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CHEMISTRY

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CHEMICAL KINETICS

4. Chemical Kinetics

1. SYLLABUS

- Rates of Chemical reactions, Order of reactions, Rate constant, Effect of concentration and Temperature, Kinetics of first–order reactions, Arrhenius Equation, Kinetics of radioactive disintegrations.

2. INTRODUCTION

- Chemical Kinetics is the branch of science that deals with rate of reaction, the factors affecting the rate of reaction mechanism Chemical reactions need varying length of time for completion depending upon nature of reactants and products and conditions under which reaction is run. Many reactions such as explosive reaction take place in a fraction of a second while the rusting of a wrecked ship may take centuries to complete. Similarly ionic reactions in solution such as that between HCl (aq) and $AgNO_3$ (aq) giving a white precipitate of silver chloride within twinkling of eye. In chemical kinetics we actually study the rates of only those reactions which are in between the above two extremes, i.e. neither so fast nor so slow.
- A chemical reaction involves breaking of bonds in reactant molecules and making of bonds in product molecules. A reaction that involves breaking of weak bond(s) is faster than one involving breaking of strong bond at a given temperature. Ionic compounds remain completely ionised in solution and in any ionic reaction no bond is to be broken. This is why an ionic reaction is so fast. Different reactions differ in respect of the strength of the bonds to be broken and hence they occur at different rates. Reactions which involve less bond rearrangements are generally faster than those which involve considerable bond rearrangements, at a given temperature.

3. RATE OF CHEMICAL REACTION

- The rate of reaction is not constant throughout the reaction but decreases with time due to decrease in the concentration of reactant and hence average rate of reaction is determined.

  Average rate :

  $$= \frac{\text{Change in concentration of reactants or products}}{\text{Time in which change takes place}}$$

  $$\text{Average} = \frac{\Delta A}{\Delta t}$$

- Where ΔA is the change in concentration in Δt time. As we have discussed in chemical equilibrium, rate of change of concentration of reactant decreases as the reaction proceeds. This means that rate of change of concentration is not constant. If the time interval is quite large then average rate will show large deviations from the actual rate.

  Consider a simple reaction

  $$A \longrightarrow B$$

- Let A_1 and A_2 be the amounts of reactant A at time t_1 and t_2 respectively. The change in the amount of A in the time interval $(t_2 - t_1)$ is equal to $[A_2 - A_1]$. Hence, the change in the amount of reactant A in unit time interval becomes:

  $$\text{Average Rate} = \frac{-\Delta A}{\Delta t}\left[\frac{A_2 - A_1}{t_2 - t_1}\right]$$

- The negative sign before $\frac{\Delta A}{\Delta t}$ is to ensure that the rate should be positive, since ΔA is negative. In general, the rate in the beginning is fast and it decreases as the reaction proceeds.
- Hence, the rate represented by above equation is an average rate over the time interval $(t_2 - t_1)$.
- If B_1 and B_2 be the amounts of product B at time t_1 and t_2 respectively, the change in the amount of B in the time interval $(t_2 - t_1)$ is equal to $[B_2 - B_1]$. Hence, the change in the amount of product B in unit time interval becomes:

  $$\text{Average Rate}' = \frac{\Delta B}{\Delta t}\left[\frac{B_2 - B_1}{t_2 - t_1}\right]$$

- As B_2 is greater than B_1, the positive sign is used in $\frac{\Delta B}{\Delta t}$. From given chemical equation it can be concluded that the decrease in the amount of A will be equal to the increase in the amount of B and thus for both the, average rate will be equal.
- **Instantaneous Rate of Reaction**

  The rate at any particular instant of time interval rather than the average rate over a time interval has much more precise value and practical application. This rate is known as the instantaneous rate and it is given as:

Instantaneous rate = Average rate as approaches zero = $\Delta t = \left[\frac{\Delta A}{\Delta t}\right]_{\Delta t \to 0} = \frac{d[A]}{dt}$

Consider the hypothetical reaction

$$A + 2B \longrightarrow 3C + D$$

Rate of disappearance of A = $-\frac{d[A]}{dt}$

Rate of disappearance of B = $-\frac{d[B]}{dt}$

Rate of appearance of C = $+\frac{d[C]}{dt}$

Rate of appearance of D = $+\frac{d[D]}{dt}$

- But from the stoichiometry it is apparent that when one mole of A is reacted, two moles of B are also consumed.
- i.e. rate of disappearance of B = 2 × rate of disappearance of A

$$-\frac{d[B]}{dt} = 2 \times -\frac{d[A]}{dt} \quad \text{or} \quad -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

Similarly we can prove that

$$-\frac{d[A]}{dt} = \frac{1}{3}\frac{d[C]}{dt}$$

So, rate of reaction

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

- We can also generalize the rate of reaction for a general reaction given as:

$$m_1A + m_2B \longrightarrow n_1C + n_2D$$

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

$$= \frac{1}{n_1}\frac{d[C]}{dt} = -\frac{1}{n_2}\frac{d[D]}{dt}$$

- **Unit of Rate of Reaction**

  From the expression of rate of reaction, it is clear that unit of rate of reaction is **concentration time^{-1}**. If concentration is in mol L^{-1} and time is in seconds than the unit will be mol L^{-1}s^{-1}.

  However, in gaseous reactions instead of concentration, pressure is also used and hence the unit will be atm time^{-1}.

- **Factors affecting rate of reaction**

  The rate of any particular reaction depends upon the following factors:

1. **Concentration of the reactants:** Greater the concentrations of the reactants, faster is the reaction. Conversely, as the concentrations of the reactants decreases, the rate of reaction also decreases.
2. **Temperature:** The rate of reaction increases with increase of temperature. In most of the cases, the rate of reaction becomes nearly double for 100 rise of temperature. In some cases, reactions do not take place at room temperature but take place at higher temperature.
3. **Presence of Catalyst:** A catalyst generally increases the speed of a reaction without itself being consumed in the reaction. In case of reversible reactions, a catalyst helps to attain the equilibrium quickly without disturbing the state of equilibrium.
4. **Surface area of the reactants:** For a reaction involving a solid reactant or catalyst, the smaller is the particle size, i.e., greater is the surface area, the faster is the reaction.
5. **Presence of light:** Some reactions do not take place in the dark but take place in the presence of light.
   e.g., $H_2 + Cl_2 \xrightarrow{hv} 2HCl$.
   Such reactions are called "photochemical reactions".

4. RATE OF EXPRESSION AND RATE OF CONSTANT

- As it is clear that the rate of reaction decreases with the time due to decrease in concentration of reactant, we can simply say that it has dependence on concentration of reactant species.
- The theoretical interpretation of rate can be done by law of mass action. According to it
- "The rate of a chemical reaction is proportional to the product of effective concentrations (active masses) of the reacting speices, each raised to a power that is equal to the corresponding stoichiometric coefficient of the reactant appearing in the chemical reaction".

  For a general chemical reaction

  $$aA + bB \longrightarrow cC + dD;$$

  rate of reaction is: $r \propto [A]^a[B]^b$

  or $r \propto k[A]^a[B]^b$

  where k is rate constant.
- Experimental determination of rate of reaction suggest that it is not always possible to say the exponents of concentration terms are equal to stoichiometric coefficient of reactants and hence rate of reaction can be given as:

  rate = k $[A]^x$ $[B]^y$

where x and y may be or may not be equal to a and b. The above expression which corelates the concentration terms with rate of reaction is known as rate law or differential rate law.

We can say that **“the rate law is the experimentally observed expression in which reaction rate is related molar concentration of reactant with each term raised to some power which may or may not be the stoichiometric coefficient of the reacting species in the balanced chemical equation.”**

- As the rate law is experimental it may not depend on the concentration of every reactant of the reaction. Also the rate law may depend on the concentration of such species which do not appear in the chemical equation of overall reaction.
- The theoretical interpretation of rate law can be done if the reaction mechanism is specified with the slow step, as it is rate determining step (rds). It can be used to write the rate law expression.
- **Rate Constant:**

  In the above mentioned rate law expression rate = k [A]x [B]y;

  k is the rate constant of reaction. Its value is constant for a constant temperature and is actually the rate of reaction when concentration of each reactant is equal to unity. k is also called velocity coefficient or specific reaction rate. Its unit can be determine by rate law expression. Let for a given reaction;

  nA $\longrightarrow$ Product; rate law is defined as:

  $$-\frac{dA}{dt} = k[A]^n - = k[\,A]n$$

  where n = order of reaction (discussed in next section)

  $$\frac{[\text{concentration}]}{\text{sec}} = k[\text{concentration}]^n$$

  $k = [\text{concentration}]^{1-n}\text{sec}^{-1}$

Example-01

N_2O_5 decomposes as follows:

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

If, $\frac{-d[N_2O_5]}{dt} = k_1[N_2O_5]$; $\frac{d[NO_5]}{dt} = k_2[N_2O_5]$;

$\frac{d[O_2]}{dt} = k_3[N_2O_5]$

Which one of the following is correct for k_1, k_2 and k_3:

(a) $k_1 + k_2 = k_3$ (b) $k_1 = k_2 + K_3$

(c) $k_1 = 2k_2 + 1/2\,k_3$ (d) $2k_1 = k_2 = 4k_3$

Solution:

(d) For the given change

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

On substituting values as given,

$$k_1[N_2O_5] = \frac{1}{2}k_2[N_2O_5] = 2k_3[N_2O_5]$$

or $2k_1 = k_2 = 4k_3$

Example-02

The rate of change in concentration of C in the reaction $2A + B \longrightarrow 2C + 3D$ was observed as 1.0 mol litre-1sec-1. Which of the following is/are correct for the rate of reaction:

(a) Rate of change of concentration of A is 1.0 mol L^{-1} $\sec^{-1}$

(b) Rate of change of concentration of B is 0.5 mol L^{-1} $\sec^{-1}$

(c) Rate of change of concentration of D is 1.5 mol L^{-1} $\sec^{-1}$

(d) Rate of reaction is 0.5 mol L^{-1} $\sec^{-1}$

Solution :(A, B, C, D)

Rate of reaction

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

As $\frac{d[C]}{dt} = 1.0\,\text{mol lit}^{-1}\sec^{-1}$

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

$$\therefore\ -\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt} = 0.5\,\text{mol lit}^{-1}\sec^{-1}$$

$$\frac{d[D]}{dt} = \frac{3}{2}\frac{d[C]}{dt} = 1.5\,\text{mol lit}^{-1}\sec^{-1}$$

Rate of reaction = $\frac{1}{2}\frac{d[C]}{dt} = 0.5\,\text{mol lit}^{-1}\sec^{-1}$

Example-03

For the reaction: $2A + B \longrightarrow A^2B$

the rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6}$ mol^{-2} L^2 s^{-1}. If the initial concentration of A and B are 0.1 mol L^{-1} and 0.2 mol L^{-1} respectively then which of the following is/are correct:

(a) Initial rate of reaction is 8×10^{-9} mol L^{-1} $\sec^{-1}$

(b) When A is reduced to 0.06 mol L^{-1} then rate becomes 3.89×10^{-9} mol L^{-1} $\sec^{-1}$

(c) When A is reduced to 0.06 mol L^{-1} then B will be 0.16 mol L^{-1}

(d) All are correct

Solution: (A, B)

Rate $= k[A]\,[B]^2$

Initial rate = $2 \times 10^{-6}\,[0.1]\,[0.2]^2$

$= 8 \times 10^{-9}$ mol L^{-1} $\sec^{-1}$

Now as [A] is reduced to 0.06 mol L^{-1} i.e. 0.04 mol L^{-1} of [A] is reacted

$\because$ 2 moles A reacts with 1 mole B.

$\therefore$ 0.04 moles of A reacts with 0.02 moles of B

$\therefore$ $[B]_{left} = 0.2 - 0.02 = 0.18$

$\therefore$ Rate $= 2 \times 10^{-6} [0.06] [0.18]^2$

$= 3.89 \times 10^{-9}$ mol^{-2} L^{-1}sec^{-1}

Example-04

The possible mechanism for the reaction

$2\ NO + Br_2 \longrightarrow 2\ NOBr$

is $NO + Br_2 \rightleftharpoons NOBr_2$ (fast);

$NOBr_2 + NO \longrightarrow 2NOBr$ (slow).

Rate law is

(a) $r = k [NO] [Br_2]$ (b) $r = k [NO]_2 [Br_2]^{-1}$

(c) $r = k [NOBr_2] [NO]$ (d) $r = k [NO]_2 [Br_2]$

Solution:(d)

As the slowest step is the rate determining step, therefore the rate law is

$r = k[NOBr_2] [NO]$

Now since $NOBr_2$ is an intermediate its concentration can be calculated from step 1 as follows:

$$K = \frac{[NOBr_2]}{[NO][Br_2]} \quad [K = \text{equilibrium constant}]$$

or $[NOBr_2] = K [NO] [Br_2]$

Substituting this value in above equation

$r = k.\ K[NO]^2[Br_2]$

Or rate $= k' [NO]^2 [Br_2]$ $[\ k' = k\ .\ K]$

rate $= k' [NO]^2 [Br_2]$

Example-05

The reaction $2A + B + C \longrightarrow D + 2E$; is found to follow the rate law as :

$r = k[A] [B]2 [C]^0$. If the concentration of A, B and C increases two times then rate of reaction becomes:

(a) Same (b) doubled

(c) Eight times (d) four times

Solution:(c)

(i) The rate law according to given information may be given as,

$$\frac{dx}{dt} = k[A]^1[B]^2[C]^0$$

(ii) When concentration of A, B and C are doubled then rate will be

$$\frac{dx}{dt} = k[2A][2B]^2[C]^0$$

$= 8k[A][B]^2[C]^0$

i.e., rate becomes 8 fold of, the original rate.

5. MOLECULARITY OF REACTION

- Chemical reactions may be classified as "elementary" (or simple) and "complicated". Reactions which occur in one and only one step are actually called elementary reactions and reactions occurring in the sequence of two or more steps are called complicated reactions. The sequence of two or more steps in which a complicated reaction occurs is called its mechanism.

Thus, complicated reaction has mechanism while elementary reaction has not. Further, each step of a complicated reaction is an elementary reaction.

- The molecularity of an elementary reaction is defined as the minimum number of molecule(s), atom(s) or ion(s) of reactant(s) required for the reaction to occur i.e. which are actually needed for transition state formation of the reaction, and is equal to the sum of the stoichiometric coefficients of the reactants as appearing in the chemical equation for the reaction. Thus, for the reaction represented by the chemical equation.

$aA + bB \longrightarrow$ Products

molecularity $= a + b$

Examples:

Reactions	Molecularity
$PCl_5 \rightleftharpoons PCl_3 + Cl_2$	1
$H_2 + I_2 \rightleftharpoons 2HI$	2

- Reactions are classified as unimolecular, bimolecular, their molecular etc according to their molecularity equal to one, two, three etc., respectively. A complicated reaction has, in fact, no molecularity of its own but molecularity of each of the steps involved in its mechanism.

For example, the reaction:

$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$, is complicated and takes place in this sequence of following three steps.

I $NO + NO \rightleftharpoons N_2O_2$ (fast and reversible)

II $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow)

III $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

- The molecularity of each step is 2 and hence we say that the reaction takes place in the sequence of three bimolecular steps.
- The rates of various elementary reactions in any reaction mechanism generally differ from one another. The rate of overall reaction and the rate of product formation evidently cannot be faster than the rate of the slowest reaction. To take analogy, suppose in a bicycle factory, the different components are manufactured at the rate of 200, 150, 50, 250 and 100 pieces per day. The rate of bicycle production cannot be more than 50 bicycles per day rather it must be exactly 50 bicycles per day. Thus, the slowest step is always the rate determining step (r.d.s.). Based on this concept there is another view regarding molecularity of a complicated reaction. According to which molecularity of a complicated reaction or better to say the overall molecularity of the reaction mechanism is given **by the number of molecules atoms or ions of reactant(s) and/or intermediates coming into contact and colliding simultaneously in the slowest step of the mechanism i.e. the r.d.s. of the reaction.**]

To understand this view let us consider the following nucleophilic substitution reaction.

$(CH_3)_3C–OH + HCl \xrightarrow{ZnCl_2} (CH_3)_3C - Cl + H_2O$

- The reaction occurring in the sequence of following three steps is said to follow SN1 i.e. substitution nucleophilic unimolecular mechanism since r.d.s. is unimolecular.

I $(CH_3)_3C - \underset{..}{O} + HCl \rightleftharpoons$

$(CH_3)_3C - \overset{\ominus}{\underset{..}{O}}H_2 + :Cl^-$ (fast)

II $(CH_3)_3C - \overset{\ominus}{\underset{..}{O}}H_2 \rightleftharpoons$

$(CH_3)_3C^{\ominus} + H_2\underset{..}{\ddot{O}}$(slow r.d.s)

III $(CH_3)_3\overset{\oplus}{C} + :\underset{..}{\ddot{Cl}}:^- \rightleftharpoons R - \underset{..}{\ddot{Cl}}:$

- The mathematical equation expressing concentration dependence of rate is commonly known as rate law or rate expression of the reaction and sum of the indices of the concentration terms appearing in the experimentally observed rate law of a reaction is known as order of the reaction.

- Thus, if for a reaction: aA + bB $\longrightarrow$ products, rate law will be as follows:
  Rate $\propto [A]^m [B]^n$
  Then
  Order w.r.t. A = m
  Order w.r.t. B = n and
  Overall order = m + n
- Note that m and n are experimental quantities which may or may not be equal to the respective stoichiometric coefficients (a and b) i.e. molecularity, so, order of reaction cannot be predicted by just seeing the chemical equation.

  Let us consider the reaction:

  $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$

  Kinetic experiment carried on the reaction has revealed following facts.

(i) Rate increases fourfold when concentration (or partial pressure) of nitric oxide (NO) is doubled keeping that of H_2 constant.

(ii) Rate gets doubled with doubling of concentration (or partial pressure) of hydrogen keeping that of NO constant.

(iii) Rate increases 8-fold when concentrations (or partial pressure) of both NO and H_2 are doubled simultaneously.

- From these facts it is evident that the reaction obeys following kinetics (rate law).
  Rate $\propto [NO]^2 [H_2]$
  Thus, order w.r.t. NO = 2
  Order w.r.t. H_2 = 1
  Overall order = 2 + 1 = 3
  Reactions are classified as zero order, 1st order, 2nd order etc.

6. ORDER OF REACTION

- Order of reaction is defined as the **"sum of the powers of the concentration terms appearing in experimentally observed rate law."**
- It should be noted that all the molecules shown in a chemical equation not necessarily used to determine the value of order of reaction, but only those molecules whose concentrations changes are included in the determination of the order of a reaction.
- In other words: "The number of reacting molecules whose concentration alters as a result of chemical reaction is termed as the order of reaction."
  For example, the kinetic experiment carried on the given reaction:
  $2NO + 2H_2(g) \longrightarrow N_2(g) + 2H_2O$ (g); has shown the following experimental observation:

(i) Rate increases 4 - fold when concentration of NO is doubled keeping the concentration of H_2 constant.

(ii) Rate gets just doubled when concentration of H_2 is doubled keeping that of NO constant,

(iii) Rate increases 8 - fold when concentrations of both NO and H_2 are doubled.

- These experimental rate data fit into following experimentally observed "Rate law" of the given reaction:
  Rate $\propto [NO]_2[H_2]$
  Thus for the above given reaction
  Order with respect to NO = 2;
  Order with respect to H_2 = 1; and
  Overall order = 2+ 1 = 3

- Let a reaction represented by the chemical equation:
  aA + bB $\longrightarrow$ Products
  Obeys the following rate law:
  Rate $\propto [A]^m [B]^n$ or Rate = $k[A]^m [B]^n$
  m and n are experimental quantities which indicates that order of reaction is m with respect to A and n with respect to B.

- If either of A or B is taken in large excess as compared to another, the order with respect to the excess reactant will be zero.
  Rate = $k'[A]^m$; where $k' = k[B]^n$,
  when B is in large excess.
  therefore Order with respect to A = m;

- Order with respect to B = 0, and over all order = m
  Also rate = k''[B]n; where k'' = k[A]m, when A is in large excess.
  Order with respect to A = 0;
- Order with respect to B = n and over all order = n
  here k' or k'' is actually known as pseudo rate constant.

- Thus, a bimolecular reaction conforms to be of first - order when one of the reactants is taken in large excess and the reaction is said to be pseudo unimolecular or pseudo first order. Hydrolysis of ester by dilute acid is the example of this type of reaction.

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

- In your syllabus zero order and first order reactions are widely discussed.
- **Zero** order reactions are relatively uncommon and they occur under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are the examples of zero order reactions. At high pressure the decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction:

  $2NH_3(g) \xrightarrow[\text{Pt catalyst}]{1130K} N_2(g) + 3H_2(g)$

  Rate = $k[NH_3]^0 = k$
- In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst and rate of the reaction independent of its concentration. Similarly the thermal decomposition of HI on gold surface is another example of zero order reaction.
- A reaction is said to be of the first order if the rate of the reaction depends upon only one concentration term. A first order reaction may be given as any one of the following reactions

  $A \longrightarrow$ Products; Rate of reaction $\propto [A]$ or

  $2A \longrightarrow$ Products; Rate of reaction $\propto [A]$ or

  $A + B \rightarrow$ Products; Rate of reaction $\propto [A]$ or $[B]$

7. EXAMPLE OF REACTION OF VARIOUS ORDER

(i) First order reactions

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

(b) $Br_2 \longrightarrow 2Br$

(c) $2HNO_3 \longrightarrow 2NO + H_2O$

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

These reactions obey following rate law.
Rate $\propto [R]$
Where R = N_2O_5, Br_2, HNO_3 and H_2O_2 for the reactions (a), (b), (c) and (d), respectively.

