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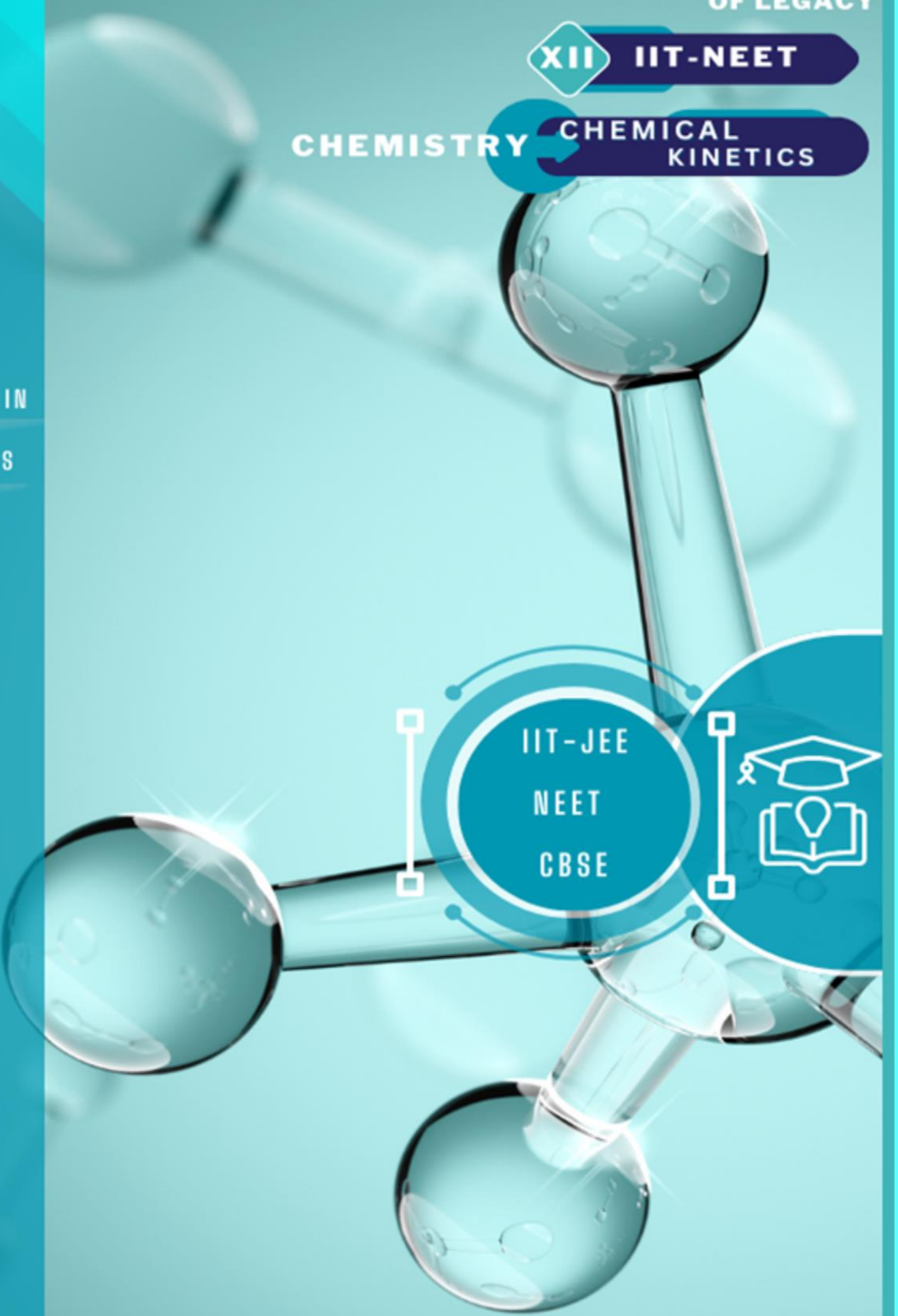

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CHEMICAL KINETICS

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CHEMICAL KINETICS

IIT-NEET-CHEMISTRY

The branch of physical chemistry which deals with the rate at which the chemical reactions occur, the mechanism by which the chemical reactions take place and the influence of various factors such as concentration, temperature, pressure, catalyst etc., on the reaction rates is called the chemical kinetics.

Types of chemical reactions

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

(1) **Very fast or instantaneous reactions :** These reactions occur at a very fast rate generally these reactions involve ionic species and known as ionic reactions. It is almost impossible to determine the rates of these reactions.

Examples

(i) $AgNO_3 + NaCl \rightarrow \underset{\text{(PPt.)}}{AgCl} + NaNO_3$ (*Precipitation reaction*)

(ii) $\underset{\text{(acid)}}{HCl} + \underset{\text{(base)}}{NaOH} \rightarrow \underset{\text{(Salt)}}{NaCl} + H_2O$ (*Neutralization reaction*)

(2) **Moderate reaction :** These reactions proceed with a measurable rates at normal temperature and it is *these reactions are studied in chemical kinetics.* Mostly these reactions are molecular in nature.

Examples

(i) *Decomposition of* H_2O_2: $2H_2O_2 \rightarrow 2H_2O + O_2$

(ii) *Decomposition of* N_2O_5: $2N_2O_5 \rightarrow 2N_2O_4 + O_2$

(3) **Very slow reactions :** These reactions are extremely slow and take months together to show any measurable change.

