   (C) 12.5   (D) 6.25

17. For a third order reaction $2A + B \rightarrow 3C$ with rate constant k (in proper units), the correct rate law is : **[NSEC-2003]**

(A) $-\dfrac{d[A]}{dt} = k\ [A]^2[B]$ (B) $-\dfrac{d[B]}{dt} = k[A]^2[B]$ (C) $-\dfrac{d[C]}{dt} = k\ [A]^2[B]$ (D) $-\dfrac{d[A]}{dt} = k\ 2[A].[B]$

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18. The correct representation of the plot of rate vs time for the reaction A → B → C is : **[NSEC-2004]**

19. A container with a radioactive isotope of half-life 3 days was sent to a laboratory. The activity of the same on 12th day was found to be 3 micro curies. (μC_1) Hence, the initial activity (μC_2) of the isotope when packed was: **[NSEC-2004]**
(A) 12   (B) 24   (C) 36   (D) 48.

20. The rate constant for a chemical reaction is related to temperature by the relation log k = 10 $-\frac{10^4 \times 5}{T}$.

If the reaction temperature is raised from 227ºC to 327ºC, the rate of this reaction would increase by a factor of about : **[NSEC-2004]**
(A) 20   (B) 46   (C) 2^{10} (D) 3.4×10^6.

21. The unit of the rate constant of a second order reaction with reactants having equal concentration is : **[NSEC-2004]**
(A) $mol\ dm^{-3}\ s^{-1}$ (B) $mol^2\ dm^{-6}\ s^{-1}$ (C) $dm^3\ mol^{-1}\ s^{-1}$ (D) s^{-1}

22. The units of rate and rate constant are identical in : **[NSEC-2005]**
(A) fractional order reactions   (B) first order reactions
(C) second order reactions   (D) zero order reactions.

23. The main function of the catalytic converter in automobiles is **[NSEC-2005]**
(A) to control the air pollutants produced by the automobile
(B) to decrease the rate of combustion of fuel
(C) to increase the rate of combustion of fuel
(D) to decrease the sound pollution.

24. Consider a decay scheme, A → B → C where A and B are radioisotopes with half lives 10 s and 20 s respectively. In an experiment, initially (t=0) there are 10,000 atoms of A and no atoms of B and C. Identify the correct statement regarding the number of atoms of A, B and C, viz. N_A, N_B and N_C at t = 30 s. **[NSEC-2005]**
(A) N_A = 2500 and N_B more than 7500   (B) N_A = 2500 and N_C less than 1000
(C) N_A = 1250 and N_C more than 7500   (D) N_A = 1250 and N_C more than 2500.

25. In 1911 Rutherford and Boltwood studied the rate of formation of helium from radium $^{226}_{88}Ra$. The first few steps in this transformation are given as Ra > 1500 year Rn 3.83 days RaA 3.05 min RaB. The species RaA and RaB are, in a modern notation respectively **[NSEC-2005]**
(A) $^{222}_{84}Po$ and $^{218}_{82}Pb$ (B) $^{210}_{85}At$ and $^{209}_{83}Bi$ (C) $^{218}_{84}Po$ and $^{214}_{82}Pb$ (D) $^{218}_{84}Po$ and $^{218}_{85}At$.

26. The units of the rate constant of a first order reaction when time is measured in seconds is: **[NSEC-2005]**
(A) s   (B) s^{-1} (C) $mol\ L^{-1}\ s^{-1}$ (D) $L\ mol^{-1}\ s^{-1}$.

27. In a multi - step reaction, rate of the overall reaction is governed by the **[NSEC-2006]**
(A) rate of the fastest step   (B) rate of the slowest step
(C) average rate of all the steps   (D) sum of the rates of all the steps.

28. A first-order reaction has a rate constant of $0.003\ s^{-1}$. The time required for completion of 75% reaction is **[NSEC-2007]**
(A) 231 s   (B) 201 s   (C) 41.7 s   (D) 462 s

29. The activation energy of a reaction is given by **[NSEC-2007]**
(A) R/(slope of a plot of ln k vs. 1/T)   (B) (slope of a plot of ln k vs. 1/T)/R
(C) (slope of a plot of ln k vs. 1/T) × R   (D) + (slope of a plot of ln vs. 1/T) × R

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30. Viscosity is a measure of resistance of a liquid to flow and viscosity- **[NSEC-2007]**
(A) decreases with increasing temperature
(B) increases with increasing temperature
(C) remains constant with temperature
(D) shows linear relation (with positive) with temperature.

31. By observing the reaction between gases A and B, the following data was obtained :

[A] mol L^1	[B] mol L^1	Initial rate mol L^{1}s^1
2.16 ×10^{-5}	1 ×10^{-5}	1 ×10^{-8}
2.14 ×10^{-5}	2.01 ×10^{-6}	2 ×10^{-9}
2.18 ×10^{-5}	3.2 ×10^{-5}	3.25 ×10^{-8}
4.31 ×10^{-5}	1.1 ×10^{-6}	4.3 ×10^{-9}
8.60 ×10^{-5}	2.1 ×10^{-5}	3.3 ×10^{-8}

The reaction orders with respect to A and B respectively are : **[NSEC-2007]**
(A) 1 and 2 (B) 0 and 2 (C) 2 and 1 (D) both are 1

32. For a reaction of the nth order, the time required for half reaction is inversely proportional to : **[NSEC-2007]**
(A) an (B) a$^{(n+1)}$ (C) a$^{(n+1)}$ (D) a

33. If the energy of a reaction is twice RT, its rate constant k is related to frequency factor A by the relation : **[NSEC-2007]**
(A) k = 0.135 A (B) k = 1.35 A (C) k = 0.0135A (D) k = 2.303A

34. For the reaction P + Q → R the following data was obtained **[NSEC-2008]**

Set	[P]	[Q]	Rate
I	0.125M	0.250M	0.01
II	0.250M	0.250M	0.04
III	0.250M	1.00M	0.08

The order of reaction is
(A) 1 (B) 2 (C) 3 (D) 2.5

35. For a chemical reaction, A + B → C + D, the following data was recorded :

Set No.	Initial Concentration of 'A' (mol.dm^{-3})	Initial Concentration of 'B' (mol.dm^{-3})	Rate of reaction (mol.dm^{-3}s^{-1})
1	4.00	3.00	0.10
2	12.00	3.00	0.90
3	12.00	6.00	0.90

The correct rate expression for the reaction is : **[NSEC-2009]**
(A) rate = k[A][B] (B) rate = k[A]^2[B]^2 (C) rate = k[A]^2 (D) rate = k[A][B]^2

36. A radioactive element has half life of 14 hours. The fraction of the radioactive isotope which will disintegrate in 56 hours is : **[NSEC-2009]**
(A) 0.75 (B) 0.875 (C) 0.9375 (D) 0.60

37. For a zero order reaction, the unit of rate constant is : **[NSEC-2009]**
(A) s^{-1} (B) mol.dm^{-3}s^{-1} (C) dm^{3}mol^{-1}s^{-1} (D) mol^2.dm^{-6}s^{-1}

38. Thorium-232 loses a total of 6α particles and 4β particles in a decay process. The isotope produced at the end is **[NSEC-2010]**
(A) $^{208}_{78}$Pt (B) $^{208}_{82}$Pb (C) $^{202}_{78}$Pt (D) $^{208}_{83}$Bi

39. For a first order reaction, the half-life t$_{(1/2)}$ is related to the rate constant (k) by the relation. **[NSEC-2010]**
(A) t$_{(1/2)}$ = $\frac{2.303}{k}$ log 2 (B) t$_{(1/2)}$ = $\frac{1}{k}$ (C) t$_{(1/2)}$ = $\frac{k}{2.303}$ log 2 (D) t$_{(1/2)}$ = $\frac{2.303}{k}$

40. The rate constants k_1 and k_2 of two reactions are in the ratio 2 : 1. The corresponding energies of activation of the two reactions will be related by : **[NSEC-2010]**
(A) $E_1 > E_2$ (B) $E_1 < E_2$ (C) $E_1 = E_2$ (D) $E_1 = 2E_2$

41. The correct statement about order of reaction is : **[NSEC-2010]**
(A) it can be predicted from the stoichiometric coefficients of the reactants.
(B) it has always positive integral values.
(C) it has always positive integral or fractional values.
(D) it has to be determined experimentally.

42. The initial activity of a radionuclide is 9750 counts per min and 975 counts after 5 min. The decay constant of the radionuclide in min^{-1} is about **[NSEC-2011]**
(A) 0.23   (B) 0.46   (C) 0.69   (D) 0.99

43. The number of α-particles emitted per second by a radioactive element reduces to 6.25% of the original value in 48 days. The half-life period of the element in days is **[NSEC-2011]**
(A) 3   (B) 8   (C) 12   (D) 16

44. The half time for a second order reaction with equal concentrations of the reactants is 35 seconds. 99% reaction will be completed in : **[NSEC-2011]**
(A) 69s   (B) 138s   (C) 1733s   (D) 3465s

45. Iodide ion is oxidized by acidified dichromate ions as shown in this equation, $Cr_2O_7^{2-}(aq) + 9I^-(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3I_3^-(aq) + 7H_2O(\ell)$. These data were obtained when the reaction was studied at a constant pH. The order of the reaction with respect to $Cr_2O_7^{2-}(aq)$ are **[NSEC-2011]**

Exeriment	$[Cr_2O_7^{2-}]$, M	$[I^-]$, M	Rate, $M.s^{-1}$
1	0.0050	0.0125	0.00050
2	0.010	0.0125	0.0010
3	0.0150	0.0250	0.0060

(A) first order with respect to both $Cr_2O_7^{2-}$ and I^-
(B) second order with respect to both $Cr_2O_7^{2-}$ and I^-
(C) second order with respect to $Cr_2O_7^{2-}$ and first order with respect to I^-
(D) first order with respect to $Cr_2O_7^{2-}$ and second order with respect to I^-

46. A first order reaction is 20% complete in 600 s. The time required to complete 75% of the same reaction will be : **[NSEC-2012]**
(A) 3120 s   (B) 3720 s   (C) 4320 s   (D) 4920 s

47. For the reaction $NH_4^+ + NO_2^- \longrightarrow N_2 + 2H_2O$ the following data was recorded. **[NSEC-2012]**

Set	NH_4^+ / M	NO_2^-	Rate / MS^{-1}
1	0.010	0.020	0.020
2	0.015	0.020	0.030
3	0.010	0.010	0.005

(A) rate = K $[NH_4^+]$ $[NO_2^-]$ (B) rate = K $[NH_4^+]^2$ $[NO_2^-]$
(C) rate = K$[NH_4^+]$ $[NO_2^-]^2$ (D) rate = K$[NH_4^+]^2$ $[NO_2]^2$

48. The rate constant of a reaction increases by 5% when the temperature is increased from 27°C to 28°C. Therefore, the energy of activation of the reaction is : **[NSEC-2012]**
(A) 36.6 kJ mol^{-1} (B) 46.6 kJ mol^{-1} (C) 16.6 kJ mol^{-1} (D) 26.6 kJ mol^{-1}

49. How old is a fossil bone whose ^{14}C content is 15.0% of that living bone ? **[NSEC-2013]**
Half life of ^{14}C isotope is 5.73×10^3yr.
(A) 25488 yr   (B) 15688 yr   (C) 388 yr   (D) 6818 yr