(ii) Second – Order Reactions

a) $H_2 + I_2 \rightleftharpoons 2HI$, Rate $\propto [H_2][I_2]$

b) $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$
Rate $\propto [CH_3COOH][C_2H_5OH]$

c) $CH_3COOEt + NaOH \longrightarrow CH_3COOH + EtOH$
Rate $\propto$ [CH3COOEt] [NaOH]

d) $2NO_2 \longrightarrow N_2O_2 + O_2$
Rate $\propto [NO_2]_2$

(iii) Fractional – order reactions

$CH_3CHO \longrightarrow CH_4 + CO$

Rate $\propto [CH_3CHO]^{3/2}$

(iv) Pseudo first – order Reactions

(a) $CH_3COOEt + H_2O \xrightarrow{H^+} CH_3COOH + EtOH$

(b) $\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{(Sucrose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$

- These reactions follow the following 1st order kinetics.

  Rate $\propto [R]$, R = CH_3COOEt and $C_{12}H_{22}O_{11}$
- **Pseudo first – order** reaction also called pseudo unimolecular reaction is a bimolecular reaction conforming to the first-order kinetics due to large excess concentration of one of the reactants.

(v) Zero-order Reactions

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

[when catalyst surface is saturated]

Reaction between chlorine and hydrogen in sunlight over water in inverted tube.

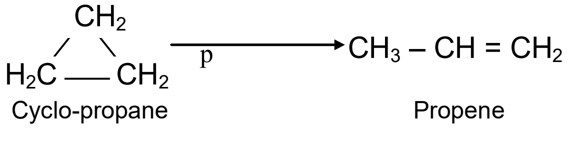
8. DISTINCTION BETWEEN ORDER AND MOLECULARITY

(i) Molecularity is a theoretical property and it concerns with mechanism while order is an experimental property and it concerns with kinetics.

(ii) Molecularity is always an integer excepting zero while order may be any number integral or fractional including zero.

(iii) Order may change with change in experimental conditions while molecularity is a fixed property of a reaction and is independent of experimental conditions.

Example: The isomerisation of cyclopropane into propene is a 1st order at high cyclopropane gas pressure but 2nd order at low cyclopropane gas pressure.



Rate $\propto$ [Cyclo-propane] … at high pressure

Rate $\propto$ [Cyclo-propane]^2 … at low pressure

- Order may differ from the molecularity if reaction is complicated or if concentrations of any of the reactants be taken in large excess as compared to other.

  For example, let us consider the reaction "the acid catalysed hydrolysis of an ester say ethyl acetate" represented by the following chemical equation.

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

- As it is evident from the chemical equation, the reaction is bimolecular. But the order of reaction is "one". It obeys the following rate law as observed experimentally.
  Rate $\propto [CH_3COOC_2H_5]$
  i.e. order w.r.t. ester = 1
  order w.r.t. water = 0
  overall order = 1 + 0 = 1
- The reaction is actually carried out taking dilute aqueous solution of ester and dilute acid (HCl). In the reaction mixture so employed, the concentration of water remains in large excess as compared to the concentration of ester. Though, ester and water both are consumed in equimolecular amounts during the reaction, the decrease in the concentration of water is negligibly small in comparison to its large initial concentration. In other words, the concentration of water remains practically constant inspite of change in its concentration during the reactions.
- As per Law of Mass Action, the rate of reaction may be given as
  Rate $\propto$ [ester] [water]
  or Rate = k [ester] [water]
  or Rate = K[ester]
  Where K = k [water] = another constant.
- The reaction is called "pseudo unimolecular" and K is called "pseudo rate constant" or apparent or observed rate constant. In the light of the above example, the order of reaction may be defined as the number of molecules of the reactant(s) whose concentration(s) alters during the chemical charge.

9. INTEGRATY RATE REACTION

- To make the easier determination of instantaneous rate, differential rate equation is integrated to get a relation between directly measured experimental data and rate constant.
- **Zero Order Reactions :**
  For zero order reaction the rate of reaction is independent of concentration of reactants.
  Let a zero order reaction is given as :

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

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^0$$

$$\text{Rate} = -\frac{d[A]}{dt} = k$$

$$d[A] = -k\,dt$$

$$\int dA = -k\int dt$$

$$[A] = -kt + I$$

Where, I is the constant of integration.

At t = 0, the concentration of the reactant $[A] = [A]_0$, where $[A]_0$ is initial concentration of the reactant.

Substituting in equation

$$[A]_0 = -k \times 0 + I$$

$$[A]_0 = I$$

Substituting the value of I in the equation

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

On solving

$$k = \frac{[A]_0 - [A]}{t}$$

- Comparing with equation of a straight line, y = mx+c, if we plot [A] against t, we get a straight line with slope = - k and intercept equal to $[A]_0$.
- **First Order Reactions**
  Let us consider a first order reaction

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

- Suppose we start with 'a' moles per litre of the reactant A. After time t, suppose x moles per litre of it, have decomposed. Therefore, the concentration of A after time t becomes (a – x) moles per litre. Then according to Law of Mass Action:
  Rate of reaction $\propto (a - x)$

i.e., $\frac{dx}{dt} \propto (a - x)$ or $\frac{dx}{dt} = k(a - x)$

where k is called the rate constant or the specific reaction rate for the reaction of the first order.

$$\frac{dx}{a - x} = kdt$$

$$\int \frac{dx}{a - x} = \int kdt$$

or $k = \frac{1}{t}\ln\frac{a}{a - x}$

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

- If the initial concentration of reactant A is $[A]_0$ and the concentration after time t is [A] then putting a = $[A]_0$ and (a – x) = [A], above equation becomes

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

or $kt = \ln\frac{[A]_0}{[A]}$

which can be written in the exponential form as

$\frac{[A]_0}{[A]} = e^{et}$ or $[A] = [A]_0\,e^{-kt}$

- **Half-Life Period of a Reaction :**
  The half-life period of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.

- **Zero order reaction:** For a zero order reaction, rate constant is given by equation

$$k = \frac{[A]_0 - [A]}{t}$$

At $t = t_{1/2}$, $[A] = \frac{1}{2}[A]_0$

The rate constant at $t_{1/2}$ becomes

$$k = \frac{[A]_0 - 1/2[A]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

Thus for zero order reaction $t_{1/2} \propto [A]_0$.

- **First order reaction:** For a first order reaction rate constant is given by equation

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

When half of the reaction is completed, x = a/2. The rate constant at $t_{1/2}$ becomes

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

$$= \frac{2.303}{k}\log 2 = \frac{0.693}{k}$$

$$\text{i .e, } t_{1/2} = \frac{0.693}{k}$$

Thus ‘a’ does not appear in this equation so that $t_{1/2}$ is independent of initial concentration a. Similarly, it can be seen that $t_{1/2}$, $t_{2/3}$ etc. will also be independent of the initial concentration.

- **n^{th} Order reaction:**

$$\begin{array}{lcc} & A \longrightarrow & \text{Product} \\ t = 0 & a & 0 \\ t = t & a - x & x \end{array}$$

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

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

$$\int^{a/2} \frac{dx}{(a-x)^n} = \int_0^{t_{1/2}} kdt$$

Let a – x = z

–dx = dz, when x = 0, z = a

When x = a/2, z = a/2

$$\int^{a/2} \frac{-dz}{Z^n} = \int_0^{t_{1/2}} kdt$$

$$\text{or} \quad -\left[\frac{Z^{-n+1}}{-n+1}\right]_a^{a/2} = kt_{1/2}$$

$$\frac{a^{1-n}}{n-1}\left[\left(\frac{1}{2}\right)^{1-n} - 1^{1-n}\right] = kt_{1/2}$$

$$\frac{1}{a^{n-1}(n-1)}[2^{n-1} - 1]$$

$$= kt_{1/2},\ (a^{n-1})t_{1/2}\left(\frac{1}{k(n-1)}(2^{n-1} - 1)\right) = k$$

- **Therefore for a nth order reaction, half life period in inversely related to initial amount**

$t_{1/2}a^{n-1} = \text{constant}$;

$t_{1/2} = \frac{\text{constant}}{a^{n-1}}$ or $t_{1/2} = \text{constant} \times a^{1-n}$

or $t_{1/2} \propto a^{1-n}$

10. PSEUDO FIRST ORDER REACTIONS

- Such reactions which are not truly of the first order but under certain conditions become reactions of the first order are called pseudo-unimolecular or pseudo first order reactions.
  Consider the following acid-catalysed reactions:

(i) Hydrolysis of ethyl acetate

$$\underset{\text{Ethylacetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} \underset{\text{Acetiacid}}{CH_3COOH} + \underset{\text{Ethylalcohol}}{C_2H_5OH}$$

(ii) Inversion of cane-sugar

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glu cos e}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Both the above reactions are bimolecular and supposed to follow the kinetics

Rate = k $[CH_3COOC_2H_5]$ $[H_2O]$

or

Rate = k $[C_{12}H_{22}O_{11}]$ $[H_2O]$

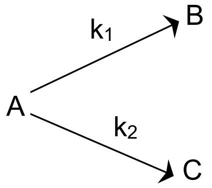
but reactions are found to be of the first order, as experimentally it is observed that it is usually carried out taking dilute aqueous solution of ester or sugar and acid (HCl) such that in the reaction mixture water exists in large excess as compared to ester. It is also say that water has almost its maximum concentration of 55.5 mole L^{-1}, so there is no appreciable change in its concentration and the same remains practically constant.

∴ Rate = $k[H_2O][CH_3COOC_2H_5]$

becomes Rate = k’ $[CH_3COOC_2H_5]$ where (k’) called pseudo rate constant. Thus, the molecularity of the above reaction is ‘two’ but its order is ‘one’.

11. SOME COMPLEX FIRST ORDER REACTION

- **Parallel Reactions**



- In such reactions (mostly organic) a single reactant gives two products B and C with different rate constants. If we assume that both of them are first order, we get.

$$\frac{-d[A]}{dt} = k_1[A] + k_2[A] = (k_1 + k_2)[A] \ldots(a)$$

$$\frac{d[B]}{dt} = k_1[A] \qquad \ldots(b)$$

and $$\frac{d[C]}{dt} = k_2[A] \qquad \ldots(c)$$

- Let us assume that in a time interval, dt, x moles / lit of B was produced and y moles / lit of C was produced.

$$\therefore \frac{d[B]}{dt} = \frac{x}{dt} \text{ and } \frac{d[C]}{dt} = \frac{y}{dt}$$

$$\therefore \frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}} = \frac{x}{y}.$$

We can also see that from (b) and (c),

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

$\therefore \frac{x}{y} = \frac{k_1}{k_2}$. This means that irrespective of how much time is elapsed, the ratio of concentration of B to that of C from the start (assuming no B and C in the beginning) is a constant equal to k_1/k_2.

- **Sequential Reactions**

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

In this A decomposes to B which in turn decomposes to C.

$$\therefore \frac{-d[A]}{dt} = k_1[A] \qquad \ldots\ldots(a)$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad \ldots\ldots(b)$$

$$\frac{d[C]}{dt} = k_2[B] \qquad \ldots..(c)$$

Integrating equation (a), we get

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

Now we shall integrate equation (b) and find the concentration of B related to time t.

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

$$\Rightarrow \frac{d[B]}{dt} + k_2[B] + k_1[A]$$

Substituting [A] as $[A]_0 e^{-k_1 t}$

$$\Rightarrow \frac{d[B]}{dt} + k_2[B] = k_1[A]_0 e^{-k_1 t} \ldots (d)$$

- Integration of the above equation is not possible as we are not able to separate the two variables, [B] and t. Therefore we multiply equation (d) by an integrating factor, on both the sides of the equation.

$$\left(\frac{d[B]}{dt} + k_2[B]\right)e^{k_2 t} = k_1[A]_0 e^{(k_2 - k_1)t}$$

- We can see that the left hand side of the equation is a differential of $[B]e^{k_2 t}$.

$$\therefore \frac{d}{dt}\left([B]e^{k_2 t}\right) = k_1[A]_0 e^{(k_2 - k_1)t}$$

$$d\left([B]e^{k_2 t}\right) = k_1[A]_0 e^{(k_2 - k_1)t} dt$$

- Integrating within the limits 0 to t.

$$\int d\left([B]e^{k_2 t}\right) = k_1[A]_0 \int_0^t e^{(k_2 - k_1)t} dt$$

$$\Rightarrow [B]e^{k_2 t} = k_1[A]_0 \left[\frac{e^{(k_2 - k_1)t}}{(k_2 - k_1)}\right]_0^t$$

$$\Rightarrow [B]e^{k_2 t} = \frac{k_1[A]_0}{(k_2 - k_1)}\left[e^{(k_2 - k_1)t} - 1\right]$$

$$\Rightarrow [B] = \frac{k_1[A]_0}{(k_2 - k_1)} e^{-k_2 t}\left[e^{(k_2 - k_1)t} - 1\right]$$

$$[B] = \frac{k_1[A]_0}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right] \quad \ldots (5)$$

- Now in order to find [C], substitute equation (5) in equation (c), we get

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A]_0}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right]$$

$$\therefore d[C] = \frac{k_1 k_2 [A]_0}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right] dt$$

On integrating

$$\int d[C] = \frac{k_1 k_2 [A]_0}{(k_2 - k_1)} \int_0^t \left[e^{-k_1 t} - e^{-k_2 t}\right] dt$$

$$\Rightarrow [C] = \frac{k_1 k_2 [A]_0}{(k_2 - k_1)}\left[\left(\frac{e^{-k_1 t}}{-k_1}\right)_0^t - \left(\frac{e^{-k_2 t}}{-k_2}\right)_0^t\right]$$

$$\Rightarrow [C] = \frac{k_1 k_2}{(k_2 - k_1)}[A]_0\left[\left(\frac{e^{-k_1 t} - 1}{-k_1}\right) - \left(\frac{e^{-k_2 t} - 1}{-k_2}\right)\right]$$

$$\Rightarrow [C] = \frac{k_1 k_2}{k_2 - k_1}[A]_0\left[\left(\frac{1 - e^{-k_1 t}}{k_1}\right) - \left(\frac{1 - e^{-k_2 t}}{k_2}\right)\right]$$

$$[C] = \frac{[A]_0}{k_2 - k_1}\left[k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})\right]$$

- **B_{max} and t_{max}:** We can also attempt to find the time when [B] becomes maximum. For this we differentiate equation (5) and find $\frac{d[B]}{dt}$ & equate it to zero.

$$\therefore \frac{d[B]}{dt} = \frac{k_1[A]_0}{(k_2 - k_1)}[e^{-k_1t}(-k_1) + e^{-k_2t}(k_2)] = 0$$

$$\Rightarrow k_1e^{-k_1t} = k_2e^{-k_2t}$$

$\frac{k_1}{k_2} = e^{(k_1-k_2)t}$, taking log of both the sides

$$\therefore t_{max} = \frac{1}{k_1 - k_2}\ln\frac{k_1}{k_2} \qquad \dots (6)$$

Substituting equation (6) in equation (5)

$$B_{max} = [A]_0\left[\frac{k_2}{k_1}\right]^{k_2/k_1-k_2}$$

12. TEMPERATURE DEPENDENCE ON THE RATE OF REACTION

- It was observed that for most of the reactions rate increases with the increase of temperature. For most of the reactions, it was found that the rate of the reaction increases two or three fold with the increase in 10ºC temperature. This increase in rate was defined by temperature coefficient.

- **Temperature Coefficient:** "Temperature coefficient of a chemical reaction is defined as the ratio of rate constants of a reaction at two temperatures differing by 10°C".

  Temperature coefficient = $\frac{k_{T+10}}{k_T} \approx 2$ to 3

  where k_T is the rate constant at temperature T K and k_{T+10} is the rate constant at temperature (T + 10) K. This ratio generally falls between 2 and 3 which means for most of the chemical reactions, the rate becomes two or three folds for every 10°C rise in temperature.

Example-06

From the following data for the reaction between A and B,

[A] in mol L^{-1}	[B] in mol L^{-1}	Initial rate in mole L^{-1} s^{-1}
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}

the order of the reaction with respect to A and with respect to B will be:

(a) 2, 1 (b) 1, 2

(c) 2, 0 (d) 1, 3/2

Solution:(a)

Let the order with respect to A be 'a' and with respect to B be 'b'. The rate law would then be represented as

Rate = k $[A]^a$ $[B]^b$

Therefore

By (i) and (ii),

$$\frac{4.0\times10^{-3}}{5.0\times10^{-4}} = \frac{k[5.0\times10^{-5}]^a[6.0\times10^{-5}]^b}{k[2.5\times10^{-4}]^a[3.0\times10^{-5}]^b}$$

$2^3 = 2_{a+b}$

$\therefore$ a + b = 3

By (ii) and (iii),

$$\frac{4.0\times10^{-3}}{1.6\times10^{-2}} = \frac{k[5.0\times10^{-4}]^a[6.0\times10^{-5}]^b}{k[1.0\times10^{-3}]^a[6.0\times10^{-5}]^b} = \frac{1}{4} = \left(\frac{1}{2}\right)^a$$

a = 2 and b = 1

Example-07

What will be the initial rate of a reaction if its rate constant is 10^{-3} min^{-1} and the concentration of reactant is 0.2 mol dm-$^{-3}$3 also calculate the amount of reactant converted into products in 200 minute is:

(a) 2 ×10^{-4}mol dm^{-3} min^{-1}, 81.97%

(b) 2 ×10^{-4} mol dm^{-3} min^{-1}, 18.03%

(c) 2 ×10^{-4} mol dm^{-3} min^{-1}, 76%

(d) 2 ×10^{-4} mol dm^{-3} min^{-1}, 24%

Solution:(b)

Since k has unit min^{-1} and thus, given reaction is of first order

Now rate = k[reactant $]^1$

initial rate = $10^{-3} \times [0.2]^1 = 2 \times 10^{-4}$ mol dm^{-3} min^{-1}

$$\text{Also} \quad k = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

$$\therefore \quad 10^{-3} = \frac{2.303}{200}\log\frac{100}{(100-x)}$$

x = 18.03%

Example-08

The half time of first order decomposition of nitramide is 2.1 hour at 15°C.

$$NH_2NO_2(s) \longrightarrow N_2O(g) + H_2O(l)$$

If 6.2 g of NH_2NO_2 is allowed to decompose, then time taken for NH_2NO_2 to decompose 99% and volume of dry N_2O produced at this point measured at STP will be

(a) 13.95 hours, 22.4 L

(b) 13.95 hours, 2.217 L

(c) 2.1 hours, 22.4 L

(d) 2.1 hours, 2.217 L

Solution:(b)

For a first-order reaction, $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$

Initial moles of nitramide = $\frac{6.2}{62} = 0.1$

$$\therefore t = \frac{2.303\times2.1}{0.693}\log\frac{0.1}{0.001} = 13.95\,\text{hours}$$

Since, the decomposition is 99%, so 99% of the initial moles of NH_2NO_2 would be converted to N_2O.

Moles of N_2O = $\frac{0.1\times99}{100}$

Volume of N_2O at STP

$$= \frac{0.1\times99\times22.4}{100} = 2.217\,\text{litre}$$

Example-09

A drug is known to be ineffective after it has decomposed to the extent of 30%. The original concentration of a sample was 500 units/ml. When analysed 20 months later, the concentration was found to be 420 units / ml. Assuming that the decomposition is of first order, what will be the expiration time of the drug sample. What is the half life of the drug?

(a) 0.00872 month,41 month
(b) 0.00872 month, 79.49 month
(c) 41 month, 79.49 month
(d) 79.49 month, 41 month

Solution:(c)

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{20}\log\left(\frac{500}{420}\right)$$

$k = 0.00872\ \text{month}^{-1}$

Expiry time $t = \frac{2.303}{0.00872} \times \log\frac{500}{350} = 14$ months

Also $t_{1/2} = \frac{0.693}{0.00872} = 79.49$ month

Example-10

A first order reaction takes 40 minute for 30% decomposition $t_{1/2}$ for the reaction is:

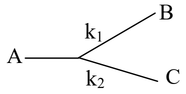
(a) 66.67 min (b) 80 min
(c) 77.70 min (d) infinite time

Solution: (c)

$t_{1/2} = 77.70$ minute

Example-11

A certain organic compound A decomposes by two parallel first order mechanisms.



