04

Chemical Kinetics

Chemical kinetics is that branch of science which deals with the speeds or the rate of chemical reactions, the factors affecting the rate of reactions and the mechanism by which reactions proceed.

Chemical Reactions

When one or more substance(s) undergoes a change which results in the formation of new product(s) that differ from the original one in composition and properties, the change is called as a chemical reaction.

Chemical reactions involve breaking and formation of bonds. Therefore, different bonds require different amount of energy for breaking and different amount of energy is evolved during bond formation. Thus, the rates of different reactions are different.

Depending upon their rates or speeds, chemical reactions can be classified as:

1. Instantaneous or Fast Reactions

These are infact very fast reactions and it is practically impossible to measure the speed of such reactions. Typical examples of such reactions include

- ionic reactions
- organic substitution reactions
- explosive reactions of oxygen with hydrogen and hydrocarbons.

2. Extremely Slow Reactions

Such reactions proceed at very slow speed and here the speed is so slow that again it is not possible to measure the speed of such reactions, e.g. rusting of iron.

IN THIS CHAPTER

- Chemical Reactions
- Rate of a Chemical Reaction
- Rate Law and Rate Constant
- Molecularity of Reaction
- Order of Reaction
- Differential and Integral Forms of Different Order Reactions
- Methods of Determination of Order of Reaction
- Effect of Temperature on Rate of Reaction
- Theories of Rate of Reaction

3. Moderately Slow Reactions

Reactions belonging to third category, i.e. **with moderate speed** are utilised for the study of chemical kinetics as in inversion of cane sugar and hydrolysis of starch.

Depending upon number of steps, chemical reactions are classified in the following ways

Elementary Reactions

A balanced chemical equation never gives us a true picture of how a reaction takes place. It can be complete in one step or in many steps. The reactions taking place in one step are called elementary reactions.

Complex Reactions

The reactions which do not take place in one step are called **complex reactions**. These are the reactions in which all the atoms, ions or molecules as represented in the balanced chemical reaction may not come together to collide simultaneously. e.g.

 $5\mathrm{Br}^{\ominus}(aq) + \,\mathrm{BrO}_3^{\ominus}(aq) + \,6\mathrm{H}^+(aq) \longrightarrow 3\mathrm{Br}_2(aq) + \,3\mathrm{H}_2\mathrm{O}(l)$

It is impossible for all the 12 ions of the reactant to come together simultaneously to collide. Such reactions take place in a sequence of a number of steps. Each of these step reaction is an elementary reaction.

Remember Different steps of complex reaction are elementary reactions.

Rate of a Chemical Reaction

The rate or speed or velocity of a reaction is the rate of change of concentration of reactants or products in unit time. When a reaction occurs, the concentration of reactant starts decreasing while the concentration of product starts increasing. Therefore,

Rate of a reaction

$$=\frac{\text{decrease in the concentration of reactant}}{\text{time interval}}$$

or Rate of reaction

 $=\frac{\text{increase in the concentration of product}}{\text{time interval}}$

In general for a reaction, $n_1A + n_2B \longrightarrow m_1C + m_2D$ The rate expression may be expressed as,

Rate of reaction
$$= -\frac{1}{n_1} \frac{\Delta[A]}{\Delta t} = -\frac{1}{n_2} \frac{\Delta[B]}{\Delta t}$$

 $= +\frac{1}{m_1} \frac{\Delta[C]}{\Delta t} = +\frac{1}{m_2} \frac{\Delta[D]}{\Delta t}$

Remember The negative sign indicates that the concentration of reactant decreases with time whereas the positive sign indicates that the concentration of product increases with time.

Types of Rate of Reactions

The rate of a reaction can be categorised into two types

(i) Average rate of reaction Average rate of a reaction is defined as the rate of change of concentration per unit time. It is calculated by dividing the total change in concentration of any one of the reactant or product by the total time taken to do so. For the reaction,

$$PCl_5 \longrightarrow Cl_2 + PCl_3$$
Average rate =
$$\frac{\text{decrease in conc. of PCl}_5}{\text{time taken}}$$

It can also be expressed in terms of increase in concentration of PCl_3 and Cl_2 as,

$$\text{Rate} = -\frac{\Delta[\text{PCl}_5]}{\Delta t} = +\frac{\Delta[\text{Cl}_2]}{\Delta t} = +\frac{\Delta[\text{PCl}_3]}{\Delta t}$$

(ii) **Instantaneous rate of reaction** The rate of reaction at any particular instant of time is known as **instantaneous rate** of reaction. It is equal to the small change in concentration (dx) in small interval of time (dt).

Rate =
$$\frac{dx}{dt}$$

In general, for a reaction,

$$n_1A + n_2B \longrightarrow m_1C + m_2D$$

Instantaneous Rate = $-\frac{1}{n_1}\frac{d[A]}{dt} = -\frac{1}{n_2}\frac{d[B]}{dt}$
+1 $d[C]$ +1 $d[D]$

$$= \frac{+1}{m_1} \frac{d[C]}{dt} = \frac{+1}{m_2} \frac{d[D]}{dt}$$

Note In aqueous solution, the rate of reaction is not expressed in terms of change of concentration of water because there is a negligible change, e.g. from 55.5 M to 55.49 M.

Example 1. For the reaction $2A + 3B + \frac{3}{2}C \rightarrow 3P$, which statement is correct ? (JEE Main 2020)

(a)
$$\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$$
 (b)
$$\frac{dn_A}{dt} = \frac{3}{2}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$$

(c)
$$\frac{dn_A}{dt} = \frac{dn_B}{dt} = \frac{dn_C}{dt}$$
 (d)
$$\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{4}{3}\frac{dn_C}{dt}$$

Sol. (*d*) For a reaction, $2A + 3B + \frac{3}{2}C \longrightarrow 3P$ For a reaction, aA + bB = cCRate of reaction,

$$\Rightarrow \qquad \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt}$$

... For given reaction,

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

Example 2. NO₂ required for a reaction is produced by the decomposition of N_2O_5 in CCl₄ 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 NO₂ is (JEE Main 2019)

(a) $4.167 \times 10^{-3} \text{ mol } \text{L}^{-1} \text{ min}^{-1}$ (b) $1.667 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ min}^{-1}$ (c) $8.333 \times 10^{-3} \text{ mol } \text{L}^{-1} \text{ min}^{-1}$ (d) $2.083 \times 10^{-3} \text{ mol } \text{L}^{-1} \text{ min}^{-1}$

Sol. (*b*) The rate of a chemical reaction means the speed with which the reaction takes place.

For
$$R \longrightarrow P$$

Rate of disappearance of $R = \frac{\text{Decrease in conc. of } R}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t}$
Rate of appearance of $P = \frac{\text{Increase in conc. of } P}{\text{Time taken}} = +\frac{\Delta[P]}{\Delta t}$

Given, $[N_2O_5]_{initial} = 3.00 \text{ mol } L^{-1}$

After 30 min, $[N_2O_5] = 2.75 \text{ mol } L^{-1}$

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

t = 30 2.75 M

From the equation, it can be concluded that

and

$$\frac{1}{2} \times \frac{-\Delta[N_2O_5]}{\Delta t} = \frac{1}{4} \times \frac{\Delta[NO_2]}{\Delta t}$$

$$= \frac{-\Delta[N_2O_5]}{\Delta t} = \frac{-(2.75 - 3.00) \text{ mol } \text{L}^{-1}}{30} \Rightarrow \frac{0.25}{30}$$

$$\frac{\Delta[NO_2]}{\Delta t} = -2 \frac{\Delta(N_2O_5)}{\Delta t} \Rightarrow \frac{\Delta[NO_2]}{\Delta t} = 2 \times \frac{0.25}{30}$$

$$= 1.667 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ min}^{-1}$$

Calculation of Rates by Graphical Method

To calculate rate, a graph is plotted between the concentration and time.

Then, rate is calculated as



Average rate =
$$\frac{\Delta x}{\Delta t} = \frac{C_2 - C_1}{t_2 - t_1}$$
; Instantaneous rate = $\frac{OP}{OQ}$

Units of Rate of Reaction

Rate of reaction has the units of concentration or molarity divided by time. Therefore,

Unit of rate of reaction $=\frac{\text{Unit of concentration}}{\text{Unit of time}}$

= mol L^{-1} s⁻¹ or mol L^{-1} min⁻¹

In case of gaseous reactions, the units of rate of reaction becomes atmosphere/sec or atmosphere/min etc.

Factors Affecting Rate of Reaction

The factors which affect the rate of reaction are as follows

- (i) **Concentration of reactants** An increase in concentration of reactant increase the reaction rate.
- (ii) Nature of Reactants The nature of bonds in a molecule influences the rate of reaction at which it changes into products.
- (iii) Temperature Reaction rates are normally favoured by increase of temperature. The temperature effect is expressed in terms of temperature coefficient which is the ratio of the velocity constant of a reaction at two temperature differing by 10°C.

 $\text{Temperature coefficient} = \frac{k_{(t+10)^{\circ}\text{C}}}{k_{t^{\circ}\text{C}}}$

For most of the reactions, the rate is doubled for every 10°C rise in temperature.

(iv) Presence of catalyst A catalyst is a substance which alters the reaction rate but itself remains unchanged in amount and chemical composition at the end of the reaction. Actually the reactants in a reaction have to cross an energy barrier to form the product. The higher the energy barrier, the slower is the reaction rate.

A catalyst provides a new reaction path with a lower energy barrier. So, that more and more reactant molecules can form the product.

- (v) **Surface area of reactants** The rate of reaction increases as the surface area of the reactant increases.
- (vi) **Presence of light** Reaction rate normally becomes faster in the presence of light. Light gives the necessary activation energy for starting the reaction.

Rate Law and Rate Constant

The mathematical relation between the rate of reaction and the concentration of the reactants is termed as the Rate Equation or Rate Law Expression.

The rate law for a given reaction has to be established by experimental study of the rate over a wide range of concentration of the reactants. The rate law thus established is also called **differential rate equation** or **rate expression**. If we consider the reaction

or

$$A + B \longrightarrow$$
 products

Now, if $[A]^{\alpha}$ and $[B]^{\beta}$ are the molar concentrations of A and B respectively, then

$$\operatorname{Rate} \propto [A]^{lpha} \, [B]^{eta}$$

Rate = $k[A]^{\alpha}[B]^{\beta}$

here, k = velocity constant or rate constant

Now, if all concentrations are taken as unity, i.e.

$$[A] = [B] = 1 \text{ mol } /L$$
 then
$$\operatorname{Rate} = k$$

Thus, **rate constant** is defined as the rate of the reaction when the concentration of each reactant is taken as unity. It is also known as specific reaction rate.

Different characteristics of rate constant are given below

- It is the measure of the rate of reaction. Greater is the value of rate constant, faster is the reaction.
- Each reaction has a particular value of rate constant at a particular temperature.
- The value of rate constant for a particular reaction changes with temperature.
- The value of rate constant for a reaction does not depend upon the concentration of the reactants.

Unit of Rate Constant

Since the dimensions of rate are concentration/time and the SI units for concentration are mol m^{-3} , mol dm^{-3} or mol L^{-1} and second for time.

For the *n*th order of a reaction,

$$nA \longrightarrow \text{Product}$$

$$\text{Rate} = k[A]^n.$$

$$k = \frac{\text{Rate}}{[A]^n}$$

Thus, the dimensions of k are equal to

 $\frac{\text{Concentration / Time}}{[\text{Concentration}]^n} = [\text{Concentration}]^{1-n} \ [\text{Time}]^{-1}$ $= (\text{mol})^{1-n} \ \text{L}^{n-1} \ \text{s}^{-1}$

where, n = order of reaction.

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Units of Rate Constants for Gaseous Reactions

In case of gaseous reactions, concentrations are expressed in terms of pressure in the units of atmosphere. Thus, the rate has the units of atm per second. Now, the unit of different rate constants would be listed in the following table.

Units of Rate Constant

Order	Unit of rate constant	for gaseous reactions
0	$\frac{(mol \ L^{-1})}{s} \times \frac{1}{(mol \ L^{-1})^0} = mol \ L^{-1}s^{-1}$	atm s^{-1}
1	$\frac{(mol \ L^{-1})}{s} \times \frac{1}{(mol \ L^{-1})} = s^{-1}$	s ⁻¹
2	$\frac{(mol \ L^{-1})}{s} \times \frac{1}{(mol \ L^{-1})^2} = mol^{-1} Ls^{-1}$	$atm^{-1} s^{-1}$
п	$\frac{(\text{mol } L^{-1})}{\text{s}} \times \frac{1}{(\text{mol } L^{-1})^n} = (\text{mol } / L)^{1-n} \text{s}^{-1}$	$\operatorname{atm}^{1-n} \operatorname{s}^{-1}$
	Order 0 1 2 n	Order Unit of rate constant 0 $\frac{(\text{mol } \text{L}^{-1})}{\text{s}} \times \frac{1}{(\text{mol } \text{L}^{-1})^0} = \text{mol } \text{L}^{-1}\text{s}^{-1}$ 1 $\frac{(\text{mol } \text{L}^{-1})}{\text{s}} \times \frac{1}{(\text{mol } \text{L}^{-1})} = \text{s}^{-1}$ 2 $\frac{(\text{mol } \text{L}^{-1})}{\text{s}} \times \frac{1}{(\text{mol } \text{L}^{-1})^2} = \text{mol}^{-1} \text{Ls}^{-1}$ n $\frac{(\text{mol } \text{L}^{-1})}{\text{s}} \times \frac{1}{(\text{mol } \text{L}^{-1})^n}$ = (\text{mol } / \text{L})^{1 - n} \text{s}^{-1} = mol^{1 - n} \text{L}^{n - 1} \text{s}^{-1}

Molecularity of Reaction

It can be defined as "The number of atoms or molecules which collide together at the same time for the reaction to occur".

Reactions are classified in terms of molecularity as unimolecular, bimolecular, termolecular, trimolecular depending upon the number of molecules involved in the reaction.

Example of these reactions are as follows Unimolecular reaction,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Bimolecular reaction,

$$CH_3COOC_2H_5 + NaOH \implies CH_3COONa + C_2H_5OH$$

Termolecular reaction,

$$2 \text{FeCl}_3 + \text{SnCl}_2 \longrightarrow 2 \text{FeCl}_2 + \text{SnCl}_4$$

Remember Only a few termolecular reactions are known while no reaction having molecularities more than three is known because more than three molecules may not mutually collide with each other.

Determination of Molecularity

In case of simple reactions (elementary reactions), the molecularity is simply the sum of the molecules of different reactants as represented by the balanced chemical equation, e.g.

$$\begin{array}{cccc} {\rm O}_2{\rm F}_2 \longrightarrow {\rm O}_2 + {\rm F}_2 & ({\rm Unimolecular}) \\ \\ 2{\rm HI} \longrightarrow {\rm H}_2 + {\rm I}_2 & ({\rm Bimolecular}) \\ \\ 2{\rm NO} + {\rm O}_2 \longrightarrow 2{\rm NO}_2 & ({\rm Termolecular}) \end{array}$$

In case of complex reactions (multistep reactions) the slowest step is the rate determining step.

So atoms, molecules or ions participating in this rate determining step, determine the molecularity of the reaction.

e.g. Consider the reaction,

 HBrO_3 + 6HI \longrightarrow HBr + 3H₂O + 3I₂

The reaction takes place through following steps

$$\begin{array}{l} \text{HBrO}_3 + \text{HI} \xrightarrow{\text{Slow}} \text{HBrO}_2 + \text{HIO} \\ \\ \text{HBrO}_2 + 4 \text{HI} \xrightarrow{\text{Fast}} \text{HBr} + 2 \text{H}_2 \text{O} + 2 \text{I}_2 \\ \\ \end{array}$$

$$HIO + HI \xrightarrow{I \text{ use}} H_2O + I_2$$

Here, 2 molecules participate in the slowest step, thus reaction is of bimolecular type.

Characteristics of Molecularity

- Molecularity of a reaction is always a whole number. It can never be fractional or zero.
- It does not provide any idea about the rate or mechanism of the reaction.
- Molecularity is defined just for elementary reactions not for complex reactions.

Order of Reaction

In chemical kinetics the reactions are generally classified in terms of their order. The order of a reaction is defined as "The sum of the concentration terms on which the rate of a reaction actually depends as observed experimentally".

Or

"The order of reaction is given as the sum of the exponents (powers) to which the concentration terms in the rate law equation are raised to express the observed rate of the reaction." In the reaction rate expression,

Rate =
$$k[A]^{\alpha} [B]^{\beta}$$

the sum $\alpha + \beta =$ order of reaction

Order of reaction is purely experimental quantity. It may be whole number, zero or in fractions. Depending upon whether $\alpha + \beta$ is equal to zero, 1, 2 or 3, the reactions are said to be of zero order, first order, second order or third order respectively.

Remember

- Order of a reaction can change with change in conditions such as temperature, pressure etc.
- When one of the reactants is present in large excess, the second order rate expression becomes a first order rate expression because the value of change in concentration for other reactant is taken as negligible.

The main differences between molecularity and order of reaction are tabulated below.

Difference between	Order and	l Molecularity
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Molecularity	Order of reaction
It is the total number of reacting species (molecules, atoms or ions) which bring the chemical change.	It is the sum of powers of molar concentrations of the reacting species in the rate equation of the reaction.
It is a theoretical concept.	It is experimentally determined.
It is always a whole number.	It may be a whole number, zero, fractional, positive or negative.
It is meaningful only for simple reactions or individual steps of a complex reaction.	It is meant for the reaction and not for its individual steps.

Differential and Integral Forms of Different Order Reactions

For a general reaction,

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

Rate $= \frac{-d[R]}{dt} = k[A]^{\alpha} [B]^{\beta}$

This form of the equation is called **differential rate** equation. It relates the rate of change of concentration with time or instantaneous rate. It is measured by the determination of the slope of the tangent at point t in the concentration *versus* time curve. This makes it difficult to determine the rate law and hence, the determination of the order of the reaction.

In order to avoid this difficulty, we can integrate the rate equation and obtain integrated rate equation that gives a relation between directly measured experimental quantities, i.e. concentrations at different times. The integrated rate equations are different for reactions of different orders.

Zero Order Reactions

Reactions in which the concentration of reactants do not change with time and the rates remain constant throughout are said to be zero order reactions. For the reaction,

$$A \xrightarrow{k} \text{products}$$

$$[A]_t = [A]_0 - kt \qquad \dots (i)$$

$$k = \frac{1}{t} \{ [A]_0 - [A]_t \}$$

or,

where, $[A]_t$ = concentration of 'A' at any time 't'

 $[A]_0 = initial concentration of 'A'$

k =rate constant of zeroth order reaction

Characteristics of Zero Order Reactions

• Any reaction of zero order must obey Eq. (i)

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

This shows that the plot of concentration of reactants against time will be a straight line.

- Also, as the rate is independent of concentration, the plot of rate *versus* concentration will be a straight line parallel to the concentration axis.
- The units of rate constant for zero order reaction is mol L^{-1} time⁻¹.
- The time required to reduce the initial concentration of the reactant to half of its initial value is called **half-life time** or **half-life period** and is denoted by t_{U2} . When $[A] = [A]_0/2, t = t_{U2}$, substituting these values in Eq. (i), we get

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

Thus, the half-life period of zero order reaction is directly proportional to initial concentration, *i.e.*, $t_{1/2} \propto [A]_0$.

Remember

or

- In zero order reaction, it is the amount of reactant that changes and not the reaction rate.
- The rate of reaction remains constant throughout the course of the reaction.



Plot of rate versus concentrations for the reaction of zero order

Some Examples of Zero Order Reactions

• Photochemical synthesis of HCl, i.e.

$$H_2(g) + Cl_2(g) \xrightarrow{n_V} 2HCl$$

• Decomposition of ammonia in the presence of a catalyst, i.e.

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

First Order Reactions

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The first order reaction is defined as "The reaction in which the reaction rate is determined by the change of one concentration term of the reactant only".