50. A plot of $1/[NO_2]$ verses time for decomposition of NO_2 was found to be linear. This means that the reaction **[NSEC-2013]**
(A) Is zero order with respect to $[NO_2]$
(B) Is first order with respect to $[NO_2]$
(C) Is second order with respect to $[NO_2]$
(D) Order cannot be determined from the information given

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51. The following data was recorded for the reaction : **[NSEC-2013]**

X + Y $\longrightarrow$ P

Set No.	[A]	[B]	Rate of the reaction
I	0.1 M	0.2 M	0.001
II	0.2 M	0.2 M	0.004
III	0.2 M	0.8 M	0.008

The order of the reaction is
(A) 1   (B) 2   (C) 2.5   (D) 3

52. As part of a diagnostic procedure for a thyroid disorder, a patient is given certain amount of iodine-131. The half life of this radioactive iodine-131 is 8.0 days. The percent fraction of iodine-131 that will remain in the body after 32 days, if there is no elimination of iodine through the body is **[NSEC-2014]**
(A) 6.25   (B) 0.0625   (C) 2.77   (D) 25

53. If k is the rate constant of the reaction and T is the absolute temperature, the correct plot is

[NSEC-2015]
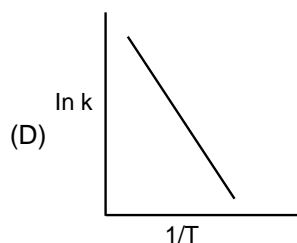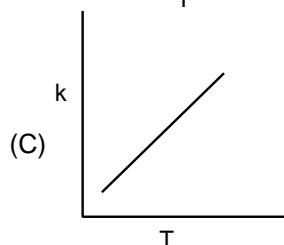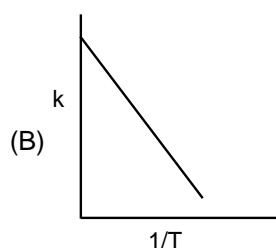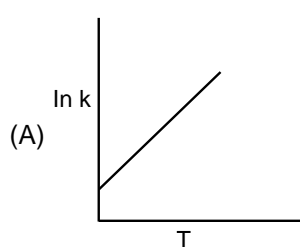
54. For a gaseous reaction, A + B $\rightarrow$ products, the energy of activation was found to be 2.27 kJ mol^{-1} at 273 K. The ratio of the rate constant (k) to the frequency factor (A) at 273 K is **[NSEC-2016]**
(A) 0.368   (B) 3.68   (C) 4.34   (D) 0.434

55. The kinetic data recorded at 278 K for the reaction **[NSEC-2016]**
NH_4^+ (aq) + NO_2^- (aq) $\rightarrow$ N_2 (g) + $2H_2O$ (*l*) is
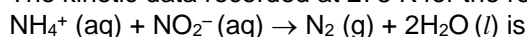
Set No.	[NH$_4^+$]/M	[NO$_2^-$]/M	Rate of reaction/ Ms^{-1}
1.	0.24	0.10	7.2×10^{-6}
2.	0.12	0.10	3.6×10^{-6}
3.	0.12	0.15	5.4×10^{-6}

The kinetic rate expression and the unit of rate constant (k) of the above reaction are respectively
(A) k [NH$_4^+$] [NO$_2^-$] and M s^{-1} (B) k [NH$_4^+$] and s^{-1}
(C) k [NH$_4^+$] [NO$_2^-$] and M^{-1} s^{-1} (D) k [NO$_2^-$] and s^{-1}

56. For an elementary rearrangement reaction A $\square$ P, the following data were recorded at 303 K, when [P]$_0$ = 0. **[NSEC-2016]**

Set No.	[A]$_0$/mol L^{-1}	Rate of conversation of A/mol L^{-1} min^{-1}
1	0.340	0.100
2	0.170	0.050
3	0.085	0.025

If the equilibrium constant of the reaction is 1.12 at 303 K, the rate constant for the reaction P$\rightarrow$ A is :
(A) 0.263 min^{-1} (B) 0.294 min^{-1} (C) 0.526 min^{-1} (D) 0.588 min^{-1}

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57. NaOH solution is added dropwise to HCl solution and the conductance of the mixture is measured after addition of each drop. The variation of conductance with volume of NaOH added is as shown below.
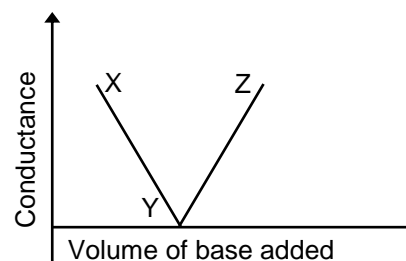
The statement that is not true for the above is **[NSEC-2016]**

(A) decrease in conductance from X $\rightarrow$ Y is due to decrease in [H^+]

(B) point Y represents the equivalence point of titration.

(C) Na^+ has the higher equivalence conductance than H_3O^+

(D) segment YZ represents the conductance due to ions from NaCl and NaOH in solution.

58. For the reaction $N_2 + 3H_2 \rightarrow$ the rate expression is $-d[NH_3]/dt = k[H_2][N_2]$

The correct statement is

I. The reaction is not elementary

II. The reaction is of second order

III. $-d[H_2]/dt = -d[NH_3]/dt$ **[NSEC-2017]**

(A) II only   (B) I and II   (C) II and III   (D) I, II and III

59. Which of the energy values marked as I, II and III in the following diagram, will change by the addition of a suitable catalyst?
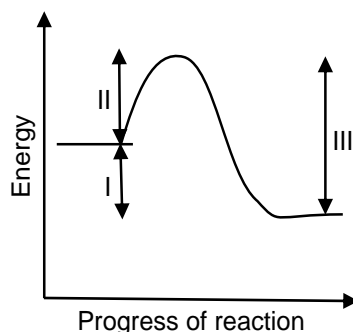
[NSEC-2018]

(A) II only   (B) I and II   (C) II and III   (D) III only

60. Urea, $CO(NH_2)_2$, decomposes at $90^\circ C$ as $CO(NH_2)_2(aq) \rightarrow NH_4^+(aq) + OCN^-(aq)$. Experimental data obtained for the reaction is given in the following plot
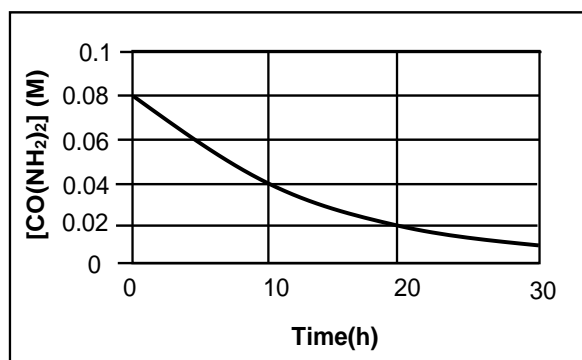
From the graph it can be inferred that **[NSEC-2018]**

(A) average rate of the reaction is the same for successive time intervals of 10 h

(B) unit of rate constant of the reaction is h^{-1}

(C) rate constant of the reaction is the lowest at 30 h

(D) the reaction is of zero order

61. The rate of the reaction between two reactants X and Y can be expressed as $R = k[X]^2[Y]$. In an experiment, the initial rate of the reaction was found to be R_1 when the initial concentrations of X and Y are [X_0] and [Y_0]. Another experiment was performed in which [X_0] was taken as $\frac{1}{2}[X_0]$. What should be [Y_0] in this experiment to get the initial rate as $0.5R_1$? **[NSEC-2018]**

(A) 4 [Y_0]   (B) 1/2 [Y_0]   (C) 2 [Y_0]   (D) [Y_0]

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PART - III : HIGH LEVEL PROBLEMS (HLP)

THEORY

COMPLICATIONS IN 1st ORDER REACTION

REVERSIBLE 1ST ORDER REACTION (both forward and backward)

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

	A	B
t = 0	a	0
t = t	a − x	x
t = t$_{eq.}$	a − x$_{eq.}$	x$_{eq.}$
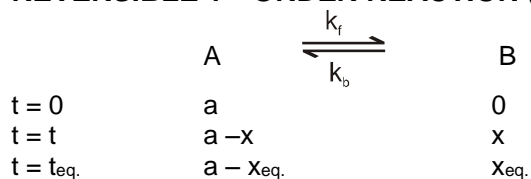
x$_{eq.}$ = eq conc. of product

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0 \qquad (\because \text{At equilibrium conc. is not changed})$$

$$\frac{d[A]}{dt} = -k_f[A] + k_b[B]$$

$$\frac{d[B]}{dt} = -k_b[B] + k_f[A]$$

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

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

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

$$-\frac{\ell n[k_f a - (k_f + k_b)x]_0^x}{k_f + k_b} = t$$

$$\Rightarrow \quad \frac{1}{k_f + k_b}\left(-\ell n\left(\frac{k_f a - (k_f + k_b)x]}{k_f a}\right)\right) = t \qquad \Rightarrow \qquad \frac{1}{k_f + k_b} \ell n\left(\frac{k_f a}{k_f a - (k_f + k_b)x]}\right) = t$$

$$\boxed{x = \frac{k_f a}{k_f + k_b}\left(1 - e^{-(k_f + k_b)t}\right)} \qquad \text{(remember)}$$

$$K_{eq.} = \frac{k_f}{k_b} = \frac{[B]_{eq.}}{[A]_{eq.}} = \frac{x_{eq.}}{(a - x_{eq.})}$$

$$\frac{k_f + k_b}{k_f} = \frac{a}{x_{eq.}}$$

$$x = x_{eq.}\left(1 - e^{-(k_f + k_b)t}\right) \qquad (t \to \infty, \ x \to x_{eq.})$$

$$\boxed{k_f + k_b = \frac{1}{t}\ell n\left(\frac{x_{eq.}}{x_{eq.} - x}\right)} \qquad \text{(remember)}$$

$$\text{Where } X_{eq} = a \times \left[\frac{k_f}{k_f + k_b}\right]$$

$$X_{eq} = \frac{k_f \times a}{k_f + k_b}.$$

if $\dfrac{k_f}{k_b} = 2$

SEQUENTIAL 1ST ORDER REACTION OR CONSECUTIVE FIRST-ORDER REACTIONS

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad \text{all first order equation}$$

t = 0	a	0	0
t	a – x	y	z
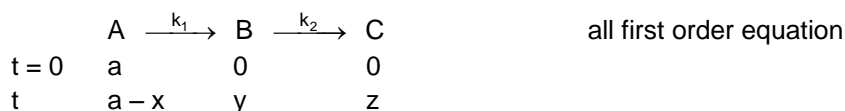
Calculate $[A]_t$, $[B]_t$ and $[C]_t$

For $\rightarrow$ A

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

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

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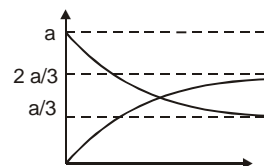
$$a - x = a \, e^{-k_1 t}$$

☞ $\quad x = a(1 - e^{-k_1 t})$

For $\rightarrow$ B

$$r_2 = k_2 [B]$$

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

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

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

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

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

$$k_2 y \, e^{k_2 t} = \left(\frac{k_1 a}{k_2 - k_1} \right) e^{(k_2 - k_1)t} + y$$