If $k_1 : k_2 = 1 : 9$ and $k_1 = 1.3 \times 10^{-5}\ s^{-1}$. The concentration ratio of C to A if an experiment is started with only A and allowed to run for one hour will be

(a) 0.626 (b) 0.3436
(c) 0.526 (d) 0.5486

Solution:(d)

Rate constant (k_T) for decomposition of

$A = k_1 + k_2 = (1.3 + 11.7) \times 10^{-5}$

$= 13 \times 10^{-5}$

moles of A decomposed into C in 1 hr. = mole of C formed in 1 hr. so

$k_2 = \frac{2.303}{3600}\log\frac{1}{1-x}$ (Let initial moles of A = 1)

$x = [C]_t = 0.3436$

Total moles of A remaining in 1 hr are calculated as

$$k_T = \frac{2.303}{3600}\log\frac{1}{[A]_t}$$

$[A]_t = 0.626$ so, $\frac{[C]_t}{[A]_t} = \frac{0.3436}{0.626} = 0.5486$

Example-12

^{227}Ac has a half-life of 22 years with respect to radioactive decay. The decay follows two parallel paths, on leading to ^{222}Th and other to ^{223}Fr. The percentage yields of these two daughter nuclides are 2 and 98 respectively. The decay constant for separate paths are:

(a) $0.693\ y^{-1}$; $0.693\ y^{-1}$ (b) $0.387\ y^{-1}$; $0.63\ y^{-1}$
(c) $0.03087\ y^{-1}$; $0.00063\ y^{-1}$
(d) 2; 98

Solution:(c)

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{22}$$

where $k = k_1 + k_2$, which are rate constant of separate paths

Also $k_1 / k_2 = 2/98$

On solving $k_2 = 0.03087\ y^{-1}$

$k_1 = 0.00063\ y^{-1}$

Example-13

Calculate the average rate of decomposition of N_2O_5 of the reaction

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

During the time interval t = 600s to t = 1200s. Use the following data:

Time	$[N_2O_5]$
600s	1.24×10^{-2} M
1200s	0.93×10^{-2} M

Solution:

We know that the decomposition of N_2O_5 is a first order reaction. Therefore,

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

or $k = \frac{2.303}{(1200-600)}\log\frac{1.24\times10^{-2}}{0.93\times10^{-2}}$

Now rate of decomposition at 600s

$-\frac{dC}{dt} = kC_1 = (4.8 \times 10^{-4} s^{-1})(1.24 \times 10^{-2} M)$

$= 5.95 \times 10^{-6}\ M\ s^{-1}$

Similarly rate of decomposition at 1200s

$= (4.8 \times 10^{-4}\ s^{-1})(0.93 \times 10^{-2}\ M)$

$= 4.46 \times 10^{-6}\ M\ s^{-1}$

Average rate of decomposition

$= \frac{5.95\times10^{-6} \times 4.46\times10^{-6}}{2} Ms^{-1}$

$= 5.205 \times 10^{-6}\ Ms^{-1}$

Example-14

Find out the order of reaction under following conditions:

(a) When $t_{1/2}$ of the reaction is halved as initial concentration of reactant is doubled.
(b) When $t_{1/2}$ of the reaction is doubled as the initial concentration of reactant is doubled.
(c) When $t_{1/2}$ of the reaction remains unchanged as initial concentration of reactant is doubled.

Solution:

(a) In present case

$t_{1/2} \propto \frac{1}{a_0^{n-1}}$ [a_0 = initial concentration] …(a)

$\frac{1}{2} \times t_{1/2} \propto \frac{1}{(2a_0)^{n-1}}$ …(b)

∴ On dividing equation (a) by equation (b)

$2 = 2^{n-1} = n - 1 = 1$ or $n = 2$

(b) In this case

$2 \times t_{1/2} \propto \frac{1}{(2a_0)^{n-1}}$ …(c)

On dividing equation (a) by equation (b)

$\frac{1}{2} = 2^{n-1} = 0.5 = 2n^{-1}$

log 0.5 = (n −1) log2

$\therefore\ n - 1 = \frac{\log 0.5}{\log 2} = n - 1 = -1$

$\therefore\ n = 0$

(c) In this case

$t_{1/2}\ \alpha \frac{1}{(2a_0)^{n-1}}$ …(d)

On dividing equation (a) by equation (d)

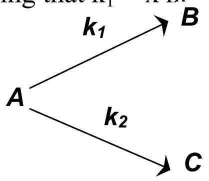
$1 = 2n^{-1}$

log1 = (n −1)log2

$\therefore\ n - 1 = \frac{\log 1}{\log 2} = 0$ or $n = 1$

Example-15

Let $k_1 : k_2 = 1 : 10$. Calculate the ratio, $\frac{[C]}{[A]_t}$ at the end of one hour assuming that $k_1 = x\ hr^{-1}$



Solution:

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

$$\therefore\ \frac{-d[A]}{dt} = (k_1 + k_2)dt$$

Integrating within the required limits, we get

$$\ln\frac{[A]_0}{[A]_t} = (k_1 + k_2)t$$

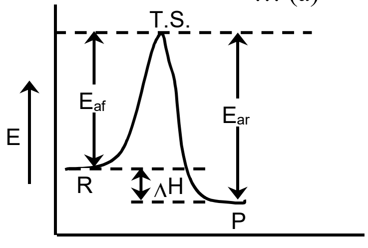
$$\therefore\ \ln\frac{[A]_t + [B] + [C]}{[A]_t} = (k_1 + k_2)t$$

Since $\frac{[B]}{[C]} = \frac{k_1}{k_2} = \frac{1}{10}$

$$\therefore\ \ln\frac{[A]_t + \frac{[C]}{10} + [C]}{[A]_t} = 11x = \frac{[C]}{[A]_t} = \frac{10}{11}(e^{11x} - 1)$$

13. ARRHENIOUS REACTION

- In 1889 Arrhenius recognised the temperature dependence of rates or rate constant. He has given an emperical relation which can be written as
$k = Ae^{-E_a/RT}$ … (a)



k is the rate constant (of any order other than zero order), A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature. Activation energy (E_a) is the minimum energy required by a reactant at a certain temperature to undergo transformation into product. Arrhenius clearly assumed that reactions occur because of collisions between atoms and molecules of the reactant. He assumed the activation energy to be the least value of energy which the colliding molecules must possess for the collision to yield a product. If we plot graph between activation energy and progress of a reaction (expressed as reaction co-ordinate),we get a graph as shown in figure.

The difference between the energies of the reactant and the transition state (TS) is called E_{a_f} .

A, the pre-exponential factor or the frequency factor or the Arrhenius constant is the number of effective collisions occurring per unit time. Effective collision is the number of collisions occurring per unit time in which orientation of the colliding molecules is proper. $e^{-E_a/RT}$ gives the fraction of the effective collision that have the sufficient activation energy. Therefore the product of A and $e^{-E_a/RT}$ gives the number of collisions per unit time that forms the product and is called its number of productive collisions which is the rate constant, k.

For all practical calculations, we shall assume that Ea and A are temperature independent. Both A and Ea are characteristics of the reaction.

- **Determination of A and E_a:**
- **First Method:**

Taking log of both sides of equation (a)

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

Converting natural log to common log,

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

If log k is plotted against 1/T, a straight line is obtained which is shown as:

The slope of this line is given by

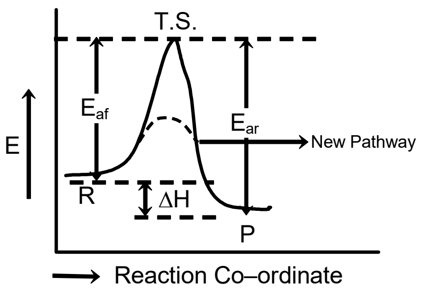
$$\text{slope} = \frac{-E_a}{2.303RT}$$

Thus, knowing the slope, the Ea can be easily calculated. The intercept of the line will give the value of log A.

- **Second Method:**
  The logarithmic form of Arrhenius equation is rearranged as
  $$\ln k = -\frac{-E_a}{RT} + \ln A$$
  Differentiating with respect to temperature, we get
  $$\frac{d\ln k}{dT} = \frac{E_a}{RT^2}$$
  Integrating within the limits of temperature T_1 and T_2, we get
  $$\int_{k_1}^{k_2} d\ln k = \int_{T_1}^{T_2} \frac{E_a}{RT^2} dT \;=\; \ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
  $$\text{or} \quad \log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \ldots \text{(b)}$$
  Where k_1 and k_2 are rate constants at temperatures T_1 & T_2 respectively. Thus, knowing these values E_a can be calculated. When the value of E_a is known, the value of A can be calculated by substituting its value in equation $k = Ae^{-E_aRT}$. In equation (b), the value of R has to be inserted in the same unit in which E_a is desired.
- **Temperature Coefficient:** "Temperature coefficient of a chemical reaction is defined as the ratio of rate constants of a reaction at two temperatures differing by 10ºC.
  $$\therefore \text{ Temperature coefficient} = \frac{k_{T+20}}{K_T} \approx 2 - 3$$
  where k_T is the rate constant at temperature T K and k_{T+10} is the rate constant at temperature (T+10) K. This ratio generally falls between 2 and 3 which means for most of the chemical reactions, the rate becomes two or three folds for every 10ºC rise in temperature.

14. ROLE OF CATALYST

- A catalyst is a substance that takes part in a reaction system by providing a new path way with a lower activation energy between the two fixed points of reactant and product.



- It is very important to understand the role of catalyst and their significance. We shall explain this with the following examples.
- There are several reactions which are catalysed by H^+ or OH^-. An example of this is the hydrolysis of an ester in the presence of an acid.
  $$\text{Ester} + H_2O \xrightarrow{H^+} \text{Acid} + \text{Alcohol}$$
  The rate of the reaction is given as
  Rate = k [Ester] [H^+]
- In this reaction H+ plays the role of the catalyst. Its concentration in the beginning of the reaction and at the end is same. In fact the rate can be written as
  Rate = k' [Ester]
  Where k' = k [H^+]
- These reactions are called pseudo first order reactions, and k' is the pseudo or effective rate constant.
- Now if we go by the well known definition of a **catalyst that 'catalysts increase the rate of reaction by their presence but their presence is not required for the reaction to occur** (of course now the reaction will occur slowly).
- If we take this definition on its face value then the absence of H^+ should not let the reaction to happen, therefore the rate of the reaction in the absence of H^+ should be,
- Rate = k [Ester]. This puts us in a spot because if concentration of H^+ is taken less than 1 molar then the rate of the reaction would become less than the rate which we had in its absence.
- This dilemma can be resolved by understanding what catalysts do. There are two types of catalyst (a) Reactant catalyst and (b) Non reactant or surface catalyst. The former increases the rate of the reaction by existing in the rate law. Therefore, this implies that in their absence the reaction rate will be zero. In fact the reactant catalysts are just like any other reactant. We call them as catalysts only because they are regenerated back at the end of the reaction. For example, during dehydration of alcohols to alkene H+ acts like a catalyst which is in first step participates in the reaction and then in second step is regenerated.
  $$CH_3 - CH_2OH + H^+ \longrightarrow CH_3 + H_2O$$
  $$CH_3 - CH_2^+ \longrightarrow H^+ + CH_2 = CH_2$$
- The non-reactant catalysts, on the other hand, do not exist in the rate expression. For example, when alkenes are hydrogenated, Pt is used as a catalyst. Now, the rate of the reaction depends on the concentration of H_2 and that of alkenes only. Changing the concentration of Pt has no effect on the rate. These catalysts increase the rate of reaction by either decreasing the activation energy or increasing the value of Arrhenius constant or by doing both.

15. TRANSITION STATE THEORY (TST)

- The Arrhenius rate law was widely used to determine energies for the reaction barrier. The Arrhenius equation arises from empirical observation and ignores any mechanistic considerations, such as whether one or more reactive intermediates are involved in the overall conversion of a reactant to a product. TST is primarily used as a qualitative basis to understand how chemical reactions take place. Transition state theory (TST) is the theory of the rates of elementary reactions which assumes a special type of equilibrium (quasi-equilibrium) between reactants and activated complexes. TST is also referred as "activated-complex theory", "absolute-rate theory", and "theory of absolute reaction rates".

- To understand TST consider the bimolecular reaction of A with B to form product P,

  $A + B \xrightarrow{k} P$

  Where k is the second order rate constant.

- Now, consider the same bimolecular reaction sequence, but in which A and B reversibly react to form an intermediate complex $(AB)^{\#}$, which irreversibly decomposes to form final product P. The species $(AB)^{\#}$, is a so-called transition state (or activated complex) whose lifetime is less than 10-13 sec.

  $A + B \underset{k_1}{\overset{k_1}{\rightleftharpoons}} (AB)^{\#} \xrightarrow{k} P$

  $\therefore d[P]/dt = k[A][B] = k'[AB^{\#}]$

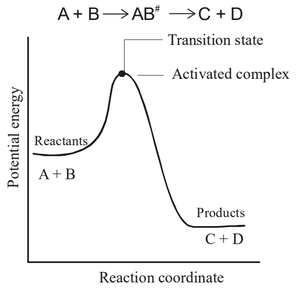
- In this equation, k is the bimolecular rate constant for conversion of A and B to P and k' is the unimolecular rate constant for decomposition of the activated complex $(AB)^{\#}$ to form P.

- Assume a thermodynamic quasi-equilibrium to exist between A, B and $(AB)^{\#}$. For this we can write an equilibrium constant and an expression for $DG_0^{\#}$, (the free energy of reaction to form the transition state normally called the standard free energy of activation)

  $$\therefore \quad K_{eq}^{\#} = \frac{[AB^{\#}]}{[A][B]}; \Delta G_0 = -RT \ln K_{eq}^{\#}$$

  $$\therefore \quad d[P]/dt = k[A][B] = k'[AB\#] = k' K_{eq}^{\#} [A][B]$$

- From this equality now we can say that the bimolecular rate constant k is given by the product of k′. Thus if we can evaluate k′ and $K_{eq}^{\#}$ we can calculate k.



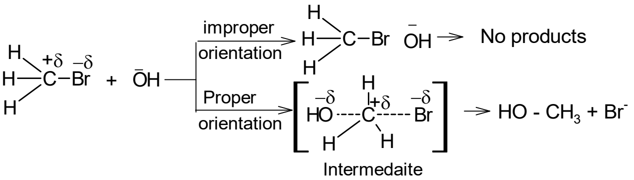
16. COLLISION THEORY OF CHEMICAL REACTION

- It is based on kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. The number of collisions per sec per unit volume of the reaction mixture is known as collision frequency (Z). The rate of chemical reactions is also affected by activation energy for a given elementary bimolecular reaction

  $A + B \longrightarrow$ Products; rate of reaction can be expressed as Rate = $Z_{AB}\, e^{-E_a/RT}$

  Where Z_{AB} represents the collision frequency of reactants, A and B and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a. If we compare the above rate equation with Arrhenius equation, we can say that A is related to collision frequency. Above equation can be used to predict the value of rate constants with fair accuracy for the elementary reactions but for complex reaction significant deviations are observed. The reason could be that all collisions do not lead to the formation of products. The effective collisions are those in which molecules collide with sufficient kinetic energy (called threshold energy) and proper orientation, so facilitate breaking of bonds between reacting species and formation of new bonds to form products. To explain the role of proper orientation example of CH_3Br and OH^- can be considered.

  $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$



Formation of methanol from bromomethane depends upon the orientation of reactant molecules. The proper orientation of reactant molecules lead to bond formation whereas improper orientation increases repulsive force and makes them simply bounce back and no products formation can take place. The effective collisions, can also corelated to a factor P, which is known as the probability or steric factor.

Hence Rate = P × $Z_{AB}\, e^{-E_a/RT}$

Thus in collision theory it can be concluded that activation energy and proper orientation of the molecules togetherly is the criteria for an effective collision and it determines the rate of a chemical reaction.

17. RADIOACTIVITY

- All radioactive decay follow 1st order kinetics and this is where the similarity ends. This will be explained in a short while.
- We measured the rate of reaction in chemical kinetics based on the rate of change of concentration of reactants or products. But this procedure will not work for calculating the rate of radioactive reaction. This is because most of the time the radioactive substance is a solid. Therefore its concentration would be a constant with time (assuming it to be pure and that the product does not remain with the reactants). Therefore the rate of radioactive reactions are measured by calculating the rate of change of nuclei of the radioactive substance. For a radioactive decay $A \longrightarrow B$, the rate of reaction is calculated as

$$\frac{-dN_A}{dt} = \lambda N_A$$

Where λ = decay constant of reaction

N_A = number of nuclei of the radioactive substance at the time when rate is calculated.

- As you can see the above rate law is very much similar to the rate law of a first order chemical reaction, but all other similarities ceases here. For example unlike a chemical reaction the decay constant (λ) does not depend on temperature. Arrhenius equation is not valid for radioactive decay.

$$\frac{-dN_A}{dt} = \lambda N_A$$

Integrating the differential rate law we get

$$\int_{N_0}^{N_t} \frac{dN_A}{dt} = \int_0^t dt = \log_e \frac{N_0}{N_t} = \lambda t$$

Where N_o = number of nuclei of A at $t = 0$
N_t = number of nuclei of A at $t = t$
λ = decay constant

The expression can be rearranged to give

$N_t = N_o e^{-\lambda t}$ … (a)

- This suggests that the number of nuclei of radioactive substance A at any instant of time can be calculated, by knowing the number of nuclei at $t = 0$, its decay constant and the time.
- **Half – Life**

Just like a 1st order reaction the half life of radioactive decay is given by

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

Note: Let us start with 10 nuclei. If the half life is 5 minutes, then at the end of first 5 minutes, number of nuclei would be 5. Now what would be the number of nuclei after next 5 minutes? Will it be 2.5 or 2 or 3? We can clearly see that it cannot be 2.5 and if it is 2 or 3 then it cannot be called as half life. This dilemma can be overcome by understanding that all formula relating to kinetics are only valid when the sample size is very large and in such a large sample size, a small difference of 0.5 will be insignificant.

- The fact that radioactive decay follows the exponential law implies that this phenomenon is statistical in nature. Every nucleus in a sample of a radionuclide has a certain probability of decaying, but there is no way to know in advance which nuclei will actually decay in a particular time span. If the sample is large enough – that is, if many nuclei are present – the actual fraction of it that decays in a certain time span will be very close to the probability for any individual nucleus to decay. To say that, a certain radioisotope has a half –life of 5 hr., then, signifies that every nucleus of this isotope has a 50 percent chance of decaying in every 5 hr. period. This does not mean a 100 percent probability of decaying in 10 hr. A nucleus does not have a memory, and its decay probability per unit time is constant until it actually does decay. A half life of 5 hr. implies a 75% probability of decay in 10 hr., which increases to 87.5% in 15 hr, to 93.75% in 20 hr, and so on, because in every 5 hr interval the probability of decay is 50 percent.
- **Average – Life Time**

Average life time is defined as the life time of a single isolated nucleus. Let us imagine a single nucleus which decays in 1 second. Assuming 1 second time interval to be very small the rate of change of nuclei would be 1/1 (because $-dN = 1$ and $dt = 1$). We can also see that since $\frac{-dN}{dt} = \lambda N$, for a single isolated nucleus $N = 1$, $\frac{-dN}{dt} = \lambda$. Therefore in this present case $\lambda = 1$.

- Now let us assume the same nucleus decays in 2 seconds, we can see that $\frac{-dN}{dt}$ i.e., λ is equal to ½.

You will also notice that in the 1st case the nucleus survived for 1 second and in the second case it survived for 2 second. Therefore the life time of a single isolated nucleus is $\frac{1}{\lambda}$.

$$\therefore\ t_{av} = \frac{1}{\lambda}$$

- **Activity**

  Activity by definition is the rate of decay of a radioactive element. It is represented as 'A' and is equal to λN. By no means should activity be confused with rate of change of radioactive nuclei represented by $\frac{-dN}{dt}$.

  This is because $\frac{-dN}{dt}$ talks about the overall change in the number of nuclei in a given instant of time while activity only talks about that change which is decay. For example if you go out to a market with Rs. 50 in your pocket and you spend Rs.20 in 5 minutes then your rate of change of money in the wallet is Rs. 4 / min and in fact the rate of spending the money is also Rs.4 / min. Here you can see both are same. But if while spending Rs. 20 in 5 minutes, somebody keeps Rs.10 in your wallet, then the rate of change of money in your wallet would became Rs. 2.5 /min, while the rate of spending the money is Rs. 4 / min. This implies that as long as the radioactive substance is only decaying the rate of change of nuclei and activity are same and equation (a) in terms of activity of a radioactive substance can be written as $A_t = A_o\ e^{-\lambda t}$. But if the radioactive substance is also being produced this $\frac{dN}{dt}$ = rate of production – activity, (Of course it's a different matter, rate of production may or may not be a constant).

- **Specific Activity**

  This is activity per unit mass of the sample. Let radioactive sample weighing w gms have a decay constant λ. The number of nuclei in the w gms would be $\frac{w}{M} \times Av$, where

  M = molecular weight of the radioactive substance and Av= Avogadro's number.

  $$\therefore \text{ specific activity} = \frac{\left(\lambda \times \frac{w}{M} \times Av\right)}{w} = \frac{\lambda \times Av}{M}$$

  It should be remembered that if a radioactive sample is pure and the product does not remain with reactant then specific activity is a constant.

- **Units of Activity:**

  The unit of radioactivity of a substance is measured as the rate at which it changes into daughter nucleus. It has been derived on the scale of disintegration of Radium.

  Let us consider 1g of radium (atomic mass = 226 and $t_{½}$=1600 yrs) undergoes decay, then

  Rate of decay of radium = λ × Number of nuclei of Ra in 1 g

  $$\frac{0.693}{1600 \times 365 \times 24 \times 60 \times 60} \times \frac{1 \times 6.023 \times 10^{23}}{226}$$

  = 3.7 × 1010 dps = 3.7 ×10 Becquerel

  = 1 curie ($\because$ 1 Ci = 3.7×10^{10} dps)

  = 3.7×10^4 Rutherford ($\because$ 1 rd = 10^6 dps)

  The SI unit of activity is dps or Becquerel.

Example-16

The decomposition of N_2O_5 is takes place as

$N_2O_5 \rightleftharpoons 2NO_2 + O_2$

If the values of the rate constants are 3.45×10^{-5} and 6.9×10^{-3} at 27°C and 67°C respectively then energy of activation will be

(a) 222.5k J (b) 122.5 kJ

(c) 112.5 kJ (d) 450 kJ

Solution:(c)

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log\frac{6.9 \times 10^3}{3.45 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{40}{300 \times 340}\right]$$

$E_a = 112.5$ kJ

Example-17

The decomposition of A into product has value of k as 4.5×10^3 sec^{-1} at 100C and the energy of activation 60 kJ mol^{-1} . At what temperature would k be 1.5 × 104 sec^{-1}.