Examples

(i) *Rusting of iron* : $Fe_2O_3 + xH_2O \rightarrow \underset{\text{Hydrated ferric oxide (Rust)}}{Fe_2O_3.xH_2O}$

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

Rate of a reaction

The rate (speed or velocity) of a reaction is the change in concentration in per unit time.

$$\frac{\Delta x}{\Delta t} \text{ or } \frac{dx}{dt} = \left(\frac{x_2 - x_1}{t_2 - t_1}\right)$$

where Δx or dx is the concentration change, *i.e.*, $(x_2 - x_1)$ in the time interval Δt or dt, *i.e.*, $(t_2 - t_1)$.

Concentration is generally expressed in active mass, *i.e.*, mole L^{-1}

- The rate measured over a long time interval is called *average rate* and the rate measured for an infinitesimally small time interval is called *instantaneous rate* and

Instantaneous rate $= (\text{Average rate})_{\Delta t \rightarrow 0}$

- For the reaction $aA + bB \rightarrow cC + dD$

Rate of disappearance of a reactant is negative

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

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

Rate of formation of a product is positive

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

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

- In terms of stoichiometric coefficient rate may be expressed as

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

- The rate of reaction is always ***positive***.
- The rate of chemical reaction decreases as the reaction proceeds.
- Unit of rate of a reaction = $\frac{\text{Unit of conc.}}{\text{Unit of time}}$ = *mole* L^{-1} *time* $^{-1}$

In term of gaseous reaction the unit is *atm time*$^{-1}$ and

Rate in *atm time*$^{-1}$= Rate in mole $L^{-1} time^{-1} \times RT$

Factors affecting rate of a reaction

The rate of a chemical reaction depends on the following things

(1) **Nature of reactants**

(i) *Physical state of reactants* : This has considerable effect over rate of reaction.

$$\xrightarrow[\text{Decreasing rate of reaction}]{\text{Gaseous satae > Liquid state > Solid state}}$$

(ii) *Physical size of the reactants* : Among the solids, rate increases with decrease in particle size of the solid.

(iii) *Chemical nature of the reactants*

(a) Reactions involving polar and ionic substances including the proton transfer reactions are usually very fast. On the other hand, the reaction in which bonds is rearranged, or electrons transferred are slow.

(b) Oxidation-reduction reactions, which involve transfer of electrons, are also slow as compared to the ionic substance.

(c) Substitution reactions are relatively much slower.

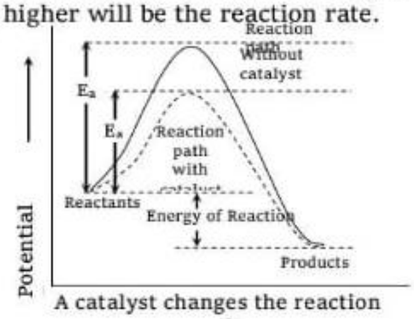
(2) **Effect of temperature :** The rate of chemical reaction generally increases on increasing the temperature. The rate of a reaction becomes almost double or tripled for every $10^\circ C$ rise in temperature.

Temperature coefficient of a reaction is defined as the ratio of rate constants at two temperatures differing by (generally 25°C and 35°C) 10°C.

$$\mu = \text{Temperature coefficient} = \frac{k \text{ at } (t+10^\circ C)}{k \text{ at } t^\circ C} = \frac{k_{35^\circ C}}{k_{25^\circ C}}$$

(3) **Concentration of reactants :** The rate of a chemical reaction is directly proportional to the concentration of the reactants means rate of reaction decreases with decrease in concentration.

(4) **Presence of catalyst :** The function of a catalyst is to lower down the activation energy. The greater the decrease in the activation energy caused by the catalyst, higher will be the reaction rate.



A catalyst changes the reaction

(5) **Effect of sunlight :** There are many chemical reactions whose rate are influenced by radiations particularly by ultraviolet and visible light. Such reactions are called photochemical reactions. For example, Photosynthesis, Photography, Blue printing, Photochemical synthesis of compounds etc.

The radiant energy initiates the chemical reaction by supplying the necessary activation energy required for the reaction.

Law of mass action and Rate constant

The rate at which a substance reacts is directly proportional to its active mass and the rate at which a reaction proceeds is proportional to the product of the active masses of the reacting substances.

- For a reaction, $aA + bB \rightarrow$ product

Rate $= \left(\frac{dx}{dt}\right) \propto [A]^a[B]^b$; $\left(\frac{dx}{dt}\right) = k[A]^a[B]^b$

Where k is called **rate constant** or **velocity constant**.

When $[A]=[B]=1\ mol/litre$, then $\frac{dx}{dt} = k$

Thus, rate constant k is also called **specific reaction rate**.

- The value of rate constant depends on, nature of reactant, temperature and catalyst. It is independent of concentration of the reactants.
- Unit of rate constant $= \left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \text{sec}^{-1} = \left[\frac{\text{mol}}{\text{litre}}\right]^{1-n} \times \text{sec}^{-1}$

Where $n =$ order of reaction.

Rate law : Molecularity and Order of a reaction

Molecularity is the sum of the number of molecules of reactants involved in the balanced chemical equation. Molecularity of a complete reaction has no significance and overall kinetics of the reaction depends upon the rate determining step. *Slowest step is the rate-determining step.* This was proposed by *Van't Hoff.*

Example : $NH_4NO_2 \rightarrow N_2 + 2H_2O$ *(Unimolecular)*

$NO + O_3 \rightarrow NO_2 + O_2$ *(Bimolecular)*

$2NO + O_2 \rightarrow 2NO_2$ *(Trimolecular)*

The total number of molecules or atoms whose concentration determine the rate of reaction is known as order of reaction.