At t = 0 $\qquad y = 0$

$$y = - \left(\frac{k_1 a}{k_2 - k_1} \right)$$

☞ $\quad \boxed{ y = \frac{k_1 a}{k_2 - k_1} \{ e^{-k_1 t} - e^{-k_2 t} \} } \qquad$ (remember)

Calculate time at which concentration of B will be maximum

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

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

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

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

☞ $\quad \boxed{ t_{max.} = \frac{1}{(k_1 - k_2)} \ell n \frac{k_1}{k_2} } \qquad$ (remember)

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

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CASE-I $k_1 \gg k_2$

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

a

a – x   x
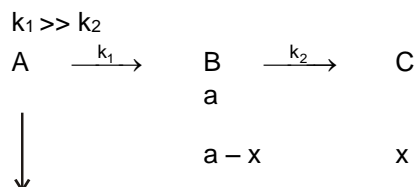
☞ $[A] = a\,e^{-k_1 t}$ (conc. is minimum)

☞ $[B] = a\,e^{-k_2 t}$

☞ $[C] = a\,(1 - e^{-k_2 t})$

∴ $k_1 t \gg k_2 t$

   $k_1 > k_2$

∴ $k_1 t \ll -k_2 t$

∴ $e^{-k_1 t} \ll e^{-k_2 t}$

   $y = \dfrac{k_1 a}{k_1}\,(-e^{-k_1 t}) = a\,e^{-k_2 t} = [B]$

Effective half life is $t_{1/2}$ for B.
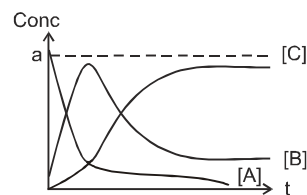
CASE-II : $k_2 \gg k_1$

                $[B]_t \to 0$

☞ $[A] = a\,e^{-k_1 t}$

☞ $[C] = a\,(1 - e^{-k_1 t})$

          $y = \dfrac{k_1}{k_2}\,a\,e^{-k_1 t} = \dfrac{k_1}{k_2}\,[A]$ $\left(\dfrac{k_1}{k_2} \to 0\right)$
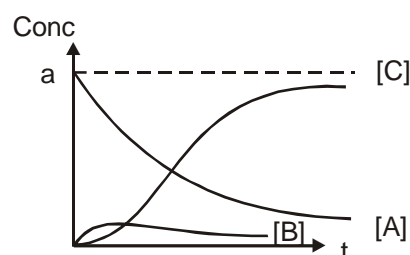
CASE-III :   If in sequential equation, $k_1 = k_2 = k$

          $y = kate^{-kt}$

          $z = a(1 - e^{-kt}) - kate^{-kt}$

—— *Solved Examples* ——

Ex.1   Starting from the equation for radioactive decay i.e. $-\dfrac{dN}{dt} = \lambda N$, derive the expression, mean life = $\dfrac{1}{\lambda}$.

Sol.   (i) $-\dfrac{dN}{dt} = \lambda N$. This on integration gives (with $N = N_0$, at $t = 0$); $N = N_0\,e^{-\lambda t}$

Mean life = $\left[\dfrac{\displaystyle\int_{t=0}^{\infty} t\,dN}{\displaystyle\int_{t=0}^{\infty} dN}\right] = \dfrac{\displaystyle\int_{t=0}^{\infty} t\,\dfrac{dN}{dt}\,dt}{\displaystyle\int_{t=0}^{\infty} \dfrac{dN}{dt}\,dt} = \dfrac{\displaystyle\int_{t=0}^{\infty} (-\lambda N_0)e^{-\lambda t}\,t\ dt}{\displaystyle\int_{t=0}^{\infty} (-\lambda N_0)e^{-\lambda t}\ dt} = \dfrac{1}{\lambda}$.   ∴ Mean life = $\dfrac{1}{\lambda}$

Ex.2   In the case of first order consecutive reactions $A \xrightarrow{\ k_1\ } B \xrightarrow{\ k_2\ } C$ (Product), one may show that the concentration of B is given by $C_B = \dfrac{k_1 C_A^0}{(k_2 - k_1)}\left[e^{-k_1 t} - e^{-k_2 t}\right]$.

The usual assumptions are $C_A = C_A^0$ at $t = 0$ while $C_B = C_C = 0$ at $t = 0$. Show that C_B has its maximum value at time $t = \left(\dfrac{2.303}{k_2 - k_1}\right)\log\left(\dfrac{k_2}{k_1}\right)$.

Sol. $\dfrac{dC_B}{dt} = \dfrac{k_1 C_A^\circ}{(k_2 - k_1)}\left[k_2 e^{-k_2 t} - k_1 e^{-k_1 t}\right]$

equating this zero $k_2 e^{-k_2 t} = k_1 e^{-k_1 t}$

∴ $\dfrac{k_2}{k_1} = e^{(k_2 - k_1)t}$ ∴ $\ell n\left(\dfrac{k_2}{k_1}\right) = (k_2 - k_1)\,t$ ∴ $t = \left(\dfrac{2.303}{k_2 - k_1}\right)\log\left(\dfrac{k_2}{k_1}\right)$

SUBJECTIVE QUESTIONS

1. For the reaction A $\to$ B, the rate law expression is $-\dfrac{d[A]}{dt} = K[A]^{1/2}$. If initial concentration of A is A_0.

Calculate :   (a) integrated form of the rate law expression
(b) nature of plot of $[A]^{1/2}$ vs time.
(c) half life period.

2. **(a)** Let there be as first-order reaction of the type, A B + C. Let us assume that all three species are gases. We are required to calculate the value of rate constant based on the following data.

Time	0	t	∞
Partial pressure of A	P_0	P_t	–

(b) Let there be a first order reaction, A B + C. Let us assume all three are gases. We are required to calculate the value of rate constant based on the following data.

Time	0	t	∞
Total pressure	P_0	P_t	–

Calculate the expression of rate constant.

(c) A(g) $\longrightarrow$ B(g) + C(g)

Time	0	t	∞
Total pressure of B + C	–	P_t	P_∞

Calculate the expression of rate constant.

(d) A(g) $\longrightarrow$ B(g) + C(s)

Time	0	t	∞
Total pressure of B	–	P_t	P_∞

Calculate the expression of rate constant.

3. For a first order reversible reaction A $\underset{K_b}{\overset{K_f}{\rightleftharpoons}}$ B , the initial concentration of A and B are $[A]_0$ and zero respectively. If concentrations at equilibrium are $[A]_{eq.}$ and $[B]_{eq.}$ derive an expression for the time taken by B to attain concentration equal to $[B]_{eq/2}$.

4. For a gaseous reaction A $\longrightarrow$ products, the half-life of the first order decomposition at 400 K is 150 minutes and the energy of activation is 65.0 kJ mole^{-1}. What fraction of molecules of A at 400 K have sufficient energy to give the products ?

5. At some temperature, the rate constant for the decomposition of HI on a gold surface is 0.1 Ms^{-1}.
2HI $\longrightarrow$ H$_2$(g) + I$_2$(g)
What is the order of the reaction? How long will it take for the concentration of HI to drop from 2M to 0.5M
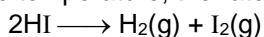
ONLY ONE OPTION CORRECT TYPE

6. A certain reaction A + B $\longrightarrow$ C, the first order with respect to each reactant k = 10^{-3}. Determine the final concentration of A after 100 s, if the initial concentration of A was 0.1 M and that of B was 0.2 M.
(A) 0.098 M   (B) 0.088 M   (C) 0.078 M   (D) 0.068 M

7. At a given temperature, $k_1 = k_2$ for the reaction, A + B $\rightleftharpoons$ C + D.

If $\left[\dfrac{dx}{dt}\right] = k_1 [A] [B] - k_2[C] [D]$ in which set of the concentration reaction ceases?

	[A]	[B]	[C]	[D]		[A]	[B]	[C]	[D]
(A)	0.1 M	0.2 M	0.3 M	0.4 M	(B)	0.4 M	0.25 M	0.2 M	0.5 M
(C)	0.2 M	0.2 M	0.3 M	0.2 M	(D)	0.2 M	0.2 M	0.4 M	0.2 M

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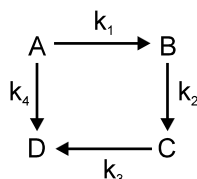**8.** For the complex, $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2^+]$

$$\left(\frac{dx}{dt}\right) = 2 \times 10^7 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1} [Ag^+] [NH_3]^2 - 1 \times 10^{-2} \text{ s}^{-1} [Ag(NH_3)_2^+]$$

Hence, ratio of rate constants of the forward and backward reactions is :
(A) 2×10^7 L^2 mol^{-2} (B) 2×10^9 L^2 mol^{-2} (C) 1×10^{-2} L^2 mol^{-2} (D) 0.5×10^{-9} L^2 mol^{-2}

9. Consider the elementary reaction sequence shown in figure. Which of the following equations are correct?

(A) $\dfrac{d[A]}{dt} = -k_1[A] + k_4[D]$ (B) $\dfrac{d[C]}{dt} = k_2[B] - k_3[C]$

(C) $\dfrac{d[D]}{dt} = k_4[D] + k_3[D]$ (D) Nothing can be said about order of reactions in this problem

10. The steady state concentration of the activated molecule [A*] in the following sequence of steps is given by :

$$A + A \xrightarrow{\ K_1\ } A + A^*$$
$$A^* + A \xrightarrow{\ K_2\ } 2A$$
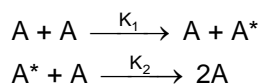
(A) $\dfrac{K_2[A]}{K_1}$ (B) $\dfrac{K_1[A]}{K_2}$ (C) $K_1K_2[A]$ (D) $\dfrac{K_1K_2}{[A]}$

11. The α activity in 1 g sample of ^{226}Ra ($t_{1/2}$ = 1600 years) is equal to :
(A) 2.19×10^{12} dpm   (B) 2.19×10^{14} dpm   (C) 2.19×10^{16} dpm   (D) 4.96×10^{12} dpm

12. In the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$\left(\frac{dx}{dt}\right) = 1 \times 10^2 [N_2] [H_2]^3 - 1 \times 10^{-3} [NH_3]^2 \text{ and at some instant if } \frac{[N_2][H_2]^3}{[NH_3]^2} = 10^{-5} \text{ M}^2$$

then at this instant value of $\left(\dfrac{dx}{dt}\right)$ is :

(A) 0   (B) 1×10^5 (C) 1×10^{-5} (D) 1×10^{-3}

13. A (aq) $\rightarrow$ B (aq) + C (aq) is a first order reaction.

Time	t	∞
moles of reagent	n_1	n_2

Reaction progress is measure with the help of titration of reagent 'R'.If all A, B and C reacted with reagent and have 'n' factors $\left[\text{n factors; eq.wt.} = \dfrac{\text{mol. wt}}{n}\right]$ in the ratio of 1 : 2 : 3 with the reagent.The k in terms of t, n_1 and n_2 is :

(A) $k = \dfrac{1}{t}\ln\left(\dfrac{n_2}{n_2 - n_1}\right)$ (B) $k = \dfrac{1}{t}\ln\left(\dfrac{2n_2}{n_2 - n_1}\right)$ (C) $k = \dfrac{1}{t}\ln\left(\dfrac{4n_2}{n_2 - n_1}\right)$ (D) $k = \dfrac{1}{t}\ln\left(\dfrac{4n_2}{5(n_2 - n_1)}\right)$

14. For A $\xrightarrow{\ K_1\ }$ B $\xrightarrow{\ K_2\ }$ C, at what time will B be present in greatest concentration ?