For the reaction,

$$A \xrightarrow{k} \text{products}$$

$$[A]_{t} = [A]_{0} e^{-kt} \qquad \dots(i)$$

$$k = \frac{2.303}{t} \log \frac{[A]_{0}}{[A]_{t}}$$

 $k = \frac{2.303}{t} \log \frac{a_0}{a_0 - x}$

where, $[A]_0 = a_0 = initial concentration$

 $[A]_t = a_0 - x =$ concentration of 'A' at any time 't'

k = rate constant for 1st order reaction

x = amount of 'A ' reacted at time 't '

Characteristics of First Order Reactions

• Any reaction of the first order must obey above equation which can also be written as,

$$\log [A] = \frac{-kt}{2.303} + \log [A]_0$$

This is the equation of a straight line (y = mx + c)

Thus, if $\log [A]$ or $\log (a - x)$ values are plotted against time *t*, the graph obtained should be a straight line.

The intercept on *y*-axis would be log $[A]_0$ and the slope of the line would be equal to $\left(\frac{-k}{2.303}\right)$, i.e. slope = $\frac{-k}{2.303}$



Plot of log
$$[A]$$
 vs time (t)

Thus, if we plot $\log \frac{|A|_0}{|A|}$ versus *t*, a staight line graph

will be obtained with slope
$$=\frac{\kappa}{2.303}$$
 as shown belown,



• The time taken for the completion of same fraction of change, i.e. half-life is independent of initial concentration. e.g. For half change,

$$x = 0.5a \text{ and } t = t_{1/2}$$

so,
$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{0.5a} = \frac{2.303}{t_{1/2}} \log 2 = \frac{0.693}{t_{1/2}}$$

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

Thus, $t_{1/2}$ is independent of initial concentration *a*.

• Since, the rate is dependent of concentration, the unit of k will be time⁻¹, i.e. s⁻¹ or h⁻¹.

or

- Average life (λ) = $\frac{1}{k} = \frac{t_{1/2}}{0.693} = 1.443 t_{1/2}$
- Relation between $t_{1/2}$ and $t_{x\%}$ (amount decomposed)

$$t_{x\% \text{ decomposes}} = \frac{2.3}{k} \log \left(\frac{100}{100 - x} \right)$$

Divide Eq. (vi) by (viii),

$$\frac{t_{1/2}}{t_{x\%}} = \frac{0.3}{\log\left(\frac{100}{100 - x}\right)}$$

Examples of First Order Reactions

• Decomposition of H₂O₂,

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

- Dissociation of N_2O_5 , $2N_2O_5 \longrightarrow 4NO_2 + O_2$
- Hydrolysis of methyl acetate, $CH_3COOCH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3OH$
- Inversion of cane sugar,

$$\begin{array}{ccc} \mathrm{C}_{12}\mathrm{H}_{22}\mathrm{O}_{11} & \xrightarrow{\mathrm{H}_{2}\mathrm{O}/\mathrm{H}^{+}} & \mathrm{C}_{6}\mathrm{H}_{12}\mathrm{O}_{6} & +\mathrm{C}_{6}\mathrm{H}_{12}\mathrm{O}_{6} \\ \mathrm{Sucrose} & & \mathrm{Glucose} & \mathrm{Fructose} \end{array}$$

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

 $^{226}_{88}$ Ra $\longrightarrow ^{4}_{2}$ He + $^{222}_{86}$ Rn

Rate = k (Ra)

If, N_0 = atoms of the radioactive element present initially N = atoms of the radioactive element present after time t

then.

 $K = \frac{2.303}{t} \log \frac{N_{\rm o}}{N}$

where, K =disintegration or decay constant and half-life $(t_{1/2}) = \frac{0.693}{K}$

Thus, half-life period of a radioactive element is independent of the initial amount of the element.

Example 3. During the nuclear explosion, one of the products is ⁹⁰Sr with half-life of 6.93 years. If 1 µg of ⁹⁰Sr was absorbed in the bones of a newly born baby in place of Ca, how much time, in years is required to reduce it by 90% if it is not lost metabolically (JEE Main 2020)

Sol. (23.03) Radioactive decay follows first order kinetics.

 \therefore Time taken for decay from N_0 to N_t is

(N =number of nuclei)

$$t = \frac{1}{\lambda} \ln \frac{N_0}{N_t}$$

$$t = \frac{1}{\lambda} \times 2.303 \log \frac{N_0}{N_t} \qquad \dots (i)$$

0.693 Also, we know $\lambda = (decay \ constant) =$

where, $t_{1/2} = 6.93$ yr (given)

...

...

Also, we know 90% nuclei are decayed

$$\therefore \qquad \frac{N_0}{N_t} = \frac{100}{10} = 10$$
Put the values of λ and $\frac{N_0}{N_t}$ in Eq. (i), we get

$$t = \frac{6.93}{0.693} \times 2.303 \times \log 10 = 23.03 \text{ (yr)}$$

Example 4. The reaction, $2 \times A \rightarrow B$ is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of X is 0.5 M, the time required to reach its final concentration of 0.2 M will be (JEE Main 2019)

Sol. (b) For zero order reaction, $[A_0] - [A_t] = kt$...(i)

where, $[A_0] =$ initial concentration

 $[A_t]$ = final concentration at time 't' k = rate constant

Also, for zero order reaction,
$$t_{1/2} = \frac{[A_0]}{2k}$$

Given,
$$t_{1/2} = 6$$
 h and $[A_0] = 0.2 M$
 $\therefore \qquad 6 = \frac{0.2}{2k} \text{ or } k = \frac{0.2}{2 \times 6} = \frac{1}{60}$
Now, from Eq. (i)
 $[A_0] - [A_t] = kt$
Given, $[A_0] = 0.5 M$, $[A_t] = 0.2 M$
 $\therefore \qquad 0.5 - 0.2 = \frac{1}{60} \times t$
 $0.3 = \frac{1}{60} \times t$
 $\Rightarrow \qquad t = 0.3 \times 60 = 18 \text{ h}$

Example 5. Decomposition of H₂O₂ follows a first order reaction. In 50 min, the concentration of H₂O₂ decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H₂O₂ reaches 0.05 M, the rate of formation of O_2 will be (JEE Main 2016)

(a)
$$6.93 \times 10^{-4}$$
 mol min⁻¹ (b) 2.66 L min⁻¹ at STP
(c) 1.34×10^{-2} mol min⁻¹ (d) 6.93×10^{-2} mol min⁻¹

Sol. (a) For first order reaction, $k = \frac{2.303}{t} \log \frac{a}{a-x}$ Given, t = 50 min, a = 0.5 M, a - x = 0.125 M $k = \frac{2.303}{50} \log \frac{0.5}{0.125} = 0.0277 \,\mathrm{min}^{-1}$ *.*.. Now, as per reaction $2H_2O_2 \longrightarrow 2H_2O + O_2$ $-\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt} = \frac{d[O_2]}{dt}$

Rate of reaction,
$$-\frac{d [H_2O_2]}{dt} = k [H_2O_2]$$

 $\therefore \qquad \frac{d [O_2]}{dt} = -\frac{1}{2} \frac{d [H_2O_2]}{dt} = \frac{1}{2} k [H_2O_2] \qquad \dots (i)$

When the concentration of $[H_2O_2]$ reaches 0.05 M,

or
$$\frac{d[O_2]}{dt} = \frac{1}{2} \times 0.0277 \times 0.05$$
 [from Eq. (i)]
$$\frac{d[O_2]}{dt} = 6.93 \times 10^{-4} \text{ mol min}^{-1}$$

Alternative Method

In fifty minutes, the concentration of $\rm H_2O_2$ decreases from 0.5 to 0.125 M or in one half-life, concentration of $\rm H_2O_2$ decreases from 0.5 to 0.25 M. In two half-lives,

concentration of H_2O_2 decreases from 0.5 to 0.125 M or $2 t_{1/2} = 50 \text{ min}$ $t_{1/2} = 25 \text{ min} \Rightarrow k = \left(\frac{0.693}{25}\right) \text{min}^{-1}$

or

$$\frac{d[O_2]}{dt} = -\frac{1}{2} \frac{d[H_2O_2]}{dt} = \frac{k[H_2O_2]}{2}$$
$$= 6.93 \times 10^{-4} \text{ mol min}^{-1}$$

Typical First Order Gas Phase Reactions

Consider a typical first order gas phase reaction

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

Let p_0 be the initial pressure of A at time t = 0 and p_t is the total pressure at time *t*. Total pressure $(p_t) = p_A + p_B + p_C$ (pressure units), where p_A , p_B , and p_C are the partial pressures of *A*, *B* and *C*, respectively.

If *x* atmosphere be the decrease in the pressure of *A* at time *t* and one mole each of *B* and *C* is being formed, then increase in the pressure of *B* and *C* will also be *x* atm each.

$$A(g) \longrightarrow B(g) + C(g)$$
At $t = 0$
 p_0 atm
 0 atm
 0 atm
 0 atm
At time t
 $(p_0 - x)$ atm
 x atm
 x atm
 $p_t = p_0 + x$
and
 $x = (p_t - p_0)$
where, and
 $p_A = 2p_0 - p_t$
 $k = \left(\frac{2.303}{t}\right) \left(\log \frac{p_0}{p_A}\right)$
or
 $= \frac{2.303}{t} \log \frac{p_0}{(2p_0 - p_t)}$
...(i)

Example 6 The following data were obtained during the first order thermal decomposition of $N_2O_5(g)$ at constant volume.

$2N_2O_5$	$(g) \longrightarrow 2N$	$V_2O_4(g) + $	O ₂ (g)
Time	(s) Tota	I pressure (at	tm)
0		0.5	
100		0.512	
Calculate the rate co	nstant.		(NCERT Exemplar)
(a) $3.39 \times 10^{-4} \text{ s}^{-1}$	1 (b) 1.39 ×10	$^{-5}$ s ⁻¹

(d) $4.98 \times 10^{-4} \text{ s}^{-1}$

(c) $5.45 \times 10^{-4} \text{ s}^{-1}$

Sol. (*d*) Let the pressure of $N_2O_5(g)$ decreases by 2x atm. As 2 moles of N_2O_5 decompose to give 2 moles of $N_2O_4(g)$ and 1 mole of $O_2(g)$, the pressure of $N_2O_4(g)$ increases by 2x atm and that of $O_2(g)$ increases by x atm.

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$
When, $t = 0$ 0.5 atm 0 atm 0 atm
At time t (0.5 - 2 x) atm 2 x atm x atm
Total pressure (p_t) = $p_{(N_2O_5)} + p_{(N_2O_4)} + p_{(O_2)}$
= (0.5 - 2 x) + 2 x + x
= 0.5 + x
 \therefore $x = p_t - 0.5$
 $p_{N_2O_5} = 0.5 - 2x$
= 0.5 - 2($p_t - 0.5$)
= 1.5 - 2 p_t
At $t = 100$ s; $p_t = 0.512$ atm
 $p_{(N_2O_5)} = 1.5 - 2 \times 0.512 = 0.476$ atm
 \therefore $k = \frac{2.303}{t} \log \left(\frac{p_0 (N_2O_5)}{p_A (N_2O_5)} \right)$
= $\frac{2.303}{100 \text{ s}} \log \left(\frac{0.5 \text{ atm}}{0.476 \text{ atm}} \right)$
= $\frac{2.303}{100 \text{ s}} \times 0.02136$
= $4.92 \times 10^{-4} \text{ s}^{-1}$

Direct or Indirect Estimation of Reactants

Sometimes volumes of reagents are given in volumetric analysis (when one of the reactant is estimated directly or indirectly, i.e. when V_{∞} is not given).

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

where, $V_0 =$ volume of the reagent used at time t = 0

 V_t = volume of the reagent used at time t

 V_{∞} = volume of reagent used at infinite time or when the reaction ends

For example, $2H_2O_2 \longrightarrow 2H_2O(l) + O_2(g)$

The rate of this first order reaction is measured by titrating a fixed volume of $\rm H_2O_2$ against a standard solution of $\rm KMnO_4$

Example 7 In the dehydration of oxalic acid by conc.
$$H_2SO_4$$

$$(COOH)_2 \longrightarrow CO + CO_2 + H_2O$$

2 mL of the solution was withdrawn at different times and titrated against 0.1 N KMnO₄ solution. Find the order of reaction.

Time (mins)		0	300	450	600
Vol of KMnO ₄ use	ed (mL)	22.0	17.0	15.0	13.4
(a) 0	(b) 1	(c) 2	(d) 3	

Sol. (b) Here, $KMnO_4$ act as oxidising agent and $(COOH)_2$ act as reducing agent. The volumes of $KMnO_4$ used for $(COOH)_2$ after regular internals of time are given in question.

Volume of KMnO₄ at t = 0 corresponds to volume of (COOH)₂ initially present $C_0 \propto V_0$

Volume of KMnO₄ used at time t_1, t_2, t_3, \dots corresponds to volume of (COOH)₂ remaining after t_1, t_2, t_3, \dots

Now, using the above expression if we calculate the values of k for different intervals t_1, t_2, \ldots, t_k (for given data), the values of k should be same if the reaction follow first order kinetics.

$$(\text{COOH})_2 \longrightarrow \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$$

$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$
(i) $k = \frac{2.303}{300} \log \frac{22}{17} = \frac{2.303 \times 0.119}{300} = 0.00085 \text{ min}^{-1}$
(ii) $k = \frac{2.303}{450} \log \frac{22}{15} = 0.00085 \text{ min}^{-1}$
(iii) $k = \frac{2.303}{600} \log \frac{22}{13.4} = 0.00085 \text{ min}^{-1}$

The value of *k* is constant. Hence, the reaction is of first order.

Direct or Indirect Estimation of Products

Consider a condition when one of the product is estimated directly or indirectly, i.e. when V_0 is not given.

For general equation, $A \longrightarrow B + C$

At time, t = 0, volume of reactant = 0

time $t = \infty$ means end of a reaction.

At time $t = \infty$, $V = V_{\infty}$, this corresponds to initial volume of reactant

Here $x = V_t$ (product formed) $C_0 - x = V_{\infty} - V_t$

:. Hence, from first order kinetics, $k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t}$

For example, in the decomposition of NH_4NO_2 , the volume of N_2 is directly measured at different intervals of time

Hydrolysis of Ester (CH₃COOR') in Acidic Medium

When V_0 is not given

Let
$$[V_{\infty} - V_0 = C_0 \text{ and } V_{\infty} - V_t = C_t]$$

When
$$t = t_1$$
, then

$$k = \frac{2.303}{t_1} \log \frac{C_0}{C_{t_1}} \qquad \dots (i)$$

Similarly, when $t = t_2$

$$k = \frac{2.303}{t_2} \log \frac{C_0}{C_{t_2}} \qquad \dots (ii)$$

Operating Eq. (i) - Eq. (ii), we get

or
$$k = \frac{2.303}{(t_1 - t_2)} \log \frac{C_{t_2}}{C_{t_1}}$$
 ...(iii)

Inversion of Sugar Cane

$$k = \frac{2.303}{t} \log \frac{r_o - r_\infty}{r_c - r_\infty}$$

where, $r_o =$ initial optical rotation of sugar cane

- $r_t = optical rotation after time t$
- r_{∞} = optical rotation at infinite time (at the end of reaction)

Example 8 Methyl acetate is hydrolysed with 0.1 N HCl at 25°C. 5 mL of the reacting mixture is withdrawn at various time intervals and is quickly titrated with 1.0 N NaOH. The volumes of NaOH consumed are as follows

Time (s)	339	1242	2745	4546	00
Volume of NaOH (mL)	26.34	27.80	29.70	31.81	39.81

Find the average rate constant (k).

(a) $4.29 \times 10^{-4} \text{ s}^{-1}$	(b) $3.29 \times 10^{-4} \text{ s}^{-1}$
(c) $8.68 \times 10^{-4} \text{ s}^{-1}$	(d) $1.23 \times 10^{-4} \text{ s}^{-1}$

Sol. (d) CH_3COOR' (Ester) + H_2O + $HCl(H^{\oplus}) \longrightarrow$

$$CH_3COOH + R'OH$$

The reaction rate is measured by titrating the acid (CH₃COOH) produced against a standard alkali solution.

Note that when a test sample is prepared from the reacting mixture, there are two acids : one is mineral acid H^{\oplus} (HCl or any other) and second is CH₃COOH produced. So, the volume of alkali used gives the titration value for both acids.

When V_0 is given,

At t = 0, V_0 is the volume NaOH used to neutralise the mineral acid present (H^{\oplus}) being used as catalyst

(At t = 0, no CH₃COOH is yet produced)

At $t = \infty$ (i.e. at the end of hydrolysis), V_{∞} is the volume of NaOH used to neutralise whole of CH₃COOH plus the volume of HCl present. At $t = \infty$, the volume of CH₃COOH corresponds to the volume of ester taken initially.

 $\Rightarrow c_0 \propto V_{\infty} - V_0$ (as $V_0 \equiv$ volume of HCl)

At $t = t_1, t_2, t_3, ..., V_1, V_2, V_3, ...$ correspond to the volume of HCl plus the volume of CH₃COOH being produced.

$$\begin{array}{ll} \Rightarrow & x \propto V_t - V_0 \\ \Rightarrow & c_0 - x \propto (V_\infty - V_0) - (V_t - V_0) \\ \Rightarrow & c_0 - x \propto V_\infty - V_t \end{array}$$

Hence, from the first order kinetics, it follows

$$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_1}$$

For ester hydrolysis, equation

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

Since, V_0 is not given

or
$$k = \frac{2.303}{(t_1 - t_2)} \log \frac{c_{t_2}}{c_{t_1}}$$

Now, find c_t .

t	339 s	1242 s	2745 s	4546 s
$c_t = V_{\infty} - V_t$	39.81 – 26.34 = 13.47 mL	39.81 – 27.80 ≈12.0 mL	39.81 – 29.70 = 10.11 mL	39.81 – 31.81 = 8.0 mL
and	$t_1 - t_2 =$	339 - 1242 =	-903 s	
	$t_1 - t_3 =$	339 - 2745 =	-2406 s	
	$t_1 - t_4 =$	339 - 4546 =	-4207 s	
Using relation	on given in Eq.	(iii) <i>,</i>		
	$k_1 = \frac{2.303}{-903} \log \frac{1}{2}$	$\frac{12.0}{13.47} = -0.00$)25 ×log (0.8	89)
	=-0.0025 ×	-0.0506 = 1.	$27 \times 10^{-4} \text{ s}^{-1}$	1
	$k_2 = \frac{2.303}{-2406} \log \frac{1}{2}$	$\frac{10.11}{13.47} = -0.0$	095 ×log (0	.75)
	= -0.00095	$\times -0.1249 = 1$	$.19 \times 10^{-4}$ s	-1

$$= -0.00095 \times -0.1249 = 1.19 \times 10^{-4}$$

$$k_3 = \frac{2.303}{-4207} \log \frac{8.0}{13.47} = -0.00054 \times \log (0.59)$$
$$= -0.00054 \times -0.2291 = 1.23 \times 10^{-4} \text{ s}^{-1}$$
$$k_{\text{average}} = 1.23 \times 10^{-4} \text{ s}^{-1}$$

Second Order Reactions

The reaction is said to be of second order, if its reaction rate is determined by the variation of two concentration terms of reactants.

For the reaction.

or

$$2A \longrightarrow \text{product}$$
$$A + B \longrightarrow \text{product}$$

If the initial concentrations of both 'A' and 'B' are

$$k = \frac{1}{t} \times \frac{x}{a_0(a_0 - x)}$$

In case, the concentrations are not equal,

$$k = \frac{2.303}{t(a-b)} \log \frac{b_0(a_0 - x)}{a_0(b_0 - x)}$$

where, a_0 = initial concentration of 'A'

$$b_0 =$$
initial concentration of 'B'

x = amount of 'A' or 'B' reacted

The units of
$$k$$
 are given as L mol⁻¹ time⁻¹

The time required to complete a certain fraction of the reaction is inversely proportional to the initial concentration of reactants in the case of second order reactions.