Order of reaction = Sum of exponents of the conc. terms in rate law

For the reaction $xA + yB \rightarrow \text{Products}$

The rate law is $\text{Rate} = [A]^x[B]^y$

Then the overall order of reaction. $n = x + y$

where x and y are the orders with respect to individual reactants.

- If reaction is in the form of reaction mechanism then the order is determined by the slowest step of mechanism.

$2A + 3B \rightarrow A_2B_3$

$A + B \rightarrow AB(\text{fast})$

$AB + B_2 \rightarrow AB_3(\text{slow})$ *(Rate determining step)*

$AB_3 + A \rightarrow A_2B_3(\text{fast})$

(Here, the overall order of reaction is equal to two.)

- Molecularity of a reaction is derived from the mechanism of the given reaction. Molecularity can not be greater than three because more than three molecules may not mutually collide with each other.
- Molecularity of a reaction can't be zero, *negative* or fractional. order of a reaction may be zero, negative, positive or in fraction and greater than three. Infinite and imaginary values are not possible.
- When one of the reactants is present in the large excess, the second order reaction conforms to the first order and is known as ***pesudo unimolecular reaction***. (Table 11.1)

Table : 11.1 Order and molecularity of some reaction

S. No.	**Chemical equation**	**Molecularity**	**Rate law**	**Order w.r.t.**		
				First reactant	**Second reactant**	**Overall**
1.	$aA + bB \rightarrow \text{product}$	a + b	$\left(\frac{dx}{dt}\right) = k[A]^a[B]^b$	a	b	a + b
2.	$aA + bB \rightarrow \text{product}$	a + b	$\left(\frac{dx}{dt}\right) = k[A]^2[B]^0$	2	zero, if B is in excess	2
3.	$2H_2O_2 \xrightarrow{Pt,\Delta} 2H_2O + O_2$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[H_2O_2]$	1*	-----	1
4.	$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[CH_3COOC_2H_5]$	1*	Zero, if H_2O is in excess	1
5.	$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[C_{12}H_{22}O_{11}]$	1*	Zero, if H_2O is in excess	1
6.	$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[(CH_3)_3CCl]$	1*	Zero, if OH^- does not take part in slow step	1
7.	$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[CH_3Cl][OH^-]$	1	1	2
8.	$C_6H_5N_2Cl \xrightarrow{\Delta} C_6H_5Cl + N_2$	1 (Unimolecular)	$\left(\frac{dx}{dt}\right) = k[C_6H_5N_2Cl]$	1	----	1
9.	$CH_3CHO \xrightarrow{\Delta} CH_4 + CO$	1 (Unimolecular)	$\left(\frac{dx}{dt}\right) = k[CH_3CHO]^{3/2}$	1.5	----	1.5
10.	$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$	5	$\left(\frac{dx}{dt}\right) = k[H_2O_2][I^-]$	1	1 ($H^+$is medium)	2
11.	$2O_3 \rightarrow 3O_2$	2 (Bimolecular)	$\left(\frac{dx}{dt}\right) = k[O_3]^2[O_2]$	1	-1 with respect to O_2	1

*Pseudo-unimolecular reactions.

Table : 11.2 Rate constant and other parameters of different order reactions

Order	Rate constant	Unit of rate constant	Effect on rate by changing conc. to m times	(Half-life period) T_{50}=
0	$k_0 = \frac{x}{t}$	conc. time^{-1} (mol L^{-1} s^{-1})	No change	$\frac{a}{2k_0}$
1	$k_1 = \frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right)$, $C = C_0e^{-k_1t}$ $N = N_0e^{-k_1t}$, $k_1 = \frac{2.303}{(t_2-t_1)}\log_{10}\frac{(a-x_1)}{(a-x_2)}$	time^{-1} (s^{-1})	m times	$\frac{0.693}{k_1}$
2	$k_2 = \frac{1}{t}\left[\frac{1}{(a-x)}-\frac{1}{a}\right] = \frac{x}{ta(a-x)}$ (for the case when each reactant has equal concentration) $k_2 = \frac{2.303}{t(a-b)}\log_{10}\left[\frac{b(a-x)}{a(b-x)}\right]$(for the case when both reactants have different concentration)	conc^{-1} time^{-1} (mol L^{-1}) s^{-1} L mol^{-1} s^{-1}	m^2 times	$\frac{1}{k_2a}$
3	$k_3 = \frac{1}{2t}\left[\frac{1}{(a-x)^2}-\frac{1}{a^2}\right]$	conc^{-2} time^{-1} (mol L^{-1})$^{-2}$ s^{-1} L^2 mol^{-2} s^{-1}	m^3 times	$\frac{3}{2k_3a^2}$
n	$k_n = \frac{1}{(n-1)t}\left[\frac{1}{(a-x)^{n-1}}-\frac{1}{(a)^{n-1}}\right]$; $n \geq 2$	conc$^{(1-n)}$ time^{-1} (mol L^{-1})$^{(1-n)}$ s^{-1} $L^{(n-1)}$ mol$^{(1-n)}$ s^{-1}	m^n times	$\frac{2^{n-1}-1}{(n-1)k_n(a)^{n-1}}$

Methods for determination of order of a reaction

(1) **Integration method** (Hit and Trial method)

(i) The method can be used with various sets of a, x and t with integrated rate equations.