(A) $\dfrac{k_1}{K_2 - K_1}$ (B) $\dfrac{1}{K_1 - K_2}\ln\dfrac{k_1}{k_2}$ (C) $\dfrac{1}{K_2 - K_1}\ln\dfrac{k_1}{k_2}$ (D) None of these

15. A $\xrightarrow{K=2\times10^{-5}\text{s}^{-1}}$ B $\xrightarrow{K=8\times10^{-6}\text{s}^{-1}}$ C $\xrightarrow{K=3\times10^{-3}\text{s}^{-1}}$ D

The rate determining step of the reaction is -
(A) A $\longrightarrow$ B   (B) C $\longrightarrow$ D   (C) B $\longrightarrow$ C   (D) A $\longrightarrow$ D

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16. A reaction is catalysed by H^+ ion;and in the rate law the dependence of rate is of first order with respect to the concentration of H^+ ions, in presence of HA rate constant is 2×10^{-3} min^{-1} and in presence of HB rate constant is 1×10^{-3} min^{-1}. HA and HB have relative strength as :
(A) 0.5   (B) 0.002   (C) 0.001   (D) 2

MATCH THE COLUMN

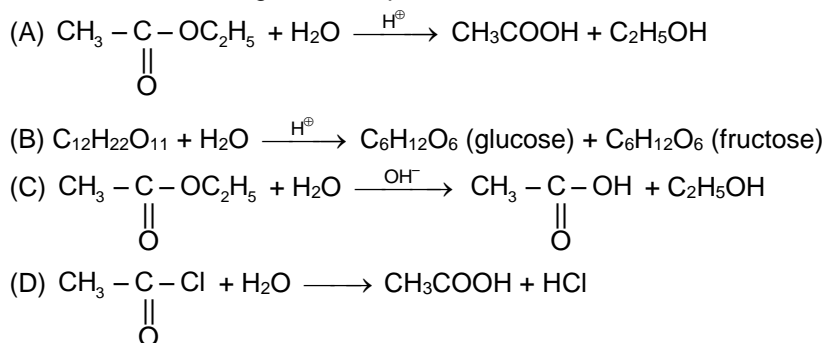**17.** Match the order of reaction (in List **I**) with its property (in List **II**) :

	List I (order)		List II (Property)
(A)	Zero	(p)	Half life $\propto \dfrac{1}{a^2}$
(B)	First	(q)	Half life $\propto \dfrac{1}{a}$
(C)	Second	(r)	Half life is doubled on doubling the initial concentration
(D)	Third	(s)	50% reaction takes same time even if concentration is halved or doubled.

SINGLE AND DOUBLE VALUE INTEGER TYPE

18. A 1 mL sample of a bacterial culture at 37ºC is taken, and diluted to 10 L. A 1mL sample of the diluted culture is spread on a culture plate. Ten minutes later, another 1mL sample taken from the original culture diluted and spread in the same way. The two plates are incubated for 24 hours. The first sample exhibits 48 colonies of bacteria, the second 72 colonies. If we assume that each colony originates with a single bacterium, what is the approx generation time in minute (time required for doubling the population).

19. Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open. Due to this, some H_2O_2 decomposed. To determine the new volume strength after 6 hours, 10 mL of this solution was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.025 M $KMnO_4$ solution under acidic conditions. Calculate the rate constant for decomposition of H_2O_2 in second^{-1}. Report your answer as k × 100. [ln $\dfrac{20}{17.5}$ = 0.1335]

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

20. Which of the following are example of Pseudo uni molecular reaction?

(A) $CH_3 - \underset{\underset{O}{\|}}{C} - OC_2H_5 + H_2O \xrightarrow{H^\oplus} CH_3COOH + C_2H_5OH$

(B) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^\oplus} C_6H_{12}O_6$ (glucose) $+ C_6H_{12}O_6$ (fructose)

(C) $CH_3 - \underset{\underset{O}{\|}}{C} - OC_2H_5 + H_2O \xrightarrow{OH^-} CH_3 - \underset{\underset{O}{\|}}{C} - OH + C_2H_5OH$

(D) $CH_3 - \underset{\underset{O}{\|}}{C} - Cl + H_2O \longrightarrow CH_3COOH + HCl$

21. A reaction takes place in three steps. The rate constant of the three steps are k_1, k_2 and k_3 respectively.

The overall rate constant k = $\dfrac{k_1 k_3}{k_2}$

The energy of activation for the three steps are 40, 30 and 20 KJ respectively. Therefore :
(A) Overall energy of activation is 10 KJ
(B) Overall energy of activation is 30 KJ

(C) The reaction mechanism is 2A $\underset{K_2}{\overset{K_1}{\rightleftharpoons}}$ A* + A ; A * $\xrightarrow[\text{rds}]{K_3}$ product and overall order is one.

(D) The reaction mechanism is A $\xrightarrow{K_1}$ B ; B $\xrightarrow{K_2}$ C ; C $\xrightarrow{K_3}$ product and overall order is one

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22. The rate expression for the reaction :

$NH_4CNO \rightleftharpoons NH_2CONH_2$ can be derived from the mechanism :

i. $NH_4CNO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_4NCO$ (Fast)

ii. $NH_4NCO \xrightarrow{k_3} NH_3 + HNCO$ (Fast)

iii. $NH_3 + HNCO \xrightarrow{k_4} NH_2CONH_2$ (Slow)
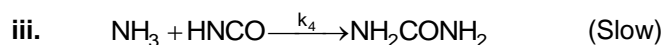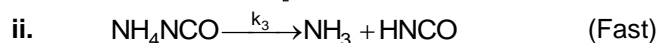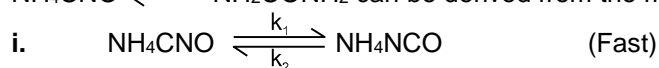
Which of the following statement(s) is/are correct about the rate expression ?

(A) $\dfrac{d_{(urea)}}{dt} = \dfrac{k_1 k_3}{k_2}[NH_4NCO]$ (B) $\dfrac{d_{(urea)}}{dt} = \dfrac{k_1 k_3}{k_2 k_4}[NH_4NCO]$

(C) $\dfrac{d_{(urea)}}{dt} = k[NH_4NCO]$ (D) $\dfrac{d_{(urea)}}{dt} = \dfrac{k_1 \times k_2}{k_3 \times k_4}[NH_4NCO]$

PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.   **Max. Marks : 63**

Important Instructions

A. General :

1. The test is of 1 hour duration.
2. The Test Booklet consists of 21 questions. The maximum marks are 63.

B. Question Paper Format :

3. Each part consists of five sections.
4. Section-1 contains 8 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5. Section-2 contains 4 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
6. Section-3 contains 5 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
7. Section-4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a partcular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
8. Section-5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme :

9. For each question in Section-1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (– 1) mark will be awarded.
10. For each question in Section-2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
11. For each question in Section-3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)
This section contains 8 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

---

1. 60 % of a first order reaction was completed in 60 min. The time taken for decompose to half of their original amount will be :

(A) $\approx$ 30 min   (B) $\approx$ 45 min   (C) $\approx$ 20 min   (D) $\approx$ 40 min

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2. The decomposition of H_2O_2 can be followed by titration with $KMnO_4$ and is found to be a first order reaction. The rate constant is 4.5×10^{-2}. In an experiment, the initial titre value was 25 mL. The titre value will be 5 mL after a lapse of

(A) $4.5 \times 10^{-2} \times 5$ min
(B) $\dfrac{\log_e 5}{4.5 \times 10^{-2}}$ min
(C) $\dfrac{\log_e 5/4}{4.5 \times 10^{-2}}$ min
(D) None of the above

3. In a second order reaction, 20% of a substance is dissociated in 40 min. The time taken by 80% of its dissociation is :
(A) 160 min
(B) 640 min
(C) 200 min
(D) 320 min

4. A simple mechanism for enzyme-catalysed reaction is given by the following set of equations

E + S	$\rightleftharpoons$	ES
(enzyme) (reactant)		(intermediate-1)
ES	$\rightleftharpoons$	EP
(intermediate-1)		(intermediate-2)
EP	$\rightleftharpoons$	E + P
(intermediate-2)		(enzyme) (product)

This is known as the Michaelis–Menten mechanism. The potential energy diagram is shown in the fig. Which of the following sets of identifications is correct ?
(Assume that the temperature and pressure are constant).

	(1)	(2)	(3)	(4)
(A)	E + P.	EP	ES	E + S
(B)	ES	Activated complex	EP	Activated complex
(C)	EP	Activated complex	ES	Activated complex
(D)	E + S	ES	EP	E + P

5. In a reaction carried out at 500 K, 0.001 % of the total number of collisions are effective. The energy of activation of the reaction is approximately
(A) 15.8 kcal mol^{-1}
(B) 11.5 kcal mol^{-1}
(C) 12.8 kcal mol^{-1}
(D) zero

6. A reaction, the rate constant is expressed as $k = Ae^{-40000/T}$. The energy of the activation is
(A) 40000 cal
(B) 88000 cal
(C) 80000 cal
(D) 8000 cal

7. For the decomposition of H_2O_2(aq) it was found that V_{O_2} (t = 15 min.) was 100 mL (at 0ºC and 1 atm) while V_{O_2} (maximum) was 200 mL (at 0ºC and 2 atm). If the same reaction had been followed by the titration method and if $V_{KMnO_4}^{(cM)}$ (t = 0) had been 40 mL, what would $V_{KMnO_4}^{(cM)}$ (t = 15 min) have been ?
(A) 30 mL
(B) 25 mL
(C) 20 mL
(D) 15 mL

8. Consider the following reactions at 300 K.
$A \rightarrow B$ (uncatalysed reaction)
$A \xrightarrow{\text{catalyst}} B$ (catalyst reaction)
The activation energy is lowered by 8.314 KJ mol^{-1} for the catalysed reaction. How many times the rate of this catalysed reaction greater than that of uncatalysed reaction ?   (Given $e^{3.33} = 28$)
(A) 15 times
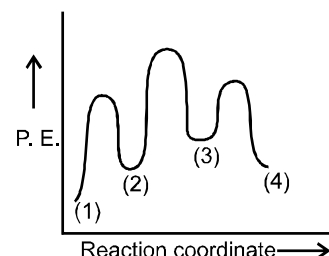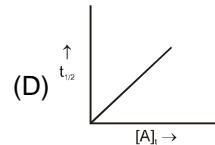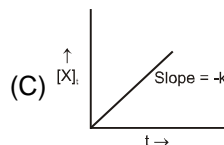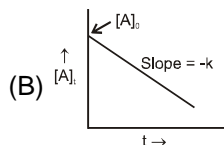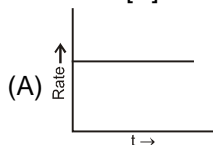(B) 38 times
(C) 22 times
(D) 28 times

Section-2 : (One or More than one options correct Type)
This section contains 4 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.
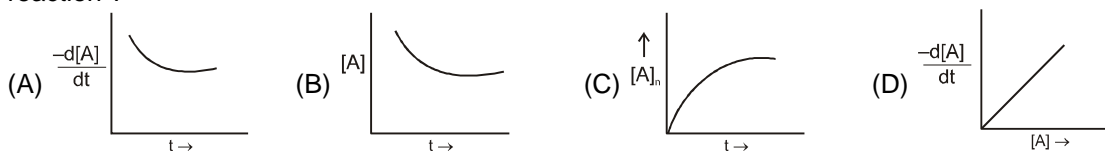
9. Which of the following graphs represents zero order if $A \longrightarrow P$
At $t = 0 \Rightarrow [A]_0$
At $t = t \Rightarrow [A]_t$

10. In a hypothetical reaction $X \rightarrow Y$, the activation energy for the forward and backward reactions in 15 and 9 kJ mol^{-1}, respectively. The potential energy of X is 10 kJ mol^{-1}. Then Plot of $t_{1/2}$ vs. concentration
(A) The heat of reaction of 6 kJ
(B) The potential energy of Y is 16 kJ.
(C) The threshold energy of the reaction is 25 kJ
(D) The reaction is endothermic.