Some examples of second order reactions are

(i) Dissociation of HI,

$$2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$$

(ii) Saponification of ethyl acetate

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COO^-Na^+ + C_2H_5OH$$

(iii) Reaction between NO and O_3 ,

$$NO + O_3 \longrightarrow NO_2 + O_3$$

(iv) Reaction between potassium persulphate and potassium iodide.

$$K_2S_2O_8 + 2KI \longrightarrow 2K_2SO_4 + I_2$$

Third Order Reactions

A reaction is said to be of third order if its rate is determined by the variation of three concentration terms. The units of rate constant for third order reaction are $L^2 \text{ mol}^{-2} \text{ time}^{-1}$.

Reactions of third and higher orders are rare, but some examples of 3rd order reactions are definitely seen. This is due to the fact that the probability of trimolecular collisions is much less as compared to unimolecular or bimolecular collisions.

Examples of third order reactions are

(i) $2NO + O_2 \longrightarrow 2NO_2$ (ii) $2NO + X_2 \longrightarrow 2NOX$ (where, X = Halogen)

(iii) $2CH_3COOAg + HCOONa \longrightarrow 2Ag + CO_2$ + CH₃COOH + CH₃COO⁻Na⁺

Reactions Involving Order in Fraction

There are some reactions, rate of which is expressed by fractions of concentration terms. e.g.

(i)
$$\operatorname{CO} + \operatorname{Cl}_2 \longrightarrow \operatorname{COCl}_2$$

Rate = $k [\operatorname{CO}]^2 [\operatorname{Cl}_2]^{1/2}$
Order = 2.5
(ii) $\operatorname{COCl}_2 \longrightarrow \operatorname{Cl}_2 + \operatorname{CO}$
Rate = $k [\operatorname{COCl}_2]^{3/2}$
Order = 1.5
(iii) Reaction between H₂ and D₂

Rate =
$$k_p H_2 (p_{D_2})^{1/2}$$

The conversion of parahydrogen to orthohydrogen at high temperature; Rate = $k(p_{\rm H_2})^{1.5}$. The non-integer values are generally due to complex nature of reaction which involves more than one elementary step. The overall rate law is obtained by combining rates of individual elementary steps.



Differential Equations, Corresponding Integral Rate Equation, $t_{1/2}$, Unit of k and Nature of Plot of Various Reactions

Negative Order Reactions

Sometimes the rate of reaction decreases as the concentration of one of the constituent is increased, e.g. transformation of ozone into oxygen, i.e. $2O_3 \longrightarrow 3O_2$.

Consecutive or Sequential Reactions

A reactant (A) decomposes to (B), which in turn decomposes to (C), i.e.

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

For the above sequential reaction we have

$$[A] = [A]_0 e^{-kt} \qquad \dots (i)$$

$$[B] = [A]_0 \frac{k_1}{k_1} (e^{-k_1 t} - e^{-k_2 t}) \qquad \dots (ii)$$

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

(where,
$$[A]_0$$
 = initial concentration of (A)

[B] is maximum, when $\frac{d[B]}{dt} = 0$ On differentiation Eq. (iii), we get $t_{\text{max}} = \frac{2.303}{k_2 - k_1} \log \left[\frac{k_2}{k_1}\right]$

- Decomposition of ethylene oxide $(CH_2)O \xrightarrow{k_1} CH_3CHO \xrightarrow{k_2} CO + CH_4$
- Pyrolysis of acetone (CH₃)CO \longrightarrow CH₄ + CH₂=C=O $\xrightarrow{k_2}$ C₂H₄ + CO

Side or Parallel or Concurrent Elementary Reactions

A single reactant gives two products B and C simultaneously with different decay constants. For first order reaction,

$$A \xrightarrow{k_1} B(90\%) \text{ (Main reaction)}$$

$$\stackrel{k_2}{\longrightarrow} C(10\%) \text{ (Side reaction)}$$

If after a time interval say x M of B and y M of C are formed, then if reaction is carried out with A, when t = 0, [B] = [C] = 0.

$$\begin{aligned} & k_1 = (\% \text{ yield of } B) \times k_{av} \\ \Rightarrow & \% \text{ yield of } B = \frac{k_1}{k_{av}} = \frac{k_1}{k_1 + k_2} \\ & k_2 = (\% \text{ yield of } C) \times k_{av} \\ \Rightarrow & \% \text{ yield of } C = \frac{k_2}{k_{av}} = \frac{k_2}{k_1 + k_2} \end{aligned}$$

Some examples

(i) Phenol $\xrightarrow{\text{Nitration}} o$ -nitrophenol + *p*-nitrophenol

(ii)
$$C_2H_5Br + KOH \longrightarrow H_2C = CH_2 + KBr + H_2O$$

 $\longrightarrow C_2H_5OH + KBr$

Opposed or Reversible Elementary Reactions

The elementary reaction given below follows opposing or reversible kinetics.

Case I First order-opposed by first order

When concentration of B = 0 at time t = 0

$$A \stackrel{k_1}{\underset{k_2}{\longrightarrow}} B$$

Case II First order-opposed by first order

When concentration of *B* is not zero at t = 0

Let concentration of B at time zero be b

Formula for both the cases is

$$t = \frac{2.303}{(k_1 + k_2)} \log \frac{X_{\rm eq}}{X_{\rm eq} - x}$$

 $(X_{eq} = [B] \text{ formed a equilibrium})$

Some examples

(i)
$$H_2 + I_2 \xrightarrow{k_1} 2HI$$

Rate $= \frac{1}{2} \frac{d[HI]}{dt} = k_1 [H_2] [I_2] - k_2 [HI]^2$
(ii) $2NO_2 \xrightarrow{k_1} N_2O_4 - \frac{d[NO_2]}{dt} = 2k_1 [NO_2]^2 - k_2 [N_2O_4]$

Pseudomolecular Reactions

There are several reactions which are considered as unimolecular, although in reality they are bi-or tri-molecular, e.g. consider the hydrolysis of methyl acetate in the presence of acid

$$CH_3COOCH_3 + H_2O \xrightarrow{Acid} CH_3COOH + CH_3OH$$

According to the law of mass action, this reaction seems to follow bimolecular process with the rate dependent on concentration of both ester and water. However, it is found that the rate is independent of water, it depends only on concentration of ester.

This can be explained on the basis of the fact that here water is present in such excess that its concentration remains practically constant during the course of reaction. Hence, reactions showing such a behaviour are called **pseudounimolecular reactions** or **pseudo first order reactions**. **Example 9.** For an elementary chemical reaction,

$$A_{2} \xrightarrow{k_{1}}{\sum_{k_{-1}}} 2A \text{, the expression for } \frac{d[A]}{dt} \text{ is} \qquad \textbf{[JEE Main 2019]}$$
(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) $k_{1}[A_{2}] + k_{-1}[A]^{2}$

follows opposing or reversible kinetics, (i) Rate of the reaction,

(ii) Again, rate of the reaction can be expressed as,

$$f = -\frac{d[A_2]}{dt} = +\frac{1}{2}\frac{d[A]}{dt}$$

So, the rate of appearance of A,

i.e.
$$\frac{d[A]}{dt} = 2r = 2k_1[A_2] - 2k_{-1}[A]^2$$
 [From Eq. (i)]

Example 10 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)

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

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

 $0 = k_1[A] - k_2[B]$

(a)
$$k_1 k_2 [A]$$
 (b) $\left(\frac{k_1}{k_2}\right) [A]$
(c) $(k_1 - k_2) [A]$ (d) $(k_1 + k_2) [A]$

Sol. (b)

 \Rightarrow

Rate of formation of *B* is

$$\int \because \text{Given}, \frac{d[B]}{dt} = 0$$

 $\Rightarrow k_2[B] = k_1[A]$ $\Rightarrow \text{Concentration of } B, \ [B] = \frac{k_1}{k_2}[A]$

Methods of Determination of Order of Reaction

Several methods are used to determine order of a reaction, like initial rate method, integration method, half-life method, Ostwald isolation method, etc.

1. Integration Method or Hit and Trial Method

In this method a, x and t are determined and substituted in kinetic equations of various orders. The equation which gives the most constant value of rate constant for a series of time intervals is the one to which the order of reaction corresponds. In this method the kinetic equation used for same molar concentration are

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$
 for first order reactions
$$k = \frac{1}{t} \left[\frac{1}{a-x} - \frac{1}{a} \right]$$
 for second order reactions

In general for the reactions of n order, given as below,

$$nA \longrightarrow \text{products}$$

the rate equation of the form given below is obtained.

$$k_n = \frac{1}{t(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$$

This equation is applicable for all orders except first order.

2. Half-life Method or Fractional Change Method

The half-life period (time required to reduce the initial concentration to half of its value) depends differently on the initial concentrations of reactants for different orders of reactions, i.e.

For zero order reaction,

$$t_{1/2} \propto [A]_i$$

For first order reaction, $t_{1/2}$ is independent of initial concentration actually it depends upon the rate constant as,

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

and and similarly For *n* order reaction

 $t_{3/4} = 2 t_{1/2}$ $t_{94.9\%} = 10 t_{1/2}$

$$t_{1/2} \propto \frac{1}{[A]_i^{n-1}}$$

Starting with two independent reactions having initial concentrations a_1 and a_2 at corresponding half-lives $(t_{1/2})_1$ and $(t_{1/2})_2$ we have

or

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

By taking log on both the sides and rearranging the equation, we obtain

$$n = 1 + \frac{\log \left[(t_{1/2})_1 / (t_{1/2})_2 \right]}{\log \left(a_2 / a_1 \right)}$$

- From this equation, n, the order of reaction is calculated.
- For gaseous equations, the initial pressure (*p*) is taken instead of initial concentration *a*, thus, for them the above formula is changed to

$$n = 1 + \frac{\log\left[(t_{1/2})_1/(t_{1/2})_2\right]}{\log\left(p_2/p_1\right)}$$



Plots between half-life period and concentration

3. Ostwald Isolation Method

This method is employed in determining the order of **complicated reactions** by isolating one of the reactants. Suppose the reaction under consideration is

 $n_1A + n_2B + n_3C \longrightarrow \text{products}$

In this reaction for the determination of any of the reactants say A, rest of the reactants, i.e. B and C are taken in large excess, so that there is no change practically in their concentrations.

The order of the reaction for A is then determined by using any of the methods written before. The procedure is likewise for B and C also. e.g.

It is observed as follows

• Keeping the concentrations of *B* and *C* constant, if concentration of *A* is doubled, the rate of reaction becomes 4 times. This means that Rate $\propto [A]^2$

i.e. order of reaction with respect to *A* is 2.

• Keeping the concentrations of A and C constant, if concentration of B is doubled, the rate of reaction becomes 2 times. This means that

Rate
$$\propto [B]$$

i.e. order of reaction with respect to B is 1.

• Keeping the concentrations of A and B constant, if the concentration of C is doubled, the rate of the reaction remains unaffected. This means that rate is independent of concentration of C, i.e. order of reaction with respect to C is zero.

Hence, the overall rate law expression will be

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

Thus, order of reaction = 2 + 1 + 0 = 3

4. Initial Rate Method

In this method, the order of a reaction is determined by varying the concentration of one of the reactants while others are kept constant The initial rate, r_1 is determined either numerically or from the slope of the curve of concentration *versus* time.

Thus, for the reaction

$$aA + bB + cC \longrightarrow \text{product}$$
$$r_i = k [A_i]^a [B_i]^b [C_i]^c$$

Now, if [B] and [C] remain constant,

$$r_i = k_i [A_i]^a$$
 where, $k_i = k[B_i]^b [C_i]^c$

Here the value of a can be determined by inspecting the rate at different values of [A] as, it we know the initial rates at different concentration of A we have

$$[r_i]_1 = k_i [A_i]_1^a, \quad [r_i]_2 = k_i [A_i]_2^a$$

where, $[r_i]_1$ and $[r_i]_2$ are the initial rates of reaction and $[A_i]_1$, and $[A_i]_2$ are initial concentrations of *A*. On dividing both the equations, we get

$$\frac{[r_i]_1}{[r_i]_2} = \left[\frac{[A_i]_1}{[A_i]_2}\right]^c$$

Taking log on both the sides, we obtain

$$\log \frac{|r_i|_1}{[r_i]_2} = a \log \frac{|A_i|_1}{[A_i]_2},$$
$$a = \frac{\log [(r_i)_1/(r_i)_2]}{\log [(A_i)_1/(A_i)_2]}$$

In this way, the order of reaction with respect to a is determined. Similarly, it can also be determined for other reactants also, The overall order of reaction is the sum of all such orders, i.e. $n = a + b + c \dots$

Example 11. The following results were obtained during kinetic studies of the reaction

 $2A + B \longrightarrow products$

Experiment	[A] (in mol L ⁻¹)	[B] (in mol L ⁻¹)	Initial rate of reaction (in mol L^{-1} min ⁻¹)
Ι.	0.10	0.20	6.93×10^{-3}
11.	0.10	0.25	6.93×10^{-3}
III.	0.20	0.30	1.386×10^{-2}
la a tima a (ina t	animutaa) ma	arrived to an	nound half of A is

The time (in minutes) required to consume half of A is (JEE Main 2019) (a) 5 (b) 10 (c) 100 (d) 1

Sol. (b) Let, the rate expression is

 $r \propto [A]^a [B]^b$.

From experiment I,

$$\frac{r_2}{r_1} = \left(\frac{0.1}{0.1}\right)^a \times \left(\frac{0.25}{0.20}\right)^b$$

$$\Rightarrow \qquad \frac{6.93 \times 10^{-3}}{6.93 \times 10^{-3}} = 1 \times \left(\frac{5}{4}\right)^b$$

$$\Rightarrow \qquad 1 = \left(\frac{5}{4}\right)^b$$

$$\Rightarrow \qquad \left(\frac{5}{4}\right)^0 = \left(\frac{5}{4}\right)^b \Rightarrow b = 0$$

From experiment II,
$$\underline{c}_{r_1} = \left(\frac{1}{0.1}\right)^{-1} \times \left(\frac{1}{0.20}\right)^{-1}$$

 $\Rightarrow \qquad \frac{1.386 \times 10^{-2}}{0.693 \times 10^{-2}} = (2)^a \times (1.5)^0$
 $\Rightarrow \qquad 2 = 2^a \times 1 \Rightarrow 2^1 = 2^a \Rightarrow a = 1$

 $\Rightarrow \text{So}, \qquad r \propto [A]^{1}[B]^{0} \Rightarrow r \propto [A]$

Order of the reaction (n) = 1

 \Rightarrow Now, let for the 1st experiment, $r_{r} = k \cdot [A]$

$$\Rightarrow \qquad k = \frac{r_1}{[A]} = \frac{6.93 \times 10^{-3}}{0.1}$$
$$= 6.93 \times 10^{-2} \text{ s}^{-1}$$
$$\Rightarrow \qquad t_{50} = \frac{0.693}{k}$$
$$= \frac{0.693}{6.93 \times 10^{-2}} = 10 \text{ s}$$

5. Graphical Method

In this method, the values of $\Delta x / \Delta t$ at different intervals of time is determined by plotting a curve between x (the amount of substance decomposed) and time t.

The value of $\Delta x/\Delta t$ at a particular time corresponding to a particular value of (a - x) is given by the slope of the curve at that curve. Linear Plots for Different Order Reactions are as

Plot of Differential Equations to Corresponding Rate Equation



If graphs are plotted between $\log\left(\frac{dx}{dt}\right)$ and $\log(a - x)$, the slope of the line gives the order of reaction.



Effect of Temperature on Rate of Reaction

Rate constants and, therefore rate of a chemical reaction depends strongly on temperature. Typically rates of all reactions increase with increase in temperature.

A rough rule, valid for many reactions in solution, is that near room temperature, rate constant (k) doubles or triples for each 10°C rise in temperature.

Arrhenius Equation

In year 1889, Arrhenius noted that k(T) data for many reactions fit the equation.

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

- Here, *A* = a constant called frequency factor (because it gives the frequency of binary collisions of the reacting molecules per second per litre). It is also called **collision number** or **pre-exponential factor**
 - R = gas constant, T = absolute temperature
 - $E_a = energy of activation$

The factor $e^{-E_a/RT}$ is referred as Boltzmann factor and gives the fraction of molecules having energy equal to or greater than activation energy.

Activation Energy

The activation energy can also be defined as, "The energy that activates passive or non-active molecules after its adsorption or minimum energy in excess to normal energy of molecules, which molecules must possess in order to form product on collision.

The concept of activation energy gives us an idea whether a given reaction is slow or fast at a given temperature. A reaction which has lower activation energy proceed at a faster rate at a given temperature or *vice-versa*. The differences in activation energy are mainly responsible for observed difference in rates of reactions. The concept of activation energy as applied to chemical reaction can be explained by plotting energy against the progress of reaction as shown in the figure below.



where, E_{th} = threshold energy (the minimum energy required over and above the energy possessed by the reactants in order to cross the energy barrier).

 E_{R} = energy possessed by the reactant.

All the molecules in the reacting species do not have the same kinetic energy and it is not easy to predict the behavior of any one molecule.

Ludwig Boltzmann and James Clark Maxwell used statistics to predict the behaviour of large number of molecules and give Maxwell and Boltzmann distribution curve.



Fraction of molecules = $\frac{N_E}{N_T}$

 N_E = number of molecules with energy E N_T = total number of molecules.

- Peak of the curve corresponds to the most probable kinetic energy. There is decrease in number of molecules with higher energies or lower energies than this peak value.
- When the temperature is raised the curve is broaden out and peak of the curve moves to the higher energy value. But area under the curve is constant since total probability must be one at all times.



• By increasing the temperature of the substance increases the fraction of molecules which collide with energies greater than E_a .

Calculation of Activation Energy

Activation energy can be calculated by knowing the rate constants at two different temperatures, assuming that E_a and A remains constant.

Taking log of both the sides in Arrhenius equation, we get

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \dots (i)$$

Now, if the values of rate constant at temperatures T_1 and T_2 are k_1 and k_2 respectively then

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \qquad \dots (ii)$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \qquad \dots (iii)$$

Subtracting the Eq. (ii) from (iii), we get

$$\begin{aligned} & \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \\ & \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \text{ [Here, } T_2 > T_1 \text{] } \dots \text{(iv)} \end{aligned}$$

This relation is used when rate constants at two different temperatures are given.

Equation (i) is also written as,
$$\frac{d \log k}{dT} = \frac{E_a}{RT^2}$$

Graphical Representation of Arrhenius Equation

Arrhenius equation is purely an empirical equation that gives a reasonably good representation of temperature dependence of the rate constant.

When $\log k$ is plotted against 1/T, we get a straight line which is represented by Arrhenius equation as,

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

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

The intercept of this line is equal to log A and slope is

equal to
$$-\frac{E_a}{2.303R}$$
. Therefore, $E_a = -2.303R \times \text{slope}$



Remember

- Different reactions have different rates because their activation energies are different. Lesser the activation energy, faster is the reaction rate.
- Activation energy can never be zero. If $E_a = 0$, then according to Arrhenius equation, k = A, i.e. every collision between molecules leads to a chemical reaction. This can never be true.

Example 12. The rate constant (k) of a reaction is measured at different temperature (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)



Sol. (d) .:.

Taking natural logarithm on both sides, the Arrhenius equation becomes.

$$\Rightarrow \ln k = \ln A - \left(\frac{E_a}{R}\right) \frac{1}{T} = \ln A - \left(\frac{E_a}{R \times 10^3}\right) \times \frac{10^3}{T}$$

Slope of a graph = $\frac{-E_a}{R \times 10^3} = \frac{-10}{5}$
 $E_a = 2R \times 10^3 \text{ J mol}^{-1} \Rightarrow E_a = 2R \text{ kJ mol}^{-1}$

Example 13 How faster would a reaction proceed at 25°C than at 0°C if the activation energy is 65 kJ?