(ii) The value of k is determined and checked for all sets of a, x and t.

(iii) If the value of k is constant, the used equation gives the order of reaction.

(iv) If all the reactants are at the same molar concentration, the kinetic equations are :

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$ *(For first order reactions)*

$$k = \frac{1}{t}\left[\frac{1}{a}-\frac{1}{a-x}\right]$$ *(For second order reactions)*

$$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2}-\frac{1}{a^2}\right]$$ *(For third order reactions)*

(2) **Half-life method :** This method is employed only when the rate law involved only one concentration term.

$$t_{1/2} \propto a^{1-n};\ t_{1/2} = ka^{1-n};\ \log t_{1/2} = \log k + (1-n)\log a$$

A plotted graph of $\log t_{1/2}$ *vs log a* gives a straight line with slope $(1-n)$, determining the slope we can find the order n. If half-life at different concentration is given then,

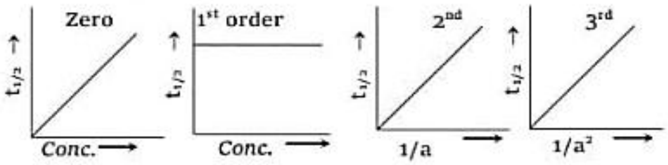
$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}};\ (t_{1/2})_2 \propto \frac{1}{a_2^{n-1}};\ \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

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

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

This relation can be used to determine order of reaction '*n*'

Plots of half-lives Vs concentrations ($t_{1/2} \propto a^{1-n}$)



(3) **Graphical method :** A graphical method based on the respective rate laws, can also be used.

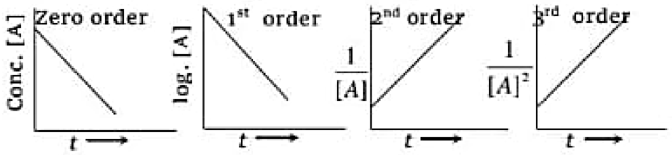
(i) If the plot of $\log(a-x)$ Vs t is a straight line, the reaction follows first order.

(ii) If the plot of $\frac{1}{(a-x)}$ Vs t is a straight line, the reaction follows second order.

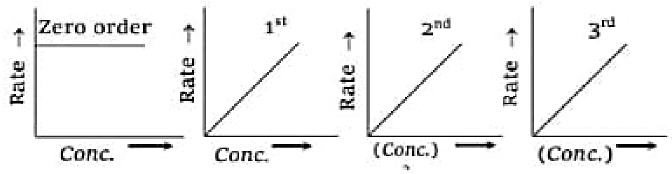
(iii) If the plot of $\frac{1}{(a-x)^2}$ Vs t is a straight line, the reaction follows third order.

(iv) In general, for a reaction of nth order, a graph of $\frac{1}{(a-x)^{n-1}}$ Vs t must be a straight line.

Plots from integrated rate equations



Plots of rate Vs concentrations [Rate = k(conc.)^n]



(4) **Van't Haff differential method :** The rate of reaction varies as the n^{th} power of the concentration Where 'n' is the order of the reaction. Thus for two different initial concentrations C_1 and C_2 equation, can be written in the form,

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

Taking logarithms,

$$\log_{10}\left(\frac{-dC_1}{dt}\right) = \log_{10} k + n\log_{10} C_1 \quad .....(i)$$

$$\text{and } \log_{10}\left(\frac{-dC_2}{dt}\right) = \log_{10} k + n\log_{10} C_2 \quad .....(ii)$$

Subtracting equation (ii) from (i),

$$n = \frac{\log_{10}\left(\frac{-dC_1}{dt}\right) - \log_{10}\left(\frac{-dC_2}{dt}\right)}{\log_{10} C_1 - \log_{10} C_2} \quad .....(iii)$$

$\frac{-dC_1}{dt}$ and $\frac{-dC_2}{dt}$ are determined from concentration Vs time graphs and the value of 'n' can be determined.

(5) **Ostwald's isolation method** (Initial rate method)

This method can be used irrespective of the number of reactants involved *e.g.,* consider the reaction, $n_1A + n_2B + n_3C \rightarrow \text{Products}$.

This method consists in finding the initial rate of the reaction taking known concentrations of the different reactants (A, B, C).

Suppose it is observed as follows,

(i) Keeping the concentrations of B and C constant, if concentration of A is doubled, the rate of reaction becomes four times. This means that, Rate $\propto [A]^2$ *i.e.,* order with respect to A is 2

(ii) Keeping the concentrations of A and C constant, if concentration of B is doubled, the rate of reaction is also doubled. This means that, Rate $\propto [B]$ *i.e.,* order with respect to B is 1

(iii) Keeping the concentrations of A and B constant, if concentration of C is doubled, the rate of reaction remains unaffected. This means that rate is independent of the concentration of C *i.e.,* order with respect to C is zero. Hence the overall rate law expression will be, Rate = $k[A]^2 [B] [C]^0$

$\therefore$ Overall order of reaction = 2 + 1 + 0 = 3.

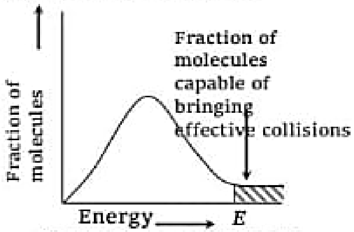
Theories of reaction rate

(1) **Collision theory**

(i) The basic requirement for a reaction to occur is that the reacting species must collide with one another. This is the basis of ***collision theory*** for reactions.