11. Which of the following plots are correctly made for the reaction $nA \rightleftharpoons (A)_n$ if it obeys first order reaction ?

(A) $\frac{-d[A]}{dt}$ vs $t \rightarrow$ (B) $[A]$ vs $t \rightarrow$ (C) $[A]_n$ vs $t \rightarrow$ (D) $\frac{-d[A]}{dt}$ vs $[A] \rightarrow$

12. A certain reaction $A \rightarrow B$ follows the given concentration (Molarity)-time graph. Which of the following statements is/are true ?
(A) The reaction is second order with respect to A
(B) The rate for this reaction at 20 s will be 7×10^{-3} M s^{-1}.
(C) The rate for this reaction at 80 s will be 1.75×10^{-3} M s^{-1}
(D) The [B] will be 0.35 M at t = 60 s
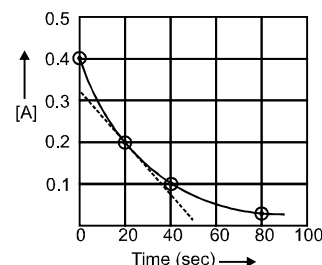
Section-3 : (One Integer Value Correct Type.)
This section contains 5 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive).

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13. At some temperature, the rate constant for the decomposition of HI on a gold surface is 0.08 M.s^{-1}.
$$2HI\,(g) \longrightarrow H_2(g) + I_2(g)$$
What is the order of the reaction ? How long will it take for the concentration of HI to drop from 1.50 M to 0.30 M ?

14. Identify the reaction order from the following rate constant :
$k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1} .

15. $3A + B \longrightarrow C + D$
Mechanism of given reaction is :
Step 1 : $A + B \xrightarrow{\;k_1\;} E$
Step 2 : $E + 2A \xrightarrow{\;k_2\;} C + D$
What is the total order of reaction considering steady state approximation.

16. A reaction take place at 300K. When catalyst is added rate of reaction increases. Calculate the change in temp (in ºC) which would have same effect on rate of reaction as that of catalyst. (Assume catalyst change the activation energy by 20%).

17. Consider the following chemical reaction and the corresponding kinetic data showing the initial reaction rate as a function of the initial concentrations of the reactants :
$$H_3AsO_4(aq) + 2H_3O^+(aq) + 3I^-(aq) \rightarrow HAsO_2(aq) + I_3^-(aq) + 4H_2O(liq)$$
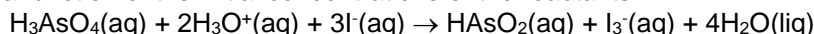
Initial Rate $\times 10^{-5}$ (M/sec)	[H₃AsO₄]	[H₃O⁺]	[I⁻]
3.7	0.001	0.01	0.10
7.4	0.001	0.01	0.20
7.4	0.002	0.01	0.10
3.7	0.002	0.005	0.20

Using the data, establish the correct reaction composite order.

SECTION-4 : Comprehension Type (Only One options correct)
This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph for Questions 18 to 20

Study the two photochemical reactions and answer the question at the end.
For the overall reaction between A and B to yield C and D, two mechanisms are proposed :

I. $A + B \; AB^* \longrightarrow C + D,$ $\qquad k_1' = 1 \times 10^{-5} \, M^{-1} \, s^{-1}$

II. $A \longrightarrow A^* \longrightarrow E,$ $\qquad k_1 = 1 \times 10^{-4} \, s^{-1}$

$\quad E + B \longrightarrow C + D,$ $\qquad k_2 = 1 \times 10^{10} \, M^{-1} \, s^{-1}$

(species with * are short-lived)

18. Rate according to mechanism I when concentration of each reactant is 0.1 M will be :
(A) $1 \times 10^{-7} \, Ms^{-1}$　　(B) $1 \times 10^{-6} \, Ms^{-1}$　　(C) $1 \times 10^{-5} \, Ms^{-1}$　　(D) $1 \times 10^{-4} \, Ms^{-1}$

19. Rate according to mechanism II when concentration of each reactant is 1 M will be:
(A) $1 \times 10^{-4} \, Ms^{-1}$　　(B) $1 \times 10^{10} \, Ms^{-1}$　　(C) $1 \times 10^{-6} \, Ms^{-1}$　　(D) $1 \times 10^{-10} \, Ms^{-1}$

20. At what concentration of B, rates of two mechanism are equal :
(A) 1 M　　　　(B) 5 M　　　　(C) 7 M　　　　(D) 10 M

SECTION-5 : Matching List Type (Only One options correct)
This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

21. Match order of the reaction (in List–**I**) with the corresponding rate constant (in List–**II**) and select the correct answer using the code given below the lists.

	List I (order)		List II (rate constant)
(P)	Zero	(1)	$k = \dfrac{1}{2t}\left[\dfrac{1}{(a-x)^2} - \dfrac{1}{a^2}\right]$
(Q)	First	(2)	$k = \dfrac{1}{t}\left[\dfrac{1}{(a-x)} - \dfrac{1}{a}\right]$
(R)	Second	(3)	$k = \dfrac{x}{t}$
(S)	Third	(4)	$k = \dfrac{1}{t}\log_e\left(\dfrac{a}{(a-x)}\right)$

Code :

	P	Q	R	S			P	Q	R	S
(A)	3	4	2	1		(B)	1	2	4	3
(C)	3	1	2	4		(D)	2	3	1	4

Practice Test-2 ((IIT-JEE (ADVANCED Pattern))
OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21									
Ans.										

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APSP Answers

PART - I

1.	(3)	**2.**	(2)	**3.**	(4)	**4.**	(4)	**5.**	(3)
6.	(1)	**7.**	(1)	**8.**	(3)	**9.**	(4)	**10.**	(4)
11.	(2)	**12.**	(3)	**13.**	(2)	**14.**	(2)	**15.**	(3)
16.	(4)	**17.**	(4)	**18.**	(4)	**19.**	(2)	**20.**	(3)
21.	(2)	**22.**	(4)	**23.**	(4)	**24.**	(4)	**25.**	(4)
26.	(3)	**27.**	(1)	**28.**	(2)	**29.**	(1)	**30.**	(2)

PART - II

1.	(C)	**2.**	(C)	**3.**	(C)	**4.**	(B)	**5.**	(D)
6.	(A)	**7.**	(C)	**8.**	(B)	**9.**	(C)	**10.**	(A)
11.	(C)	**12.**	(A)	**13.**	(B)	**14.**	(A)	**15.**	(B)
16.	(C)	**17.**	(B)	**18.**	(C)	**19.**	(D)	**20.**	(C)
21.	(C)	**22.**	(D)	**23.**	(A)	**24.**	(D)	**25.**	(C)
26.	(B)	**27.**	(B)	**28.**	(D)	**29.**	(C)	**30.**	(A)
31.	(C)	**32.**	(B)	**33.**	(A)	**34.**	(D)	**35.**	(C)
36.	(C)	**37.**	(B)	**38.**	(B)	**39.**	(A)	**40.**	(B)
41.	(D)	**42.**	(B)	**43.**	(C)	**44.**	(D)	**45.**	(D)
46.	(B)	**47.**	(C)	**48.**	(A)	**49.**	(B)	**50.**	(C)
51.	(C)	**52.**	(A)	**53.**	(D)	**54.**	(A)	**55.**	(C)
56.	(A)	**57.**	(C)	**58.**	(B)	**59.**	(C)	**60.**	(B)
61.	(C)								

PART - III

1. **(a)** $\sqrt{A_t} = \left(\sqrt{A_0} - \dfrac{k}{2}t\right)$ **(b)** straight line with slope $-\dfrac{k}{2}$ **(c)** $\dfrac{\sqrt{2}(\sqrt{2}-1)}{K}\sqrt{[A]_0}$

2. **(a)** $k = \dfrac{1}{t}\ln\left(\dfrac{P_0}{P_t}\right)$ **(b)** $k = \dfrac{1}{t}\ln\left(\dfrac{P_0}{2P_0 - P_t}\right)$ **(c)** $k = \dfrac{1}{t}\ln\left(\dfrac{P_\infty}{P_\infty - P_t}\right)$ **(d)** $k = \dfrac{1}{t}\ln\left[\dfrac{P_\infty}{P_\infty - P_t}\right]$

3. $t = \dfrac{0.693}{K_f + K_b}$

4. $\dfrac{K}{A} = e^{-Ea/RT} = 3.13 \times 10^{-6}$. = Fraction of Molecule Having Sufficient Energy. **5.** t = 7.5 sec

6.	(A)	**7.**	(B)	**8.**	(B)	**9.**	(B)	**10.**	(B)
11.	(A)	**12.**	(A)	**13.**	(D)	**14.**	(B)	**15.**	(C)

16. (D) **17.** (A) → (r) ; (B) → (s) ; (C) → (q) ; (D) → (p) **18.** 17

19. 80 **20.** (AB) **21.** (BC) **22.** (AC)

PART - IV

1.	(B)	**2.**	(B)	**3.**	(B)	**4.**	(D)	**5.**	(B)
6.	(C)	**7.**	(A)	**8.**	(D)	**9.**	(ABCD)	**10.**	(ABCD)
11.	(ABCD)	**12.**	(BD)						

13. From the unit of k given, the reaction is of zero order.
As this reaction is of the type $2A \rightarrow$ Products, we apply,

$k_0 = \dfrac{x}{nt}$ where n = 2   or $k_0 = \dfrac{a-(a-x)}{nt}$ or $0.08 = \dfrac{1.50-0.30}{2t}$ $\Rightarrow$ t = 7.5 s

14. Second order **15.** 2   **16.** 75   **17.** 4   **18.** (A)

19. (A)   **20.** (D)   **21.** (A)

▮ APSP Solutions

PART - I

1.
$$\begin{array}{cccc} & A(g) & + & 2B(g) & \rightarrow & C(g) \\ t = 0 & 0.4\ atm & & 1\ atm & & 0\ atm \\ t = t & (0.4-0.3)atm & & (1-0.6)atm & & 0.3\ atm \end{array}$$

Since reaction is elementary.
So, Rate of reaction w.r.t. A & B will be of order equal to stoichiometric coefficient
Rate = K [A] [B]^2
Rate$_{(Initial)}$ = K [0.4] [1]^2
Rate$_{(after\ t = t)}$ = K [0.1][0.4]^2

$\dfrac{R_{(t=t)}}{R_{(t=o)}} = \dfrac{K[0.1][0.4]^2}{K[0.4][1]} = \dfrac{1}{25}$

2. Rate constant change on changing temperature.

4. $K_{eq} = \dfrac{K_f}{K_b} = \dfrac{\text{Conc. of products as per rate law}}{\text{Conc. of reactants as per rate law}}$ stoichiometry of reaction is required.