(a) 283 K (b) 293 K

(c) 297.02 K (d) 293.8 K

Solution: (c)

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log\frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60 \times 10^3}{2.303 \times 8.314}\left[\frac{T_2 - 283}{283 \times T_2}\right]$$

On solving $T_2 = 297.02$ K

Example-18

For the decomposition of dimethyl ether, A in the Arrhenious equation $k = Ae^{-Ea/RT}$ has a value of 1.26×10^{13} s^{-1} and E_a value of 58.5 kcal. The half life period for first order decomposition at 527°C is

(a) 525 sec (b) 636 sec

(c) 800 sec (d) 425 sec

Solution:(a)

$$\log k = \log A - \frac{E_a}{2.303RT} \qquad \ldots (i)$$

Given $A = 1.26 \times 10^{13}$

$E_a = 58.5$ kcal

T = 527 + 273 = 800 K

Substituting these value in Equation (i), we get

$$\log k = \log(1.26 \times 10^{13}) - \frac{58.5 \times 10^3}{2.303 \times 1.987 \times 800}$$

$= 13.1003 - 15.9799$

$= -2.8796$

$k = 1.3194 \times 10^{-3}\ \text{sec}^{-1}$

$$t_{1/2} = \frac{0.693}{1.3194} \times 10^3\ \text{sec} = 525\ \text{sec}$$

Example-19

Two substances A and B are present such that $[A_0] = 4[B_0]$ and half-life of A is 5 minute and that of B is 15 minute. If they start decaying at the same time following first order kinetics how much time later will the concentration of both of them would be same.

(a) 30 min (b) 60 min

(c) 15 min (d) 10 min

Solution:(c)

Amount of A left in n_1 halves = $\left(\frac{1}{2}\right)^{n_1}[A_0]$

Amount of B left in n_2 halves = $\left(\frac{1}{2}\right)^{n_2}[B_0]$

At the end, according to the question

$$\frac{[A_0]}{2^{n_1}} = \frac{[B_0]}{2^{n_2}} \Rightarrow \frac{4}{2^{n_1}} = \frac{4}{2^{n_2}},\ [A_0] = 4[B_0]$$

$$\therefore \quad \frac{2^{n_1}}{2^{n_2}} = 4 \Rightarrow 2^{n_1 - n_2} = (2)^2$$

$\therefore \quad n_1 - n_2 = 2$

$\therefore \quad n_2 = (n_1 - 2) \quad \ldots(a)$

Also $t = t = n_1 \times t_{1/2(A)} t = n_2 \times_{1/2(B)}$

(Let concentration of both become equal after time t)

$$\therefore \quad \frac{n_1 \times t_{1/2(A)}}{n_2 \times t_{1/2(B)}} = 1 \Rightarrow \frac{n_1 \times 5}{n_2 \times 15} = 1 \Rightarrow \frac{n_1}{n_2} = 3 \ldots(b)$$

For equation (a) and (b)

$n_1 = 3,\ n_2 = 1$

$t = 3 \times 5 = 15$ minute

Example-20

A radioactive isotope has an initial activity of 2×10^6 disintegration / min. After 4 days its activity is 9×10^5 dis/min. The activity after 40 days will be

(a) 699.31 dpm (b) 680.81 dpm

(c) 670 dpm (d) 500 dpm

Solution:(b)

Initial activity $a_0 = 2 \times 10^6$ dpm

activity after 4 days at $= 9 \times 10^5$ dpm

$$\lambda = \frac{2.303}{4} \log \frac{2 \times 10^6}{9 \times 10^5} = 0.19967\ \text{day}^{-1}$$

Activity after 40 days

$$0.19967 = \frac{2.303}{40} \log \frac{2 \times 10^6}{a_t}$$

$a_t = 680.81$ dpm

Example-21

A carbon radio isotope ${}_ZX^A$ (half life 10 days) decays to give ${}_{Z-2}Y^{A-4}$. If 1.00 gm atom of ${}_ZX^A$ is kept in a sealed tube, how much helium will accumulate in 20 days in STP:

(a) 22400 cc (b) 24400 cc (c) 16800 cc (d) 17600 cc

Solution:(c)

Initial concentration (N_0) of radio-isotope is 1 gm atom. Concentration remained after 20 days may be calculated as

$$N_t = N_0\left(\frac{1}{2}\right)^n$$

Where n = number of half lives = 20/10 = 2

$$N_t = 1\left(\frac{1}{2}\right)^n = \frac{1}{4}$$

Concentration decayed to -particles = $1 - \frac{1}{4} = \frac{3}{4}$ gm atom. An α-particle takes 2 electron from air and from helium gas. Thus,

Helium formed = $\frac{3}{4}$ gm atom

$= \frac{3}{4} \times 22400$ cc = 16800cc

18. KEY CONCEPT

1. The rate of a chemical reaction is the change in the concentration of reactants or products over time. The rate is not constant but varies continuously as concentration changes.

2. The rate law expresses the relationship of the rate of a reaction to the rate constant (k) and the concentration of the reactants raised to appropriate power. The k value for a given reaction changes only with temperature.
   rate = k[Reactant]^n

3. Overall reaction order is the sum of the powers to which reactant concentrations are raised in the rate law. The rate law and the reaction order can be determined experimentally only and not using the stoichiometry of the reaction.
   rate = $k[A]^m[B]^n$
   Order = m + n.

4. The integrated form of a zero order reaction is given by $k = \frac{[A]_0 - [A]}{t}$
   The half -life of a zero order reaction is given by $t_{1/2} = \frac{[A]_0}{2k}$.
   The integrated form of a first order reaction is given by $k = \frac{1}{t} \ln \frac{a}{a - x}$
   The half -life of a first order reaction is given by $t_{1/2} = \frac{0.693}{k}$.

5. The rate constant and activation energy are related by Arrhenius equation, as $k = Ae^{-E_a/RT}$. The variation of rate constant at two different temperatures is given by

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

6. A catalyst speeds up a reaction either by increasing value of A or by lowering the value of E_a or by doing both.

7. As per collision theory, activation energy and proper orientation of the molecules togetherly is the criteria for an effective collision and it determines the rate of a chemical reaction.

8. All radioactive decays follow first order kinetics. Activity is the rate of decay of a radioactive substance and is proportional to the number of nuclei of the radioactive species.

Example-22

Rate of reaction: aA + bB $\longrightarrow$ Product, is given as a function of different initial concentration of A and B.

	[A] (mole dm^{-3})	[B] (mole dm^{-3})	Initial rate (mol dm^{-3} min^{-1})
(i)	0.01	0.01	0.005
(ii)	0.02	0.01	0.010
(iii)	0.01	0.02	0.005

[A] Determine the order of reaction w.r.t. A and w.r.t. B. What is the half life of A in the reaction?

Solution:

From the kinetic data given in question it is evident that

(i) rate is doubled by doubling the concentration of A when concentration of B is constant i.e.

Rate $\propto$ [A] when [B] is constant

So, order w.r.t. A = 1, and

(ii) rate remains unchanged when concentration of B is changed keeping that of A constant so

Rate $\propto [B]^0$ when [A] is constant

So, order w.r.t. B = 0

The rate law of the reaction may, therefore, be put as

Rate = $k[A][B]^0 = k[A]$

$$\text{or } k = \frac{\text{Rate}}{[A]} = \frac{0.005}{0.01} = 0.5 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.5} = 1.386 \text{ min}$$

- **Alternatively:**

Let the rate r be given as

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

Where m and n are individual order w.r.t. A and B, respectively.

Putting the data as given in (i) and (ii) in the above rate equation one by one and then dividing one by another, we get

$$\frac{0.005}{0.010} = \left(\frac{0.01}{0.02}\right)^m \left(\frac{0.01}{0.01}\right)^n \text{ or } \frac{1}{2} = \left(\frac{1}{2}\right)^m \quad \therefore m = 1$$

Again putting the data as given in (i) and (iii) in the rate law as mentioned above in turn and the dividing one by another, we get

$$\frac{0.005}{0.005} = \left(\frac{0.01}{0.01}\right)^m \left(\frac{0.01}{0.02}\right)^n \text{ or } 1 = 1^m . \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^n$$

$\therefore n = 0$

Example-23

From the following data for the reaction between A and B.

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

Solution:

(i) Let the rate law be

Rate = $k[A]^m [B]^n$

Where m and n are the order w.r.t. A and B respectively, and k = rate constant of the reaction, a constant at constant temperature.

From (a): $5.0 \times 10^{-4} = k(2.5 \times 10^{-4})m\ (3.0 \times 10^{-5})^n$

From (b): $4.0 \times 10^{-3} = k(5.0 \times 10^{-4})m\ (6.0 \times 10^{-5})^n$

Dividing one by another

$$\frac{4.0\times10^{-3}}{5.0\times10^{-4}} = \left(\frac{5.0\times10^{-4}}{2.5\times10^{-4}}\right)\left(\frac{5.0\times10^{-5}}{3.0\times10^{-5}}\right)^n$$

or $2^m . 2^n = 8$

From (c): $1.6 \times 10^{-2} = k(1 \times 10^{-3})m\ (6 \times 10^{-5})^n$

Dividing this by the rate law from (b), we get

$$\frac{1.6\times10^{-2}}{4.0\times10^{-3}} = \frac{(1\times10^{-3})^m (6\times10^{-5})^n}{(5\times10^{-4})^m (6\times10^{-5})^n}$$

or $2^m = 4 \quad \therefore m = 2$

Putting the value of m in the above equation

$2^2 \times 2^n = 8$, or n = 1

(ii) Rate = $k[A]^2\,[B]$

$$\therefore\ k = \frac{\text{Rate}}{[A]^2[B]} = \frac{5.0\times10^{-4}}{(2.5\times10^{-4})^2(3\times10^{-5})}$$

$= 2.674 \times 10^8\ L^2\ mol^{-2}\ s^{-1}$

(iii) $$\log\frac{r_{T_2}}{r_{T_1}} = \frac{E_a}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$= \log\frac{2.0\times10^{-3}}{5.0\times10^{-4}} = \frac{E_a}{2.303\times8.314}\left(\frac{20}{320\times310}\right)$$

upon solving: $E_a = 55333\ J\ mol^{-1}$

= 55.333 kJ mol–1

(iv) $k = Ae^{-E_a/RT}$

or $2.67 \times 10^8 = A\exp\left(\frac{-55333}{8.314\times300}\right)$

or $A = 1.145 \times 10^{18}$

Example-24

The half-life of first order decomposition of nitramide is 2.1 hours at 15ºC.

$NH_2NO_2\,(aq) \longrightarrow N_2O(g) + H_2O(l)$

If 6.2 g of NH_2NO_2 is allowed to decompose calculate

(i) time taken for NH_2NO_2 to decompose 99% and

(ii) the volume of dry N_2O produced at this point, measured at STP.

Solution:

(i) $$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1} = 0.33h^{-1}$$

Let t be the time for 99% decomposition. This means at the expiry of time t; x = 99 when a = 100. So,

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

$$0.33 = \frac{2.303}{t}\log\frac{100}{1}$$

$\therefore\ t = 13.96$ h

(ii) No. of mole of NH_2NO_2 taken $= \frac{6.2}{62} = 0.1$

No. of mole of NH_2NO_2 decomposed

$= 0.99 \times 0.1 = 0.099$

From stoichiometry: $NH_2NO_2 \equiv N_2O$

$\therefore$ No. of mole of N_2O evolved = 0.099

Volume of N_2O evolved at STP

= 0.099 × 22.4

= 2.2176 L

Example-25

The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is a first order reaction.

(i) After 55 seconds at 400 K, the pressure of Cl_2O^{-7} falls from 0.062 to 0.044 atm. Calculate the rate constant.

(ii) Calculate the pressure of Cl_2O_7 after 100 seconds of decomposition at this temperature.

Solution:

(i) $$k = \frac{2.303}{t}\log\frac{P_0}{P_t}$$

$$= \frac{2.303}{55}\log\frac{0.062}{0.044} = 6.2 \times 10^{-3}\ s^{-1}$$

(ii) Again t = 100 s, P_t = ?

$$6.2 \times 10^{-3} = \frac{2.303}{100}\log\frac{0.062}{P_t}$$

or Pt = 0.033 atm

Example-26

Show that for 1st order reaction the time required for completion of 75% reaction is twice that for 50% reaction.

Solution:

$$\frac{2.303}{t_{3/4}}\log\frac{10}{100-75} = \frac{2.303}{t_{1/2}}\log\frac{100}{100-50}$$

$$\therefore\ \frac{2\log2}{t_{3/4}} = \frac{\log}{t_{1/2}} \qquad \therefore\ t_{3/4}\ t_{1/2} = 2$$

Example-27

The time required for 10% completion of first order reaction at 298 K is equal to that required for its 25% completion at 308K. If the pre-exponential factor for the reaction is $3.56 \times 10^9\ s^{-1}$, calculate its rate constant at 318 K and also the energy of activation.

Solution:

For first order reactions, $t = \frac{2.303}{K}\log\frac{N_0}{N_1}$

At 298 k; $t = \frac{2.303}{K_{298}}\log\frac{100}{90}$

At 309 K; $t = \frac{2.303}{K_{308}}\log\frac{100}{25}$

Since time is the same hence,

$$\frac{2.303}{K_{298}}\log\frac{100}{90} = \frac{2.303}{K_{308}}\log\frac{100}{25}$$

or $\frac{0.0458}{K_{298}} = \frac{0.1249}{K_{308}}$ or $\frac{K_{308}}{K_{298}} = \frac{0.1249}{0.0458} = 2.73$

According to Arrhenius equation

$$2.303\log\frac{K_{308}}{K_{298}} = \frac{E_a}{8.314}\left[\frac{1}{298}-\frac{1}{208}\right]$$

or $2.303\log 2.73 = \frac{E_a}{8.314}\left[\frac{10}{298\times398}\right] = 76.65kJ$

and $K_{318} = 9.036 \times 10^{-4}\ s^{-1}$

Example-28

Show that following reaction is of first order with the help of data given below

$2H_2O_2 \longrightarrow 2H_2O + O_2$

Time (min)	***0***	***10***	***20***
Volume of $KMnO_4$ (ml)	***22.9***	***13.9***	***8.4***

Solution:

Here volume of $KMnO_4$ used is proportional to the concentration of H_2O_2 present

or $V_0 \propto a$

$V_t \propto a - x$

$$\therefore \quad K = \frac{2.303}{t}\log\frac{V_0}{V_t}$$

When t = 10 min

$$K = \frac{2.303}{10}\log\frac{22.9}{13.9} = \frac{2.303}{10}\log 1.647$$

$$= \frac{2.303}{10} \times 0.217 = 0.04998\,\text{min}^{-1}$$

When t = 20

$$K = \frac{2.303}{20}\log 2.726 = \frac{2.303}{20} \times 0.4355 = 0.0502\ \text{min}^{-1}$$

Thus K, comes out to be nearly constant, we can say that reaction is of first order.

Example-29

5 ml of ethyl acetate was added to a flask containing 100 ml of 0.1 N HCl placed in a thermostat maintained at 30°C. 5 ml of the reaction mixture was withdrawn at different intervals of time and after chilling, titrated against a standard alkali. The following data were obtained :

Time (minutes)	0	75	119	183	∞
Volume of alkali used in ml	9.62	12.10	1.10	14.75	21.05

Show that hydrolysis of ethyl acetate is a first order reaction.

Solution :

The hydrolysis of ethyl acetate will be a first order reaction if the above data confirm to the equation.

$$k_1 = \frac{2.303}{t}\log\frac{V_\infty - V_0}{V_\infty - V_t}$$

Where V_0, V_t and V_∞ represent the volumes of alkali used at the commencement of the reaction, after time t and at the end of the reaction respectively, Hence

$V_\infty - V_0 = 21.05 - 9.62 = 11.43$

Time	$V_\infty - V_\infty$	k_1
75 min	$21.05 - 12.10$ $= 8.95$	$\frac{2.303}{75}\log\frac{11.43}{8.95}$ $= 0.003259\ \text{min}^{-1}$
119 min	$21.05 - 13.10$ $= 7.95$	$\frac{2.303}{119}\log\frac{11.43}{7.95}$ $= 0.003051\ \text{min}^{-1}$
183 min	$21.05 - 14.75$ $= 6.30$	$\frac{2.303}{183}\log\frac{11.43}{6.30}$ $= 0.003254\ \text{min}^{-1}$

A constant value of k shows that hydrolysis of ethyl acetate is a **first order** reaction.

Example-30

The optical rotations of sucrose in 0.5 N HCl at 35°C at various time intervals are given below. Show that the reaction is of first order :

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

Solution:

The inversion of sucrose will be first order reaction if the above data confirm to the equation ,

$$k_1 = \frac{2.303}{t}\log\frac{r_0 - r_\infty}{t_t - r_\infty}$$

Where r_0, r_t and r_∞ represent optical rotations initially, at the commencement of the reaction after time t and at the completion of the reaction respectively

In the case $a_0 = r_0 - r_\infty = +32.4 - (-11.1) = +43.5$

The value of k at different times is calculated as follows:

Time	r_t	$r_t - r_\infty$	k
10 min	+28.8	39.9	$\frac{2.303}{10}\log\frac{43.5}{39.9}$ $= 0.00864\ \text{min}^{-1}$
20 min	+25.5	36.6	$\frac{2.303}{20}\log\frac{43.5}{36.6}$ $= 0.008637\ \text{min}^{-1}$
30 min	+22.4	33.5	$\frac{2.303}{30}\log\frac{43.5}{33.5}$ $= 0.008702\ \text{min}^{-1}$
40 min	+19.6	30.7	$\frac{2.303}{40}\log\frac{43.5}{30.7}$ = 0.008714 min 1

The constancy of k_1 indicates that the inversion of sucrose is a **first order** reaction.

Example-31

The reaction given below, involving the gases is observed to be first order with rate constant 7.48×10^{-3} sec^{-1}.Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm and also find the total pressure after 100 sec.

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

Solution:

$$\begin{array}{llll} & 2A(g) & \longrightarrow 4B(g) + & C(g) \\ \text{initial} & P_0 & 0 & 0 \\ \text{at time t} & P_0 - P' & 2P' & P'/2 \end{array}$$

$$P_{total} = P_0 - P' + 2P' + P'/2 = P_o + \frac{3P'}{2}$$

$$P' = \frac{2}{3}(0.145 - 0.1) = 0.03 \text{ atm}$$

$$k = \frac{2.303}{t}\log\frac{P_0}{P_0 - P'}$$

$$t = \frac{2.303}{7.48\times10^{-3}}\log\left(\frac{0.1}{0.07}\right)$$

t = 47.7 sec

$$\text{Also, } k = \frac{2.303}{t}\log\left(\frac{0.1}{P_0 - P'}\right)$$

$$7.48 \times 10^{-3} = \frac{2.303}{100}\log\left(\frac{0.1}{01 - P'}\right)$$

$$0.1 - P' = 0.047$$

$$P' = 0.053$$

$$P_{total} = 0.1 + \frac{3}{2}(0.053) \approx 0.180 \text{ atm.}$$

Example-32

What will be the ratio of rate constants for two reactions that have same A value but Ea values at room temperature differ by

(a) 1 kcal/mol (b) 10 kcal/mol

Solution:

$$\text{(a)}\ \frac{K_1}{K_2} = \frac{Ae^{-Ea_1/RT}}{Ae^{-Ea_2/RT}} = \exp\frac{Ea_2 - Ea_1}{RT}$$

$$= \exp\frac{1\text{kcal mol}^{-1}}{1.987\times10^{-3}\text{kcal mol}^{-1}\text{K}^{-1}\times298\text{K}} = 5.4$$

$$\text{(b)}\ \frac{K_1}{K_2} = \exp\frac{10\text{kcal mol}^{-1}}{1.987\times10^{-3}\text{kcal mol}^{-1}\text{K}^{-1}\times298\text{K}}$$

$$= 2 \times 10^7$$

Example-33

^{227}Ac has a half-life of 22.0 years with respect to radioactive decay. The decay follows two parallel paths, one leading to ^{222}Th and the other to ^{223}Fr. The percentage yields of these two daughter nuclides are 2.0 and 98.0 respectively. What are the decay constants (λ) for each of the separate paths?

Solution:

The rate constant of the decay is

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{22}$$

If k_1 and k_2 are the rate constants of the reactions leading to ^{222}Th and ^{223}Fr, respectively we have

$$k_1 + k_2 = \frac{0.693}{22} = \frac{k_1}{k_2} = \frac{2}{98}$$

On solving for k_1 and k_2, we get

$$k_2 = 0.03087\ y^{-1}$$

$$k_1 = 0.00063\ y^{-1}$$

Example-34

At 278ºC the half life period for the first order thermal decomposition of ethylene oxide is 363 min and the energy of activation of the reaction in 52,00 cal/mole. From these data estimate the time required for ethylene oxide to be 75% decomposed at 450°C.

Solution:

$$\ln\frac{k_{450}}{k_{278}} = \frac{5200}{2}\left[\frac{1}{551} - \frac{1}{723}\right] = 1.122$$

$$\frac{k_{450}}{k_{278}} = 3.07 = \frac{363}{t_{1/2}(\text{at}450^{\circ}\text{C})}t_{1/2}\,(\text{at } 450°\text{C})$$

=118.24 min.

$$\text{Now } t_{0.75} = \frac{1}{k}\ln\frac{A_0}{A_0/4} = \frac{1}{k}\ln 4 = \frac{1.386}{k}$$

$$\therefore\ t_{0.75} = \frac{1.386}{0.693}\times118.24 = 236.48 \text{ min}$$

Example-35

The nucleidic ratio of ${}^3_1$H to ${}^1_1$H in a sample of water is 8.0 × 10^{-18}:1. Tritium undergoes decay with half life period of 12.3 years. How many tritium atoms would 10.0 g of such a sample contains 40 years after the original sample in collected.