(ii) The number of collisions that takes place per second per unit volume of the reaction mixture is known as ***collision frequency*** (Z). The value of collision frequency is very high of the order of 10^{25} to 10^{28} in case of binary collisions.

(iii) Every collision does not bring a chemical change. The collisions that actually produce the product are ***effective collisions***. The effective collisions, which bring chemical change, are few in comparison to the total number of collisions. The collisions that do not form a product are ***ineffective elastic collisions***, *i.e.,* molecules just collide and disperse in different directions with different velocities.



Distribution of energies at a definite temperature

(iv) For a collision to be effective, the following two barriers are to be cleared,

(a) *Energy barrier : "The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as* ***threshold energy***".

- In the graph '*E*' corresponds to minimum or threshold energy for effective collision.
- There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy to cross the energy barrier.

(b) *Orientation barrier* : The colliding molecules should also have proper orientation so that the old bonds may break and new bonds are formed. For example, $NO_2(g)+NO_2(g)\rightarrow N_2O_4(g)$. During this reaction, the products are formed only when the colliding molecules have proper orientation at the time of collisions. These are called effective collisions.

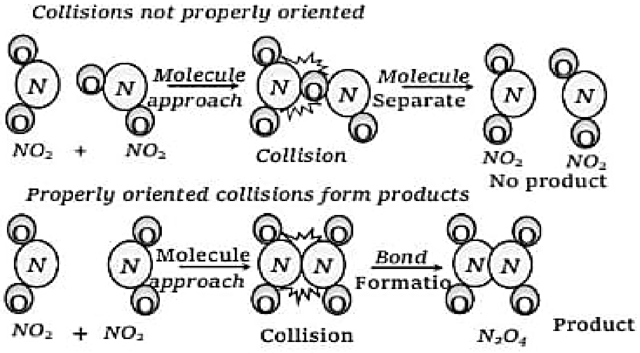


Fig. 11.1

(v) Thus, the main points of ***collision theory*** are as follows,

(a) For a reaction to occur, there must be collisions between the reacting species.

(b) Only a certain fraction of the total number of collisions is effective in forming the products.

(c) For effective collisions, the molecules should possess sufficient energy as well as orientation.

(vi) The fraction of effective collisions, under ordinary conditions may vary from nearly zero to about one for ordinary reactions. Thus, the rate of reaction is proportional to :

(a) The number of collisions per unit volume per second (Collision frequency, *Z*) between the reacting species

(b) The fraction of effective collisions (Properly oriented and possessing sufficient energy), *f* i.e.,

$$\text{Rate}=\frac{-dx}{dt}=f\times Z$$

Where *f* is fraction of effective collision and *Z* is the collision frequency.

(vii) The physical meaning of the activation energy is that it is the minimum relative kinetic energy which the reactant molecules must possess for changing into the products molecules during their collision. This means that the fraction of successful collision is equal to $e^{-E_a/RT}$ called ***Boltzmann factor***.

(viii) It may be noted that besides the requirement of sufficient energy, the molecules must be properly oriented in space also for a collision to be successful. Thus, if Z_{AB} is the collision frequency, *P* is the ***orientation factor*** (Steric factor) then, $k=PZ_{AB}.e^{-E_a/RT}$. If we compare this equation with Arrhenius equation. $k=A\,e^{-E_a/RT}$

We know that pre-exponential form '*A*' in Arrhenius equation is, $A=PZ_{AB}$.

Concept of activation energy

The excess energy (Over and above the average energy of the reactants) which must be supplied to the reactants to undergo chemical reactions is called ***activation energy*** (E_a),

$$E_a=E_{(\text{Threshold energy})}-E_{(\text{Reactants})}$$

Activation energy = Threshold energy – Average kinetic energy of the reacting molecules.

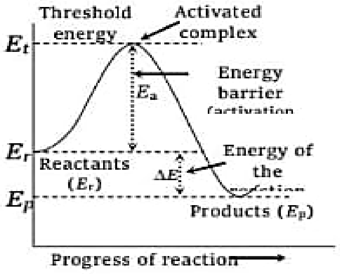
(a) *Zero activation energy* = Fraction of effective collision (*f*) will be very large = Very fast reaction (Instantaneous reaction).

(b) *Low activation energies* = Fraction of effective collision (*f*) will be large = Fast reactions.

(c) *High activation energies* = Fraction of effective collision (*f*) will be small = Slow reaction.

The activation energy (E_a) *depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products.*

According to the concept of activation energy, the react [illegible] t change directly into the products. The reactant first absorb energy equal to activation energy and form activated complex. At this state, the molecules must have energy at least equal to the threshold energy. This means that the reaction involves some energy barrier which must be overcome before products are formed. The energy barrier is known as ***activation energy barrier***.



(2) Transition state theory

(i) According to transition state theory the activated complex is supposed to be in equilibrium with the reactant molecules.

(ii) Once the transition state is formed it can either return to the initial reactants or proceed to form the products.

(iii) Assuming that once formed the transition state proceeds to products we can say that rate is proportional to concentration of transition state.

Mathematically, Rate ∝ Transition state

Rate= Constant × Transition state

(iv) The activation energy for the forward reaction, (E_a^f) and the activation energy for the reverse reaction (E_a^r) are related to the enthalpy (ΔH) of the reaction by the equation $\Delta H = E_a^f - E_a^r$.