5. As $t_{50\%}$ is constant. Hence order of reaction is 1.

$t_{50\%} = \dfrac{0.693}{K} \Rightarrow$ n = 1, $t_{1/2} = \dfrac{0.693}{K}$

10. $K_{eq} = \dfrac{k_f}{k_b} = \dfrac{[CH_3]^2}{[C_2H_6]}$ $\therefore$ $[CH_3] = \dfrac{10^{-4}}{10} = 10^{-5}$ M

$\dfrac{1.57 \times 10^{-3}}{k_b} = \dfrac{(10^{-5})^2}{1}$ $\Rightarrow$ $k_b = 1.57 \times 10^7$ L mol^{-1}s^{-1}

11. $k = \dfrac{2.303}{t} \log\left(\dfrac{C_{A_0}}{C_A}\right)$

$2.303 \times 1 = 2.303 \log\left(\dfrac{C_{A_0}}{C_A}\right) \Rightarrow$ $\dfrac{C_{A_0}}{C_A} = 10$

$\therefore$ $CA \Rightarrow \dfrac{1}{10} = 0.1$ rate after 1 min $r_1 = k.C_A$ $\Rightarrow$ $2.0303 \times 0.1 \Rightarrow 0.2303$ min^{-1}

12. $r_1 = k[A]^2 [B]$; $r_2 = k[2A]^2 [2B] = 8 r_1$

13.   A $\longrightarrow$ B + 2C + 3D

Optical rotation – θ_1 θ_2 θ_3

		θ_1	θ_2	θ_3	
t=0	a	0	0	0	Optical rotation at t = 0 is zero.
t=t	a–x	x	2x	3x	Optical rotation at time = t is $(x.\theta_1 + 2x.\theta_2 + 3x.\theta_3)$.
t=∞	0	a	2a	3a	Optical rotation at time = ∞ is $(a.\theta_1 + 2a.\theta_2 + 3a.\theta_3)$.

$(x.\theta_1 + 2x.\theta_2 + 3x.\theta_3) = r_t$; $(a.\theta_1 + 2a.\theta_2 + 3a.\theta_3) = r_\infty$

$x = \dfrac{r_t}{\theta_1 + 2\theta_2 + 3\theta_3}$; $a = \dfrac{r_\infty}{\theta_1 + 2\theta_2 + 3\theta_3}$; $k = \dfrac{1}{t}\ln\left[\dfrac{a}{a-x}\right] = \dfrac{1}{t}\ln\left[\dfrac{r_\infty}{r_\infty - r_t}\right]$

14.   0.2 M $\xrightarrow[t_{1/2}=5\ hr]{}$ 0.1 M $\xrightarrow[t_{1/2}=5\ hr]{}$ 0.05 M   From 0.2 M $\xrightarrow[t = 10\ hr]{}$ 0.05 M
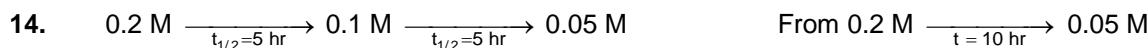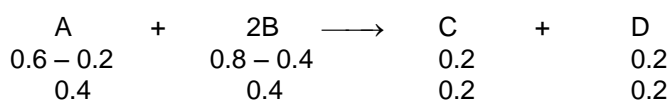
So $t_{1/2}$ is constant which is characteristic of first order reaction. Hence, $t_{1/2} \propto (1)^0$.

15.   First step is slow (require large activation energy) second step is fast (less activation energy) and overall reaction exothermic, so product energy level should be less as compare to reactants.

17. $r_1 = k[A][B]^2 = k[0.6][0.80]^2$
After reaction

A	+	2B	$\longrightarrow$	C	+	D
0.6 – 0.2		0.8 – 0.4		0.2		0.2
0.4		0.4		0.2		0.2

$\dfrac{r_2}{r_1} = \dfrac{k(0.4)(0.4)^2}{(0.6)(0.8)^2} = \dfrac{1}{6}$

18.   We know $-\dfrac{d(BrO_3^-)}{dt} = -\dfrac{1}{5}\dfrac{d(Br^-)}{dt} = -\dfrac{1}{6}\dfrac{d(H^+)}{dt} = +\dfrac{d(Br_2)}{dt}$ Then by this relation $\dfrac{d[Br_2]}{dt} = -\dfrac{3}{5}\dfrac{d[Br^-]}{dt}$

19.   Rate = k [conc]^n $\longrightarrow$ Independent of conc. of A.

20.   More is the activation energy less is the rate of reaction.

21. $t_{1/2} = \dfrac{t}{4}$; $t_{1/2} = T \ln 2$ so $\dfrac{t}{4} = T \ln 2$; t = 4T ln 2

22.   Isotones have same number of neutron; 17 – 9 = B – 8 ; B = 16
Isobars have same mass number A = B = 16
Number of neutrons 16 – 8 = 8

23.   Slow step is the rate determining step (RDS) and (N_2O_2) is the reactive intermediate.
$\therefore$ $r = k_2 [N_2O_2][O_2]$ .....(i)
From reversible reaction, $[N_2O_2]$ is

$\dfrac{k_1}{k_{-1}} = \dfrac{[N_2O_2]}{[NO]^2}$ .....(ii)

substitute $[N_2O_2]$ in equation (i), $r = k_2\left(\dfrac{k_1}{k_{-1}}\right)[NO]^2[O_2]$ Hence, rate constant $= k_2\left(\dfrac{k_1}{k_{-1}}\right)$

24.   For nth order, $t_{1/2} \propto (1)^{1-n}$.

$\Rightarrow$ $\dfrac{t_{1/2}}{(a)^{1-n}}$ or $t_{1/2} \times (a)^{n-1} =$ Constant $\therefore$ Given $t_{1/2} \times (a)^{n-1} =$ Constant

$\Rightarrow$ $(a)^{n-1} = (a)^2$ n – 1 = 2 $\Rightarrow$ n = 3   Hence, third order reaction.

25.   Unit of rate = mol L^{-1} t^{-1} ;   Unit of zero order = mol L^{-1} t^{-1}
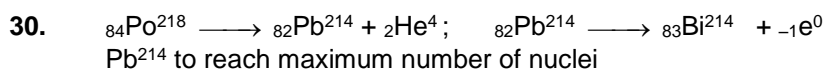
26.   It is fact.

27.   For zero order reaction, $t_{1/2} \propto (a)^1$

28. $\lambda = \lambda_1 + \lambda_2$; $\lambda = \dfrac{0.693}{22}$ and $\dfrac{\lambda_1}{\lambda_2} = \dfrac{2}{98}$; $\lambda_1 = 0.00063$ year^{-1} ; $\lambda_2 = 0.03087$ year^{-1}

29. $\lambda_A N_A = \lambda_B N_B$ ($\because$ rate of disintegration are same) $\quad \dfrac{N_A}{N_B} = \dfrac{\lambda_B}{\lambda_A} = \dfrac{2}{1}$

30. $_{84}Po^{218} \longrightarrow \,_{82}Pb^{214} + \,_{2}He^4$; $\quad _{82}Pb^{214} \longrightarrow \,_{83}Bi^{214} + \,_{-1}e^0$
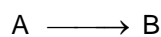Pb^{214} to reach maximum number of nuclei

$$t_{maximum} = \dfrac{1}{\lambda_1 - \lambda_2} \ln \dfrac{\lambda_1}{\lambda_2} = 247.5 \text{ sec.}$$

where, $\lambda_1 = \dfrac{0.693}{183}$; $\lambda_2 = \dfrac{0.693}{161}$

PART - III

1. **(a)** $A \longrightarrow B$

$$\dfrac{-d[A]}{dt} = K[A]^{\frac{1}{2}}$$

$A \longrightarrow B$
$t = 0 \quad a = C_O$
$t = t \quad (a-x) = C_t$

$$\dfrac{-d[A]}{dt} = K[A]^{\frac{1}{2}}$$

$$\int_{A_0}^{A_t} \dfrac{1}{(A_t)^{\frac{1}{2}}} \, dA_t = -\int_{o}^{t} K\,dt$$
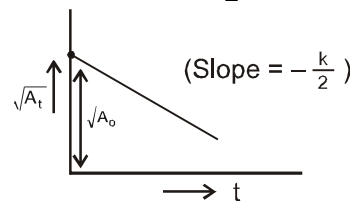
$$\left[\dfrac{(A_t)^{\frac{1}{2}}}{\left(\frac{1}{2}\right)}\right]_{C_O}^{C_t} = -kt \qquad\qquad 2\left[(C_t)^{\frac{1}{2}} - (C_O)^{\frac{1}{2}}\right] = -kt$$

$$(A_t)^{\frac{1}{2}} - (A_o)^{\frac{1}{2}} = \dfrac{kt}{2} \qquad = \sqrt{A_t} - \sqrt{A_o} - \dfrac{kt}{2} \qquad \sqrt{A_t} = \sqrt{A_o} - \dfrac{kt}{2}$$

(b) $\quad \sqrt{A_t} = \left(\dfrac{-k}{2}\right) t + \sqrt{A_o}$

(Slope = $-\dfrac{k}{2}$)
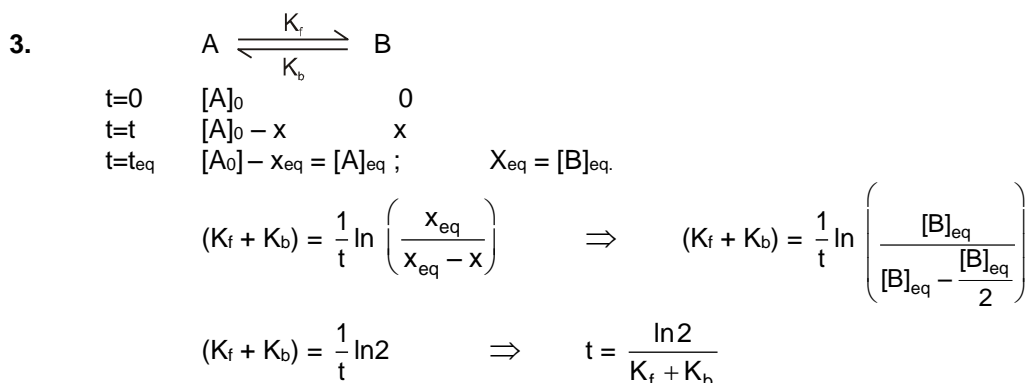
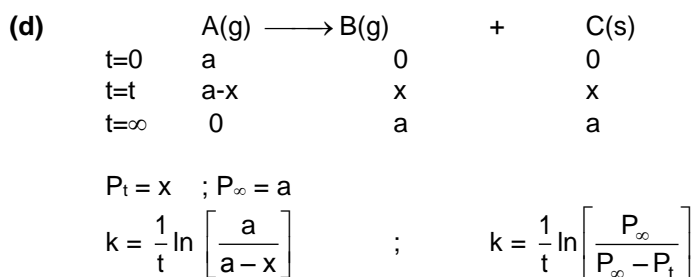**(c)** For Half life $A_t = \left(\dfrac{A_0}{2}\right)$

$$\sqrt{\dfrac{A_0}{2}} = \sqrt{A_0} - \dfrac{kt_{1/2}}{2} \Rightarrow \dfrac{kt_{1/2}}{2} = \sqrt{A_0} - \sqrt{\dfrac{A_0}{2}}$$

$$t_{\frac{1}{2}} = \dfrac{2}{k}\left[\dfrac{\sqrt{2}\sqrt{A_0} - \sqrt{A_0}}{\sqrt{2}}\right] \qquad \Rightarrow \qquad t_{\frac{1}{2}} = \dfrac{2}{k}\left[\dfrac{\sqrt{2}-1}{\sqrt{2}}\right] = \sqrt{A_0} = \dfrac{\sqrt{2}(\sqrt{2}-1)\sqrt{A_0}}{k} t_{1/2}$$