(a) 11 times (b) 9 times (c) 6 times (d) 2 times

Sol. (a) 2.303 log
$$\frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

∴ 2.303 log $\frac{k_2}{k_1} = \frac{65 \times 10^3}{8.314} \left[\frac{25}{298 \times 273} \right] \Rightarrow \frac{k_2}{k_1} = 11.05$

Example 14 Milk turns sour at 40°C three times faster as at 0°C. The energy of activation for souring of milk is

(a) 5.683 kcal (b) 2.532 kcal (c) 4.693 kcal (d) 4.246 kcal

Sol. (c) 2.303 log
$$\frac{k_2}{k_1} = \frac{E_a}{R} \frac{[T_2 - T_1]}{T_1 T_2}$$

∴ 2.303 log 3 = $\frac{E_a}{2} \frac{[313 - 273]}{313 \times 273}$ ⇒ E_a = 4.693 kcal

Theories of Rate of Reaction

Following theories are given to explain the rate of a reaction.

Collision Theory of Bimolecular Reactions

The collision theory states that

• If two molecules are to react together, they must collide with each other.

or

- The collision between all molecules do not lead to chemical reaction.
- The collisions in which the molecules acquire energy greater than the activation energy, results in chemical reaction.



Properly oriented collisions to form products





- The colloiding molecules must posses certain minimum energy (**threshold energy**) to make the collision effective.
- The additional energy required by the molecule to attain threshold energy is called **activation energy**. During the collisions, this energy is acquired by the molecules as a result of interchange of energies. Thus, Activation energy = threshold energy – energy of colliding molecules
- If we assume that the rate of reaction is equal to the rate of collisions per unit volume per unit time multiplied by the fraction of collisions (that have sufficient relative kinetic energy to overcome the energy barrier E^*) then the rate constant is given by the expression

$$k = Z_{AB} \cdot e^{-E^*/I}$$

Here, $Z_{AB} =$ collision frequency factor, i.e. the number of collisions between reactant molecules *A* and *B* per unit volume per unit time divided by N_A and N_B , the number of molecules per unit volume of *A* and *B* respectively.

For a successful collision, however it is also important that the molecules must be oriented properly in space alongwith their energy requirements. Thus, if P is the **orientation factor** (also called steric factor) then above rate equation can be changed as.

$$K = P \overline{Z}_{AB} e^{-E_a/RT}$$

Now, if we compare above equation, with Arrhenius equation we get

$$A = PZ_{AB}$$

where, A = Arrhenius collision factor

Remember This theory explains the results of a number of reactions but it does not give satisfactory explanation in some cases as it consider atoms/molecules to be hard sphere and ignores their structural aspect.

Transition State Theory

This theory is also known as **absolute reaction rate theory** or **activated complex theory**. This theory is based on the idea that bond breaking and bond making involved in a chemical reaction must occur continuously or simultaneously. According to this theory

- The reactant molecules must come together to form an activated complex, whose energy is higher than the reactant molecules.
- The activated complex is supposed to be in equilibrium with the reactant molecules and has all the attributes of normal molecule except that one of the vibrational degree of freedom is converted into translational degree of freedom.
- This complex though unstable, has a transient existence and its potential energy is maximum. Finally it decomposes into products.
- The energy of activation according to this theory is the additional energy which the reacting molecules must acquire to form the activated complex.



Energy profile diagram of an exothermic reaction

Action of Catalyst

A catalyst can increase the rate of a chemical reaction by lowering the activation energy as shown below :



Energy profile diagram in the absence and presence of catalyst

Practice Exercise

ROUND I Topically Divided Problems

Rate of Reaction and Factors Affecting It

- Consider the reaction, 2A + B → products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is (AIEEE 2007)

 (a) L mol⁻¹ s⁻¹
 (b) no unit
 (c) mol L⁻¹ s⁻¹
 (d) s⁻¹
- **2.** For a reaction $\frac{1}{2}A \longrightarrow 2B$, rate of disappearance

of 'A' is related to the rate of appearance of 'B' by the expression (AIEEE 2008)

(a)
$$-\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$$
 (b) $-\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$
(c) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (d) $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$

3. For the reaction : $H_2 + I_2 \longrightarrow 2HI$, the differential rate law is (AIEEE 2002)

(a)
$$-\frac{d [H_2]}{dt} = -\frac{d [I_2]}{dt} = 2 \frac{d [HI]}{dt}$$

(b) $-2 \frac{d [H_2]}{dt} = -2 \frac{d [I_2]}{dt} = \frac{d [HI]}{dt}$
(c) $-\frac{d [H_2]}{dt} = -\frac{d [I_2]}{dt} = \frac{d [HI]}{dt}$
(d) $-\frac{d [H_2]}{2dt} = -\frac{d [I_2]}{2dt} = \frac{d [HI]}{dt}$

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

$$+\frac{1}{2}\frac{d[C]}{dt} = -\frac{1}{5}\frac{d[D]}{dt} = +\frac{1}{3}\frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

The reaction is
a) $4A + B \longrightarrow 2C + 3D$
b) $B + 5D \longrightarrow 3A + 2C$
c) $4A + 2B \longrightarrow 2C + 3D$
d) $B + \frac{1}{2}D \longrightarrow 4A + 2C$

5. The rate equation for the reaction $2A + B \rightarrow C$ is found to be rate = k[A][B]

The correct statement in relation to this reaction is that the (AIEEE 2004)

- (a) unit of k must be s^{-1}
- (b) $t_{1/2}$ is a constant
- (c) rate of formation of C is twice the rate of disappearance of A
- (d) value of k is independent of the initial concentrations of A and B
- 6. Which of the following expression is correct for the rate of reaction given below? (NCERT Exemplar)

$$\begin{array}{l} 5\mathrm{Br}^{-}(aq)+\mathrm{BrO}_{3}^{-}(aq)+6\mathrm{H}^{+}(aq) \longrightarrow 3\mathrm{Br}_{2}(aq)\\ +3\mathrm{H}_{2}\mathrm{O}\left(l\right)\end{array}$$

(a)
$$\frac{\Delta [Br^{-}]}{\Delta t} = 5 \frac{\Delta [H^{+}]}{\Delta t}$$
 (b) $\frac{\Delta [Br^{-}]}{\Delta t} = \frac{6}{5} \frac{\Delta [H^{+}]}{\Delta t}$
(c) $\frac{\Delta [Br^{-}]}{\Delta t} = \frac{5}{6} \frac{\Delta [H^{+}]}{\Delta t}$ (d) $\frac{\Delta [Br^{-}]}{\Delta t} = 6 \frac{\Delta [H^{+}]}{\Delta t}$

7. A graph of volume of hydrogen released *vs* time for the reaction between zinc and dil.HCl is given in figure. On the basis of this mark the correct option.



- **8.** Which of the following statements is correct ? (NCERT Exemplar)
 - (a) The rate of a reaction decreases with passage of time as the concentration of reactants decreases
 - (b) The rate of a reaction is same at any time during the reaction
 - (c) The rate of a reaction is independent of temperature change
 - (d) The rate of a reaction decreases with increase in concentration of reactant(s)
- **9.** Consider the graph given in Q. 7. Which of the following options does not show instantaneous rate of reaction at 40th second? (NCERT Exemplar)

(a)
$$\frac{V_5 - V_2}{50 - 30}$$
 (b) $\frac{V_4 - V_2}{50 - 30}$
(c) $\frac{V_3 - V_2}{40 - 30}$ (d) $\frac{V_3 - V_1}{40 - 20}$

10. The rate constant for the reaction,

 $\begin{array}{rl} 2N_2O_5 & \longrightarrow & 4NO_2 + O_2 \mbox{ is } 3.0 \times 10^{-5} \mbox{ s}^{-1}. \mbox{ If the rate is } 2.40 \times 10^{-5} \mbox{ then the concentration of } N_2O_5 \mbox{ (in mol/L) is } \mbox{ (a) } 1.4 \mbox{ (b) } 1.2 \mbox{ (c) } 0.04 \mbox{ (d) } 0.8 \end{array}$

11. For a chemical reaction $2X + Y \longrightarrow Z$, the rate of appearance of Z is 0.05 mol L⁻¹ min⁻¹. The rate of disappearance of X will be (a) 0.05 mol L⁻¹ h⁻¹ (b) 0.05 mol L⁻¹ min⁻¹ (c) 0.1 mol L⁻¹ min⁻¹ (d) 0.25 mol L⁻¹ min⁻¹

Molecularity and Rate Law Expression

- 12. Units of rate constant of first and zero order reactions in terms of molarity *M* unit are respectively
 (a) s⁻¹, M s⁻¹ (b) s⁻¹, M (c) M s⁻¹, s⁻¹ (d) M, s⁻¹
- 13. For which type of reaction order and molecularity have the same value? (NCERT Exemplar)(a) First order reaction (b) Bimolecular reaction
 - (c) Termolecular reaction (d) Elementary reaction
- **14.** The rate of the reaction,

$$CCl_3CHO + NO \longrightarrow CHCl_3 + NO + CO$$

is equal to rate $k[CCl_3CHO][NO]$. If concentration is expressed in mol/L, the unit of k is (a) L mol⁻¹ s⁻¹ (b) mol L⁻¹ s⁻¹

(c) $L^2 \mod^{-2} s^{-1}$ (d) s^{-1}	(u)	LI IIIOI	0	(\mathcal{D})	mor L	0
	(c)	$L^2 \text{ mol}^{-2}$	s^{-1}	(d)	s^{-1}	

15. Rate law for the reaction $A + 2B \longrightarrow C$ is found to be Rate = k[A][B]

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate

constant will be	(NCERT Exemplar)
(a) the same	(b) doubled
(c) quadrupled	(d) halved

- **16.** The conversion of molecules x to y follows second order kinetics. If concentration of x is increased to three times, the rate of formation of y will (NCERT)
 - (a) increase by three times
 - (b) decrease by three times
 - (c) increase by nine times
 - (d) decrease by nine times
- 17. The rate of a gaseous reaction is equal to k[A][B]. The volume of the reaction vessel containing these gases is reduced by one-fourth of the initial volume. The rate of the reaction would be

(a)
$$\frac{1}{16}$$
 (b) $\frac{16}{1}$ (c) $\frac{1}{8}$ (d) $\frac{8}{16}$

18. For a first order reaction, the graph log [*A*] *vs t* is given below.





19. The hydrolysis of ethyl acetate was carried out separately with 0.05 M HCl and 0.05 M H₂SO₄. The rate constants were found to be (k_1) and (k_2) respectively then

(a) $k_1 < k_2$ (b) $k_1 > k_2$ (c) $k_1 = k_2$ (d) $k_2 = 2k_1$

20. In the sequence of reaction,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$$

 $k_3>k_2>k_1$ then the rate determining step of the reaction is

(a) $A \longrightarrow B$	(b)	B	\longrightarrow	C
(c) $C \longrightarrow D$	(d)	A	\longrightarrow	D

21. Given the hypothetical reaction mechanism

$$A \xrightarrow{I} B \xrightarrow{II} C \xrightarrow{III} D \xrightarrow{IV} E$$

and the data as,

Species formed	Rate of its formation
В	0.002 mol/h, per mole of A
C	0.030 mol/h, per mole of B
D	0.011 mol/h, per mole of C
E	0.042 mol/h, per mole of D

The rate determining step is (a) step I (b) step II (c) step III (d) step IV

- A reaction involving two different reactants can never be (AIEEE 2005)
 (a) bimolecular reaction
 (b) second order reaction
 - (c) first order reaction (d) unimolecular reaction
- **23.** Consider the reaction,

 $Cl_2(aq) + H_2S(aq) \longrightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)$ The rate equation for this reaction is,

rate =
$$k$$
[Cl₂] [H₂S]

Which of these mechanisms is/are consistent with this rate equation? (AIEEE 2010)

 $\begin{array}{ll} \text{(A)} & \text{Cl}_2 + \text{H}_2\text{S} \longrightarrow \text{H}^+ + \text{Cl}^+ + \text{Cl}^+ + \text{HS (slow)} \\ & \text{Cl}^+ + \text{HS}^- \longrightarrow \text{H}^+ + \text{Cl}^- + \text{S} & \text{(fast)} \\ \text{(B)} & \text{H}_2\text{S} \longmapsto \text{H}^+ + \text{HS} & \text{(fast equilibrium)} \\ & \text{Cl}_2 + \text{HS} \longrightarrow 2\text{Cl}^- + \text{H}^+ + \text{S} & \text{(slow)} \\ \text{(a)} & \text{(B) only} & \text{(b) Both (A) and (B)} \\ & \text{(c) Neither (A) or (B)} & \text{(d) (A) only} \\ \end{array}$

24. For the reaction system,

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

volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO; the rate of reaction will (AIEEE 2003)

- (a) diminish to one-fourth of its initial value
- (b) diminish to one-eight of its initial value
- (c) increase to eight times of its initial value
- (d) increase to four times of its initial value

25. For the reaction,

 $2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$ the observed rate expression is, rate = $k_f [NO]^2 [H_2]$. The rate expression for the reverse reaction is (JEE Main 2020)

(a)	$k_b [N_2] [H_2 O]^2 / [H_2]$	(b) $k_b [N_2] [H_2 O]$
(c)	$k_b [N_2] [H_2O]^2 / [NO]$	(d) $k_b [N_2] [H_2 O]^2$

26. For the reaction, $2A + B \longrightarrow C$, 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)

$\begin{matrix} \textbf{[A]} \\ (\text{mol } \text{L}^{-1}) \end{matrix}$	$[B] \pmod{\operatorname{L}^{-1}}$	$\begin{array}{c} \textbf{Initial rate} \\ (mol \ L^{-1}s^{-1}) \end{array}$
0.05	0.05	0.045
0.10	0.05	0.090
0.20	0.10	0.72
(a) rate = $k [A][B]^2$	(b) rate =	$= k \ [A]^2 [B]^2$
(c) rate = $k [A][B]$	(d) rate =	$= k [A]^2 [B]$

Order of Reaction



29. For a general reaction, $A \longrightarrow B$, plot of

concentration of A vs time is given in figure. What are the units of rate constant?



(d) mol⁻² L² s⁻¹

(JEE Main 2020)

30. It is true that

(c) s^{-1}

- (a) a second order reaction is always a multistep reaction
- (b) a zero order reaction is a multistep reaction
- (c) a first order reaction is always a single step reaction
- (d) a zero order reaction is a single step reaction

31. Higher order (>3) reactions are rare due to

- (a) low probability of simultaneous collision of all the reacting species
- (b) increase in entropy and activation energy as more molecules are involved
- (c) shifting of equilibrium towards reactants due to elastic collisions
- (d) loss of active species on collision
- **32.** Which of the following statements is not correct about order of a reaction? (NCERT Exemplar)
 - (a) The order of a reaction can be a fractional number.
 - (b) Order of a reaction is experimentally determined quantity.
 - (c) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.
 - (d) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

- **33.** Radioactive decay is a
 - (a) first order reaction(b) zero order reaction(c) second order reaction(d) third order reaction
- **34.** The rate law for the reaction,

RCl + NaOH $\longrightarrow R$ OH + NaCl is given by

Rate = k [RCl]. The rate of this reaction

- (a) is doubled by doubling the concentration of NaOH(b) is halved by reducing the concentration of *R*Cl by one half
- (c) is increased by increasing the temperature of the reaction
- (d) in unaffected by change in temperature
- **35.** The reaction $L \longrightarrow M$ is started with 10.0 g of L. After 30 and 90 min, 5.0 g and 1.25 g of Lrespectively are left. The order of the reaction is (a) 0 (b) 1 (c) 2 (d) 3
- **36.** The rate constant of a zero order reaction is $0.2 \text{ mol dm}^{-3} \text{ h}^{-1}$. If the concentration of the reactant after 30 min is 0.05 mol dm⁻³, then its initial concentration would be (a) 0.01 mol dm^{-3} (b) 0.15 mol dm^{-3}
 - (c) 0.25 mol dm^{-3} (d) 4.00 mol dm^{-3}
- **37.** What is the two third life of a first order reaction having $k = 5.48 \times 10^{-14} \text{ s}^{-1}$? (a) $2.01 \times 10^{13} \text{ s}$ (b) $2.01 \times 10^{12} \text{ s}$ (c) $4.02 \times 10^{13} \text{ s}$ (d) $4.02 \times 10^{26} \text{ s}$
- **38.** Sucrose decomposes in acid solution into glucose
and fructose according to the first order rate law,
with $t_{1/2} = 3.00$ h. What fraction of sample of
sucrose remains after 8 h? (NCERT)
(a) 1.023 M (b) 0.8725 M
(c) 0.023 M (d) 0.1576 M
- **39.** Consider the following reactions

 $A \rightarrow P1; B \rightarrow P2; C \rightarrow P3; D \rightarrow P4,$

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:



Among the following, the correct sequence for the order of the reactions is (JEE Main 2020)

(a) D	>A>B>C	(b) $A > B > C > D$
(c) C	>A>B>D	(d) $D > B > A > C$

- 40. In a second order reaction when the concentrations of both the reactants are equal, the reaction is completed 20% in 500 s. How long will it take for the reaction to go to 60% completion?
 (a) 1000 s
 (b) 300 s
 (c) 3000 s
 (d) 2000 s
- **41.** 1 g of $_{79}$ Au¹⁹⁸ ($t_{1/2}$ = 65 h) gives stable mercury by β-emission. What amount of mercury will left after 260 h? (a) 0.9375 g (b) 0.3758 g
- (c) 0.7586 g (d) 0.9000 g **42.** A first order reaction is 50% completed in $1.26 \times 10^{14} \text{ s}$. How much time would it take for 100% completion? *(NCERT Exemplar)* (a) $1.26 \times 10^{15} \text{ s}$ (b) $2.52 \times 10^{14} \text{ s}$
- 43. The rate of a first order reaction is 1.5 × 10⁻² mol L⁻¹ min⁻¹ at 0.5 M concentration of the reactant. The half-life of the reaction is
 (a) 13.6 min (b) 42.5 min (c) 23.1 min (d) 32.5 min

(d) Infinite

44. The time for half-life period of a certain reaction, $A \rightarrow$ products is 1 h. When the initial concentration of the reactant 'A' is 2.0 mol L⁻¹, how much time does it take for its concentration to come from 0.50 to 0.25 mol L⁻¹, if it is a zero order reaction? (AIEEE 2010)

(a) 4 h	(b) 0.5 h
(c) 0.25 h	(d) 1 h

45. Rate constant, k of the first order reaction when initial concentration (C_0) and concentration at time t, (C_t) is given by the equation

(AIEEE 2002)

$$kt = \log C_0 - \log C_t$$

Graph is a straight line if we plot

(a) $t vs \log C_0$ (b) $t vs \log C_t$

(c) 2.52×10^{28} s

- (c) $t^{-1} vs \log C_t$
- (d) $\log C_0 vs \log C_t$
- **46.** The rate constant for a first order reaction is 60 s^{-1} . How much time will it take to reduce the initial concentration of the reactant to its 1/16th value? *(NCERT)*

(a) 0.046 s	(b) 0.025 s
(c) 0.098 s	(d) 0.060 s

47. A flask contains a mixture of compounds *A* and *B*. Both compounds decompose by first-order kinetics. The half-life 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

concentra	tion of A to b	e four times	that of B (in s) is	,
(Use ln 2 :	= 0.693)		(JEE Main 2020)	1
(a) 120	(b) 180	(c) 300	(d) 900	

48. The given plots represent the variation of the concentration of a reaction *R* with time for two different reactions (i) and (ii). The respective orders of the reactions are (JEE Main 2019)



49. For the reaction, $2A + B \longrightarrow$ products When concentration of both (*A* and *B*) becomes double, then rate of reaction increases from 0.3 mol L⁻¹ s⁻¹ to 2.4 mol L⁻¹ s⁻¹.

When concentration of only \boldsymbol{A} is doubled, the rate of reaction increases from

(JEE Main 2019)

 $0.3 \ \mathrm{mol} \ \mathrm{L^{-1}} \ \mathrm{s^{-1}}$ to $0.6 \ \mathrm{mol} \ \mathrm{L^{-1}} \ \mathrm{s^{-1}}$

Which of the following is true?