(a) *For endothermic reactions*, $\Delta H > 0$, so that $E_a^r < E_a^f$

(b) *For exothermic reaction*, $\Delta H < 0$, so that $E_a^r > E_a^f$.

Arrhenius equation

Arrhenius proposed a quantitative relationship between rate constant and temperature as,

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

The equation is called ***Arrhenius equation***.

In which constant A is known as ***frequency factor***. This factor is related to number of binary molecular collision per second per litre.

E_a is the activation energy.

T is the absolute temperature and

R is the gas constant

Both A and E_a are collectively known as ***Arrhenius parameters***.

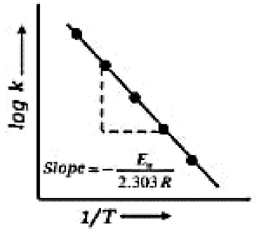
Taking logarithm equation (i) may be written as,

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

The value of activation energy (E_a) increases, the value of k decreases and therefore, the reaction rate decreases.

When log k plotted against $1/T$, we get a straight line. The intercept of this line is equal to log A and slope equal to $\frac{-E_a}{2.303\ R}$.

Therefore $E_a = -2.303\ R \times \text{slope}$.



Rate constants for the reaction at two different temperatures T_1 and T_2,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad .....(iii)$$

where k_1 and k_2 are rate constant at temperatures T_1 and T_2 respectively $(T_2 > T_1)$.

Mechanism of the reaction

(1) Reaction involving first order consecutive reactions

(i) In such reactions, the reactions form a stable intermediate compound before they are finally converted into the products.

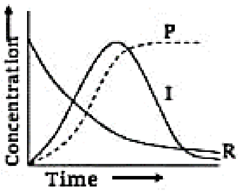
(ii) For example, reactants (R) are first converted to intermediate (I) which is then converted to product (P) as

$$R \xrightarrow{k_1} I \xrightarrow{k_2} P$$

Therefore, the reaction takes place in two steps, both of which are first order i.e.,

Step I : $R \xrightarrow{k_1} I$; Step II : $I \xrightarrow{k_2} P$

This means that I is produced by step I and consumed by step II. In these reactions, each stage will have its own rate and rate constant the reactant concentration will always decrease and product concentration will always increase as shown in fig.



Concentration profile of reactants (R), intermediate (I) and products (P) as a

(2) Reaction involving slow step : When a reaction occurs by a sequence of steps and one of the step is slow, then the rate determining step is the slow step. For example in the reaction

$R \xrightarrow{k_1} I$; $I \xrightarrow{k_2} P$, if $k_1 << k_2$ then I is converted into products as soon as it is formed, we can say that

$$\frac{-d[R]}{dt} = \frac{d[P]}{dt} = k_1[R]$$

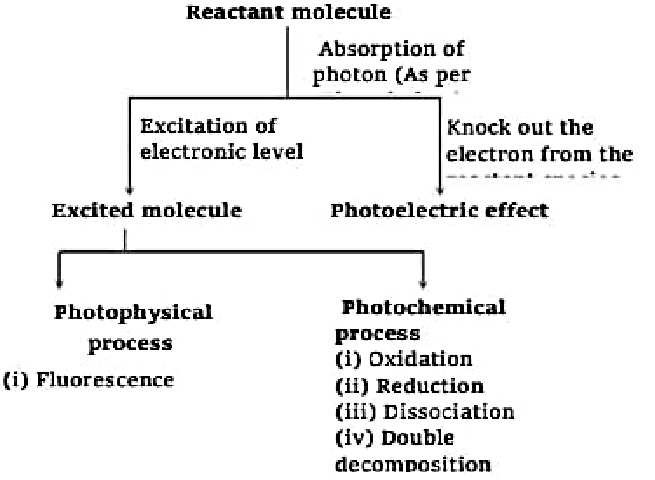
(3) Parallel reactions : In such type of reactions the reactants are more reactive, which may have different orders of the reactions taking place simultaneously. For example, in a system containing

NO_2 and SO_2, NO_2 is consumed in the following two reactions, $2NO_2 \xrightarrow{k_1} N_2O_4$; $NO_2 + SO_2 \xrightarrow{k_2} NO + SO_3$

The rate of disappearance of NO_2 will be sum of the rates of the two reactions *i.e.*, $-\frac{d[NO_2]}{dt} = 2k_1[NO_2]^2 + k_2[NO_2][SO_2]$

Photochemical reaction

Absorption of radiant energy by reactant molecules brings in photophysical as well as photochemical changes. According to ***Einstein's law*** of photochemical equivalence, the basic principle of photo processes, each reactant molecule is capable of absorbing only one photon of radiant energy. The absorption of photon by a reactant molecule may lead to any of the photo process.



The chemical reactions, which are initiated as a result of absorption of light, are known as photochemical reactions. In such cases, the absorbed energy is sufficient to activate the reactant molecules to cross the energy barrier existing between the reactants and products or in other words, energy associated with each photon supplies activation energy to reactant molecule required for the change.

(1) Characteristics of photochemical reactions

(i) Each molecule taking part in a photo process absorbs only one photon of radiant energy thereby increasing its energy level by $h\nu$ or $\frac{hc}{\lambda}$

(ii) Photochemical reactions do not occur in ***dark***.