2. **(a)**
$$\begin{array}{lcccl}
 & A \longrightarrow & B & + & C \\
t=0 & a & 0 & & 0 \qquad a\,P_0 \\
t=t & a-x & x & & x \qquad (a-x)\,P_t
\end{array}$$

$$Kt = \ln\left(\dfrac{a}{a-x}\right) \Rightarrow \qquad k = \dfrac{1}{t}\ln\left(\dfrac{P_0}{P_t}\right)$$

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(b)   A $\longrightarrow$ B   +   C

t=0   a   0   0 $a \propto P_0$

t=t   a-x   x   x $(a+x) \propto P_t$ $\Rightarrow$ $x \propto (P_t - P_0)$

$$Kt = \ln\left(\frac{a}{a-x}\right) \Rightarrow k = \frac{1}{t}\ln\left(\frac{P_0}{P_0 - (P_t - P_0)}\right) \Rightarrow k = \frac{1}{t}\ln\left(\frac{P_0}{2P_0 - P_t}\right)$$

(c)   A $\longrightarrow$ B   +   C

t=0   a   0   0

t=t   a-x   x   x $2x \propto P_t$ $\Rightarrow$ $x \propto \frac{P_t}{2}$

t=∞ 0   a   a $2a \propto P_\infty$ $\Rightarrow$ $a \propto \frac{P_\infty}{2}$

$$Kt = \ln\left(\frac{a}{a-x}\right) \Rightarrow k = \frac{1}{t}\ln\left(\frac{P_\infty}{P_\infty - P_t}\right)$$

(d)   A(g) $\longrightarrow$ B(g)   +   C(s)

t=0   a   0   0

t=t   a-x   x   x

t=∞ 0   a   a

$P_t = x$; $P_\infty = a$

$$k = \frac{1}{t}\ln\left[\frac{a}{a-x}\right] \quad ; \quad k = \frac{1}{t}\ln\left[\frac{P_\infty}{P_\infty - P_t}\right]$$

3.   A $\underset{K_b}{\overset{K_f}{\rightleftharpoons}}$ B

t=0 $[A]_0$ 0

t=t $[A]_0 - x$ x

t=t_{eq} $[A_0] - x_{eq} = [A]_{eq}$; $X_{eq} = [B]_{eq.}$

$$(K_f + K_b) = \frac{1}{t}\ln\left(\frac{x_{eq}}{x_{eq} - x}\right) \quad \Rightarrow \quad (K_f + K_b) = \frac{1}{t}\ln\left(\frac{[B]_{eq}}{[B]_{eq} - \frac{[B]_{eq}}{2}}\right)$$

$$(K_f + K_b) = \frac{1}{t}\ln 2 \quad \Rightarrow \quad t = \frac{\ln 2}{K_f + K_b}$$

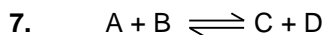**5.**   From the unit of k given, the reaction is of zero order. As this reaction is of the type 2A $\rightarrow$ Products, we apply

$k_0 = \frac{x}{nt}$ where n = 2   or $k_0 = \frac{a - (a-x)}{nt}$ or $0.1 = \frac{(2 - 0.5)}{2t}$

t = 7.5 sec

6.   A   +   B $\longrightarrow$ C

t = 0   a = 0.1 M   b = 0.2 M   0

t = 100s   a – x   b – x   x

From question, r = k[A][B] and hence

$$k_t = \frac{1}{b-a}\ln\frac{a(b-x)}{b(a-x)}$$

or, $10^{-3} \times 100 = \frac{1}{0.2 - 0.1} \times 2.303 \times \log\frac{0.1(0.2-x)}{0.2(0.1-x)}$

          x $\approx$ 0.002 $\therefore$ [A] = 0.1 – x = 0.098 M

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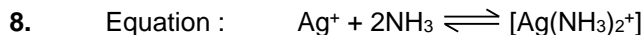
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7. $A + B \rightleftharpoons C + D$
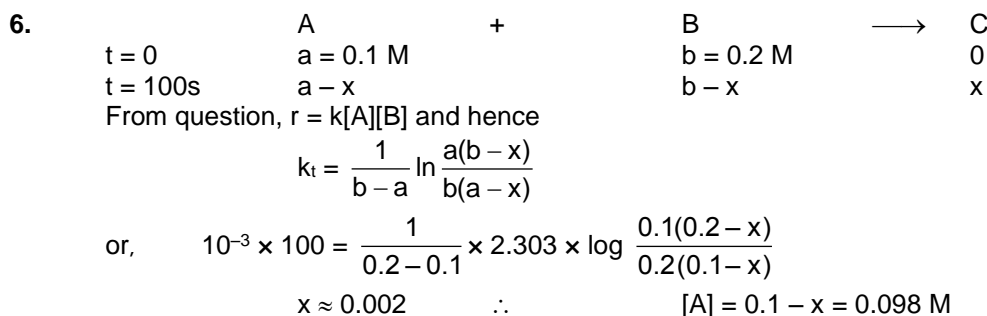
$$\left[\dfrac{dx}{dt}\right] = 0$$

$k_1[A][B] - k_2[C][D] = 0$; $k_1[A][B] = k_2[C][D]$

$[A][B] = [C][D]$

$0.4 \times 0.25 = 0.2 \times 0.5 \quad \Rightarrow \quad 1 = 1$.

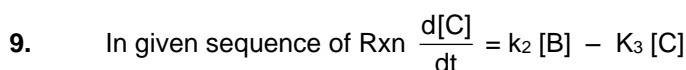**8.** Equation : $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2^+]$

Given, $\dfrac{dx}{dt} = 2 \times 10^7 \, L^2 \, mol^{-2} \, s^{-1} [Ag^+][NH_3]^2 - 1 \times 10^{-2} \, s^{-1} [Ag(NH_3)_2^+]$

For equilibrium $\dfrac{dx}{dt} = 0$

$2 \times 10^7 [Ag^+][NH_3]^2 - 1 \times 10^{-2} [Ag(NH_3)_2^+] = 0$

$\dfrac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \dfrac{2 \times 10^7}{1 \times 10^{-2}} = 2 \times 10^9 \, L^2 \, mol^{-2}$.

9. In given sequence of Rxn $\dfrac{d[C]}{dt} = k_2[B] - K_3[C]$

10. $A + A \xrightarrow{K_1} A + A^* \qquad A^* + A \xrightarrow{K_2} 2A$

Rate of decomposition

$\qquad\qquad\qquad A = K_1[A]^2$

Rate of formation $A = K_2[A][A^*]$

At equilibrium rate of decomposition = rate of formation

$\qquad\qquad K_1[A]^2 \quad = \qquad K_2[A][A^*]$

$\qquad\qquad [A^*] \quad = \qquad \dfrac{K_1}{K_2}[A]$

11. Activity $= \lambda N_0 \qquad = \dfrac{0.693}{t_{1/2}} \times \dfrac{1}{226} \times N_A$

12. Given Rxn

$\qquad\qquad\qquad N_2 + 3H_2 \rightleftharpoons 2NH_3$
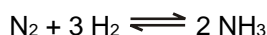
$\qquad \dfrac{dx}{dt} = 1 \times 10^2 [N_2][H_2]^3 - 1 \times 10^{-3} [NH_3]^2$

when $\dfrac{dx}{dt} = 0$ then $\dfrac{[N_2][H_2]^3}{[NH_3]^2} = 10^{-5}$

Hence the reaction will be at equilibrium at the given instant.

13.
$$A\,(aq) \longrightarrow B\,(aq) + C\,(aq)$$
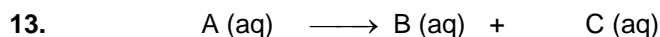
	A	B	C
t=0	a	0	0
t=t	a–x	x	x
t=∞	0	a	a

$(a - x) + 2x + 3x \propto n_1$

$a + 4x \propto n_1$ .....(i)

$2a + 3a \propto n_2$

$a \propto \dfrac{n_2}{5}$ .....(ii)

$k = \dfrac{1}{t} \ln\left[\dfrac{a}{a-x}\right] \qquad \Rightarrow \qquad k = \dfrac{1}{t} \ln \dfrac{\left(\dfrac{n_2}{5}\right)}{\left(\dfrac{n_2 - n_1}{4}\right)} = \dfrac{1}{t} \ln \dfrac{4(n_2)}{5(n_2 - n_1)}$

14. $y = \dfrac{k_1 a}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right]$

$\dfrac{dy}{dt} = 0.$

$- k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0$ So, $t_{max} = \dfrac{1}{K_1 - K_2} \ln \dfrac{k_1}{k_2}$

15. Slow step is rate determining step.

16. We know
Rate = k [conc.]
Given Rxn catalysed by HA and HB
Rate constant $k_A = k_1 [H^+]_A$
$k_B = k_1 [H^+]_B$
Then relative strength of acids A and B is

$\dfrac{k_A}{k_B} = \dfrac{[H^+]_A}{[H^+]_B}$

$\dfrac{2}{1} = \dfrac{[H^+]_A}{[H^+]_B}$ = strength of $\dfrac{[Acid\,A]}{[Acid\,B]}$

17. $t_{1/2} \propto \dfrac{1}{(\text{initial conc.})^{\text{order}-1}}$

18. $t_1 = \dfrac{1}{k} \ln \left(\dfrac{a + x_1}{a} \right)$

$t_2 = \dfrac{1}{k} \ln \left(\dfrac{a + x_1}{a} \right)$

$(t_2 - t_1) = \dfrac{1}{k} \ln \left(\dfrac{a + x_2}{a + x_1} \right)$

$k = \dfrac{1}{t_2 - t_1} \ln \left(\dfrac{a + x_2}{a + x_1} \right)$

$k = \dfrac{1}{10} \ln \left(\dfrac{72}{48} \right)$

$k = \dfrac{1}{10} \ln \left(\dfrac{3}{2} \right)$

$k = \left(\dfrac{\ln 3 - \ln 2}{10} \right)$

$\dfrac{\ln 2}{(t_{1/2})} = \left(\dfrac{\ln 3 - \ln 2}{10} \right)$

$\dfrac{0.80}{(t_{1/2})} = \dfrac{0.48 - 0.30}{10}$

$\dfrac{0.30}{(t_{1/2})} = \dfrac{0.18}{10}$

$t_{1/2} = \dfrac{30 \times 10}{18}$ = 17 minutes (Approx.)