Solution:

18 g H_2O has 2H atom in it = 6.023 × 10^{23}× 2

18 g H_2O has atoms = 8 ×10^{-18} × 6.023 ×10^{23} × 2

∴ 10 g H_2O has atoms

$$= \frac{8\times10^{-18}\times6.023\times10^{23}\times2\times10}{18}$$

i.e No of ${}^3_1$H = 5.354 × 10^6 atoms

$$\text{Now } t = \frac{2.303}{K}\log\frac{N_0}{N}$$

$$40 = \frac{2.303}{0.693}\log\frac{5.354\times10^6}{N} = 5.624 \times 10^5 \text{ atoms}$$

Example-36

On analysis a sample of Uranium was found to contain 0.277 g of $_{82}Pb^{206}$ and 1.667 g of $_{92}U^{238}$. The half life period of $_{92}U^{238}$ is 4.51×10^9 years. If all the lead were assumed to have come from decay of $_{92}U^{238}$, what is the age of the earth?

Solution:

$$_{92}U^{238} = 1.667\text{ g} = \frac{1.667}{238}\text{ mole}$$

$$_{82}Pb_{206} = 0.227\text{g} = \frac{0.227}{206}\text{ mole}$$

∵ All the lead have come from decay of U.

∴ Moles of Pb formed = $\frac{0.227}{206}$

∴ Moles of U decayed = $\frac{0.227}{206}$

∴ Total moles of Uranium

$$= \frac{1.667}{238} + \frac{0.277}{206}, \text{ ie } N_0$$

Also N for $U^{238} = \frac{1.667}{238}$

$$\because \text{ for } U^{238}\ t = \frac{2.803}{k}\log\frac{N_0}{N}$$

$= t = 1.143 \times 10^9$ yrs .

EXERCISE # 1

Based On **Rate of reaction, rate law and rate constant**

1. The instantaneous rate of disappearance of the MnO_4^- ion in the following reaction is 4.56 × 10^{-3} Ms^{-1}.

$2MnO_4^- + 10\,I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

The rate of appearance of I_2 is –

(A) 1.14 × 10^{-3} Ms^{-1} (B) 5.7 × 10^{-3} Ms^{-1}

(C) 4.56 × 10^{-4} Ms^{-1} (D) 1.14 × 10^{-2} Ms^{-1}

2. For a gas reaction at T(K) the rate is given by $-\dfrac{dp_A}{dt} = k'\,p_A^2$ atm/hr. If the rate equation is expressed as : $-\,r_A = -\dfrac{1}{V}\dfrac{dn_A}{dt} = kC_A^2$, mol/(litre–hr), the rate constant k is given by–

(A) k = k' (B) k = k' RT

(C) k = k'/RT (D) k = k' $(RT)^2$

where R = ideal gas law constant, cal/g mol. K

3. In the following reaction : $xA \longrightarrow yB$

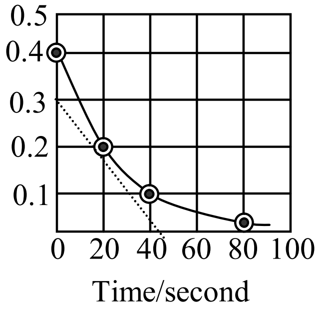
$$\log\left[-\frac{d[A]}{dt}\right] = \log\left[\frac{d[B]}{dt}\right] + 0.3$$

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

4. A reaction follows the given concentration (C) vs time graph. The rate for this reaction at 20 seconds will be –



(A) 4 × 10^{-3} Ms^{-1} (B) 8 × 10^{-2} Ms^{-1}

(C) 2 × 10^{-2} Ms^{-1} (D) 7 × 10^{-3} Ms^{-1}

5. The rate of the simple reaction $2NO + O_2 \rightarrow 2NO_2$, when the volume of the reaction vessel is doubled –

(A) Will grow eight times of its initial rate

(B) Reduce to one-eighth of its initial rate

(C) Will grow four times of its initial rate

(D) Reduce to one-fourth of its initial rate

6. The rate expression for the reaction $A(g) + B(g) \rightarrow C(g)$ is rate = $kC_A^2\,C_B^{1/2}$. What changes in the initial concentration of A and B will cause the rate of reaction increase by a factor of eight -

(A) C_A × 2; C_B × 2 (B) C_A × 2; C_B × 4

(C) C_A × 1; C_B × 4 (D) C_A × 4; C_B × 1

7. For a given reaction $3A + B \longrightarrow C + D$ the rate of reaction can be represented by

(A) $-\dfrac{1}{3}\dfrac{d[A]}{dt} = \dfrac{-d[B]}{dt} = \dfrac{+d[C]}{dt} = \dfrac{+d[D]}{dt}$

(B) $-\dfrac{1}{3}\dfrac{d[A]}{dt} = -\dfrac{d[C]}{dt} = k[A]^m[B]^n$

(C) $+\dfrac{1}{3}\dfrac{d[A]}{dt} = \dfrac{-d[C]}{dt} = k[A]^n[B]^B$

(D) All of these

8. For a chemical reaction $A + 3B \longrightarrow$ Product

It was observed that rate of reaction increases nine times when concentration of B increased three times by keeping concentration of A as constant. On doubling concentration of both rate increases eight times. Differential rate equation can be given as

(A) r = k [A] $[B]^3$ (B) r = k [A] $[B]^2$

(C) r = $k[A]^2[B]$ (D) r = $k[A]^2[B]^{1/3}$

9. The kinetic datas for the reaction:

$2A + B_2 \longrightarrow 2AB$ re as given below:

[A] mol L^{-1}	[B_2] mol L^{-1}	Rate mol L^{-1} min^{-1}
0.5	1.0	2.5 ×10^{-3}
1.0	1.0	5.0 ×10^{-3}
0.5	2.0	1 ×10^{-2}

Hence the order of reaction with respect to A and B_2 are, respectively,

(A) 1 and 2 (B) 2 and 1

(C) 1 and 1 (D) 2 and 2

10. Units of rate constant of first and zero order reactions in terms of molarity unit are respectively

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

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

11. Rate law for the following reaction;

Ester + H^+ $\rightleftharpoons$ Acid + Alcohol; is

$\dfrac{dx}{dt} = k\,[\text{ester}]^1\,[H^+]^0$. What would be the effect on the rate if concentration of H^+ ion is doubled ?

(A) Same (B) doubled

(C) Half (D) data insufficient

12. For the reaction, $4A + B \longrightarrow 2C + 2D$, The statement not correct is:
(A) The rate of disappearance of B is one fourth the rate of disappearance of A
(B) The rate of appearance of C is half the rate of disappearance of B
(C) The rate of formation of D is half the rate of consumption of A
(D) The rates of formation of C and D are equal

Based On Order & Molecularity

13. Select the rate law that corresponds to the data shown for the following reaction–
$A + B \longrightarrow C$

Expt. No.	$[A]_0$	$[B]_0$	Initial rate
1.	0.012	0.035	0.10
2.	0.024	0.070	0.80
3.	0.024	0.035	0.10
4.	0.012	0.070	0.80

(A) Rate = $k[B]^3$ (B) Rate = $k\,[B]^4$
(C) Rate = $k\,[A][B]^3$ (D) Rate = $k\,[A]^2[B]^2$

14. The reaction $2Na + Cl_2 \rightleftharpoons 2NaCl$ is found to follow III order kinetics. Its molecularity is–
(A) 1 (B) 2
(C) 3 (D) 4

15. Diazonium salt decomposes as
$C_6H_5N_2^+Cl^- \longrightarrow C_6H_5Cl + N_2$. At 0ºC, the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is –
(A) A first order reaction
(B) A second order reaction
(C) Independent of the initial concentration of the salt
(D) A zero order reaction

16. For the chemical reaction $A + B + C \xrightarrow{K} D$, it was found that the rate of the reaction doubled when the concentration of B was doubled, that the rate of reaction doubled when the concentration of both A and B were doubled, and quadrupled when the concentration of both B and C were doubled. The order of the reaction is –
(A) 2 (B) 3 (C) 4 (D) 6

17. The rate constant (k) for the reaction
$2A + B \rightarrow$ Products , was found to be
2.58×10^{-5} l mol^{-1} s^{-1} after 15 sec,
2.60×10^{-5} l $mol^{-1}s^{-1}$ after 30 sec and
2.55×10^{-5} l mol^{-1} s^{-1} after 50 sec. Hence the order of the reaction is –
(A) 0 (B) 1 (C) 2 (D) 3

18. For the reaction : $A + B \longrightarrow$ product,
$\frac{dx}{dt} = k[A]^a[B]^b$ if $\frac{dx}{dt} = k$, then the order of the reaction is:
(A) 4 (B) 2 (C) 1 (D) 0

19. 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:
(A) 10 min (B) 20 min
(C) 30 min (D) 40 min

20. In the formation of sulphur trioxide by the contact process.
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
The rate of reaction is expressed as
$$-\frac{d(O_2)}{dt} = 2.5 \times 10^{-4}\ mole^{-1}L^{-1}\ sec^{-1}$$
The rate of disappearance of (SO_2) will be
(A) $5.0\ \ 10^{-4}$ mol L^{-1} s^{-1}
(B) $-2.25\ \ 10^{4}$ mol L^{-1} s^{-1}
(C) $3.75\ \ 10^{-4}$ mol L^{-1} s^{-1}
(D) $50.0\ \ 10^{-4}$ mol L^{-1} s^{-1}

21. In the reaction
$2N_2O_5 \longrightarrow 4NO_2 + O_2$, $+\frac{d[NO_2]}{dt}$
at any time t was found to be 2.4×10^{-4} mole L^{-1} min^{-1} with rate constant 4.4×10^{-4} min^{-1}. Hence at the same time t and the corresponding rate constant of the reactions respectively would be
(A) 1.2×10^{-4} mole L^{-1} min^{-1} and $2.2 \times 10^{-4} min^{-1}$
(B) 1.2×10^{-4} mole L^{-1} min^{-1} and 8.8×10^{-4} min^{-1}
(C) 4.8×10^{-4} mole L^{-1} min^{-1} and 2.2×10^{-4} min^{-1}
(D) 2.4×10^{-4} mole L^{-1} min^{-1} and $4.4 \times 10^{-4} min^{-1}$

Based On Integral rate equation

22. For a first order reaction, the plot of 't' against log C gives a straight line with slope equal to–
(A) (k/2.303) (B) $-\frac{2.303}{k}$
(C) (ln k/2.303) (D) – k

23. In a first order reaction the reactant 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 of concentration

24. Two substances A ($t_{1/2}$ = 5min) and ($t_{1/2}$ = 15 min) are taken in such a way that initially [A] = 4[B]. The time after which both the concentration will be equal is (assuming reactions are of 1st order) :

(A) 5 min
(B) 15 min
(C) 20 min
(D) concentration can never be equal

25. The rate constant for the reaction $A \rightarrow B$ is 2×10^{-4} lt. mol^{-1}. The concentration of A at which rate of the reaction is $(1/12) \times 10^{-5}$ M sec^{-1} is–

(A) 0.25 M (B) $(1/20)\sqrt{5/3}$ M
(C) 0.5 M (D) None of these

26. $A(g) \longrightarrow B(g) + C(g)$

$\frac{-d[A]}{dt} = k[A]$; At the start pressure is 100 mm and after 10 min, pressure is 120 mm. Hence rate constant (min^{-1}) is:

(A) $\frac{2.303}{10}\log\frac{120}{100}$
(B) $\frac{2.303}{10}\log\frac{100}{20}$
(C) $\frac{2.303}{10}\log\frac{100}{80}$
(D) $\frac{2.303}{10}\log\frac{100}{120}$

27. Consider a reaction, $A \longrightarrow B + C$. If the initial concentration of A was reduced from 2M to 1M in 1 hr. and from 1M to 0.25 M in 2 hours, the order of reaction is

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

28. Thermal decomposition of a compound is of first order. If 50% of a sample of compound is decomposed in 120 minutes, how long will it take for 90% of compound to decompose ?

(A) 299 min (B) 399 min
(C) 99 min (D) 9.9 min

29. The half life period for catalytic decomposition of AB3 at 50 mm is found to be 4 hrs and at 100 mm it is 2.0 hrs. The order of reaction is

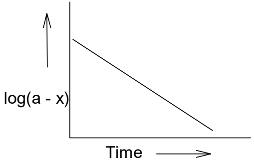
(A) 3 (B) 1 (C) 2 (D) 0

30. For the 1st order reaction: $A_{(g)} \longrightarrow 2B_{(g)} + C(s)$ the $t_{1/2}$ = 24 min. The reaction is carried out taking certain mass of A enclosed in a vessel in which it exerts a pressure of 400 mm Hg. The pressure of the reaction mixture after expiry of 48 min will be

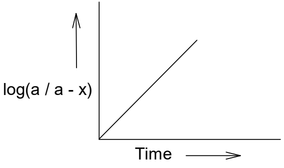
(A) 700 mm (B) 600mm
(C) 800 mm (D) 1000 mm

31. Which represent 1st order reaction out of (I) , (II) and (III) ?

(I)



(II)



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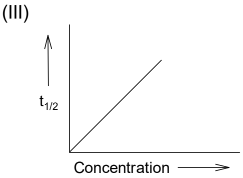


(A) I, II and III (B) I and II
(C) II and III (D) I and III

32. In the first order reaction the concentration of reactant decreases from 2 M to 0.50 M in 20 minutes. The value of specific rate is

(A) 69.32 (B) 6.932
(C) 0.6932 (D) 0.06932

33. For a first order reaction the ratio of t0.75 to t0.50 would be

(A) 4 : 3 (B) 3 : 2 (C) 2 : 1 (D) 1 : 2

Based On Monitoring the progress of reaction

34. The decomposition of a gaseous substance (A) to yield gaseous products (B) and (C) follows first order kinetics. If initially only (A) is present and 10 minutes after the start of the reaction the pressure of (A) is 200 mm Hg and that of over all mixture is 300 mm Hg, then the rate constant for $2A \rightarrow B + 3C$ is –

(A) (1/600) ln 1.25 sec^{-1}
(B) (2.303/10) log 1.5 min^{-1}
(C) (1/10) ln 1.25 sec^{-1}
(D) none of these

35. The kinetic of hydrolysis of methyl acetate in excess dilute HCl at 25° were followed by withdrawing 2mL. 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

$[\ln\frac{22.79}{17.83} = 0.2454, \ln\frac{22.79}{15.43} = 0.39,$

$\ln\frac{22.79}{9.8} = 0.8439]$

(A) 3.27×10^{-3} min^{-1} (B) 3.27×10^{-3} sec^{-1}
(C) 1.5×10^{-3} min^{-1} (D) 1.5×10^{-3} sec^{-1}

36. For a reaction, A → 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 dextro rotatory. Calculate the rate constant of this first order reaction –

(A) $k = 0.695\ \text{min}^{-1}$ (B) $k = 0.0693\ \text{sec}^{-1}$
(C) $k - 0.0693\ \text{min}^{-1}$ (D) $k = 0.00693\ \text{sec}^{-1}$

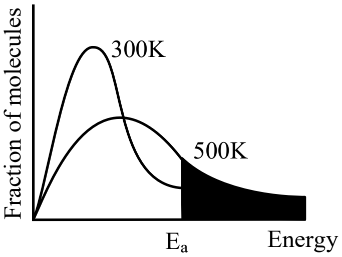
37. The decomposition of hydrogen peroxide in an aqueous solution is a reaction of first order. It can be followed by titrating 10 ml portions of reaction mixture at various times from the beginning of reaction against a standard solution of $KMnO_4$. Volume of $KMnO_4$ solution used in each case is proportional to the remaining concentration of H_2O_2. From the following data, calculate the rate constant of the reaction.

Time (in second)	0	600	1200
$KMnO_4$ used (in ml)	22.8	13.8	8.20

(A) $k = 8.44 \times 10^{-4}\ \text{sec}^{-1}$
(B) $k = 8.44 \times 10^{-2}\ \text{sec}^{-1}$
(C) $k = 2.44 \times 10^{-6}\ \text{sec}^{-1}$
(D) $k = 2.22 \times 10^{-4}\ \text{sec}^{-1}$

Based On Effect of temperature on rate constant (Arrhenius equation)

38. The distribution of molecular kinetic energy at two temperature is as shown in the following graph.



Which of the following conclusions are correct–

(A) The number of molecules with energy E_a or greater is proportional to the shaded area for each temperature
(B) The number of molecules with energy E_a or less is proportional to the shaded area for each temperature
(C) The number of molecules with energy E_a is the mean of all temperatures
(D) The graph is not according to the Maxwell-Boltzmann energy distribution law

39. Which is incorrect from the theory of Arrhenius's equation ?

(A) The number of effective collisions is proportional to the number of molecules above a certain threshold energy
(B) As the temperature increases, the number of molecules with energies exceeding the threshold energy increases
(C) The rate constant is a function of temperature
(D) Activation energy and pre-exponential factors are temperature-dependent

40. The activation energy for a chemical reaction mainly depends upon –

(A) Temperature
(B) Nature of reacting species
(C) Concentration of the reacting species
(D) Collision frequency

41. $A \longrightarrow B$, $\Delta H = -10\ \text{kJ mol}^{-1}$ $E_a = 50\text{kJ mol}^{-1}$ then E_a of $B \longrightarrow A$ will be –

(A) $40\ \text{kJ mol}^{-1}$ (B) $50\ \text{kJ mol}^{-1}$
(C) $-50\ \text{kJ mol}^{-1}$ (D) $60\ \text{kJ mol}^{-1}$

42. The velocity of a reaction is doubled for every 10ºC rise in temperature. If the temperature is raised by 50ºC, the reaction velocity increases by about –

(A) 12 times (B) 16 times
(C) 32 times (D) 50 times

Based On Series, Parallel & Reversible Reactions

43. For the consecutive unimolecular-type first-order reaction $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, the concentration of component R, C_R at any time t is given by –

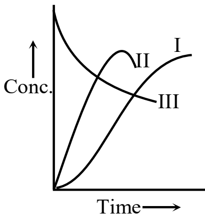
$$C_R = C_{AO}\,K_1\left[\frac{e^{-k_1t}}{(k_2-k_1)}+\frac{e^{-k_2t}}{(k_1-k_2)}\right]$$

if $C_A = C_{AO}$, $C_R = C_{RO} = 0$ at $t = 0$

The time at which the maximum concentration of R occurs is –

(A) $t_{max} = \dfrac{k_2 - k_1}{\ln(k_2/k_1)}$ (B) $t_{max} = \dfrac{\ln(k_2/k_1)}{k_2 - k_1}$
(C) $t_{max} = \dfrac{e^{k_2/k_1}}{k_2 - k_1}$ (D) $t_{max} = \dfrac{e^{k_2 - k_1}}{k_2 - k_1}$

44. A first order homogeneous reaction of the type X → Y → Z (consecutive reaction) is carried out in a CSTR. Which of the following curves respectively show the variation of the concentration of X, Y and Z with time –



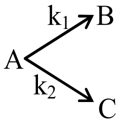
(A) I, II, III (B) III, II, I
(C) III, I, II (D) II, III, I

45. For the consecutive unimolecular-type first order reaction $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, the concentration of component A, C_A at any time t is given by -

(A) $C_A = C_{A_0} e^{(k_1+k_2)t}$ (B) $C_A = C_{A_0} e^{-(k_1+k_2)t}$

(C) $C_A = C_{A_0} e^{-k_1 t}$ (D) $C_A = C_{A_0} e^{k_1 t}$

46. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as -



$k_1 = 1.26 \times 10^{-4}\ s^{-1}$ and
$k_2 = 3.8 \times 10^{-5}\ s^{-2}$

The percentage distributions of B and C are –

(A) 80% B and 20%
(B) 76.83% B and 23.17% C
(C) 90% B and 10% C
(D) 60% B and 40% C

Based On Mechanism of Reaction

47. For the reaction $NO_2 + CO \rightarrow CO_2 + NO$ the experimental rate expression is $-\frac{dc}{dt} = k[NO_2]^2$ the number of molecules of CO involves in the slowest step will be –

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

48. The reaction, $X + 2Y + Z \rightarrow N$ occurs by the following mechanism

(i) $X + Y \rightleftharpoons M$ (very rapid equilibrium)
(ii) $M + Z \rightarrow O$ (slow)
(iii) $O + Y \rightarrow N$ (very fast)

What is the rate law for this reaction

(A) Rate = k[Z]
(B) Rate = $k[X]\,[Y]^2\,[Z]$
(C) Rate = k[N]
(D) Rate = k [X] [Y] [Z]

Based On Radioactivity

49. During a negative -decay

(A) An atomic electron is ejected
(B) An electron which is already present within the nucleus is ejected
(C) A neutron in the nucleus decays emitting an electron
(D) A part of the binding energy of the nucleus is converted into an electron

50. Identify the missing product in the given reaction ${}^{235}_{92}U + {}^{1}_{0}n \longrightarrow ? + {}^{92}_{36}Kr + 3\,{}^{1}_{0}n$

(A) ${}^{141}_{56}Ba$ (B) ${}^{139}_{56}Ba$
(C) ${}^{139}_{54}Ba$ (D) ${}^{141}_{54}Ba$

51. A certain zero order reaction has k = 0.025 M sec^{-1} for the disappearance of A. What will be the concentration of A after 15 seconds if initial concentration is 0.5 M

(A) 0.5 M (B) 0.32 M
(C) 0.125 M (D) 0.06 M

52. In the first order reaction, the concentration of the reactant is reduced to 25% in one hour. The half life period of the reaction is

(A) 2 hr (B) 4hr
(C) 1/2 hr (D) 1/4 hr

53. A radioactive element resembling iodine in properties is

(A) Astatine (B) Lead
(C) Radium (D) Thorium

54. The radiations from a naturally occurring radioactive substance, as seen after deflection by a magnetic field in one direction are:

(A) definitely alpha rays
(B) definitely beta rays
(C) both alpha and beta rays
(D) either alpha or beta rays

Based On Miscellaneous Questions

55. 75% of a Ist order reaction was completed in 32 minutes. When was 50% of the reaction completed?