(iii) Each photochemical reaction requires a definite amount of energy which is characteristic of a particular wavelength of photon. For example, reactions needing more energy are carried out in presence of *UV* light (lower λ, more E/Photon). A reaction-taking place in *UV* light may not occur on exposure to yellow light (lower λ and lesser E/Photon)

(iv) The rate of photochemical reactions depend upon the intensity of radiation's absorbed.

(v) The ΔG values for light initiated reactions may or may not be ***negative***.

(vi) The temperature does not have marked effect on the rate of light initiated reactions.

(2) Mechanism of some photochemical reactions

(i) ***Photochemical combination of H₂ and Cl₂*** : A mixture of H_2 and Cl_2 on exposure to light give rise to the formation of *HCl*, showing a chain reaction and thereby producing 10^6 to 10^8 molecules of *HCl* per photon absorbed.

$$H_2 + Cl_2 \xrightarrow{sunlight} 2HCl$$

The mechanism leading to very high yield of *HCl* as a result of chemical change can be as follows. Chlorine molecules absorb radiant energy to form an excited molecule which decomposes to chlorine free radicals (*Cl*) to give chain initiation step.

Light absorption step : $Cl_2 \xrightarrow{h\nu} Cl_2^{*}$ ....(i)

Chain initiation step : $Cl_2^{*} \rightarrow Cl^{\bullet} + Cl^{\bullet}$ ....(ii)

The chlorine free radical then combines with H_2 molecule to form *HCl* and $H^{\bullet}$ free radical. The $H^{\bullet}$ free radical so formed again combines with another Cl_2 molecule to give *HCl* and $Cl^{\bullet}$ free radical back resulting into chain propagation step.

Chain propagation step : $Cl^{\bullet} + H_2 \rightarrow HCl + H^{\bullet}$ ....(iii)

$$H^{\bullet} + Cl_2 \rightarrow HCl + Cl^{\bullet}$$

The combination of two $Cl^{\bullet}$ free radicals leads to chain terminating step.

Chain terminating step : $Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$ ....(iv)

(ii) ***Photochemical combination of H₂ and Br₂*** : The combination of H_2 and Br_2 to form *HBr* in presence of light is also an example of chain reaction like photochemical combination of H_2 and Cl_2. Here two Br_2 molecules absorb photon, however, inspite of chain reaction only one molecule of *HBr* is formed for each 100 photon absorbed by 100 molecules of Br_2.

$$H_2 + Br_2 \xrightarrow{light} 2HBr$$

Mechanism

Light absorption step : $Br_2 + h\nu \rightarrow Br_2^{*}$ ....(i)

Chain initiation step : $Br_2^{*} \rightarrow Br^{\bullet} + Br^{\bullet}$ ....(ii)

Chain propagation step : $Br^{\bullet} + H_2 \rightarrow HBr + H^{\bullet}$ ....(iii)

$$H^{\bullet} + Br_2 \rightarrow HBr + Br^{\bullet}$$ ....(iv)

Chain termination step : $Br^{\bullet} + Br^{\bullet} \rightarrow Br_2$ ....(v)

The lower values of *HBr* formation per photon of light absorbed has been attributed to the fact that step (III) is highly endothermic and thus before step (III) can take place most of the bromine free radicals recombine as per step (V) to give Br_2 molecule and thus providing less feasibility for step (IV) *i.e.* steps regenerating free radicals. Also the decomposition of *HBr* increases with increase in temperature.

(3) **Quantum yield** (or quantum efficiency) **:** The quantum efficiency or yield (ϕ) of a photochemical reaction may be expressed as,

$$\phi = \frac{\text{No. of molecules reacted or product formed}}{\text{No. of photon absorbed}}$$

(4) **Application of photochemistry :** Photochemistry has significant role in our daily life. Some of the photochemical reactions commonly known as cited below,

(i) Photosynthesis in plants
(ii) Photography
(iii) The formation and destruction of ozone layer
(iv) Photoetching in electronic industry
(v) Many polymerization reactions.
(vi) Modern printing technology
(vii) Free radical combinations to obtain many compounds.

Tips & Tricks

✍ Different reactions have different rates because their activation energies are different. Lesser the activation energy faster is the reaction.

✍ The reaction, $NO + \frac{1}{2}O_2 \rightarrow NO_2$, exhibits a small negative temperature coefficient and the rate of reaction decreases with increase of temperature.

✍ Fuels in contact with oxygen do not burn by themselves. This is because they need activation energy (provided by the flame) to initiate the reaction. Thus, fuels are thermodynamically unstable (ΔG is –ve) but kinetically stable.

✍ Quantum efficiency of the photochemical reaction, $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$ is very high while that of $H_2 + Br_2 \xrightarrow{h\nu} 2HBr$, is very low. This is because after the chain initiating step $\left(X_2 \xrightarrow{h\nu} 2X\right)$ $Cl + H_2 \rightarrow HCl + H$ is exothermic whereas $Br + H_2 \rightarrow HBr + H$ is endothermic.

✍ **Drapper's effect :** $H_2 + Cl_2 \rightarrow 2HCl$, Such reactions are accompanied by the increase in the volume. This is called Drapper's effect. The reason is that the reaction is exothermic and heat released raises the temperature and gas expands resulting in the increase in volume.

✍ **Actinometer :** A device which is used to measure the intensity of radiation is konwn as actimometer. *e.g.*, Uranyl oxalate actinometer.

✍ Amount of the substance left after 'n' half lives $= \frac{A_0}{2^n}$.