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19. Molarity of $H_2O_2 = \dfrac{11 \cdot x}{11.2} = \dfrac{20}{11.2} = 1.786$

For titration, $[M_1V_1]$ V.F$_1 = [M_2V_2]$ V.F$_2$

$M_1 \times 10 \times 2 = 0.025 \times 25 \times 5$

$M_1 = 0.15625$

Now molarity of diluted solution = 0.15625

So molarity of original solution = 1.563

So, $K = \dfrac{1}{t} \ln\left(\dfrac{C_0}{C_t}\right)$

$K = \dfrac{2.303}{6} \log\left(\dfrac{1.786}{1.563}\right)$

$K = 80$ sec^{-1}

21. $K = \dfrac{K_1 K_3}{K_2}$

$Ae = \dfrac{-(E_a)_{overall}}{RT} = \dfrac{A_1 e^{-\frac{E_1}{RT}} \times A_3 e^{-\frac{E_3}{RT}}}{A_2 e^{-\frac{E_2}{RT}}}$

$Ae\, \dfrac{-(E_a)_{overall}}{RT} = \left(\dfrac{A_1 A_3}{A_2}\right) e^{-\frac{[E_1 + E_3 - E_2]}{RT}}$

$(E_a)_{overall} = E_1 + E_3 - E_2 = 30$ KJ/mole

$2A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} A^* + A$ \qquad [Fast]

$\dfrac{K_1}{K_2} = \dfrac{[A^*][A]}{[A]^2}$ or $[A^*] = \dfrac{K_1}{K_2}[A]$

rate $= K_3[A^*] = \dfrac{K_1 K_3}{K_2}[A]$

22. $\dfrac{d}{dt}[NH_2CONH_2] = k_4[NH_3][HNCO]$ from (iii)

Applying steady state approximation to HNCO or NH$_3$

$\dfrac{d[HNCO]}{dt} = O = k_3[NH_4NCO] - k_4[NH_3][HNCO]$

$\therefore \quad \dfrac{k_3}{k_4} = \dfrac{[NH_3][HNCO]}{[NH_4CNO]}$

$\dfrac{d[urea]}{dt} = k_4 \times [NH_3][HNCO] = k_4 \times \dfrac{k_3}{k_4}[NH_4NCO]$

Also, $[NH_4NCO] = \dfrac{k_1}{k_2} \times [NH_4CNO]$

$\therefore \quad \dfrac{d[urea]}{dt} = k_3 \times \dfrac{k_1}{k_2} \times [NH_4CNO] = k[NH_4CNO]$

PART - IV

1. $t_{1/2} = \dfrac{0.69}{k} = \dfrac{0.3 \times 2.3}{k}$

$t_{60\%} = \dfrac{2.3}{k}\log\dfrac{100}{100-60} = \dfrac{2.3}{k}\log\dfrac{10}{4}$

$$k = \frac{2.3}{60} \log \frac{10}{4}$$

$$\frac{0.3 \times 2.3}{t_{1/2}} = \frac{2.3}{60} \log \frac{10}{4}$$

$$\frac{0.3}{t_{\frac{1}{2}}} = \frac{1}{60}[1 - 2\log 2] = \frac{1}{60}[1 - 0.6]$$

$$\frac{0.3}{t_{1/2}} = \frac{0.4}{60} \qquad \therefore \qquad t_{1/2} = \frac{60 \times 0.3}{0.4} = 45 \, min$$

Use direct relation

$$t_{1/2} = 0.3, \quad t_{x\%} = \left(\log \frac{100}{100 - x} \right)$$

$$t_{60\%} = \log \frac{10}{4} = (0.4)$$

$$\frac{t_{1/2}}{t_{60\%}} = \frac{0.3}{0.4} \qquad \therefore \qquad t_{1/2} = t_{60\%} \times \frac{0.3}{0.4} = \frac{60 \times 3}{4} = 45 \, min$$

2. Use the formula

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

$$= \frac{1}{k} \ln \frac{V_0}{V_t} = \frac{1}{4.5 \times 10^{-2} \, min^{-1}} \ln \frac{25 \, mL}{5 \, mL} = \frac{\log_e 5}{4.5 \times 10^{-2}} \, min$$

3. For second order reaction,
When x = 20%, (a − x) = 80%, a = 100%

$$k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)} = \frac{1}{40} \times \frac{20}{100 \times (100 - 20)} = \frac{1}{2 \times 100 \times 80}$$

When x = 80%, (a − x) = 20%

$$k_2 = \frac{1}{t} \times \frac{80}{100 \times 20} = \frac{1}{25}t$$

From equations (i) and (ii),

$$t = \frac{2 \times 100 \times 80}{25} = 640 \, min$$

4. Intermediate and product have less potential energy than activated complex.

5. The fraction of molecules having energy equal to or greater than E_a is :

$$x = \frac{n}{N} = e^{-E_a/RT} \left(x = \frac{n}{N} = 0.001\% = \frac{0.001}{100} = 10^{-5} \right)$$

$$\therefore \qquad \log x = \frac{-E_a}{2.3 \times RT} \quad (R = 2 \, cal \, mol^{-1} \, K^{-1}, \, T = 500 \, K)$$

$$\log 10^{-5} = \frac{-E_a}{2.3 \times 2 \times 500}$$

$E_a = 11.5 \times 10^3 \, cal \, mol^{-1} = 11.5 \, kcal \, mol^{-1}$

6. $k = Ae^{-E_a/RT}$ ....(i)

$k = Ae^{-40000/RT}$ ....(ii)

from (i) and (ii)

$$\frac{E_a}{RXT} = \frac{40000}{T}$$

$E_a = 40,000 \times 2 \, cal \qquad \Rightarrow \qquad E_a = 80,000 \, cal$

7. V_{O_2} (t = 15 min.) = 100 ml (at 1 atm, 0ºC)

∴ $\quad$ x ∝ 100 ml

V_{O_2} (t = ∞) = 200 ml (at 2 atm, 0ºC)

$\qquad$ = 400 ml (at 1 atm, 0ºC)

∴ $\quad$ a ∝ 400 ml

i.e., in 15 min 25% of reaction proceeds. Hence V_{KMnO_4} will be $\frac{3}{4}$ × 40 = 30 mL.

8. A → B $\quad$ (uncatalysed reaction)

A $\xrightarrow{\text{catalyst}}$ B $\quad$ (catalyst reaction)

$K = A\, e^{-E_a/RT}$

$K_{cat.} = A\, e^{-E_{a(cat.)}/RT}$

$\dfrac{K_{cat.}}{K} = e^{(E_a - E_a')\times\frac{1}{RT}}$

$\dfrac{K_{cat.}}{K} = e^{\frac{8.314\times10^3}{8.314\times300}} = e^{3.33} = 28$ times

9. $t_{1/2} \propto (a)^{1-n}$; $[A]_t = [A]_0 - kt$ and $X = kt$ are integrated form of zero order.

10. For reaction X → Y
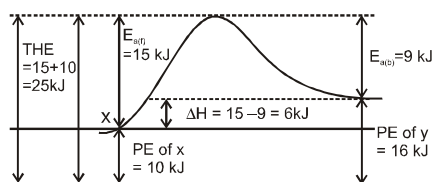
$E_{a(f)}$ = 15 kJ mol^{-1}, $E_{a(b)}$ = 9 kJ mol^{-1}
Heat of reaction $E_{a(f)} - E_{a(b)}$ = 15 – 9 = 6 kJ mol^{-1}
Potential energy of Y is = 10 + 6 = 16 kJ
Thershold energy of the reaction = PE of X + $E_{a(f)}$ = 10 kJ + 15 kJ = 25 kJ
The reaction is endothermic beacuse $E_{a(f)} > E_{a(b)}$

12. Use initial rate law method, let the reaction be first order,

So, $\quad k = \dfrac{2.303}{t}\log\dfrac{a}{a-x}$

(B) At t = 20 s, $k_1 = \dfrac{2.303}{20}\log\left(\dfrac{0.4}{0.2}\right)$

and at t = 40 s, $k_2 = \dfrac{2.303}{40}\log\left(\dfrac{0.4}{0.1}\right) = k_1$

⇒ $\quad$ Assumption is corret ($k_1 = k_2$)

Rate at 20s = k[A] = $\dfrac{0.693}{20}\times0.2$ = 0.0063 ≈ 7 × 10^{-3} Ms^{-1}

Clearly, half life $t_{1/2}$ = 20s

(D) In 60 s, number of life = $\dfrac{60}{20} = 3$

⇒ $\quad$ [B] at 60 s = $0.4 - 0.4\left(\dfrac{1}{2}\right)^3$ = 0.35 M

13. From the unit of k given, the reaction is of zero order.
As this reaction is of the type 2A → Products, we apply,

$\qquad k_0 = \dfrac{x}{nt}$ where n = 2 $\quad$ or $\quad k_0 = \dfrac{a-(a-x)}{nt}$ $\quad$ or $\quad 0.08 = \dfrac{1.50 - 0.30}{2t}$

$\qquad$ t = 7.5 s

15. From steady state approximation

$$\frac{dE}{dt} = K_1 [A] [B] - K_2[E] [A]^2 = 0$$

$$[E] = \frac{K_1[A][B]}{K_2[A]^2} = \frac{k_1}{k_2} \frac{[B]}{[A]} \qquad So \qquad -\frac{dB}{dt} = k_1[A] [B]$$

or $\qquad -\frac{dA}{dt} = k_1[A] [B] + 2k_2[E] [A]^2 = k_1[A] [B] + 2 k_2 \times \frac{k_1}{k_2} \frac{[B]}{[A]} [A]^2 = 3k_1[A][B]$

$$-\frac{1}{3} \frac{dA}{dt} = k_1[A] [B]$$

16. $\ell n \frac{K_2}{K_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad ....(i)$

$\ell n \frac{K_C}{K_1} = \frac{E_a - E_{ac}}{RT_1} \qquad$ for effect of catalyst new $K_C = K_2$

$\ell n \frac{K_2}{K_1} = \frac{E_a - E_{ac}}{RT_1} \qquad ....(ii)$

from (i) and (ii) $\frac{E_a - E_{ac}}{RT_1} = \frac{E_a}{R} \cdot \left(\frac{1}{T_1} , \frac{1}{T_2} \right)$

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{E_a - E_{ac}}{E_a . T_1}$$

$$\frac{1}{300} - \frac{1}{T_2} = \frac{100 - 80}{100 \times 300} = \frac{20}{100 \times 300} = \frac{1}{1500}$$

$$\frac{1}{T_2} = \frac{1}{300} - \frac{1}{1500} = \frac{5 - 1}{1500} = \frac{4}{1500}$$

$T_2 = 375$

change in temp = 375 – 300 = 75 Ans.

17. Assume rate law

$\qquad r = K[H_3AsO_4]^x [H_3O^+]^y [I^-]^z$

Solving by the help of various experiements

$\qquad x = 1, \qquad\qquad y = 2 \quad$ and $\quad z = 1$

total order = 4

18. (I). Rate law for mechanism I

Rate = k_1^1 [A] [B]

Rate = 1×10^{-5} [.1] [.1] = 1×10^{-7} m/sec.

19. (II). Rate = $1 \times 10^{-4} \times [1] = 1 \times 10^{-4}$

20. (III). Rate I = Rate II

k_1^1 [A] [B] = k_1 [A]

B = $\frac{k_1}{k_1^1}$ = 10 M

21. Zero order, $\qquad\qquad$ x = kt

First order, $\qquad\qquad$ K = $\frac{1}{t} ln \frac{a}{(a - x)}$

Second order, $\qquad\qquad$ K = $\frac{1}{t} \left[\frac{1}{(a - x)} - \frac{1}{a} \right]$

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