(A) 24 min (B) 4 min
(C) 16 min (D) 8 min
(E) none of these

56. The half life of a second order reaction is

(A) $t_{1/2} = 0.693 / k$ (B) $t_{1/2} = k/[A]_o$
(C) $t_{1/2} = [A]_0/k$ (D) $t_{1/2} = \frac{1}{k[A]_0}$

57. What will be the fraction of ${}^{n}_{m}X$ ($t_{1/2}$ = 25 min) left after 100 minutes?

(A) 1/2 (B) 1/4
(C) 1/3 (D) 1/16

58. 50% of the amount of a radioactive substance decomposes in 5 years. The time required for the decomposition of 99.9% of the substance will be

(A) 10 years
(B) between 10 and 50 years
(C) less than 10 years
(D) between 49 and 50 years

59. Which one of the following statements is wrong regarding molecularity of the reaction?

(A) It is calculated from the reaction mechanism
(B) It may be either a whole number or fraction
(C) It is the number of molecules of the reactants taking part in a single step chemical reaction
(D) It depends on the rate determining step of the reaction.

60. 1.386 hours are required for the disappearance of 75% of a reactant of first – order reaction. What is the rate constant of the reaction?
(A) $3.6 \times 10^{-3}\ s^{-1}$ (B) $7.2 \times 10^{-3}\ s^{-1}$
(C) $2.7 \times 10^{-4}\ s^{-1}$ (D) $1.8 \times 10^{-3}\ s^{-1}$

61. The terms rate of reaction and rate of appearance (or disappearance) of reactant (or product)
(A) Represent one and the same physical quantity
(B) Differ by constant factor
(C) Are positive parameters and have same value
(D) May or may not have same value depending upon the stoichiometric coefficient of reactants (or products) in the balanced chemical equation.

62. For the first order reaction $A(g) \longrightarrow 2B(g) + C(g)$, the initial pressure is P_A = 90 mm Hg, the pressure after 10 minutes is found to be 180 mm Hg. The rate constant of the reaction is
(A) $1.15 \times 10^{-3}\ sec^{-1}$ (B) $2.3 \times 10^{-3}\ sec^{-1}$
(C) $3.45 \times 10^{-3}\ sec^{-1}$ (D) $6 \times 10^{-3}\ sec^{-1}$

63. The rate law for the reaction
$RCl + NaOH\ (aq) \longrightarrow ROH + NaCl$
is given by Rate = k[RCl]. The rate of the reaction will be
(A) Unaffected by increasing temperature of the reaction
(B) Doubled on doubling the concentration of NaOH
(C) Halved on reducing the concentration of NaOH to one half
(D) Halved on reducing the concentration of RCl to one half

64. For a given reaction of first order, it takes 20 minutes for the concentration to drop from 1.0 mol $litre^{-1}$ to 0.6 mol $litre^{-1}$. The time required for the concentration to drop from 0.6 mol $litre^{-1}$ to 0.36 mol $litre^{-1}$ will be
(A) More than 20 minutes
(B) Less than 20 minutes
(C) Equal to 20 minutes
(D) Infinity

65. The unit of rate constant of a reaction having order 1.5 would be
(A) $(mol\ L^{-1})^{-1/2} s^{-1}$ (B) $(mol\ L^{-1})^{-3/2}\ s^{-1}$
(C) $(conc)^{-0.5}\ time^{-1}$ (D) $(conc)^{-0.75}\ time^{-1}$

66. The half–life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduce to
(A) (1/2) g (B) (1/4) g
(C) (1/8) g (D) (1/16) g

67. For a second order reaction of the type rate = $k\ [A]^2$, the plot of $[A]_t$ versus t is linear with a
(A) positive slope and zero intercept
(B) positive slope and non zero intercept
(C) negative slope and zero intercept
(D) negative slope and non zero intercept

68. In the inversion of cane-sugar
$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$, the molecularity of reaction will be
(A) 1 (B) 2
(C) 3 (D) 0

69. In a first order reaction $k = \frac{1}{t}\log_e\left(\frac{a}{a-x}\right)$ if the concentration units are changed to some other units, which are (say) m times the first. Then the value of velocity co-efficient will
(A) Increase m – times
(B) Decrease m – times
(C) Not alter
(D) None of these

70. In decomposition of carbonyl sulphide in water $COS + H_2O \longrightarrow CO_2 + H_2S$. The rate is found to be dependent on carbonyl sulphide and independent of water. Such reaction will be of
(A) Zero order
(B) Second order
(C) Pseudo-unimolecular
(D) Unimolecular

71. Decomposition of N_2O_5 occurs in the following manner. $2N_2O_5 \longrightarrow 4NO_2 + O_2$ its rate is expressed in three ways.

(i) $-\frac{d[N_2O_5]}{dt} = k(N_2O_5)$

(ii) $\frac{d(NO_2)}{dt} = k'(N_2O_5)$

(iii) $\frac{d(O_2)}{dt} = k''\ (N_2O_5)$

What is the relation between k & k′
(A) k = k′ (B) k = 2k′
(C) k′ = 2k (D) k′ = 1/3 k

72. The rate constant of a reaction depends on
(A) Temperature (B) mass
(C) Density (D) time

73. The rate at which a substance reacts depends on its
(A) atomic mass (B) equivalent mass
(C) molecular mass (D) active mass

74. The rate expression for a reaction is
rate = $k[A]^{3/2}\ [B]^{-1}$, the order of reaction is
(A) 0 (B) 1/2
(C) 3/2 (D) 5/2

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

(A) Rate = k(Cx) (Cy) (Cz)

(B) Rate = k $(Cx)^{0.5}$ $(Cy)^{0.5}$ $(Cz)^{0.5}$

(C) Rate = $k(Cx)^{1.5}$ $(Cy)^{-1}(Cz)^{0}$

(D) Rate = $\frac{R(Cx)(Cz)^{o}}{(Cy)^{2}}$

76. The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.60$ and $P_B = 0.80$ atm. When $P_C = 0.2$ atm the rate of reaction relative to the initial rate is

(A) 1/48 (B) 1/24 (C) 9/16 (D) 1/6

77. If concentration are measured in mole/lit and time in minutes, the unit for the rate constant of a 3rd order reaction are

(A) mol lit^{-1} min^{-1} (B) lit^{2} $mol^{-2}min^{-1}$

(C) lit.mol^{-1} min^{-1} (D) min^{-1}

78. A radioactive element has a half life period of 4 days. How much of it will remain after 16 days

(A) $\frac{1}{32}$ (B) $\frac{1}{16}$ (C) $\frac{1}{4}$ (D) $\frac{1}{6}$

79. For a first order reaction the plot of log $[A]_t$ Vs t is linear with a

(A) Positive slope and zero intercept

(B) Positive slope and non zero intercept

(C) Negative slope and zero intercept

(D) Negative slope and non zero intercept

80. For a hypothetical reaction $A + B \longrightarrow C+D$, the rate = $k[A]^{-1/2}$ $[B]^{3/2}$. On doubling the concentration of A and B the rate will be

(A) 4 times (B) 2 times

(C) 3 times (D) none of these

81. In a reaction the threshold energy is to equal to

(A) Average energy of the reactants

(B) Activation energy

(C) Activation energy + average energy of the reactants

(D) Activation energy – average energy of the reactants

82. The temperature coefficient of most of the reactions lies between

(A) 1 and 2 (B) 2 and 3

(C) 3 and 4 (D) 2 and 4

83. Select the rate law that corresponds to the data shown for the following reaction

$A + B \longrightarrow C$.

Experiment	[A]	[B]	Initial Rate
1.	0.012	0.035	0.10
2.	0.024	0.070	0.80
3.	0.024	0.035	0.10
4.	0.012	0.070	0.80

(A) Rate = k $[B]^{4}$ (B) Rate = k [A] $[B]^{3}$

(C) Rate = k $[A]^{2}$ $[B]^{2}$ (D) Rate = k $[B]^{3}$

84. For a first reaction $t_{0.75}$ is 138.6 seconds. Its specific rate constant (in sec^{-1}) is

(A) 10^{-2} (B) 10^{-4}

(C) 10^{-5} (D) 10^{-6}

85. Half life period for a first–order reaction is 20 minutes. How much time is required to change the concentration of the reactants from 0.08M to 0.01M

(A) 20 min (B) 60 min

(C) 40 min (D) 50 min

EXERCISE # 2

Question | One or More Than One Correct Answer Type Questions

1. Which of the following factors affect the rate of reaction?
(A) Nature of reactant (B) Pressure
(C) Volume of reaction vessel
(D) Radiation

2. For the reaction A + 3B $\longrightarrow$ C the differential form of the rate law is
(A) $\frac{d[C]}{dt} = \frac{-d[A]}{dt}$ (B) $\frac{3d[C]}{dt} = \frac{-d[B]}{dt}$
(C) $\frac{-3d[B]}{dt} = \frac{-d[C]}{dt}$ (D) $\frac{d[A]}{dt} = \frac{d[C]}{dt}$

3. The rate of a reaction?
(A) Decreases with time
(B) Decreases with decrease in conc. of reactant
(C) Decreases with increase in time and decreases in conc. of reactant
(D) Does not depend on time

4. Consider a chemical reaction 2A + B $\longrightarrow$ A_2B. the reactant A will decreases at
(A) The same rate at which B will decreases
(B) Twice the rate at which B will decrease
(C) Half the rate at which B will decreases
(D) Twice the rate at which A_2B will form

5. Select the rate law that corresponds to the data shown for the following reaction:
A + B $\longrightarrow$ C

Expt.No.	$[A]_0$ mole L^{-1}	$[B]_0$ mole L^{-1}	Initial rate
1.	0.012	0.035	0.10
2.	0.024	0.070	0.80
3.	0.024	0.035	0.10
4.	0.012	0.070	0.80

(A) The rate law expression for the given reaction is Rate = k $[B]^3$
(B) The order with respect to [A] is zero
(C) The order with respect to [A] is one
(D) The rate law expression for the given reaction is Rate = $k[A][B]^3$

6. Rate law for the chemical reaction is
Rate = $K[A]^{1/2}[B]^1$.
Choose the correct options among the following
(A) Order of the reaction is 3/2.
(B) unit of its rate constant is litre1/2 $mol^{-1/2}$ sec^{-1}.
(C) unit of rate is mole $litre^{-1}sec^{-1}$.
(D) its molecularity is always 3.

7. Which of the following statements are correct
(A) When $T \to \infty$ the rate constant becomes equal to frequency factor.
(B) Rate constant (k) always increases with the increase in temperature
(C) Larger the value of activation energy, higher is the value of rate constant
(D) Rate constant (k) is inversely proportional to the frequency factor (A)

8. Which of the following expression are correct for a first order reaction with rate constant 'k' initial concentration 'a' and half life $t_{1/2}$.
(A) $t_{1/2} = \frac{In2}{k}$ (B) $k \propto a$
(C) $k = \frac{2.303}{t_{1/2}}\log 2$ (D) $t_{1/2} = \frac{1}{k \times a}$

9. Which of the following statements are corrects:
(A) The unit of rate constant for a zero order reaction is mole $litre^{-1}$ sec^{-1}.
(B) Half life of a first order reaction is inversely proportional to rate constant.
(C) For zero order reaction rate constant is equal to the rate of reaction at all concentrations.
(D) For a first order reaction, the rate constant (k) is related to half life ($t_{1/2}$) as $k = \frac{0.693}{t_{1/2}}$

10. For a reaction X $\longrightarrow$ Y, the rate law is Rate = $k[A]^{1/2}$. Which of the following statements are correct?
(A) Half life of the reaction is inversely proportional to the initial concentration.
(B) Half life of the reaction is directly proportional to the square root of the initial concentration.
(C) The rate constant of the reaction is constant at a particular temperature for this reaction
(D) $\xrightarrow{\frac{k_{t+10}}{k_t}} = 2 \sim 3$ and this is defined as the temperature coefficient of the reaction

11. Which of the following statements is/are correct :
(A) If a reaction can give both kinetically and thermodynamically controlled products, the rate constant for the kinetically controlled is generally greater.
(B) The molecularity of a reaction cannot be negative.
(C) For zero order reaction the graph between log (reactant) versus time is a straight line.
(D) For Endothermic reaction ΔH is positive, but activation energy is not.

12. Which of the following reactions is/are of the first order?
(A) The decomposition of ammonium nitrate in an aqueous solution
(B) The inversion of cane-sugar in the presence of an acid
(C) The acidic hydrolysis of ethyl acetate
(D) All radioactive decays

13. Which of the following are examples of pseudo-unimolecular reactions?

(A) $CH_3CO_2C_2H_5 + H_2O \xrightarrow{H^+} CH_3CO_2H + C_2H_5OH$

(B) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(frutose)}}{C_6H_{12}O_6}$

(C) $CH_3COCl + H_2O \longrightarrow CH_3CO_2H + HCl$

(D) $CH_3CO_2C_2H_5 + H_2O \xrightarrow{OH^-} CH_3CO_2H + C_2H_5OH$

14. Which of the following statement(s) about the Arrhenius equation is/are correct?

(A) The pre-exponential factor becomes equal to the rate constant of the reaction at extremely high temperature.

(B) When the activation energy of the reaction is zero, the rate becomes independent of temperature.

(C) The term $e^{-E_a/RT}$ represents the fraction of the molecules having energy in excess of 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.

15. A catalyst:

(A) Increases the average kinetic energy of reacting molecules

(B) Decreases the activation energy

(C) Alters the reaction mechanism

(D) Increases the frequency of collisions of reacting species

16. Which of the following expressions give correct relation between the rate constant and activation energy.

(A) $k = Ae^{-E_a/RT}$ (B) $\ln k = \ln A - \frac{E_a}{RT}$

(C) $\log k = \log A - \frac{E_a}{2.303RT}$

(D) $\ln\frac{k}{A} = -\frac{E_a}{RT}$

17. In acidic medium, the rate of reaction between and is given by the expression $-\frac{d[BrO_3^-]}{dt}$ $= k[BrO_3^-][Br^-][H^+]^2$. It means

(A) Rate constant of the reaction depends upon the concentration of H^+ ions only.

(B) Rate of reaction is independent of the concentration of the acid added.

(C) The change in pH of the solution will affect the rate of reaction.

(D) Doubling the concentration of H^+ ions will increase the reaction rate by 4 times.

18. Arhenius equation may be represented as

(A) $\ln\left(\frac{A}{k}\right) = \frac{E_a}{RT}$ (B) $\log A = \log k + \frac{E_a}{2.303RT}$

(C) $\frac{d}{dT}(\ln k) = \frac{E}{RT^2}$ (D) $\log\left(\frac{-E_a}{RT}\right) = \frac{k}{A}$

19. Which of the following are the correct statements regarding the catalysed and uncatalysed reactions at constant temperature?

(A) Catalysed reaction does not alter ΔH of the reaction.

(B) At constant temperature, ΔG^0 of the catalysed and uncatalysed reaction is same.

(C) Catalysed reaction alters equilibrium constant even at constant temperature.

(D) Catalysed reaction alters r_f and r_b values equally at constant temperature

20. The catalyst provides a new pathway involving lower amount of activation energy, to make the reaction fast. Which of the following is/are the result of catalytic action.

(A) Catalyst decreases E_a/RT value.

(B) Catalyst increases $-E_a/RT$ value.

(C) Catalyst increases value.

(D) Catalyst increases k of reaction

21. $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

Half-life period is independent of concentration of zinc at constant pH. For the constant concentration of Zn, rate becomes 100 times when pH is decreased from 3 to 2. Hence

(A) $\frac{dx}{dt} = k[Zn]^0[H^+]^2$ (B) $\left(\frac{dx}{dt}\right) = k[Zn][H^+]^2$

(C) rate is not affected if concentration of zinc is made four times and that of H^+ ion is halved.

(D) rate becomes four times if concentration of H^+ ion is doubled at constant Zn concentration.

22. Which of the following statements is/are correct?

(A) The order of a reaction is the sum of the components of all the concentration terms in the rate equation.

(B) The order of a reaction with respect to one reactant is the ratio of the change of logarithm of the rate of the reaction to the change in the logarithm of the concentration of the particular reactant, keeping the concentrations of all other reactants constant.

(C) Orders of reactions can be whole numbers or rational numbers.

(D) The order of a reaction can only be determined from the stoichiometric equation for the reaction.

23. Which of the following statements are correct about half-life period.

(A) it is proportional to initial concentration for zeroth order

(B) Average life = 1.44 × half-life; for first order reaction

(C) Time of 75% reaction is thrice of half-life period in first order reaction

(D) 99.9% reaction takes place in 100 minutes for the case when rate constant is 0.0693 min^{-1}

24. In a pseudo first order acid catalysed hydrolysis of ester in water the following results were obtained:

t/s	0	30	60	90
[ester]/M	0.55	0.31	0.17	0.085

Which of the following is/are correct for the given reaction.

(A) The average rate of reaction between time interval 30 to 60 seconds is 4.67×10^{-3}mol L^{-1} s-1

(B) Order of reaction is 2

(C) Pseudo first order rate constant for the acid catalysed hydrolysis of ester is $1.92 \times 10^{-2}\ s^{-1}$

(D) All are correct

25. Which of the following statements about zero order reaction is/are not true

(A) Unit of rate constant is sec-1

(B) The graph between log (reactant) versus time is a straight line

(C) The rate of reaction increases with the increase in concentration of reactants

(D) Rate of reaction is independent of concentration of reactants

26. The basic theory behind Arrhenius equation is that

(A) The number of effective collisions is proportional to the number of molecules above a certain threshold energy

(B) As the temperature increases, so does the number of molecules with energies exceeding the threshold energy

(C) The rate constant is a function of temperature

(D) The activation energy and pre-exponential factor are always temperature-independent

27. In Arrhenius equation, $k = Ae^{-E_a/RT}$. A may be termed as the rate constant at

(A) Very low temperature

(B) Very high temperature

(C) Zero activation energy

(D) The boiling temperature of the reaction mixture

28. For a first order reaction

(A) The degree of dissociation is equal to $1 - e^{-kt}$

(B) A plot of reciprocal of concentration of reactant vs. time gives a straight line

(C) The time taken for the completion of 75% of reaction is thrice the t1/2 of the reaction

(D) The pre-exponential factor in the Arrhenius equation has the dimensions of time--.

29. The calculation of the pre-exponential factor is based on the

(A) idea that, for a reaction to take place, the reactant species must come together

(B) calculation of the molecularity of the reaction

(C) idea that the reactant species must come together, leading to the formation of the transition state which then transforms into the products

(D) calculation of the order of the reaction

30. Nuclear reactions accompained with emission of neutron(s) are :

(A) $^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{15}P$

(B) $^{12}_{6}Al + ^{1}_{1}He \longrightarrow ^{13}_{7}N$

(C) $^{30}_{15}P \longrightarrow ^{30}_{14}Si + ^{0}_{1}e$

(D) $^{241}_{95}Am + ^{4}_{2}He \longrightarrow ^{244}_{97}Bk + ^{0}_{1}e$

31. Taking the reaction, A + 2B Products, to be of second order, which of the following may be the correct rate law expressions?

(A) $\frac{dx}{dt} = k[A][B]$ (B) $\frac{dx}{dt} = k[A][B]^2$

(C) $\frac{dx}{dt} = k[A]^2$ (D) $\frac{dx}{dt} = k_1[A] + k_2[B]^2$

32. The reaction between A and B is first order with respect to A and zero order with respect to B. Analyze the given data for the same reaction

Experiment	[A] in mol L^{-1}	[B] in mol L^{-1}	Initial rate in mol L^{-1} min^{-1}
I	0.1	0.1	2×10^{-2}
II	–	0.2	4×10^{-2}
III	0.4	0.4	–
IV	–	0.2	2×10^{-2}

Which of the following is/are correct for the above data :

(A) concentration of A in II experiment is 1×10^{-1} mol L^{-1}

(B) half life period of B is independent of initial concentration

(C) initial rate for experiment III is 3.2×10^{-2} mol L^{-1} min^{-1}

(D) concentration of A in experiment IV is 5×10^{-2} mol L^{-1}

33. Which of the following statements is/are correct?

(A) The rate of the reaction involving the conversion of ortho-hydrogen to para-hydrogen is $-\frac{d[H_2]}{dt} = k[H_2]^{3/2}$

(B) The rate of the reaction involving the thermal decomposition of acetaldehyde is $k[CH_3CHO]^{3/2}$

(C) In the formation of phosgene gas from CO and Cl_2, the rate of the reaction is $k[CO][Cl_2]^{1/2}$

(D) In the decomposition of H_2O_2, the rate of the reaction is $k[H_2O_2]$

34. A reaction is catalysed by H^+ ion. 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 both being strong acids, we may conclude that:

(A) Equilibrium constant is 2

(B) HA is stronger acid than HB

(C) Relative acidic strength of HA and HB is 2

(D) HA is weaker acid than HB and relative strength is 0.5

35. Rate constant k varies with temperature as given by equation: $\log k\ (min^{-1}) = 5 - \frac{2000K}{T}$. We can conclude

(A) Pre-exponential factor A is 5

(B) E_a is 2000 kcal

(C) Pre-exponential factor A is 105

(D) E_a is 9.152 kcal

Question Passage Based Type Questions

Passage # 1 (Q. 36 to Q. 38)

Ozone is prepared in laboratory by passing silent electric discharge through pure and dry oxygen in an apparatus known as ozoniser. This conversion from oxygen to ozone is a reversible and endothermic reaction. When oxygen is subjected to an ordinary electric discharge, most of the O_3 produced will get decomposed. When any insulating material such as glass, is inserted in the space between the two electrodes and high current density is applied, silent electric discharge passes on between the two electrodes. By this process no spark is produced and much less heat is generated, and as a result the decomposition of the produced ozone is much retarded.