(a) The whole reaction is of 4th order

(b) The order of reaction w.r.t B is one

(c) The order of reaction w.r.t *B* is 2

- (d) The order of reaction w.r.t A is 2
- **50.** For a first order reaction given is, $(A) \longrightarrow$ products

. The concentration of A changes from 0.1 M to 0.025 M in 40 min. The rate of reaction when the concentration of A is 0.01 M is (AIEEE 2012) (a) 1.73×10^{-5} M / min (b) 3.47×10^{-4} M / min (c) 3.47×10^{-5} M / min (d) 1.73×10^{-4} M / min

- **51.** 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) 2 (b) 3 (c) 1 (d) 0
- **52.** Compounds '*A*' and '*B*' react according to the following chemical equation.

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

Concentration of either 'A' or 'B' were changed keeping the concentrations of one of the reactants constant and rates were measured as a function of initial concentration. Following results were obtained.

Experiment	Initial concentration of [A]/mol L ⁻¹	Initial concentration of [<i>B</i>]/mol L ⁻¹	Initial rate of formation of [C]/mol L^{-1} s ⁻¹
1.	0.30	0.30	0.10
2.	0.30	0.60	0.40
3.	0.60	0.30	0.20

Choose the correct option for the rate equations for this reaction. (NCERT Exemplar) (a) Rate = $k[A]^2[B]$ (b) Rate = $k[A][B]^2$ (c) Rate = k[A][B] (d) Rate = $k[A]^2[B]^0$

53. A bacterial infection in an internal wound grows as $N'(t) = N_0 \exp(t)$, where the time *t* is in hours. A dose of antibiotic, taken orally, needs 1 hour to reach the wound. Once it reaches there, the bacterial population goes down as $\frac{dN}{dt} = -5N^2$.

What will be the plot of $\frac{N_0}{N} vs t$ after 1 hour ? (JEE Main 2019)



Effect of Temperature on Rate of Reaction

54. Arrhenius equation may not be represented as

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

(b) $\frac{d \ln k}{dT} = \frac{E}{RT^2}$
(c) $\log A = \log k + \frac{E_a}{2.303 RT}$
(d) $\log \left[-\frac{E_a}{RT} \right] = \frac{k}{A}$

55. When a graph is plotted between $\ln k$ and 1/T for a first order reaction, a straight line is obtained. The slope of the line is equal to

(a)
$$-\frac{E_a}{2.303}$$
 (b) $-\frac{E_a}{2.303R}$
(c) $-\frac{2.303}{E_a R}$ (d) $-\frac{E_a}{R}$

56. According to Arrhenius equation rate constant k is equal to $Ae^{-E_a/RT}$. Which of the following options represents the graph of $\ln k vs \frac{1}{T}$?

(a) $\ln k$ (b) $\ln k$ $1/T \rightarrow$ (c) $\ln k$ $1/T \rightarrow$ $1/T \rightarrow$ (d) $\ln k$ $1/T \rightarrow$ $1/T \rightarrow$

57. Which of the following graphs represents exothermic reaction?



- (a) (i) only (b) (ii) only (c) (iii) only (d) (i) and (ii) $\left(\begin{array}{c} \label{eq:alpha} \end{array} \right)$
- **58.** The rate constant (k') of one of the reaction is found to be double that of the rate constant (k'') of another reaction. Then the relationship between the corresponding activation energies of the two reactions $(E_a' \text{ and } E_a'')$ can be represented as (a) $E_a' > E_a''$ (b) $E_a' = 4E''$ (c) $E_1' = E_a''$ (d) $E_a' < E_a''$
- 59. Consider the Arrhenius equation given below and mark the correct option. (NCERT Exemplar)

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

- (a) Rate constant increases exponentially with increasing activation energy and decreasing temperature
- (b) Rate constant decreases exponentially with increasing activation energy and decreasing temperature

- (c) Rate constant increases exponentially with decreasing activation energy and decreasing temperature
- (d) Rate constant increases exponentially with decreasing activation energy and increasing temperature
- **60.** In Arrhenius equation, $k = Ae^{-E_a/RT}$; A may be
 - called the rate constant at
 - (a) very low temperature
 - (b) zero activation energy
 - (c) the boiling temperature of reaction mixture
 - (d) All of the above
- **61.** Rate of a reaction can be expressed by Arrhenius equation as

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

In this equation, *E* represents [AIEEE 2006]

- (a) the energy above which all the colliding molecules will react
- (b) the energy below which colliding molecules will not react
- (c) the total energy of the reacting molecules at a temperature, ${\cal T}$
- (d) the fraction of molecules with energy greater than the activation energy of the reaction

62. Consider figure and mark the correct option.



- (a) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.
- (b) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant
- (c) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product.
- (d) Activation energy of backward reaction is $E_1 \mbox{ and } product \mbox{ is more stable than reactant }$
- 63. An endothermic reaction A → B has an activation energy of 15 kcal/mol and the energy of reaction is 5 kcal/mol. The activation energy for the reaction B → A is
 (a) 20 kcal/mol
 - (b) 15 kcal/mol
 - (c) 10 kcal/mol
 - (1) 10 Kcal/III
 - (d) zero

- **64.** If the reaction rate at a given temperature becomes slower then
 - (a) the free energy of activation is higher
 - (b) the free energy of activation is lower
 - (c) the entropy changes
 - (d) the initial concentration of the reactants remains constant
- **65.** Which of the following statements is incorrect about the collision theory of chemical reaction?

(NCERT Exemplar)

(JEE Main 2019)

(JEE Main 2019)

- (a) It considers reacting molecules or atoms to be hard spheres and ignores their structural features
- (b) Number of effective collisions determines the rate of reaction
- (c) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation
- (d) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective
- **66.** Consider the given plot of enthalpy of the following reaction between *A* and *B*.

 $A + B \longrightarrow C + D$

Identify the incorrect statement.



- (a) *D* is kinetically stable product.
- (b) Formation of *A* and *B* from *C* has highest enthalpy of activation.
- (c) C is the thermodynamically stable product.
- (d) Activation enthalpy to form C is 5 kJ mol⁻¹ less than that to form D.
- **67.** Consider the given plots for a reaction obeying Arrhenius equation (0°C < T < 300°C) : (k and E_a are rate constant and activation energy, respectively)



Choose the correct option.

- (a) Both I and II are wrong
- (b) Both I and II are correct
- (c) I is wrong but II is right
- (d) I is right but II is wrong

- **68.** If a reaction follows the Arrhenius equation, the plot $\ln k vs 1/(RT)$ gives straight line with a gradient (-y) unit. The energy required to activate the reactant is (JEE Main 2019)
 - (a) $\frac{y}{R}$ unit (b) -y unit (c) yR unit (d) y unit
- **69.** Consider the following plots of rate constant *versus* $\frac{1}{T}$ for four different reactions. Which of the

following orders is correct for the activation energies of these reactions? (JEE Main 2020)



(a)
$$E_b > E_a > E_d > E_c$$

(b)
$$E_a > E_c > E_d > E_l$$

$$(1) \quad E = E = E$$

(d)
$$E_c > E_a > E_d > E_b$$

- **70.** The energies of activation for forward and reverse reactions for $A_2 + B_2 \implies 2AB$ are 180 kJ mol⁻¹ and 200 kJ mol⁻¹ respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol⁻¹. The enthalpy change of the reaction $(A_2 + B_2 \rightarrow 2AB)$ in the presence of catalyst will be (in kJ mol⁻¹) (AIEEE 2007) (a) 300 (b) 120 (c) 280 (d) 20
- **71.** A reactant (*A*) forms two products

 $A \xrightarrow{k_1} B$, Activation energy E_{a_1}

 $A \xrightarrow{k_2} C$, Activation energy E_{a_2}

If $E_{a_{3}} = 2 \; E_{a_{1}}$, then k_{1} and k_{2} are related as (AIEEE 2011)

(a)
$$k_1 = 2k_2 e^{E_{a_2}/RT}$$
 (b) $k_1 = k_2 e^{E_{a_1}/RT}$
(c) $k_2 = k_1 e^{E_{a_2}/RT}$ (d) $k_1 = A k_2 e^{E_{a_1}/RT}$

- **72.** Consider an endothermic reaction $X \to Y$ with the activation energies E_b and E_f for the backward and forward reactions respectively. In general (AIEEE 2005)
 - (a) there is no definite relation between E_b and E_f
 - (b) $E_b = E_f$
 - (c) $E_b > E_f$
 - (d) $E_b < E_f$

73. For the reaction of H_2 with I_2 , the rate constant is $2.5\times10^{-4}~\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ at 327°C and $1.0 \text{ dm}^3 \text{mol}^{-1} \text{ s}^{-1}$ at 527°C. The activation energy for

the reaction, in kJ mol⁻¹ is $(R = 8.314 \text{ [Heel}^{1} \text{ main}^{-2} \text{)})$

- (b) 72 (a) 59
- (c) 150 (d) 166
- **74.** For a reaction, consider the plot of $\ln k$ versus 1/Tgiven in the figure. If the rate constant of this

ROUND II Mixed Bag

1. The chemical reaction $2O_3 \longrightarrow 3O_2$ proceeds as follows

 $0_3 \rightleftharpoons 0_2 + 0$ (fast)

$$0 + O_3 \longrightarrow 2O_2$$
 (slow)

The rate law expression should be

(a) $r = k [O_3]^2$ (b) $r = k [O_3]^2 [O_2]^{-1}$ (d) unpredictable (c) $r = k [O_3][O_2]$

2. Two first order reactions have half-lives in the ratio 8 : 1. Calculate the ratio of time intervals $t_1 : t_2$. The time t_1 and t_2 are the time period for (1/4) th and (3/4)th completion.

(a) 1 : 0.602	(b) 2 : 301
(c) 0.256 : 0.603	(d) 0.2 : 0.301

3. The rate constant of a reaction is given by $k = 2.1 \times 10^{10} \exp(-2700 RT).$

It means that

- (a) $\log k vs 1/T$ will be a curved line with slope 2700= -2.303R
- (b) $\log k vs 1/T$ will be a straight line with intercept on log k axis = log 2.1×10^{10}
- (c) the number of effective collisions are $2.1 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$
- (d) half-life of the reaction increases with increase of temperature
- **4.** Which of the following statements are correct?
 - 1. Order of a reaction can be known from experimental result and not from the stoichiometry of reaction.
 - 2. Overall molecularity of a reaction may be determined in a manner similar to overall order of reaction.
 - 3. Overall order of reaction,

$$A^m + B^n \longrightarrow AB_x$$
 is $(m + n)$

reaction at 400 K is 10^{-5} s⁻¹, then the rate constant at 500 K is (JEE Main 2019) Slope = -4606ln k



Select the correct answer by using the codes given below.

(a) 1 and 3	(b) 1, 2 and 3
(c) 2 and 3	(d) 1 and 2

5. An exothermic chemical reaction occurs in two steps as follows

(i) $A + B \longrightarrow X$ (fast) (ii) $X \longrightarrow AB$ (slow) The progress of the reaction can be best represented by



- 6. The decomposition of hydrocarbon follows the equation $k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000} \text{ K/T}$. Calculate the activation energy E_a . (NCERT) (b) 425.25 kJ mol⁻¹ (a) 232.79 kJ mol⁻¹ (c) 300 kJ mol⁻¹ (d) 885.2 kJ mol⁻¹
- **7.** The rate law for a reaction between the substances A and B is given by rate = $k [A]^a [B]^b$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as

(a) $2^{\overline{a+b}}$ (d) $2^{(a-b)}$ (b) a + b(c) a-b

8. For a chemical reaction, $A \rightarrow B$, the rate of reaction increases by a factor of 1.837 when the concentration of A is increased by 1.5 times. The order of reaction with respect to A is (8

a) 0 (b) 1 (c)
$$1.5$$
 (d) 2

9. The rate constant *k*, for the reaction

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g) \text{ is } 2.3 \times 10^{-2} \text{ s}^{-1}.$$

Which equation given below describe the change of $[N_2O_5]$ with time? $[N_2O_5]_0$ and $[N_2O_5]_t$ correspond to concentration of N_2O_5 initially and at time *t*.

(a)
$$[N_2O_5]_t = [N_2O_5]_0 + kt$$

(b) $[N_2O_5]_t = [N_2O_5]_0 e^{kt}$
(c) $\ln \frac{[N_2O_5]_0}{[N_2O_5]_0} = kt$

- (d) $\log_{10}[N_2O_5]_t = \log_{10}[N_2O_5]_0 kt$
- **10.** A substance undergoes first order decomposition. The decomposition follows the parallel first order reactions as

$$A \xrightarrow{k_1 \to B} k_1 = 1.26 \times 10^{-4} \text{ s}^{-1}$$
$$A \xrightarrow{k_2 \to C} k_2 = 3.8 \times 10^{-5} \text{ s}^{-1}$$

 The percentage distribution of B and C are

 (a) 76.83, 23.17
 (b) 24.9, 75.1

 (c) 60, 40
 (d) 50, 50

- **11.** For a reaction $A + B \longrightarrow C + D$, if the
 - concentration of *A* is doubled without altering the concentration of *B*, the rate gets doubled. If the concentration of *B* is increased by nine times without altering the concentration of *A*, the rate gets tripled. The order of the reaction is (a) 1 (b) 1.5 (c) 2 (d) -1
- **12.** The half-time of a first order decomposition of nitramide is 2.1 h at 15°C.

 $\mathrm{NH}_2\mathrm{NO}_2(aq) \longrightarrow \mathrm{N}_2\mathrm{O}(g) + \mathrm{H}_2\mathrm{O}(l)$

If 6.2 g of nitramide is allowed to decompose then time taken for it to decompose 99% will be (a) 2.1 h (b) 12 h (c) 13.96 h (d) 33 h

13. The activation energy for the given reaction $2\text{HI}(g) \longrightarrow \text{H}_2(g) + \text{I}_2(g) \text{ is } 209.5 \text{ kJ mol}^{-1} \text{ at}$ 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy. (NCERT) (a) 1.82×10^{-18} (b) 1.47×10^{-19}

(00)	1.01.10	(~)	11111111
(c)	2.67×10^{-16}	(d)	3.89×10^{-19}

14. In the following reaction; $xA \rightarrow yB$

A and B respectively can be

$$\log_{10}\left[-\frac{d[A]}{dt}\right] = \log_{10}\left[\frac{d[B]}{dt}\right] + 0.3010$$

(JEE Main 2019)

(a) *n*-butane and isobutane (b) C_2H_2 and C_6H_6 (c) C_2H_4 and C_4H_8 (d) N_2O_4 and NO_2

15. For following reactions

$$A \xrightarrow{700 \text{ K}} \text{Product};$$
$$A \xrightarrow{500 \text{ K}} \text{Product}$$

It was found that the 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): (JEE Main 2020)

(a)	198 kJ/mol	(b)	105 kJ/mol
(c)	75 kJ/mol	(d)	135 kJ/mol

16. The results given in the below table were obtained during kinetic studies of the following reaction : $2A + B \rightarrow C + D$

D • (FA1/ 1T-1	11111 -1	Initial rate/mol L^{-1}
Experiment	A /mol L	B/mol L	 –1

			111111
Ι	0.1	0.1	$6.00 imes10^{-3}$
II	0.1	0.2	$2.40 imes 10^{-2}$
III	0.2	0.1	$1.20 imes 10^{-2}$
IV	X	0.2	$7.20 imes 10^{-2}$
V	0.3	Y	2.88×10^{-1}

X and *Y* in the given table are respectively (*JEE Main 2020*) (a) 0.4, 0.4 (b) 0.4, 0.3 (c) 0.3, 0.4 (d) 0.3, 0.3

- **17.** The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of *A* is $4 \times 10^{10} \text{ s}^{-1}$. Calculate *k* at 318 K. (NCERT) (a) $2.89 \times 10^{-2} \text{ s}^{-1}$ (b) $3.26 \times 10^{-2} \text{ s}^{-1}$ (c) $1.03 \times 10^{-2} \text{ s}^{-1}$ (d) $0.03 \times 10^{-2} \text{ s}^{-1}$
- **18.** The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.

$$\frac{\text{SO}_2\text{Cl}_2(g) \longrightarrow \text{SO}_2(g) + \text{Cl}_2(g)}{\text{Experiment}}$$

$$\frac{\text{Time/s}^{-1}}{pressure/atm}$$

 1
 0
 0.5

 2
 100
 0.6

 Calculate the rate of the reaction when total pressure is 0.65 atm. (NCERT Exemplar)

(a) 2.84×10^{-7} atm s⁻¹ (b) 7.80×10^{-4} atm s⁻¹ (c) 4.42×10^{-7} atm s⁻¹ (d) 5.62×10^{-4} atm s⁻¹

19. For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained. Calculate the rate constant. (NCERT)

t (s)	p (mm of Hg)
0	35.0
360	54.0
720	63.0

(a) $2.21 \times 10^{-3} \text{ s}^{-1}$	(b) $3.48 \times 10^{-3} \text{ s}^{-1}$
(c) $1.26 \times 10^{-3} \text{ s}^{-1}$	(d) $8.46 \times 10^{-3} \text{ s}^{-1}$

20. The rate of a certain biochemical reaction at physiological temperature (T) occurs 10^6 times faster with enzyme than without. The change in the activation energy upon adding enzyme is : (JEE Main 2020)

(a) $+ 6 RT$	(b) $- 6(2.303) RT$
(c) + 6 (2.303) RT	(d) $- 6 RT$

21. For the non-stoichiometric reaction, $2A + B \longrightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K. (JEE Main 2014)

Initial concentration (A)	Initial concentration (B)	Initial rate of formation of C (mol L ⁻¹ s ⁻¹)
$0.1 \mathrm{M}$	$0.1 \mathrm{M}$	1.2×10^{-3}
$0.1 \mathrm{M}$	$0.2 \mathrm{M}$	1.2×10^{-3}
$0.2 \mathrm{M}$	$0.1 \mathrm{M}$	2.4×10^{-3}

The rate law for the formation of Cis

(a) $\frac{dc}{dt} = k [A] [B]$	(b) $\frac{dc}{dt} = k [A]^2 [B]$
(c) $\frac{dc}{dt} = k [A] [B]^2$	(d) $\frac{dc}{dt} = k [A]$

22. A first order reaction is 50% completed in 30 min at 27°C and in 10 min at 47°C. Calculate the activation energy of the reaction.

(a) 43.8 kJ mol⁻¹

- (b) 4.38 kJ mol⁻¹
- (c) 0.438 kJ mol⁻¹
- (d) 438 kJ mol⁻¹
- **23.** The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25° C are 3.0×10^{-4} s⁻¹, 104.4 kJ mol⁻¹ and 6.0×10^{14} s⁻¹ respectively. The value of the rate constant at $T \to \infty$ is (a) 2.0×10^{18} s⁻¹ (b) 6.0×10^{14} s⁻¹ (c) 3.6×10^{30} s⁻¹ (d) infinity

Numeric Value Questions

- **24.** The half-life of two samples are 0.1 and 0.8 sec. Their respective concentration are 400 and 50 respectively. The order of the reaction is
- **25.** A and B decompose via first order kinetics with half-lives 54.0 min and 18.0 min respectively. Starting from an equimolar non-reactive mixture of A and B, the time taken for the concentration of A to become 16 times that of B is min. (JEE Main 2021)

- **26.** The decomposition of formic acid on gold surface follows first order kinetics. If the rate constant at 300 K is 1.0×10^{-3} s⁻¹ and the activation energy $E_a = 11.488$ kJ mol⁻¹, the rate constant at 200 K is× 10⁻⁵ s⁻¹. (Given : R = 8.314 J mol⁻¹ K⁻¹) (JEE Main 2021)
- 27. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about (times). (AIEEE 2011)
- **28.** In a first order reaction the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 min. The time taken for the concentration to change from 0.1 M to 0.025 M is (min).
- **29.** 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

(Take;
$$R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$$
, $\ln 3.555 = 1.268$)
(JEE Main 2020)

- 30. The half-life for radioactive decay of ¹⁴C is 5730 yr. An archaeological artifact containing wood had only 80% of the ¹⁴C found in a living tree. The age of the sample is yr. (NCERT)

- **33.** 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 activation energy (in kJ/mol) for this process is closest to (Given, $R = 8.3 \text{ J mol}^{-1}\text{K}^{-1} \ln\left(\frac{2}{3}\right) = 0.4, e^{-3} = 4.0$)
 (JEE Main 2020)
- **34.** The decomposition of *A* into product has values of *k* as 4.5×10^3 s⁻¹ at 10°C and energy of activation 60 kJ mol⁻¹. The temperature at which *k* would be 1.5×10^4 sec⁻¹ is
- **35.** The rate constant of the chemical reaction doubled for an increase of 10 K in absolute temperature from 295 K. The value of E_a will be kJ mol⁻¹.