The decomposition of ozone is believed to occur by the following mechanism:

$$O_3 \underset{K_b}{\overset{K_f}{\rightleftharpoons}} O_2 + O \quad \text{(fast step)}$$

$$O_3 + O \xrightarrow{K_f} 2O_2 \quad \text{(Slow)}$$

36. Order of the reaction is

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

37. Molecularity of reaction is defined by

(A) slow step

(B) reversible step

(C) from overall reaction

(D) fast step

38. When the concentration of O_2 is increased, for the same concentration of ozone, its rate

(A) increases

(B) decreases

(C) remains the same

(D) cannot be answered

Passage # 2 (Q. 39 to Q. 41)

The rate law for the decomposition of gaseous N_2O_5 is $N_2O_5 \longrightarrow 2NO_2 + O_2$. Reaction mechanism has been suggested as follows

$$N_2O_5 \overset{K_{aq}}{\rightleftharpoons} \text{(fast equilibrium)}$$

$$NO_2 + NO_3 \xrightarrow{k_1} \text{(slow)}$$

$$NO + NO_3 \xrightarrow{k_2} 2NO_2 \text{ (fast)}$$

39. Order of the reaction is

(A) 0 (B) –1 (C) 1 (D) 3/2

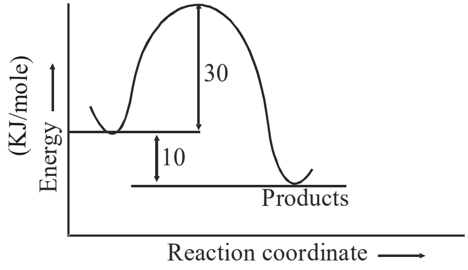
40. In 20 minutes of 80% of N_2O_5 is decomposed. Rate constant is:

(A) 0.08 (B) 0.05 (C) 0.12 (D) 0.2

41. At the equilibrium state N_2O_5, NO_2 and NO_3 concentrations are 0.2, 0.4 and 0.4 M respectively k_1 is

(A) 0.1 (B) 0.2 (C) 1 (D) 2

Passage # 3 (Q. 42 to Q.44)



The above graph represents the energy profile diagram for a first order reaction taking place at a constant temperature of 47ºC. The specific rate constant for the forward and backward reaction is 10^{-4} min^{-1} and 10^{-6} min^{-1} respectively.

42. The energy of activation for the backward reaction is :

(A) 30 kJ mol^{-1} (B) 20 kJ mol^{-1}

(C) 10 kJ mol^{-1} (D) 40 kJ mol^{-1}

43. In overall reaction heat is

(A) liberated (B) absorbed

(C) no change in heat (D) cannot be predicted

44. The maximum rate constant for the forward reaction is

(A) 5.46 (B) 7.94 (C) 1.23 (D) 9.83

EXERCISE # 3

Question Column Match Type Questions

1. Match column I with column II (for first-order reaction)

Column – I	**Column – II**
(A) $t_{63/64}$	(P) $6t_{1/2}$
(B) $t_{15/16}$	(Q) $2t_{3/4}$
(C) $t_{31/32}$	(R) $t_{7/8}$
(D) $t_{255/256}$	(S) $2t_{15/16}$

2. Match column – I with column - II

Column – I	**Column - II**
(A) decomposition of H_2O_2	(P) $10t_{1/2}$
(B) $\frac{k_{308}}{k_{298}}$	(Q) first order
(C) arrhenius equation	(R) temperature coefficient
(D) $t_{99.9\%}$ for first order	(S) $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$
	(T) 2 - 3

3. Match column I with column II

Column I	**Column II**
(A) $_{11}Na^{23} + ... \to {}_{11}Na^{24} + ...$	(P) $_0n^1$
(B) $2\,{}_1H^3 \to {}_2He^4 + 2....$	(Q) $_1h^1$
(C) $_{92}U^{238} \to {}_{90}Th^{234} + ...$	(R) $_2He^4$
(D) $_{29}Cu^{63} \to {}_{28}Ni^{63} + ...$	(S) $_1e^0$
	(T) $_1h^2$

4. Match the items of column A to those of column B:

	Column-A		Column-B
(A)	Negative sign used in expressing the rate of reaction indicates that	(p)	Mol $L^{-1}s^{-1}$
(B)	The units of rate of reaction is	(q)	Increases with increase in temperature
(C)	Rate of a reaction	(r)	Independent of Pressure
(D)	Equilibrium const K_p for an exothermic reactions	(s)	The concentration of the reactant is decreasing with time

5.

	Column-A		Column-B
(A)	For an elementary reaction A+2B→ product, the molecularity is	(p)	Pseudo unimolecular reaction
(B)	Certain biomolecular reactions which follow the kinetics of first order are called	(q)	Positive
(C)	Energy of activation of an exothermic reaction is	(r)	3
(D)	Inversion of cane sugar with excess of water	(iv)	gives glucose & fructose

6.

	Column-A		Column-B
(A)	$A + B \longrightarrow C + D$ $r = K_1 [A] [B]$	(p)	Unit of rate constant possess concentration unit.
(B)	$A + B \to C + D$ $r = k_2 [A] [B]^o$	(q)	Rate constant for the reaction of both the reactants are equal
(C)	$A + B \to C + D$ $r = K_3 [A]^o [B]^o$	(r)	Rate of consumption of atleast one of the reactant is equal to rate of production of atleast one of the products.
(D)	$2A + B \to 2C + 3D$ $r = K_3 [A]^o [B]^o$	(s)	If both reactants are taken in stoichiometric ratio, half life for both reactants are equal

Question Numerical Type Questions

7. Rate constant for reaction P→Q is 0.693 mole lit^{-1} sec^{-1}. If initial concentration of P is 6.93 mole/lit, find half life period of reaction (in seconds).

8. In the reaction $A \longrightarrow P$, concentration of A was registered after equal intervals of time. If these values followed A.P., then order of reaction will be :

9. Temperature of some reaction is increased form T_1 to T_2. If product of T_1 and T_2 is equal to E_a / 0.0693 R and $(T_2 - T_1)$ is 10. Then value of K_{45} / K_{25} for the reaction will be :

10. Consider a reaction aG + bH $\longrightarrow$ Product. 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 constant, the rate is doubled. The overall order of the reaction is:

11. The inversion of Cane sugar proceeds with constant half-life of 500 minutes at p^H = 5 for any concentration of sugar. However if p^H = 6, the half-life changes to 50 minutes. For this reaction rate equation is rate = k $[sugar]^m$ $[H^+]^n$. The value of"n" is.

12. A sample contains two radioactive substances A and B in the ratio of 4 : 1 . If their half lives are 12 and 16 hours, respectively, then after 2 days the ratio of A and B is.

13. Half - life period of the decomposition of a compound is 20 minutes. If the initial concentration is doubled, the half - life period is reduced to 10 mins. What is the order of the reaction?

EXERCISE # 4

Question **Previous Year (JEE Main)**

1. 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 J k^{-1} and log 2 = 0.301)

[JEE Main-2013]

(A) 60.5 kJ mol^{-1} (B) 53.6 kJ mol^{-1}
(C) 48.6 kJ mol^{-1} (D) 58.5 kJ mol^{-1}

2. For the non-stoichiometeic 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 [A]	Initial rate of formation of C (mol $L^{-1}S^{-1}$)
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]

(A) $\frac{dC}{dt} = k[A]$ (B) $\frac{dC}{dt} = k[A][B]$

(C) $\frac{dC}{dt} = k[A]^2[B]$ (D) $\frac{dC}{dt} = k[A][B]^2$

3. Higher order (>3) reactions are rare due to

[JEE Main-2015]

(A) Shifting of equilibrium towards reactants due to elastic collisions
(B) Loss of active species on collision
(C) Low probability of simultaneous collision of all the reacting species
(D) Increase in entropy and activation energy as more molecules are involved.

4. 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]**

(A) 6.93×10^{-2} mol min^{-1}
(B) 6.93×10^{-4} mol $L^{-1}min^{-1}$
(C) 2.66 L min^{-1} at STP0
(D) 1.34×10^{-2} mol min^{-1}

5. Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 10 kJ mol^{-1}. If k_1 and k_2 are rate constants for reactions R_1 and R_2 respectively at 300 K. then In(k_2/k_1) is equal to (R = 8.314 J mol^{-1} K^{-1}) **[JEE Main-2017]**

(A) 6 (B) 4 (C) 8 (D) 12

6. 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]

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

7. For the reaction $2A + B \rightarrow C$, the values of initial rate at different reactant concentrations are given in the table below. The rate law for the reaction is : **[JEE Main-2019]**

[A] (mol L^{-1})	[B] (mol L^{-1})	Initial Rate (mol $L^{-1}s^{-1}$)
0.05	0.05	0.045
0.10	0.05	0.090
0.20	0.10	0.72

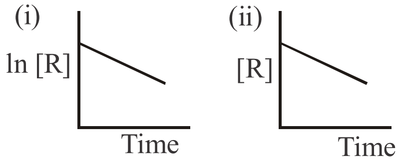
(A) Rate = k [A][B] (B) Rate = k $[A]^2[B]^2$
(C) Rate = k $[A][B]^2$ (C) Rate = k $[A]^2[B]$

8. For a reaction scheme $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, if the rate of formation of B is set to be zero then the concentration of B is given by :

[JEE Main-2019]

(A) (k_1 / k_2) [A] (B) $(k_1 + k_2)$ [A]
(C) k_1k_2 [A] (D) $(k_1 - k_2)$ [A]

9. The given plots represent the variation of the concentration of a reactant R with time for two different reactions (i) and (ii). The respective orders of the reactions are : **[JEE Main-2019]**



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

10. For the reaction of H_2 with I_2, the rate constant is $2.5 \times 10^{-4}dm^3$ mol^{-1} s^{-1} at 327°C and 1.0 dm^3 mol^{-1} s^{-1} at 527°C. The activation energy for the reaction, in kJ mol^{-1} is: **[JEE Main-2019]**
(R = 8.314 J K^{-1} mol^{-1})

(A) 72 (B) 166 (C) 150 (D) 59

11. NO_2 required for a reaction is produced by the decomposition of N_2O_5 in CCl_4 as per the equation $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$
The initial concentration of N_2O_5 is 3.00 mol L^{-1} and it is 2.75 mol L^{-1} after 30 minutes. The rate of formation of NO_2 is : **[JEE Main-2019]**

(A) 2.083×10^{-3} mol L^{-1} min^{-1}
(B) 4.167×10^{-3} mol L^{-1} min^{-1}
(C) 8.333×10^{-3} mol L^{-1} min^{-1}
(D) 1.667×10^{-2} mol L^{-1} min^{-1}

12. The following results were obtained during kinetic studies of the reaction :
$2A + B \rightarrow$ 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}

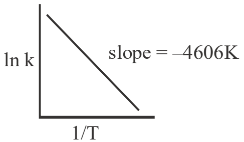
The time (in minutes) required to consume half of A is : **[JEE Main-2019]**
(A) 10 (B) 5 (C) 100 (D) 1

13. For the reaction, $2A + B \rightarrow$ products, when the concentrations of A and B both wrere doubled, the rate of the reaction increased from 0.3 mol $L^{-1}s^{-1}$ to 2.4 mol L^{-1} s^{-1}. When the concentration of A alone is doubled, the rate increased from 0.3 mol $L^{-1}s^{-1}$ to0.6 mol $L^{-1}s^{-1}$. Which one of the following statements is **correct ?** **[JEE Main-2019]**
(A) Order of the reaction with respect to B is 2.
(B) Order of the reaction with respect to A is 2.
(C) Total order of the reaction is 4.
(D) Order of the reaction with respect to B is 1.

14. For an elementary chemical reaction,
$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A$, the expression for $\frac{d[A]}{dt}$ is – **[JEE Main-2019]**
(A) $2k_1[A_2] - k_{-1}[A]^2$ (B) $k_1[A_2] - k_{-1}[A]^2$
(C) $2k_1[A_2] - 2k_{-1}[A]^2$ (D) $k_1[A_2] + k_{-1}[A]^2$

15. Decomposition of X exhibits a rate constant of 0.05 mg/year. How many years are required for the decomposition of 5 mg of X into 2.5 μg ? **[JEE Main-2019]**
(A) 50 (B) 25 (C) 20 (D) 40

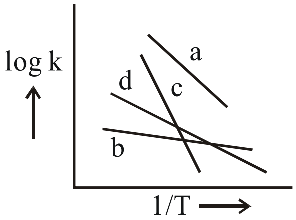
16. For a reaction consider the plot of ln k versus 1/T given in the figure. If the rate constant of this reaction at 400 K is 10^{-5} s^{-1}, then the rate constant at 500K is : **[JEE Main-2019]**



(A) 2×10^{-4} s^{-1} (B) 10^{-4} s^{-1}
(C) 10^{-6} s^{-1} (D) 4×10^{-4} s^{-1}

17. For the reaction **[JEE Main-2020]**
$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$
the observed rate expression is,
rate = $k_f [NO]^2[H_2]$. The rate expression of the reverse reaction is :
(A) $k_b[N_2][H_2O]^2/[NO]$ (B) $k_b[N_2][H_2O]$
(C) $k_b[N_2][H_2O]^2$ (D) $k_b[N_2][H_2O]^2/[H_2]$

18. Consider the following plots of rate constant versus 1/T for four different reactions. Which of the following orders is correct for the activation energies of these reactions? **[JEE Main-2020]**



(A) $E_b > E_d > E_c > E_a$ (B) $E_a > E_c > E_d > E_b$
(C) $E_c > E_a > E_d > E_b$ (D) $E_b > E_a > E_d > E_c$

19. Rate of a reaction increases by 10^6 times when a reaction is carried out in presence of enzyme catalyst at same temperature. Determine change in activation energy. **[JEE Main-2020]**
(A) -6×2.303 RT (B) $+6 \times 2.303$RT
(C) + 6 RT (D) –6RT

20. A sample of milk splits after 60 min. at 300 K and after 40 min. at 400 K when the population of *lactobacillus acidophilus* in it doubles. The activa tion energy (in kJ/ mol) for this process is closest to__________. **[JEE Main-2020]**
(Given, R = 8.3 J mol^{-1} K^{-1}, ln (2/3) = 0.4, $e^{-3} = 4.0$)

21. For the following reactions **[JEE Main-2020]**
$A \xrightarrow{700\ K}$ Product
$B \xrightarrow[\text{catalyst}]{500\ K}$ Product
it was found that E_a is decreased by 30 kJ/mol in the presence of catalyst. If the rate remains unchanged, the activation energy for catalysed reaction is (Assume pre exponential factor is same):
(A) 135 kJ/mol (B) 105 kJ/mol
(C) 198 kJ/mol (D) 75 kJ/mol

22. The results given in the below table were obtained during kinetic studies of the following reaction: **[JEE Main-2020]**
$2A + B \rightarrow C + D$

Experiment	[A]/molL^{-1}	[B]/molL^{-1}	Initial rate/molL^{-1} min^{-1}
I	0.1	0.1	6.00×10^{-3}
II	0.1	0.2	2.40×10^{-2}
III	0.2	0.1	1.20×10^{-2}
IV	X	0.2	7.20×10^{-2}
V	0.3	Y	2.88×10^{-1}

X and Y in the given table are respectively :
(A) 0.3, 0.4 (B) 0.4, 0.3
(C) 0.4, 0.4 (D) 0.3, 0.3

23. It is true that : **[JEE Main-2020]**

(A) A zero order reaction is a single step reaction

(B) A second order reaction is always a multistep reaction.

(C) A first order reaction is always a single step reaction.

(D) A zero order reaction is a multistep reaction.

24. For the reaction $2A + 3B + (3/2)\ C \rightarrow 3P$, which statement is correct ? **[JEE Main-2020]**

(A) $\frac{dn_A}{dt} = \frac{dn_B}{dt} = \frac{dn_C}{dt}$

(B) $\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$

(C) $\frac{dn_A}{dt} = \frac{3}{2}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$

(D) $\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{4}{3}\frac{dn_C}{dt}$

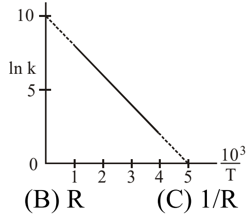
25. If 75% of a first order reaction was completed in 90 minutes, 60% of the same reaction would be completed in approximately (in minutes) ________. (Take : log 2 = 0.30; log 2.5 = 0.40) **[JEE Main-2020]**

26. The number of molecules with energy greater than the threshold energy for a reaction increases five fold by a rise of temperature from 27 °C to 42 °C. Its energy of activation in J/mol is _________. **[JEE Main-2020]**
(Take ln 5 = 1.6094; R = 8.314 J $mol^{-1}K^{-1}$)

27. A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives for A and B are 300 s and 180 s, respectively. If the concentrations of A and B are equal initially, the time required for the concentration of A to be four times that of B(in s) : (Use ln 2 = 0.693) **[JEE Main-2020]**

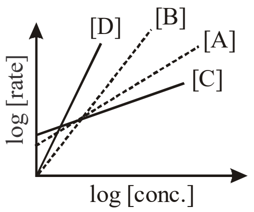
(A) 180 (B) 120 (C) 300 (D) 900

28. The rate constant (k) of a reaction is measured at different temperatures (T), and the data are plotted in the given figure. The activation energy of the reaction in kJ mol^{-1} is : (R is gas constant) **[JEE Main-2020]**



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

29. Consider the following reactions :
$A \rightarrow P_1$; $B \rightarrow P_2$; $C \rightarrow P_3$; $D \rightarrow P_4$
The order of the above reactions are a, b, c, and d, respectively. The following graph is obtained when log [rate] vs. log [conc] are plotted: **[JEE Main-2020]**



Among the following , the correct sequence for the order of the reactions is:

(A) a > b > c > d (B) c > a > b > d

(C) d > b > a > c (D) d > a > b > c

30. The rate of a reaction decreased by 3.555 times when the temperature was changed from 40°C to 30°C. The activation energy (in kJ mol^{-1}) of the reaction is_ _ _ _ _ _. **[JEE Main-2020]**
Take; R=8.314 J mol^{-1} K^{-1}, ln 3.555 = 1.268

31. The following data was obtained for chemical reaction given below at 975 K.

$2NO\ (g) + 2H_2\ (g) \rightarrow N_2(g) + 2H_2O(g)$

	[NO] mol L^{-1}	[H_2] mol L^{-1}	Rate mol $L^{-1}s^{-1}$
(A)	8×10^{-5}	8×10^{-5}	7×10^{-9}
(B)	24×10^{-5}	8×10^{-5}	2.1×10^{-8}
(C)	24×10^{-5}	32×10^{-5}	8.4×10^{-8}

The order of the reaction with respect to NO is _____. (Integer answer) **[JEE Main-2021]**

32. The reaction rate for the reaction

$[PtCl_4]^{2-} + H_2O \rightleftharpoons [Pt(H_2O)Cl_3]^{-} + Cl^{-}$

was measured as a function of concentrations of different species. It was observed that

$\frac{-d\,[[PtCl_4]^{2-}]}{dt} = 4.8\times10^{-5}[[PtCl_4]^{2-}]-2.4\times10^{-3}$

$[[Pt(H_2O)Cl_3]^{-}]\ [Cl^{-}]$ **[JEE Main-2021]**

where square brackets are used to denote molar concentrations. The equilibrium constant K_c = _______. (Nearest integer)

33. The reaction that occurs in a breath analyser, a device used to determine the alcohol level in a person's blood stream is

$2K_2Cr_2O_7 + 8H_2SO_4 + 3C_2H_6O \rightarrow$

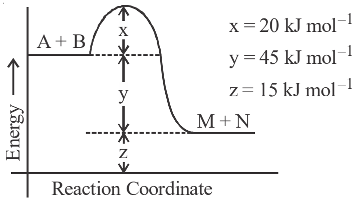
$2Cr_2(SO_4)_3 + 3C_2H_4O_2 + 2K_2SO_4 + 11H_2O$

If the rate of appearance of $Cr_2(SO_4)_3$ is 2.67 mol min^{-1} at a particular time, the rate of disappearance of C_2H_6O at the same time is _____ mol min^{-1}. (Nearest integer) **[JEE Main-2021]**

34. The first order rate constant for the decomposition of $CaCO_3$ at 700 K is 6.36×10^{-3} s^{-1} and activation energy is 209 kJ mol^{-1}. Its rate constant (in s^{-1}) at 600 K is $x \times 10^{-6}$. The value of x is _____. (Nearest integer)
[Given R = 8.31 J K^{-1} mol^{-1}; log 6.36×10^{-3} = –2.19, $10^{-4.79} = 1.62 \times 10^{-5}$]**[JEE Main-2021]**

35. For a first order reaction, the ratio of the time for 75% completion of a reaction to the time for 50% completion is _______. (Integer answer) **[JEE Main-2021]**

36. According to the following figure, the magnitude of the enthalpy change of the reaction $A + B \rightarrow M + N$ in kJ mol^{-1} is equal to ___. (Integer answer) **[JEE Main-2021]**

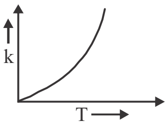


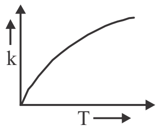
37. For the reaction $A \rightarrow B$, the rate constant k (in s^{-1}) is given by **[JEE Main-2021]**

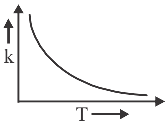
$$\log_{10}k = 20.35 - \frac{2.47 \times 10^3}{T}$$

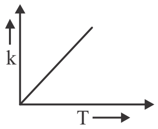
The energy of activation in kJ mol^{-1} is ________.
(Nearest integer) [Given : R = 8.314 JK^{-1} mol^{-1}]

38. Which one of the following given graphs represents the variation of rate constant (k) with temperature (T) for an endothermic reaction? **[JEE Main-2021]**

(A)


(B)


(C)


(D)


39. $2NO + 2H_2 \rightarrow N_2 + 2H_2O$
The above reaction has been studied at 800°C. The related date are given in the table below

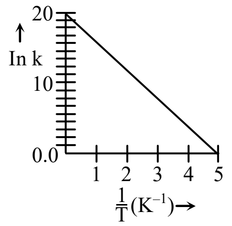
Reaction serial number	**Initial Pressure of H_2/kPa**	**Initial Pressure of NO/kPa**	**Initial rate $\left(\frac{-dp}{dt}\right)$ / (kPa/s)**
1.	65.6	40.0	0.135
2.	65.6	20.1	0.033
3.	38.6	65.6	0.214
4.	19.2	65.6	0.106

The order of the reaction with respect to NO is ______. (Nearest integer)
(Given: R = 2 cal K^{-1} mol^{-1}) **[JEE Main-2022]**

40. $[A] \longrightarrow [B]$
Reactant Product
If formation of compound [B] follows the first order of kinetics and after 70 minutes the concentration of [A] was found to be half of its initial concentration. Then the rate constant of the reaction is $x \times 10^{-6}$ s^{-1}. The value of x is __________ . (Nearest Integer) **[JEE Main-2022]**

41. For the given first order reaction $A \rightarrow B$, the half life of the reaction is 0.3010 min. The ratio of the initial concentration of reactant to the concentration of reactant at time 2.0 min will be equal to ______. (Nearest integer) **[JEE Main-2022]**

42. For a reaction, given below is the graph of ln k vs $\frac{1}{T}$. The activation energy for the reaction is equal to____ cal mol^{-1}. **[JEE Main-2022]**



43. For a first order reaction $A \rightarrow B$, the rate constant, $k = 5.5 \times 10^{-14}$ s^{-1}. The time required for 67% completion of reaction is $x \times 10^{-1}$ times the half life of reaction. The value of x is _____. (Nearest integer) **[JEE Main-2022]**

44. The reaction between X and Y is first order with respect to X and zero order with respect to Y. **[JEE Main-2022]**

Experiment	$\frac{[X]}{mol\,L^{-1}}$	$\frac{[Y]}{mol\,L^{-1}}$	$\frac{\text{Initial rate}}{mol\,L^{-1}\,min^{-1}}$
I.	0.1	0.1	2×10^{-3}
II.	L	0.2	4×10^{-3}
III.	0.4	0.4	$M \times 10^{-3}$
IV	0.1	0.2	2×10^{-3}

Examine the data of table and calculate ratio of numerical values of M and L. (Nearest Integer)

45. The activation energy of one of the reactions in a biochemical process is 532611 J mol^{-1}. When the temperature falls from 310 K to 300 K, the change in rate constant observed is $k_{300} = x \times 10^{-3}\,k_{310}$. The value of x is ______.
[Given: ln10 = 2.3, R = 8.3 JK^{-1} mol^{-1}] **[JEE Main-2022]**

46. The number of terminal oxygen atoms present in the product B obtained from the following reaction is ________.
$FeCr_2O_4 + Na_2CO_3 + O_2 \rightarrow A + Fe_2O_3 + CO_2$
$A + H+ \rightarrow B + H_2O + Na^+$ **[JEE Main-2022]**

47. The equation $k = (6.5 \times 10^{12} s^{-1})e^{-26000K/T}$ is followed for the decomposition of compound A. The activation energy for the reaction is ______ kJ mol^{-1}. [nearest integer]
(Given : $R = 8.314$ J K^{-1} mol^{-1}]**[JEE Main-2022]**

48. The number of correct statement/s from the following is __________.
A. Larger the activation energy, smaller is the value of the rate constant.
B. The higher is the activation energy, higher is the value of the temperature coefficient.
C. At lower temperatures, increase in temperature causes more change in the value of k than at higher temperature.
D. A plot of ln k vs $\frac{1}{T}$ is a straight line with slope equal to $-\frac{E_a}{R}$. **[JEE Main-2023]**

49. A student has studied the decomposition of a gas AB_3 at 25°C. He obtained the following data.

p (mm Hg)	50	100	200	400
relative $t_{1/2}$ (s)	4	2	1	0.5

The order of the reaction is **[JEE Main-2023]**
(A) 1 (B) 0 (C) 2 (D) 0.5

50. It compound A reacts with B following first order kinetics with rate constant 2.011×10^{-3} s^{-1}. The time taken by A (in seconds) to reduce from 7 g to 2 g will be ________ . (Nearest Integer)
[log 5 = 0.698, log 7 = 0.845, log 2 = 0.301]
[JEE Main-2023]

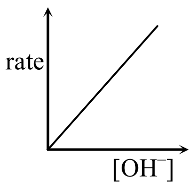
51. $A \rightarrow B$
The rate constants of the above reaction at 200 K and 300 K are 0.03 min^{-1} and 0.05 min^{-1} respectively. The activation energy for the reaction is __________ J (Nearest integer)
(Given : ln 10 = 2.3 **[JEE Main-2023]**
R = 8.3 J K^{-1} mol^{-1}
log 5 = 0.70
log 3 = 0.48
log 2 = 0.30)

52. The rate constant for a first order reaction is 20 min^{-1}. The time required for the initial concentration of the reactant to reduce to its $\frac{1}{32}$ level is ________ $\times 10^{-2}$ min. (Nearest integer)
Given : ln 10 = 2.303 **[JEE Main-2023]**
log 2 = 0.3010

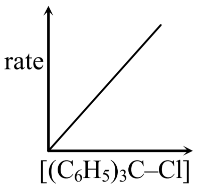
53. The graph which represents the following reaction is : **[JEE Main-2023]**

$$(C_6H_5)_3C\text{–}Cl \xrightarrow[\text{Pyridine}]{OH^-} (C_6H_5)_3C\text{–}OH$$

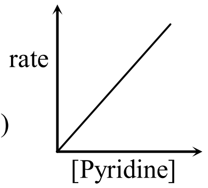
(A)



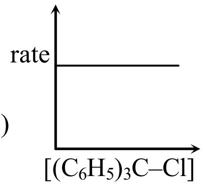
(B)



(C)



(D)



54. $A \rightarrow B$
The above reaction is of zero order. Half life of this reaction is 50 min. The time taken for the concentration of A to reduce to one-fourth of its initial value is _________ min.
[JEE Main-2023]

55. Time required for completion of 99.9% of a First order reaction is ______ times of half life ($t_{1/2}$) of the reaction. **[JEE Main-2024]**

56. Consider the following first order gas phase reaction at constant temperature
$A(g) \rightarrow 2B(g) + C(g)$
If the total pressure of the gases is found to be 200 torr after 23 sec. and 300 torr upon the complete decomposition of A after a very long time, then the rate constant of the given reaction is____$\times 10^{-2}$ s^{-1} (nearest integer) [Given : $\log_{10}(2) = 0.301$]
[JEE Main-2024]

57. Time required for 99.9% completion of a first order reaction is ____ time the required for completion of 90% reaction. (nearest interger).
[JEE Main-2024]

58. Consider the following transformation involving first order elementary reaction in each step at constant temperature as shown below.

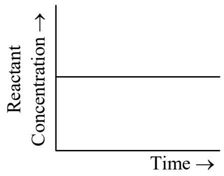
$$A + B \underset{\text{Step3}}{\overset{\text{Step I}}{\rightleftharpoons}} C \xrightarrow{\text{Step 2}} P$$

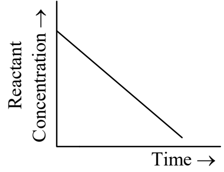
Some details of the above reaction are listed below.

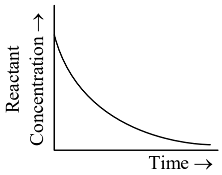
Step	**Rate constant (sec^{-1})**	**Activation energy (kJ mol^{-1})**
1	k_1	300
2	k_2	200
3	k_3	Ea_3

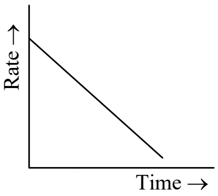
If the overall rate constant of the above transformation (k) is given as $k = \frac{k_1k_2}{k_3}$ and the overall activation energy (E_a) is 400 kJ mol^{-1}, then the value of Ea_3 is ______ kJ mol^{-1} (nearest integer) **[JEE Main-2024]**

59. Which of the following graphs most appropriately represents a zero order reaction ? **[JEE Main-2025]**

(A)


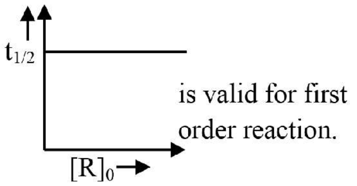
(B)


(C)


(D)


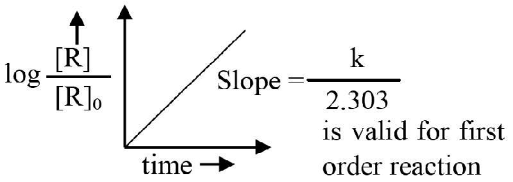
60. Given below are two statements : **[JEE Main-2025]**

Statement(I) :



is valid for first order reaction.

Statement(II) :



is valid for first order reaction

In the light of the above statements, choose the **correct** answer from the options given below :

(A) Both **Statement I** and **Statement II** are false
(B) **Statement I** is false but **Statement II** is true
(C) Both **Statement I** and **Statement II** are true
(D) **Statement I** is true but **Statement II** is false

61. The reaction $A_2 + B_2 \rightarrow 2\ AB$ follows the mechanism

$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + A$ (fast)

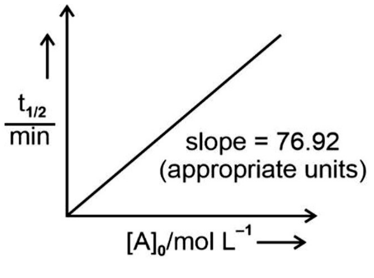
$A + B_2 \xrightarrow{k_2} AB + B$ (slow)

$A + B \rightarrow AB$ (fast)

The overall order of the reaction is: **[JEE Main-2025]**

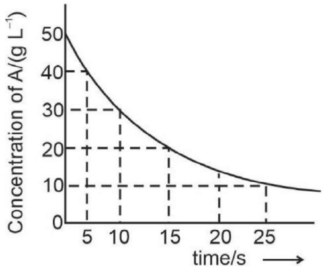
(A) 1.5 (B) 3 (C) 2.5 (D) 2

62. For the reaction A → products. **[JEE Main-2025]**



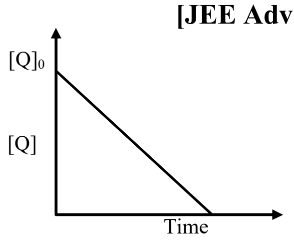
The concentration of A at 10 minutes is ___ $\times 10^{-3}$ mol L^{-1} (nearest integer).
The reaction was started with 2.5 mol L^{-1} of A.

63. For the reaction A → B the following graph was obtained. The time required (in seconds) for the concentration of A to reduce to 2.5 g L^{-1} (if the initial concentration of A was 50 g L^{-1}) is _______. (Nearest integer) Given: log 2 = 0.3010 **[JEE Main-2025]**



Question | Previous Year (JEE Advanced)

64. In the reaction, $P + Q \rightarrow R + S$ 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]**



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

65. For the elementary reaction $M \rightarrow N$, the rate of disappearance of M increases by a factor by afactor of 8 upon doubling the concentration of M. the order of the reaction with respect to M is **[JEE Advanced-2014]**

(A) 4 (B) 3 (C) 2 (D) 1

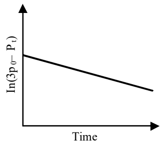
66. According to the Arrhenius equation, **[JEE Advanced-2016]**

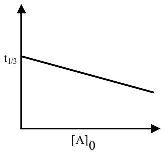
(A) a high activation energy usually implies fast reaction
(B) rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy
(C) higher the magnitude of activation energy, stronger id the temperature dependence of the rate constant
(D) the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.

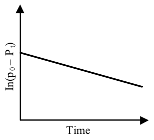
67. In a bimolecular reaction, the satiric factor P was experimentally determined to be 4.5. the correct option(s) among the following is (are) **[JEE Advanced-2017]**

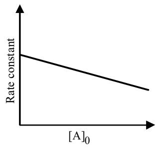
(A) Experimentally determined value of frequency factor is higher then that predicted by Arrhenius equation
(B) The value of frequency factor predicted by experimentally
(C) The activation energy of the redaction is unaffected by the value of the satiric factor
(D) Since P = 4.5, the reaction will not proceed unless an effective catalyst is used.

68. 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 1/3rd of its initial value. The correct option(s) is (are)
(Assume that all these gases behave as ideal gases) **[JEE Advanced-2018]**

(A)


(B)


(C)


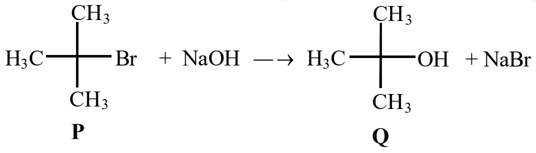
(D)


69. Consider the kinetic data given in the following table for the reaction $A + B + C \rightarrow$ Product.

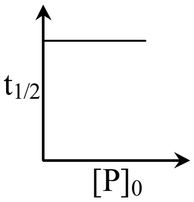
Experiment No.	[A] (mol dm^{-3})	[B] (mol dm^{-3})	[B] (mol dm^{-3})	Rate of reaction (mol dm^{-3}s^{-1})
1	0.2	0.1	0.1	6.0×10^{-5}
2	0.2	0.2	0.1	6.0×10^{-5}
3	0.2	0.1	0.2	1.2×10^{-4}
4	0.3	0.1	0.1	9.0×10^{-5}

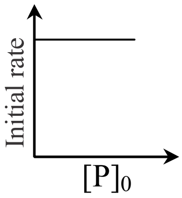
The rate of the reaction for [A] = 0.15 mol dm^{-3}, [B] = 0.25 mol dm^{-3} and [C] = 0.15 mol dm^{-3} is found to be Y × 10^{-5} mol dm^{-3} s^{-1}. The value of Y is _________ **[JEE Advanced-2019]**

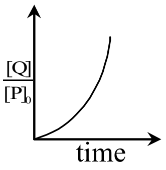
70. Which of the following plots is(are) correct for the given reaction?
($[P]_0$ is the initial concentration of P)
[JEE Advanced-2021]

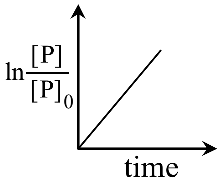


$\underset{\mathbf{P}}{H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Br} + NaOH \longrightarrow \underset{\mathbf{Q}}{H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH} + NaBr$

(A)


(B)


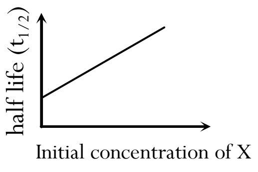
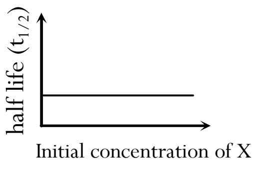
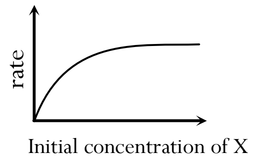
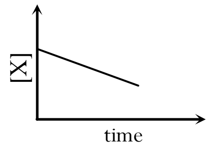
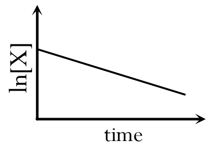
(C)


(D)


71. For the following reaction : $2X + Y \xrightarrow{k} P$
the rate of reaction is $\frac{d[P]}{dt} = k[X]$. Two moles of X are mixed with one mole of Y to make 1.0 L of solution. At 50 s, 0.5 mole of Y is left in the reaction mixture. The correct statement(s) about the reaction is(are)
(Use : ln 2 = 0.693) **[JEE Advanced-2021]**

(A) The rate constant, k, of the reaction is $13.86 \times 10^{-4} s^{-1}$.
(B) Half–life of X is 50s.
(C) At 50 s, $-\frac{d[X]}{dt} = 13.86 \times 10^{-3}$ mol L^{-1} s^{-1}.
(D) At 100 s, $-\frac{d[Y]}{dt} = 3.46 \times 10^{-3}$ mol L–1 s–1.

72. Match the rate expressions in LIST-I for the decomposition of X with the corresponding profiles provided in LIST-II. X_s and k are constants having appropriate units.
[JEE Advanced-2022]

	List-I		**List-II**
(I)	rate = $\frac{k[X]}{X_s + [X]}$ under all possible initial concentrations of X	(P)	
(II)	rate = $\frac{k[X]}{X_s + [X]}$ where initial concentrations of X are much less than X_s	(Q)	
(III)	rate = $\frac{k[X]}{X_s + [X]}$ where initial concentrations of X are much higher than X_s	(R)	
(IV)	rate = $\frac{k[X]^2}{X_s + [X]}$ where initial concentrations of X are much higher than X_s	(S)	
		(T)	

(A) I → P; II → Q; III → S; IV → T
(B) I → R; II → S; III → S; IV → T
(C) I → P; II → Q; III → Q; IV → R
(D) I → R; II → S; III → Q; IV → R

73. Consider the following reaction,

$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$

which follows the mechanism given below:

$$2NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$$

fast equilibrium

$$N_2O_2(g) + H_2(g) \overset{k_2}{\rightleftharpoons} N_2O(g) + H_2O(g)$$

slow reaction

$$N_2O(g) + H_2(g) \overset{k_3}{\rightleftharpoons} N_2(g) + H_2O(g)$$

fast reaction

The order of the reaction is ______.

[JEE Advanced-2024]

74. Consider a reaction A + R → Product. The rate of this reaction is measured to be $k[A][R]$. At the start of the reaction, the concentration of R, $[R]_0$, is 10-times the concentration of A, $[A]_0$. The reaction can be considered to be a pseudo first order reaction with assumption that $k[R] = k'$ is constant. Due to this assumption, the relative error (in %) in the rate when this reaction is 40 % complete, is ______.

[k and k' represent corresponding rate constants]

[JEE Advanced-2025]

ANSWER KEY

EXERCISE-1

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Ans.	D	D	B	D	B	B	A	B	A	A	A	B	B	C	A	A	C
Que.	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
Ans.	D	C	A	A	B	B	B	B	C	A	B	C	A	B	D	C	A
Que.	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51
Ans.	A	C	A	A	D	B	D	C	B	B	C	B	A	D	C	A	C
Que.	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68
Ans.	C	A	D	C	D	D	D	B	C	B	A	D	C	C	D	B	B
Que.	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85
Ans.	C	C	C	A	D	B	C	D	B	B	D	B	C	B	D	A	B

EXERCISE-2

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	A,B,C,D	A,B	A,B,C	B,D	A,B	A,B,C	A,B	A,C	A,B,C,D	B,C,D	A,B,C	A,B,C,D	A,B,C	A,B,C	B,C
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	A,B,C,D	C,D	A,B,C	A,B,D	A,B,D	B,C,D	A,B,C	A,B,D	A,C	A,C	A,B,C	B,C	A,D	A,C	A,D
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	
Ans.	A,C	A,D	A,B,C,D	B,C	C,D	A	A	B	C	A	A	B	A	B	

EXERCISE-3

1. (A) → (P); (B) → (Q); (C) → (R) ; D → (S)

2. (A) → (Q); (B) → (R, T); (C) → (S) ; D → (P)

3. (A) → (Q,T); (B) → (P); (C) → (R) ; D → (S)

4. (A) → (P); (B) → (Q); (C) → (R) ; D → (S)

5. (A) → (R); (B) → (P); (C) → (Q) ; D → (S)

6. (A) → (P, Q, R, S); (B) → (Q, R, S); (C) → (R) ; D → (S)

7. [5] 8. [0] 9. [4] 10. [3] 11. [0] 12. [2] 13. [2]

EXERCISE-4

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	21
Ans.	B	A	C	B	B	C	3	A	A	B	D	B	A	C	A	B	D	C	A	D
Que.	22	23	24	25	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42
Ans.	A	D	D	60	D	A	C	100	1	0	4	16	2	45	47	A	2	165	100	8
Que.	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62
Ans.	16	40	1	6	216	3	C	623	2520	17	B	75	10	3	3	100	B	D	A	2435.00
Que.	63	64	65	66	67	68	69	70	71	72	73	74								
Ans.	47.00	D	B	B,C,D	A,C	A,D	6.75	A	B,C,D	A	3	4.17								

20. [3.98 to 3.99 or –3.98 to –3.99] 26. [84297.47 or 84297.48]