Answers

Round I									
1. (a)	2. (b)	3. (b)	4. (b)	5. (d)	6. (c)	7. (c)	8. (a)	9. (b)	10. (d)
11. (c)	12. (a)	13. (d)	14. (a)	15. (a)	16. (c)	17. (b)	18. (c)	19. (a)	20. (a)
21. (a)	22. (d)	23. (d)	24. (c)	25. (a)	26. (a)	27. (c)	28. (a)	29. (a)	30. (b)
31. (a)	32. (c)	33. (a)	34. (b)	35. (b)	36. (b)	37. (a)	38. (d)	39. (d)	40. (c)
41. (a)	42. (d)	43. (c)	44. (c)	45. (b)	46. (a)	47. (d)	48. (d)	49. (c)	50. (b)
51. (a)	52. (b)	53. (a)	54. (d)	55. (d)	56. (a)	57. (a)	58. (d)	59. (d)	60. (b)
61. (b)	62. (a)	63. (c)	64. (a)	65. (c)	66. (d)	67. (b)	68. (d)	69. (d)	70. (d)
71. (b)	72. (d)	73. (d)	74. (c)						

Round II

1. (b)	2. (a)	3. (b)	4. (d)	5. (c)	6. (a)	7. (d)	8. (c)	9. (c)	10. (a)
11. (b)	12. (c)	13. (b)	14. (c)	15. (c)	16. (c)	17. (c)	18. (b)	19. (a)	20. (b)
21. (d)	22. (a)	23. (b)	24. (2)	25. (108)	26. (10)	27. (32)	28. (30)	29. (100)	30. (1845)
31. (60)	32. (84297.5)	33. (3.98)	34. (24.02)	35. (51.8)					

Solutions

6.

Round I

1. $2A + B \longrightarrow$ products

[B] is doubled, half-life didn't change, i.e. half-life is independent of change in conc. of reactant, i.e. first order. First order wrt to B.

When [A] is doubled, rate increased by two times

 \Rightarrow First order wrt A

Hence, net order of reaction = 1 + 1 = 2

Unit for the rate constant = conc.⁽¹⁻ⁿ⁾ t^{-1}

$$= (\text{mol } \text{L}^{-1})^{-1} \cdot \text{s}^{-1} = \text{L} \cdot \text{mol}^{-1} \text{ s}^{-1}$$

 $\frac{1}{2}A \longrightarrow 2B$

For the given reaction

$$-\frac{2d [A]}{dt} = \frac{1}{2} \frac{d [B]}{dt} = \text{Rate of reaction}$$

Rate of disappearance of A
=
$$-\frac{d [A]}{dt} = \frac{1}{2 \times 2} \frac{d[B]}{dt} = \frac{1}{4} \frac{d [B]}{dt}$$

3.
$$H_2 + I_2 \longrightarrow 2HI$$

Rate of reaction $= \frac{-d [H_2]}{dt} = \frac{-d [I_2]}{dt} = \frac{1}{2} \frac{d [HI]}{dt}$
or $\frac{-2d [H_2]}{dt} = \frac{-2d [I_2]}{dt} = \frac{d [HI]}{dt}$

4.
$$B + 5D \longrightarrow 3A + 2C$$

 $\frac{-d [5]}{at} = \frac{-1}{5} \frac{d [D]}{at} = \frac{+1}{3} \frac{d [A]}{dt} = \frac{+1}{2} \frac{d [C]}{dt}$

5. $2A + B \longrightarrow C$

Rate = k [A] [B]

It represents second order reaction.

Thus, unit of k is M^{-1} s⁻¹.

 $t_{1/2}$ is dependent of concentration but not constant.

 Δt

and
$$-\frac{1}{2}\frac{d[A]}{dt} = \frac{d[C]}{dt}$$

$$\operatorname{Rate} = -\frac{1}{5} \frac{\Delta [\operatorname{Br}^{-}]}{\Delta t} = -\frac{1}{6} \frac{\Delta [\operatorname{H}^{+}]}{\Delta t}$$
or
$$\Delta [\operatorname{Br}^{-}] = +\frac{5}{5} \Delta [\operatorname{H}^{+}]$$

or
$$\Delta t = \pm \frac{1}{6} \frac{1}{\Delta t}$$

7. Average rate $= \frac{\Delta R}{\Delta t} = \frac{V_3}{40}$

8. Rate of reaction = $\frac{-\Delta[R]}{\Delta t}$

Where negative sign shows that rate of reaction decreases as concentration of reactants decreases.

9. Instantaneous speed = $\frac{x_2 - x_1}{t_2 - t_1}$ $\therefore \text{ Instantaneous speed} = \frac{V_5 - V_2}{50 - 30}$ $=\frac{V_{3}-V_{2}}{40-30}$ $=\frac{V_{3}-V_{1}}{40-20}$ $= \frac{V_4 - V_2}{45 - 30}$

10. For a first order reaction,

rate = k [reactant]
[reactant] =
$$\frac{\text{rate}}{k}$$

conc. of N₂O₅³ = $\frac{2.40 \times 10^{-5}}{3.0 \times 10^{-5}}$ = 0.8

11. For the reaction,

$$2X + Y \longrightarrow Z$$

Rate = $-\frac{1}{2} \frac{d[X]}{dt} = \frac{d[Z]}{dt}$
= 0.05 mol L⁻¹ min⁻¹
 $-\frac{1}{2} \frac{d[X]}{dt} = 0.05$
 $-\frac{d[X]}{dt} = 2 \times 0.05$
= 0.1 mol L⁻¹ min⁻¹

12. For *n*th order reaction,

$$k = (\text{mol } \mathbf{L}^{-1})^{1-n} \mathbf{s}^{-1}$$

13. If the reaction is an elementary reaction, order = molecularity.

14. Rate =
$$\frac{dx}{dt}$$
 = k [CCl₃CHO][NO]
 $k = \frac{dx}{dt \times [CCl_3CHO][NO]}$
 $= \frac{\text{mol} / L}{\text{s} \times \text{mol} / L \times \text{mol} / L}$
 $k = L \text{mol}^{-1} \text{ s}^{-1}$

- **15.** Value of rate constant remains unaffected from change in concentration.
- **16.** For second order kinetics, rate = k [reactant]², So make two equation first by taking initial rate and concentration, second by taking tripled concentration and unknown rate (r'). Compare them to find a relation between r and r'.

For the reaction, $x \longrightarrow y$ Reaction rate $(r) = k [x]^2$...(i) If the concentration of *x* is increased three times, then

Reaction rate $(r') = k [3x]^2 = k \times [9x^2]$...(ii) Dividing Eq. (ii) by Eq. (i);

$$\frac{r'}{r} = \frac{k \times [9x^2]}{k \times [x^2]} = 9$$

It means that the rate of formation of *y* will increase by **nine times**.

17. Rate (r) = k [A][B] = kab

When volume is reduced by one fourth then concentration becomes 4 times.

Hence,
$$r' = k(4a)(4b) = 16kab$$

 \therefore $r' = 16r$

18. For first order reaction,

$$\log[A] = \frac{-kt}{2.303} + \log[A]_0$$

$$interpretation \int_{100}^{100} A \int_{100}^{100} Slope = \frac{-k}{2.303}$$

19. In the presence of acid, hydrolysis of ethyl acetate is a pseudo-unimolecular reaction but the actual value of k depends upon the concentration of H⁺ ion. As H₂SO₄ is stronger acid than HCl and moreover H⁺ ions produced from 0.05 M H₂SO₄ is double than 0.05 M HCl therefore, $k_1 < k_2$.

20.
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$$

÷

If

If

$$k_3 > k_2 > k_1$$

As k_1 is smallest hence reaction is slowest therefore $A \longrightarrow B$ is the rate determining step of the reaction.

- **21.** The slowest step is the rate determining step. Formation of *B* (i.e. step I) is the slowest step, therefore, step I is the rate determining step.
- **22.** There are two different reactants (say A and B).

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

Thus, it is a bimolecular reaction.

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

it is second order reaction

$$\left(\frac{dx}{dt}\right) = k [A] \text{ or } = k [B]$$

it is first order reaction.

Molecularity is independent of rate, but is the sum of the reacting substances, thus it cannot be unimolecular reaction.

23. Slowest step is the rate determining step. Thus, in case (*A*), rate law is given as rate = $k [Cl_2][H_2S]$ While for the reaction given in case (*B*), rate law is given as,

rate =
$$k [H_2S][Cl_2][H^+]^{-1}$$
.

Hence, only mechanism (A) is consistent with the given rate law.

24.
$$\left(\frac{dx}{dt}\right) = k \left[\text{NO}\right]^2 \left[\text{O}_2\right]$$
$$= k \left(\frac{n_{\text{NO}}}{V}\right)^2 \left(\frac{n_{\text{O}_2}}{V}\right)$$
$$\left(\frac{dx}{dt}\right) = \frac{k}{V^3} (n_{\text{NO}})^2 (n_{\text{O}_2})$$
$$\left(\frac{dx}{dt}\right) = \frac{k (n_{\text{NO}})^2 (n_{\text{O}_2})}{\left(\frac{V}{2}\right)^3} = 8 \left(\frac{dx}{dt}\right)$$

25. $2H_2(g) + 2NO(g) \Longrightarrow N_2(g) + 2H_2O(g)$

Rate law for forward reaction is given as:

Rate = $k_f [NO]^2 [H_2]$

Rate of forward reaction is equal to rate of reverse reaction at equilibrium and also,

at equilibrium $(K) = \frac{k_f}{r}$

where, K (equilibrium constant)

$$= \frac{[N_2] [H_2O]^2}{[H_2]^2 [NO]^2} \Rightarrow \frac{k_f}{k_b} = \frac{[N_2] [H_2O]^2}{[H_2]^2 [NO]^2}$$

Rearranging :

$$k_f [H_2] [NO]^2 = k_b [N_2] [H_2O]^2 / [H_2]$$

∴ Rate of reverse reaction =
$$k_b$$
 [N₂] [H₂O]²/[H₂]

26. Let the rate equation be $k [A]^{x} [B]^{y}$

From Ist values,

 $0.045 = k[0.05]^x [0.05]^y$...(i) From 2nd values,

$$0.090 = k \ [0.10]^x \ [0.05]^y$$
 ...(ii)
From 3rd values,

$$0.72 = k[0.20]^x [0.10]^y \dots$$
(iii)

On dividing equations (i) by (ii), we get

$$\frac{0.045}{0.09} = \left[\frac{0.05}{0.10}\right]^x \implies \left[\frac{0.05}{0.10}\right]^1 = \left[\frac{0.05}{0.10}\right]^x$$
$$x = 1$$

Similarly on dividing Eq. (ii) by (iii) we get

$$\frac{0.09}{0.72} = \left[\frac{0.1}{0.2}\right]^x \left[\frac{0.05}{0.10}\right]^y \implies \frac{0.01}{0.08} = \frac{0.1}{0.2} \left[\frac{0.05}{0.1}\right]^y$$
$$0.25 = \left[\frac{0.05}{0.10}\right]^y \implies 0.25 = [0.5]^y$$
$$[0.5]^2 = [0.5]^y \implies y = 2$$

Hence, the rate law for the reaction Rate = $k [A] [B]^2$

28.

:.

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

When,

$$n-1 = 3 \implies n = 3+1 = 4$$

Hence, order of reaction = 4

- **29.** From the graph it is clear that the reaction is of zero order and hence, the units of rate constant = mol $L^{-1}\ s^{-1}$
- **32.** Order of reaction may or may not equal to the sum of stoichiometric coefficient of reactants in a balanced chemical equation.
- **34.** $RCl + NaOH \longrightarrow ROH + NaCl$

$$Rate = k [RCl]$$

For this reaction, rate of reaction depends upon the concentration of RCl.

It means, the rate of reaction is halved by reducing the concentration of RCl by one half.

36. For zero order reaction, x = kt

=

$$0.2 \text{ mol } dm^{-3} \text{ h}^{-1} \times \frac{30}{60} \text{ h}$$

 $= 0.1 \text{ mol dm}^{-3}$ Now, concentration = 0.05 mol dm^{-3} Hence, initial concentration = 0.1 + 0.05 $= 0.15 \text{ mol dm}^{-3}$

37. For 2/3 of a reaction,

$$[A]_0 = a, \quad [A] = a - \frac{2}{3}a = \frac{a}{3}$$

$$\therefore \qquad t_{2/3} = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$$

$$= \frac{2.303}{5.48 \times 10^{-14}}\log\frac{a}{a/3}$$

$$= \frac{2.303}{5.48 \times 10^{-14}}\log 3$$

$$t_{2/3} = 2.01 \times 10^{13} \text{ s}$$

38. For first order reactions,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(3.0 \text{ h})}$$

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

or

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

$$\log \frac{[A]_0}{[A]} = \frac{0.693}{3 \text{ h}} \times \frac{(8 \text{ h})}{2.303} = 0.8024$$

$$\frac{[A]_0}{[A]} = \text{Antilog } 0.8024 = 6.345$$

$$[A]_0 = 1 \text{ M}; [A] = \frac{[A]_0}{6.345} = \frac{1 \text{ M}}{6.345}$$

39. We know that,

Rate = k (concentration)ⁿ

 \log (Rate) = $\log k + n \log$ [concentration]

Slope of graph is the order of reaction. Greater the slope, greater is the order of reaction.

: Correct sequence for the order of reaction is D > B > A > C.

Hence, the correct option is (d).

40.
$$k = \frac{1}{t} \left[\frac{x}{a(a-x)} \right]$$
$$k = \frac{1}{500} \left[\frac{0.2 a}{a(a-0.2 a)} \right] = \frac{1}{2000a}$$
$$\frac{1}{2000a} = \frac{1}{t} \left[\frac{0.6a}{a(a-0.6 a)} \right]$$
$$t = 3000 \text{ s}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{65}$$
After 260 hr,

$$k = \frac{2.303}{260} \log \frac{a}{a-x}$$

$$\frac{0.693}{65} = \frac{2.303}{260} \log \frac{a}{a-x}$$

$$\frac{a}{a-x} = 16 \implies \frac{1}{1-x} = 16$$

$$x = \frac{15}{16} = 0.9375 \text{ g}$$

42. Since, the reaction is 50% completed in 1.26×10^{14} s.

$$t_{1/2} = 1.26 \times 10^{14} \text{ s}$$
$$k = \frac{0.693}{t_{12}} = \frac{0.693}{1.26 \times 10^{14}}$$

For 100% completion,

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$
$$t = \frac{2.303 \times 1.26 \times 10^{14}}{0.693} \log \frac{100}{0} = \infty$$

43. For a first order reaction,

Rate = k (concentration)

$$\therefore k = \frac{\text{Rate}}{\text{concentration}} = \frac{1.5 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ min}^{-1}}{0.5 \text{ mol } \text{L}^{-1}}$$

$$= 3 \times 10^{-2} \text{min}^{-1}$$

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

$$= \frac{69.3}{3} \text{ min or } 23.1 \text{ min}$$
44. For a zero order reaction, $k_0 = \frac{[A]_0}{2}$

 $k_0 = 1$ $k_0 = \frac{\Delta x}{t}$

Since, $[A]_0 = 2 \text{ M}, t_{1/2} = 1 \text{ h}$

So,

and

45. $kt = -\log_e C_t + \log_e C_0$

$$t = -\frac{1}{k}\log_e C_t + \log_e C_0$$

 $t = \frac{0.50 - 0.25}{1} = 0.25 \text{ h}$

y = mx + c, straight line, negative slope.

46. For first order reaction,

$$t = \frac{2.303}{k} \log \frac{a}{(a-x)} \qquad \dots (i)$$
 Given, $(a-x) = \frac{a}{16}$; $k = 60 \text{ s}^{-1}$

Placing the given values in Eq. (i)

$$t = \frac{2.303}{60 \text{ s}^{-1}} \log \frac{a \times 16}{a} = \frac{2.303}{60 \text{ s}^{-1}} \log 16 = \frac{2.303}{60 \text{ s}^{-1}} \log 2^4$$
$$= \frac{2.303}{60 \text{ s}^{-1}} \times 4 \log 2 = \frac{2.303}{60 \text{ s}^{-1}} \times 4 \times 0.3010$$
$$= 4.62 \times 10^{-2} \text{ s}$$
Time = $4.62 \times 10^{-2} \text{ s}$

47. We know that, $N = N_0 e^{-Kt}$

K can be calculated as

$$K = \frac{\ln 2}{t_{1/2}}$$
 (Here, $t_{1/2}$ = half-life)

 \therefore The time required for the concentration of *A* to be four times that of *B*. Hence,

$$\begin{split} A &= 4B \\ N_0 e^{\frac{-\ln 2t}{300}} &= 4 \cdot N_0 e^{\frac{-\ln 2t}{180}} \Rightarrow -\frac{\ln 2t}{300} = \ln 4 - \frac{\ln 2t}{180} \\ \Rightarrow \ln 2t \left[\frac{1}{180} - \frac{1}{300} \right] &= 2\ln 2; \\ \Rightarrow \qquad t &= \frac{2 \times 180 \times 300}{120} = 900 \text{ s} \end{split}$$

48. In first order reaction, the rate expression depends on the concentration of one species only having power equal to unity.

$$\begin{array}{c} nr \longrightarrow \text{products} \\ \frac{-d[r]}{dt} = k \ [r] \end{array}$$

On integration, $-\ln[r] = kt - \ln[r_0]$

or $\ln(r) = \ln(r_0) - kt \implies y = c + mx$ $m = \text{slope} = -k \text{ (negative); } c = \text{intercept} = \ln(r_0)$

The graph for first order reactions is



In zero order reaction,

 $[r] \longrightarrow \text{product}$

:..

If

:..

$$\frac{-d[r]_t}{dt} = k \text{ or } -d[r]_t = kdt$$

On integrating, $-[r]_t = kt + c$

$$t = 0, [r]_t = [r]_0$$

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

 $\Rightarrow \qquad [r]_t = [r]_0 - kt$

Thus, the graph plotted between $[r]_t$ and t gives a straight line with negative slope (-k) and intercept equal to $[r]_0$.

41.

:..

The graph for zero order reaction is



49. For the reaction, $2A + B \longrightarrow$ products. Let, the rate expression is $r \propto [A]^a [B]^b$

Expt. 1
$$\frac{r_2}{r_1} = \left(\frac{2A}{A}\right)^a \left(\frac{2B}{B}\right)^b$$

$$\Rightarrow \qquad \frac{2.4}{0.3} = 2^a \times 2^b \Rightarrow 2^3 = 2^{a+b}$$

$$\Rightarrow \qquad 3 = a+b \qquad \dots (i)$$
Expt. 2
$$\frac{r_2}{r_1} = \left(\frac{2A}{A}\right)^a \left(\frac{B}{B}\right)^b$$

$$\Rightarrow \qquad \frac{0.6}{0.3} = 2^a \times 1 \Rightarrow 2^1 = 2^a \Rightarrow a = 1 \qquad \dots (ii)$$

$$\therefore \qquad \text{From Eq. (i), } 1+b=3 \Rightarrow b=2$$

$$\Rightarrow \text{ Order of the reaction } (n) = a+b=1+2=3$$

- \Rightarrow Order of the reaction wrt. A = 1
- \Rightarrow Order of the reaction wrt. B = 2
- **50.** Rate constant for the first order reaction is given by,

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

$$a = 0.1 \text{ M}$$

$$(a - x) = 0.025 \text{ M} \implies t = 40 \text{ min}$$

$$k = \frac{2.303}{40} \log\frac{0.1}{0.025 \text{ M}} = 0.0347 \text{ min}^{-1}$$

$$\text{Rate} = \left(\frac{dx}{dt}\right) = k[A]^1 = 0.0347 \times 0.1$$

$$= 3.47 \times 10^{-4} \text{ M min}^{-1}$$

51. For the reaction,

$$CH_3CHO(g) \xrightarrow{Decomposes} CH_4 + CO$$

Let order of reaction with respect to CH_3CHO is m. Its given, $r_1 = 1$ torr/sec when CH_3CHO is 5% reacted i.e. 95% unreacted. Similarly, $r_2 = 0.5$ torr/sec when CH_3CHO is 33% reacted, i.e. 67% unreacted.

Use the formula, $r \propto (a - x)^m$

where (a - x) = amount unreacted

so,
$$\frac{r_1}{r_2} = \frac{(a - x_1)^m}{(a - x_2)^m}$$
 or $\frac{r_1}{r_2} = \left[\frac{a - x_1}{a - x_2}\right]^m$

Now, putting the given values

$$\frac{1}{0.5} = \left(\frac{0.95}{0.67}\right)^m$$

 \Rightarrow 2 = (1.41)^m or m = 2

52. Let the order of reaction with respect to A is x and B is y.

\therefore rate law, $r = k [A]^x [B]^y$	(iv)
On putting values, we get	
$0.10 = k [0.30]^{x} [0.30]^{y}$	(i)
$0.40 = k [0.30]^{x} [0.60]^{y}$	(ii)
$0.20 = k \ [0.60]^x \ [0.30]^y$	(iii)
From Eq. (i) and (ii) we get	

$$\frac{0.1}{0.4} = \left(\frac{0.30}{0.30}\right)^x \left(\frac{0.30}{0.60}\right)^y$$
$$\frac{1}{4} = \left(\frac{1}{2}\right)^y$$
$$4 = 2^y$$

$$(2)^2 = 2^y$$
 or $y = 2$

From Eq. (ii) and (iii), we get

or

$$\frac{0.40}{0.20} = \left(\frac{0.30}{0.60}\right)^x \left(\frac{0.60}{0.30}\right)^y$$
$$2 = \left(\frac{1}{2}\right)^x (2)^y$$

On putting the values of *y*, we get

$$2 = \left(\frac{1}{2}\right)^{x} (2)^{2}$$
$$\frac{2}{4} = \left(\frac{1}{2}\right)^{x} \Rightarrow \left(\frac{1}{2}\right)^{1} = \left(\frac{1}{2}\right)^{x}$$

or

- On putting the values of x and y in Eq. (iv), we get $r = k [A]^{1}[B]^{2} = k [A][B]^{2}$
- **53.** The expression for bacterial growth is

x = 1

$$N = N_0 e^t \implies \frac{N_0}{N} = e^{-t}$$

From 0 to 1 hour $N'(t) = N_0 e^t$

From 1 hour onwards,
$$\frac{dN}{dt} = -5N^2$$

On differentiating the above equation from N' to N we get.

$$\int_{eN_0}^{N} N^{-2} dN = -5 \int_{1}^{t} dt \qquad [:: At 1 hour, N' = eN_0]$$
$$\frac{1}{N} - \frac{1}{eN_0} = 5(t-1)$$

Multiply both sides by N_0 , we get

$$\frac{N_0}{N} - \frac{1}{e} = 5N_0(t-1) \text{ or}, \frac{N_0}{N} = 5N_0(t-1) + \frac{1}{e}$$

$$\frac{N_0}{N} = 5N_0t + \left[\frac{1}{e} - 5N_0\right]$$

On comparing the above equation with equation of straight line, y = mx + c

we get,
$$m = 5N_0$$
 $c = \frac{1}{e} - 5N_0$
 \therefore Plot of $\frac{N_0}{N}$ vs t is shown in graph (a).

55. Arrhenius equation is

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

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

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

$$\text{Slope} = -\frac{E_a}{R}$$

$$\uparrow$$

$$\downarrow$$

$$\sum_{i=1}^{N} \text{Slope} = -\frac{E_a}{R}$$

56. $k = Ae^{-E_a/RT}$

On taking log, we get

$$\log k = \log A - \frac{E_a}{2.203RT}$$
$$\ln k = \ln A - \frac{E_a}{RT}$$

or

:. A graph between $\ln k vs 1/T$ is a straight line (according to equation of straight line *viz*. y = mx + c) with $-\frac{E_a}{k}$ slope (negative slope) and $\ln A$ intercept.

 \therefore Correct graph is graph (a).

In all other graphs slope is positive.

57. For exothermic reaction,

Energy of reactants > energy of product, which is the case given in (i).

58. : Rate constant (k') > rate constant (k'')

Greater the rate constant lesser will be the activation energy.

 $\therefore \qquad E_a' < E_a''$

- **59.** The given equation clearly has shown that the rate constant k increases exponentially with decreasing activation energy and increasing temperature.
- **61.** $k = Ae^{-E/RT}$

E is activation energy. It is that energy, which molecule must have to give the product.

- **62.** Activation energy of backward reaction = E_1

 - :. Products are less stable than reactants.
- 63. For endothermic reaction, A → B
 Activation energy = 15 kcal/mol
 Energy of reaction = 5 kcal/mol
 Hence, activation energy for the reaction B → A is 15 5 = 10 kcal/mol



66. Only statement (d) is incorrect. Corrected statement is; "Activation enthalpy to form *C* is 15 kg mol⁻¹ more than 5 kg mol^{-1} that is required to form A + B." It can be easily explained by following graph.



Activation enthalpy (or energy) is the extra energy required by the reactant molecules that result into effective collision between them to form the products.

67. The Arrhenius equation is, $k = A \cdot e^{-E_a/RT}$

From the equation, it is clear that k decreases exponentially with E_a . So, the plot-I is correct.

In the plot-II, k is plotted with temperature (in °C but not in K). So, at 0°C, $k \neq 0$ and k will increase exponentially with temperature upto 300°C. Therefore, the plot-II is also correct.

68. The temperature dependence of rate of a chemical reaction is expressed by Arrhenius equation as,

$$k = A e^{-E_a/RT} \qquad \dots (i)$$

where, A = Arrhenius factor or frequency factor or pre-exponential factor

 $R = Gas constant, E_a = Activation energy$

Taking log on both sides of the Eq. (i), the equation becomes

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

On comparing with equation of straight line (y = mx + c), the nature of the plot of $\ln k vs \frac{1}{RT}$ will be

(i) Intercept = $C = \ln A$

(ii) Slope/gradient = $m = -E_a = -y \Rightarrow E_a = y$

So, the energy required to activate the reactant, (activation energy of the reaction, E_a is = y)

69. According to Arrhenius equation,

$$k = Ae^{-E_a/RT} \implies \log k = \log A - \frac{E_{act}}{2.303RT}$$

 $E_{\rm act}$ = activation energy

Slope of the graph of 'log k' vs
$$\frac{1}{T}$$
 is $\frac{-E_{act}}{2.303R}$

Greater the value of $E_{\rm act},$ more will be the negative slope.

From the graph,

most –ve slope = c, followed by a, d and b.

:. Order of activation energies must be

$$E_c > E_a > E_d > E_b$$

 $k_2 = A' e^{-E_{a2}/RT}.$

71. $A \xrightarrow{k_1} B, A \xrightarrow{k_2} C,$

By Arrhenius equation, $k_1 = A' e^{-E_{a_1}/RT}$

and

(A' is Arrhenius constant.)

(Since, $E_{a_2} = 2E_{a_1}$) . $k_2 = A' e^{-2E_a/RT}$

...

...

$$\frac{k_1}{k_2} = \frac{A' e^{-E_{a_1}/RT}}{A' e^{-2Ea_1/RT}} = e^{E_{a_1}/RT}$$
$$k_1 = k_2 e^{E_{a_1}/RT}$$

72. $X \rightarrow Y$ is an endothermic reaction, $\Delta H = +$ ve



 $E_b = \text{energy of activation of backward reaction}$ $E_f = \text{energy of activation of forward reaction}$ $\Delta H = \text{heat of reaction}$

Thus, $E_f = E_b + \Delta H$ Thus, $E_f > E_b$

73. For the reaction, $H_2 + I_2 \longrightarrow 2HI$ Given $k_1 = 2.5 \times 10^{-4} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$
$$\begin{split} T_1 &= (273+327)\,\mathrm{K} = 600\,\mathrm{K} \\ k_2 &= 1\,\mathrm{dm}^3\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}\,\mathrm{at}\,T_2 = (273+527)\,\mathrm{K} = 800\,\mathrm{K} \\ \mathrm{The}\,\mathrm{Arrhenius}\,\mathrm{equation}\,\mathrm{for}\,\mathrm{rate}\,\mathrm{constants} \\ \mathrm{at}\,\mathrm{two}\,\mathrm{different}\,\mathrm{temperatures}\,\mathrm{is} \end{split}$$

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

$$\Rightarrow \log \frac{1}{2.5 \times 10^{-4}} = \frac{E_a}{2.303 \times 8.314 \times 10^{-3}} \left(\frac{800 - 600}{600 \times 800}\right)$$

$$\Rightarrow \log \frac{(10 \times 10^3)}{2.5} = \frac{E_a}{0.019} \times \frac{200}{48 \times 10^4}$$

$$\Rightarrow \log 4 + 3 \log 10 \approx E_a \times 0.022$$

 $\Rightarrow \quad E_a = \frac{2 \times \log 2 + 3}{0.022} = \frac{3.6}{0.022} \simeq 163.6 \text{ kJ mol}^{-1}$

74. The temperature dependence of a chemical reaction is expressed by Arrhenius equation,

$$k = A e^{-E_{\hat{a}}/RT} \qquad \dots (i)$$

Taking natural logarithm on both sides, the Arrhenius equation becomes, $\ln k = \ln A - \frac{E_a}{RT}$

where, $-\frac{E_a}{R}$ is the slope of the plot and $\ln A$ gives the intercept.

Eq. (i) at two different temperatures for a reaction becomes,

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad ...(ii)$$

 \Rightarrow In the given problem,

$$T_1$$
 = 400 K, T_2 = 500 K, k_1 = 10 $^{-5}$ s $^{-1}, k_2$ = ?
$$-\frac{E_a}{R} \text{ (Slope)} = - 4606$$

On substituting all the given values in Eq. (ii), we get

$$\ln \frac{k_2}{10^{-5}} = 4606 \left(\frac{1}{400} - \frac{1}{500} \right)$$
$$\ln \frac{k_2}{10^{-5}} = 2.303$$
$$\frac{k_2}{10^{-5}} = 10 \implies k_2 = 10^{-4} \text{ s}^{-1}$$

Therefore, rate constant for the reaction at 500 K is 10^{-4} s⁻¹.

Round II

1. Rate depends upon the slowest step. Hence, from equation

$$\begin{array}{ccc} \mathrm{O} + \mathrm{O}_3 & \longrightarrow & 2\mathrm{O}_2 \\ r = k \; [\mathrm{O}_3][\mathrm{O}] \\ \mathrm{and \; from \; equation} & \mathrm{O}_3 \; \rightleftharpoons \; \mathrm{O}_2 + \mathrm{O} \\ K_{\mathrm{eq}} = \frac{[\mathrm{O}_2][\mathrm{O}]}{[\mathrm{O}_3]} \end{array}$$

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

$$\therefore \qquad r = k [O_3] \frac{K_{eq} [O_3]}{[O_2]} = k' [O_3]^2 [O_2]^{-1}$$

2. $t_1 = \frac{2.303 (t_{1/2})_1}{0.693} \log\left(\frac{1}{1 - (1/4)}\right)$
and $t_2 = \frac{2.303 (t_{1/2})_2}{0.693} \log\left(\frac{1}{1 - (3/4)}\right)$

$$\frac{t_1}{t_2} = \frac{8}{1} \times \frac{\log (4/3)}{\log 4}$$

$$= \frac{8 \times 0.125}{0.602} = 1:0.602$$

3. $k = 2.1 \times 10^{10} \exp(-2700/RT)$

i.e. $\log k vs 1/T$ will be straight line intercept of log k axis = log 2.1×10^{10}

4.
$$A^m + B^n \longrightarrow ABx$$

In this case,

overall order of reaction may or may not be = m + nHence, code 3 is wrong.

5. The reaction occurring in two steps has two activation energy peaks. The first step, being fast needs less activation energy. The second step being slow, needs more activation energy. Therefore, second peak will be higher than the first.

6. According to Arrhenius equation,

$$k = Ae^{-E_a/RT} \qquad \dots (i)$$

According to the available data

 $k = (4.5 \times 10^{11} \text{s}^{-1}) e^{-28000} \text{ K} / T$

On comparing both equations;

$$-\frac{E_a}{RT} = \frac{-28000 \text{ K}}{T}$$

$$E_a = (28000 \text{ K}) \times R = (28000 \text{ K}) \times (8.314 \text{ K}^{-1} \text{J mol}^{-1})$$

$$= 232792 \text{ kJ mol}^{-1}$$

$$E_a = 232.792 \text{ kJ mol}^{-1}$$

$$\begin{aligned} r_1 &= k \, [A]^a \, [B]^b \\ r_2 &= k \, [2A]^a \left[\frac{B}{2} \right]^b = k \, [A]^a \, [B]^b \, 2^{(a-b)} \\ \vdots & \frac{r_2}{2} = 2^{(a-b)} \end{aligned}$$

 r_1

7.

8.

$$r_1 = k [A]^n$$

$$r_2 = 1.837 r_1 = k [1.5 A]^n$$
∴
$$\frac{r_2}{r_1} = 1.837 = (1.5)^n$$

$$\Rightarrow n = \frac{3}{2} = 1.5 \qquad \text{(On solving by logarithmic method)}$$

9.
$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

Rate constant = $2.3 \times 10^{-2} \text{ s}^{-1}$

The unit of rate constant (i.e. s^{-1}), shows that reaction is of first order.

For first order reaction,

or

$$\begin{aligned} k &= \frac{1}{t} \ln \frac{a}{a - x} \implies k = \frac{1}{t} \ln \frac{[N_2 O_5]_0}{[N_2 O_5]_t} \\ & \ln \frac{[N_2 O_5]_0}{[N_2 O_5]_t} = kt \end{aligned}$$

10. % distribution of
$$B = \frac{k_1}{k_1 + k_2} \times 100$$

 $= \frac{1.26 \times 10^{-4}}{1.26 \times 10^{-4} + 3.8 \times 10^{-5}} \times 100$
 $= 76.83\%$
and, % distribution of $C = \frac{k_2}{k_1 + k_2} \times 100$
 $= \frac{3.8 \times 10^{-5}}{1.26 \times 10^{-4} + 3.8 \times 10^{-5}} \times 100$
 $= 23.17\%$

11. For reaction, $A + B \longrightarrow C + D$

 $r_1 = k [A]^a [B]^b$...(i) $r_2 = 2r_1 = k [2A]^a [B]^b$...(ii) $r_3 = 3r_1 = k[A]^a \ [9B]^b$ and ...(iii) From (i) and (ii) a = 1Form (i) and (iii), $b = \frac{1}{2}$ Order = $a + b = 1 + \frac{1}{2} = \frac{3}{2} = 1.5$ *:*.. **12.** For first order reaction, 0.693 0.22 h⁻¹

...(ii)

$$k = \frac{1}{t_{1/2}} = \frac{1}{2.1} = 0.33 \text{ h}^{-1}$$

and
$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

or
$$t = \frac{2.303}{k} \log_{10} \frac{100}{(100-99)}$$
$$= \frac{2.303}{0.33} \times \log_{10} 100 = \frac{2.303}{0.33} \times 2 = 13.96 \text{ h}$$

13. Fraction of molecules (*x*) having energy equal to or more than activation energy may be calculated as follows

$$x = n/N = e^{-E_a/RT}$$

ln $x = \frac{-E_a}{RT}$ or $\log x = -\frac{E_a}{2.303 RT}$
or $\log x = -\frac{209.5 \times 10^3 \text{ J mol}^{-1}}{2.303 \times (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times 581 \text{ K}}$
 $= -18.8323$
 $x = \text{Antilog} (-18.8324) = \text{Antilog } \overline{19.1677}$
 $= 1.471 \times 10^{-19}$
Fraction of molecules $= 1.471 \times 10^{-19}$

14. In the given reaction; $x A \longrightarrow y B$

$$\log_{10}\left[\frac{-d[A]}{dt}\right] = \log_{10}\left[\frac{d[B]}{dt}\right] + 0.3010$$

Value of $\log 2 = 0.3010$ Substituting 0.3010 by $\log 2$

$$\log_{10} \left[-\frac{d[A]}{dt} \right] = \log_{10} \left[\frac{d[B]}{dt} \right] + \log 2$$

Using logarithm rules,

$$\left[\frac{-d[A]}{dt}\right] = 2 \times \left[\frac{d[B]}{dt}\right] \Longrightarrow -\frac{1}{2} \left[\frac{d[A]}{dt}\right] = \left[\frac{d[B]}{dt}\right] \qquad \dots (i)$$

Using the rate equation (i) to determine the reaction involved is

$$2A \longrightarrow B$$

Option that fits correct in the above reaction is (c).

$$2C_2H_4 \longrightarrow C_4H_8$$

15. For catalysed reaction, let E_a be x.

Then, for uncatalysed reaction,

 $E_a=x+30 \qquad {\rm (given~in~question)} \label{eq:expansion}$ Also, rate of reaction at 700 K (without catalyst) = rate of reaction at 500 K (with catalyst).

:. k at 700 K without catalyst = k at 500 K with catalyst.

Using relation,

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

 E_a = Activation energy.

$$\therefore \qquad Ae^{-(x+30)/700R} = Ae^{-x/500R}$$

$$\therefore \qquad \frac{x+30}{700} = \frac{x}{500} \Rightarrow 7x = 5x + 150$$

$$2x = 150 \Rightarrow x = 75 \text{ kJ mol}^{-1}$$

16. Let, the rate law is : $r \propto [A]^a [B]^b$

:. *a* and *b* are the order of reaction w.r.t *A* and *B* respectively.

 \Rightarrow Comparing first three (I, II, III) experiments :

$$\frac{r_{\rm II}}{r_{\rm I}} = \left(\frac{0.1}{0.1}\right)^{a} \times \left(\frac{0.2}{0.1}\right)^{b} \Rightarrow \frac{2.4 \times 10^{-2}}{6 \times 10^{-3}} = 1 \times 2^{b}$$

$$\Rightarrow 2^{b} = 4 \Rightarrow b = 2$$

$$\frac{r_{\rm III}}{r_{\rm I}} = \left(\frac{0.2}{0.1}\right)^{a} \times \left(\frac{0.1}{0.1}\right)^{2} \Rightarrow \frac{1.2 \times 10^{-2}}{6 \times 10^{-3}} = 2^{a} \times 1$$

$$\Rightarrow 2^{a} \times 2 \Rightarrow a = 1$$

$$\Rightarrow r_{\rm I} = k \times (0.1)^{1} (0.1)^{2} \Rightarrow 6 \times 10^{-3} = k \times 10^{-3}$$

$$\Rightarrow k = 6 \ L^{2} \ \text{mol}^{-2} \ \text{min}^{-1}$$

$$\Rightarrow \text{Expt. IV} : r_{\rm II} = 6 \times (X)^{1} \times (0.2)^{2}$$

$$\Rightarrow 7.2 \times 10^{-2} = 6 \times (X) \times (4 \times 10^{-2})$$

$$\Rightarrow X = 0.3 \ \text{mol } L^{-1}$$

$$\Rightarrow \text{Expt. V} : r_{\nu} = 6 \times (0.3)^{1} \times (Y)^{2}$$

$$\Rightarrow Y = 0.4 \ \text{mol } L^{-1}$$
17. For first order reaction : $k = \frac{2.303}{t} \log \frac{[A]_{0}}{[A]}$

At 298 K,
$$k_1 = \frac{2.303}{t} \log \frac{100}{90}$$
 ...(i)

At 308 K,
$$k_2 = \frac{2.303}{t} \log \frac{100}{75}$$
 ...(ii)
Dividing eq. (ii) by (i);

$$\frac{k_2}{k_1} = \frac{\log \frac{100}{75}}{\log \frac{100}{90}} = \frac{0.1249}{0.0458} = 2.73$$
According to Arrhenius theory,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \times \frac{T_2 - T_1}{T_1 T_2}$$

$$\log 2.73 = \frac{E_a}{2.303 R} \left[\frac{308 - 298}{298 \times 308} \right]$$

$$E_a = \frac{0.4361 \times 2.303 \times (8.314 \text{ J mol}^{-1}) \times 298 \times 308}{10}$$

$$E_a = 76640 \text{ Jmol}^{-1} = 76.640 \text{ kJ mol}^{-1}$$
Now, according to Arrhenius equation

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

$$\log k = \log (4 \times 10^{10})$$

$$- \frac{76640 \text{ J mol}^{-1}}{2.303 \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times (318 \text{ K})}$$

$$\log k = 10.6021 - 12.5870 = -1.9849$$

$$k = \text{Antilog} (-1.9849)$$

$$= \text{Antilog} (2.0151) = 1.035 \times 10^{-2} \text{ s}^{-1}$$

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$
Initially p_i 0 0
After time t $p_i - p$ p p
Total pressure after time t , i.e.

$$p_t = p_i - p + p + p = p_i + p$$
So, $a = p_i$
 $a - x = p_i - (p_t - p_i)$
 $= p_i - p_t + p_i = 2p_i - p_t$
Substitutions of the value of a and $(a - x)$ gives,

$$k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_i)}$$
(a) Calculation of rate constant k

18.

Given,
$$p_i = 0.5 \text{ atm}$$
; $p_t = 0.6 \text{ atm}$

$$k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)} = \frac{2.303}{(100 \text{ s})} \log \frac{0.5 \text{ atm}}{0.4 \text{ atm}}$$

$$= \frac{2.303}{(100 \text{ s})} \log 1.25 = \frac{2.303}{(100 \text{ s})} \times 0.0969$$

$$= 2.23 \times 10^{-3} \text{ s}^{-1}$$

(b) Calculation of reaction rate when total pressure is 0.65 atm

$$\begin{split} p_{\mathrm{SO}_2\mathrm{Cl}_2} &= 0.5 - (0.65 - 0.50) \\ &= (1 - 0.65) = 0.35 \text{ atm} \\ k &= 2.23 \times 10^{-3} \text{ s}^{-1} \\ \mathrm{Rate} &= k \times p_{\mathrm{SO}_2\mathrm{Cl}_2} = (2.23 \times 10^{-3} \text{ s}^{-1}) \times (0.35 \text{ atm}) \\ \mathrm{Rate} &= 7.8 \times 10^{-4} \text{ atm s}^{-1} \end{split}$$

19. $(CH_3)_2CHN = NCH(CH_3)_2(g) \longrightarrow N_2(g) + C_6H_{14}(g)$ Initial pressure p_i 0 0 pAfter time t $p_i - p$ p

Total pressure after time t,

i.e.
$$(p_t) = (p_i - p) + p + p = p_i + p_i$$

or $p = p_t - p_i$

 $a = p_i$; $(a - x) = p_i - p$ on substituting the values of p; $(a - x) = p_i - (p_t - p_i)$, i.e. $(a - x) = 2p_i - p_t$

The decomposition reaction is of gaseous nature and the rate constant k can be calculated as,

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

Substitution of value of *a* and (a - x) gives

$$k = \frac{2.303}{t} \log\left(\frac{p_i}{2p_i - p_t}\right)$$

(i) Rate constant after 360 s = k_1

$$k_{1} = \frac{2.303}{(360 \text{ s})} \log \frac{(35 \text{ atm})}{(70 - 54) \text{ atm}}$$
$$= \frac{2.303}{(360 \text{ s})} \log \frac{35}{16} = \frac{2.303}{(360 \text{ s})} \log 2.1875$$
$$= \frac{2.303 \times 0.33995}{(360 \text{ s})} = 2.17 \times 10^{-3} \text{ s}^{-1}$$

(ii) Rate constant after 720 s = k_2

$$k_2 = \frac{2.303}{(720 \text{ s})} \log \frac{(35 \text{ atm})}{(70 - 63) \text{ atm}}$$
$$= \frac{2.303}{(720 \text{ s})} \log 5 = \frac{2.303 \times 0.6990}{(720 \text{ s})}$$
$$= 2.24 \times 10^{-3} \text{ s}^{-1}$$

Average rate constant $k = \frac{(2.17 + 2.24) \times 10^{-3} \text{ s}^{-1}}{2}$

$$k = 2.21 \times 10^{-3} \text{ s}^{-3}$$

20. Let the activation energy with and without enzyme be E_a^* and E_a .

Rate constant of reaction without catalyst is given by Arrhenius equation.

$$k = A e^{-E_a/RT}$$

Taking log on both sides, we get

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

With catalyst, rate constant is 10^6 times more

$$\therefore \qquad 10^6 k = A e^{\frac{-E_a}{RT}}$$
$$\log k + \log 10^6 = \log A - \frac{E_a^*}{RT(2.303)}$$

:.
$$\log k = \log A - \frac{E_a^*}{RT(2.303)} - 6$$
 ...(ii)

Comparing Eqs. (i) and (ii)

...

$$\frac{E_a}{RT(2.303)} = \frac{E_a^*}{RT(2.303)} + 6$$
$$E_a^* - E_a = -6 (2.303)RT$$

21. Rate law equation is given by,
$$\frac{dc}{dt} = k [A]^x [B]^y$$

 $\therefore \frac{dc}{dt}$ for *C* at various concentrations are

$$1.2 \times 10^{-3} = k(0.1)^{x}(0.1)^{y} \qquad \dots (i)$$

$$1.2 \times 10^{-3} = k(0.1)^{x}(0.2)^{y}$$
 ...(ii)
 $2.4 \times 10^{-3} = k(0.2)^{x}(0.1)^{y}$...(iii)

$$2.4 \times 10^{-3} = k(0.2)^{x}(0.1)^{y}$$
 ...(iii)

Solving for x [divide Eq. (iii) by Eq. (i)]

$$\frac{2.4 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k (0.2)^{x} (0.1)^{y}}{k (0.1)^{x} (0.1)^{y}}$$

$$2 = (2)^{x} \implies x = 1$$

Solving for y [divide Eq. (iii) by Eq. (i)]
$$\frac{2.4 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k (0.2)^{x} (0.1)^{y}}{k (0.1)^{x} (0.2)^{y}} \implies 2 = (2)^{x} \left(\frac{0.1}{0.2}\right)^{y}$$

Put x = 1 in above Eq., we get

$$2 = (2)' \left(\frac{0.1}{0.2}\right)^{y} \implies 1 = (0.5)^{y}$$
$$(1)^{0} = (0.5)^{y} \implies y = 0$$
Thus, $\frac{dc}{dt} = k [A]^{1} [B]^{0} \implies \frac{dc}{dt} = k [A]^{1}$

22. At 27°C,
$$t_{1/2} = 30 \min$$

$$k_1 = \frac{0.693}{30} = 0.0231$$

and at 47°C,
$$t_{1/2} = 10 \min k_2 = \frac{0.693}{10} = 0.0693$$

From,
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

 $\Rightarrow \log \frac{0.0693}{0.0231} = \frac{E_a}{2.303 \times 8.314} \left[\frac{1}{300} - \frac{1}{320} \right]$
or $\log 3 = \frac{E_a}{2.303 \times 8.314} \left[\frac{20}{300 \times 320} \right]$

or
$$0.4771 = \frac{L_a \times L^2}{2.303 \times 8.314 \times 300 \times 320}$$

or $E_a = 43848 \text{ J mol}^{-1} = 43.8 \text{ kJ mol}^{-1}$

23. Given,
$$T_1 = 25^{\circ} \text{ C} = 298 \text{ K}$$
, $T_2 = T$ (say)
 $E_a = 104.4 \text{ kJ mol}^{-1} = 104.4 \times 10^3 \text{ J mol}^{-1}$
 $k_1 = 3 \times 10^{-4} \text{ s}^{-1}$, $k_2 = ?$

$$\begin{array}{ll} \mbox{From}, & \log \frac{k_2}{k_1} = \frac{E_a}{2.303 \, R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \\ & \log \frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3}{2.303 \times 8.314} \left[\frac{1}{298} - \frac{1}{T} \right] \\ \mbox{or} & \log \frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3}{2.303 \times 8.314} \times \frac{1}{298} \left[\mbox{as} \ T \to \infty, \frac{1}{T} \to 0 \right] \\ \mbox{or} & \log \frac{k_2}{3 \times 10^{-4}} = 18.297 \\ \mbox{or} & \frac{k_2}{3 \times 10^{-4}} = 1.98 \times 10^{18} \\ \mbox{or} & k_2 = 1.98 \times 10^{18} \times 3 \times 10^{-4} \\ & = 5.94 \times 10^{14} \approx 6 \times 10^{14} \mathrm{s}^{-1} \end{array}$$

24. We know that,

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

where, n = order of the reation

Given
$$(t_{1/2}) = 0.1$$
 sec, $a_1 = 400$

25. Given, $t_{(1/2)A} = 54 \text{ min}$ $t_{(1/2)B} = 18 \min$

$$\begin{array}{ccc} A & B \\ t = 0 \text{ 'x' M} & t = 0 \text{ 'x' M} \\ \Rightarrow \text{ To calculate : } [A_t] = 16 \times [B_t] \dots (1) \text{ time } = ? \\ \Rightarrow \text{ For I order kinetic : } \boxed{[A_t] = \frac{A_0}{(2)^n}} \\ n \to \text{no. of half lives} \\ \Rightarrow \text{ Now, from the relation (1)} \\ [A_t] = 16 \times [B_t] \\ \Rightarrow & \frac{x}{(2)^{n_1}} = \frac{x}{(2)^{n_2}} \times 16 \Rightarrow (2)^{n_2} = (2)^{n_1} \times (2)^4 \\ \Rightarrow & n_2 = n_1 + 4 \Rightarrow \frac{t}{(t_{1/2})_2} = \frac{t}{(t_{1/2})_1} + 4 \\ \Rightarrow & t \left(\frac{1}{18} - \frac{1}{54}\right) = 4 \Rightarrow t = \frac{4 \times 18 \times 54}{36} \\ \Rightarrow & \boxed{t = 108 \text{ min}} \end{array}$$

26.
$$K_{300} = 10^{-4}$$
 $K_{200} = ?$
 $E_a = 11.488 \text{ kJ/mol}$ $R = 8.314 \text{ J/mol-K}$
So, $\ln\left(\frac{K_{300}}{K_{200}}\right) = \frac{E_a}{R} \left(\frac{1}{200} - \frac{1}{300}\right)$
 $\ln\left(\frac{K_{300}}{K_{200}}\right) = \frac{11.488 \times 1000 \times 100}{8.314 \times 200 \times 300} = 2.303 = \ln 10$
So, $\frac{K_{300}}{K_{200}} = 10$
 $K_{200} = \frac{1}{10} \times K_{300} = 10^{-4} = 10 \times 10^{-5} \text{ sec}^{-1}$

27. For every 10°C rise of temperature, rate is doubled. Thus, temperature coefficient of the reaction = 2When temperature is increased by 50°, rate becomes

$$=2^{(50/10)}=2^5$$
 times $=32$ times

28. Order = 1

m

Concentration changes from 0.8 M to 0.4 M in (50%) 15 min, thus half-life = 15 min = T_{50}

A change from 0.1 M to 0.025 M is 75% and for first order reaction

$$\begin{array}{rl} T_{75} = 2 \times T_{50} = 2 \times 15 = 30 \ \mathrm{min} \\ \mathrm{or} & T_{50} = 15 \ \mathrm{min} \\ & k = \frac{2.303 \ \mathrm{log} \ 2}{T_{50}} = \frac{2.303 \ \mathrm{log} \ 2}{15} \\ & a = 0.1 \ \mathrm{M} \\ & (a - x) = 0.025 \ \mathrm{M} \\ \mathrm{For \ first \ order}: & k = \frac{2.303}{t} \ \mathrm{log} \left(\frac{a}{a - x}\right) \\ & \frac{2.303 \ \mathrm{log} \ 2}{15} = \frac{2.303}{t} \ \mathrm{log} \left(\frac{0.1}{0.025}\right) \\ & = \frac{2.303 \ \mathrm{log} \ 2}{15} = \frac{2 \times 2.303 \ \mathrm{log} \ 2}{t} \\ & \vdots & \frac{2.303 \ \mathrm{log} \ 2}{15} = \frac{2 \times 2.303 \ \mathrm{log} \ 2}{t} \end{array}$$

29. The Arrhenius eqaution is

.•.

R =

30.

$$\ln\left(\frac{KT_2}{KT_1}\right) = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Given,
$$\frac{KT_2}{KT_1} = 3.555$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$T_1 = 30 + 273 = 303 \text{ K}; T_2 = 40 + 273 = 313 \text{ K}$$

Substituting the given values in the Arrhenius equation,
$$\ln (3.555) = \frac{E_a}{8.314} \left[\frac{1}{303} - \frac{1}{313}\right] \qquad (\ln 3.555 = 1.268)$$

 $t = 30 \min$

$$1.268 = \frac{E_a}{8.314} \left[\frac{313 - 303}{303 \times 313} \right]$$
$$E_a = \frac{1.268 \times 8.314 \times 303 \times 313}{10}$$
$$= 99980.7 = 99.98 \text{ kJ/mol}$$
Decay constant (k) = $\frac{0.693}{t_{1/2}} = \frac{0.693}{5730} \text{ yr}^{-1}$

All radioactive decay follow first order kinetics $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$

Given, [A] = 80% It means that $[A]_0 = 100\%$

$$t = \frac{2.303 \times 5730}{0.693} \text{ yr} \times \log \frac{100}{80}$$
$$= \frac{2.303 \times 5730 \times 0.0969}{0.693} = 1845 \text{ yr}$$

Estimated age = 1845 yr

31. Given, first order reaction,

 $t_{75} = 90$ minute $\Rightarrow t_{60} = ?$ Consider the following reaction

$$\begin{array}{c} A & \longrightarrow B \\ (\text{Reactant}) & (\text{Product}) \\ \text{Time}, & t = 0 \quad 100 \\ t_{15\%} = 90 \text{ min } (100 - 75) = 25 \\ t_{60\%} = ? & (100 - 60) = 40 \\ & \text{For first order reaction,} \\ t = \frac{2.303}{k} \log \left(\frac{a_0}{a}\right) \begin{bmatrix} a_0 = \text{Initial concentration} \\ a = \text{Concentration} \end{bmatrix} \end{array}$$

For 75%,

$$t_{75\%} = \frac{2.303}{k} \log\left(\frac{100}{25}\right) \dots \text{(i)} \begin{bmatrix} \text{Initial conc.} = 100\\ \text{Conc.} = 100 - 75 = 25 \end{bmatrix}$$

For 60%,

$$t_{60\%} = \frac{2.303}{k} \log\left(\frac{100}{40}\right) \dots \text{(ii)} \begin{bmatrix} \text{Initial conc.} = 100\\ \text{Conc.} = 100 - 60 = 40 \end{bmatrix}$$

On equating Eqs. (i) and (ii),

$$\frac{t_{60\%}}{t_{75\%}} = \frac{\frac{2.303}{k} \log\left(\frac{100}{40}\right)}{\frac{2.303}{k} \log\left(\frac{100}{25}\right)}$$
$$t_{60\%} = t_{75\%} \times \left(\frac{0.3979}{0.602}\right) \implies t_{60\%} = 90 \times \frac{0.3979}{0.602}$$
$$t_{60\%} = 59.48 \text{ minute} \approx 60 \text{ min}$$

32. Given, temperature rise 27°C to 42°C

Hence,
$$T_1 = 273 + 27 = 300 \text{ K}$$

 $T_2 = 273 + 42 = 315 \text{ K}$
 $\{\ln 5 = 1.6094 R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}\}$

According to question $k_{T_2} = 5k_{T_1}$ as molecules activated are increased five times so k will increases 5 times. Now, $k = Ae^{-E_a/RT}$ (Arrhenius equation)

On apply log both sides, $\ln\left(\frac{k_{T_2}}{k_{T_1}}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

Here,

$$\begin{split} \frac{k_{T_2}}{k_{T_1}} &= 5\\ \ln 5 &= \frac{E_a}{R} \left(\frac{1}{300} - \frac{1}{315}\right)\\ \ln 5 &= \frac{E_a}{8314} \left(\frac{315 - 300}{300 \times 315}\right)\\ \ln 5 &= \frac{E_a}{8.314} \times \frac{15}{300 \times 315} \end{split}$$

$$\begin{split} 1.6094 = & \frac{E_a}{8.314} \times \frac{15}{300 \times 315} \\ E_a = & \frac{1.6094 \times 8.314 \times 300 \times 315}{15} \\ E_a = & 84297.47 \ 50 \ \text{Joules /mol} \end{split}$$

33. Time taken for milk to split $\propto \frac{1}{k}$

where, k = rate constant of the processand, k at 2 different temperatures and activation energy are related.

$$\ln \frac{k_2}{k_1} = \frac{-E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \ln \frac{t_1}{t_2}$$

$$\therefore \quad \ln \left(\frac{60}{40} \right) = \frac{-E_a}{83} \left(\frac{1}{400} - \frac{1}{300} \right)$$

$$E_a = 0.4 \times 8.3 \times 1200$$

$$= 3984 \text{ J mol}^{-1} = 3.984 \text{ kJ mol}^{-1}$$

Given, $\ln \frac{2}{3} = 0.4 \implies \ln \frac{3}{2} = -0.4$

(These are wrong values, because $\ln \frac{2}{3}$ is -ve and $\ln \frac{3}{2}$ is +ve, but assume them to be correct).

34. It is given that the decomposition of '*A*' into product has value of $K = 4.5 \times 10^3 \text{ s}^{-1}$ at 10°C.

$$\log\left(\frac{K'}{K}\right) = \frac{E_a}{2.303R} \left(\frac{T'-T}{TT'}\right)$$

$$\Rightarrow \log\left(\frac{1.5 \times 10^4}{4.5 \times 10^3}\right) = \frac{60 \times 10^3}{2.303 \times 8.314} \left(\frac{T'-283}{283 T'}\right)$$

$$\Rightarrow 0.5228 = 3132.62 \left[\frac{T'-283}{283 T'}\right]$$

$$\Rightarrow T'-283 = 0.0472 T'$$

$$\Rightarrow T' = 297.02 \text{ K}$$

$$\Rightarrow T' = 297.02 \text{ K} - 273 \text{ K} = 24.02^{\circ} \text{ C}$$

35. According to Arrhenius equation,

$$\begin{split} \log\!\left(\frac{K_2}{K_1}\right) &= \frac{E_a}{2303\,R} \!\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \\ \Rightarrow \quad \frac{K_2}{K_1} &= 2\ ; \\ T_1 &= 295\ \mathrm{K}, \, T_2 &= 305\ \mathrm{K} \\ R &= 8.314\ \mathrm{J}\ \mathrm{K}^{-1}\mathrm{mol}^{-1} \\ \therefore \quad \log{(2)} &= \frac{E_a}{2.303 \times (8.314)} \times \!\left[\frac{1}{295} - \frac{1}{305}\right] \\ \mathrm{or}, \quad 0301 &= \frac{E_a}{8.314\ \mathrm{J}\ \mathrm{K}^{-1}\mathrm{mol}^{-1}} \times \frac{10}{295 \times 305} \\ \mathrm{or}, \quad E_a &= \frac{0.301 \times 2.303 \times 8.314 \times 295 \times 305}{10} \\ &= 51.860\ \mathrm{J}\ \mathrm{mol}^{-1} \\ &= 51.86\ \mathrm{mol}^{-1} \end{split}$$