✍ Free energy change (ΔG) for thermochemical reactions is always negative but remember, ΔG for photochemical reaction may not always be negative. It may be +ve also because a part of the light energy absorbed is converted into the free energy of the products.

✍ Negative catalysts or inhibitors are those substances which decrease the rate of a reaction.

✍ Example of fourth order reaction, $4KClO_3 = 3KClO_4 + KCl$

✍ **Grothus-Draper law :** When light falls on a substance, a part of light is absorbed, a part is reflected and a part is transmitted. only that part of light which is absorbed causes a particular reaction to occur.

✍ **Stark's Einstein law of photochemical equivalence** According to this law, every atom or molecule taking part in photochemical reaction absorbs only one quantum of radiaton.

✍ Kinetics of fast reactions can be studied by (i) Relaxation method (ii) Flash photolysis technique etc.

✍ Enzyme catalysed reactions are faster than metal catalysed reactions, the former has lower activation energy.

ROUND UP:

CHEMICAL KINETICS

1. CLASSIFICATION OF REACTIONS : [IN TERMS OF RATES]

(i) There are certain reactions which are too slow e.g. rusting of iron, weathering of rocks.

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

(iii) Neither too fast nor too slow e.g. combination of H_2 and Cl_2 in presence of light, hydrolysis of ethyl acetate catalysed by acid, decomposition of azomethane

2. RATE OF REACTION :

The change in concentration of either reactant or product per unit time.

Formula : $v = \pm \dfrac{dc}{dt}$

dc = change in concentration in a small interval dt.

[–] sign is used when we refer to reactant concentration.

[+] sign is used when we refer to product concentration.

◆ **Example :** $N_2 + 3H_2 \rightarrow 2NH_3$

(i) Rate of formation of ammonia $= +\dfrac{d[NH_3]}{dt}$

(ii) Rate of disappearance of nitrogen $= -\dfrac{d[N_2]}{dt}$

(iii) Rate of disappearance of hydrogen $= -\dfrac{d[H_2]}{dt}$

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

Thus, $\text{Rate of reaction} = -\dfrac{d[N_2]}{dt} = \dfrac{1}{2}\dfrac{d[NH_3]}{dt}$

or rate of formation of ammonia = Twice the rate of disappearance of nitrogen

i.e. $\dfrac{d[NH_3]}{dt} = \dfrac{2}{3}\left[-\dfrac{d[H_2]}{dt}\right]$

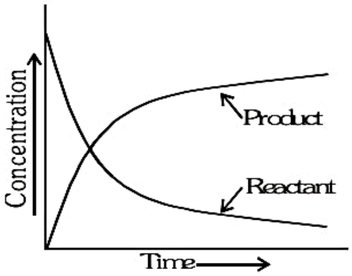
3. AVERAGE VELOCITY OF REACTION :

Change in the concentration of reactants or products per unit time is called average reaction velocity. If Δc is the change in the concentration of reactants and product in Δt time, then

$$\text{Average velocity} = \pm\frac{\Delta c}{\Delta t}$$

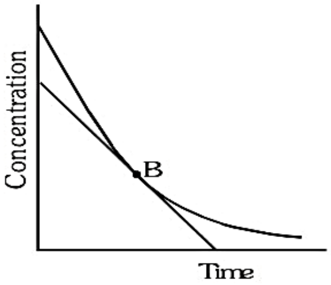
or $\text{Average velocity} = \dfrac{(-)\text{Change in the concentration of reactants}}{\text{Time}}$

(+)Change in the concentration of products



Unit of average velocity = $\dfrac{\text{Unit of concentration}}{\text{Unit of time}} = \dfrac{\text{gram mole}}{\text{litre}\ \ \text{Second}}$ = gram mole litre^{-1} second^{-1}

4. INSTANTANEOUS RATE OF THE REACTION :



The rate of reaction determined at specified concentration or specified time is called **instantaneous rate**.

The instantaneous rate of the reaction can be determined by measuring concentration of reactant or product at a instant of time and plotting concentration versus time.

The instantaneous rate at any time is determined by the slope of the tangent at a point on the time-concentration curve corresponding to the specified time. The slope of the tangent at a point is the limiting value of $\dfrac{\Delta c}{\Delta t}$.

$$\lim_{\Delta t \to 0} \frac{\Delta c}{\Delta t} = \frac{dc}{dt}$$

In terms of the concentration of reactant, the rate of the reaction = $-\dfrac{dc}{dt}$. The –sign indicates that the concentration of reactant decreases with time.

In terms of the concentration of product, the rate of the reaction = $+\dfrac{dc}{dt}$. The +sign indicates that the concentration of product increases with time. In the reaction if at a time t the concentration of product is x and at time t + dt, the concentration becomes x + dx then the reaction rate = $\dfrac{dx}{dt}$.

◆ **For example the rate of reaction :** $N_2 + 3H_2 \rightleftharpoons 2NH_3$

in terms of the concentrations of N_2, H_2 and NH_3 can be expressed as :

$$-\frac{d[N_2]}{dt},\ -\frac{1}{3}\frac{d[H_2]}{dt},\ +\frac{1}{2}\frac{d[NH_3]}{dt}$$

Ex.1 What should be (a) the rate of disappearance of B and (b) the rate of formation of C, if the rate of disappearance of A for the reaction A + B → 2C is 10^{-2} mole/litre/second at a particular temperature ?

Sol. (a) Rate of disappearance of A = Rate of disappearance of B

= 10^{-2} mole/litre/second

(b) Rate of disappearance of A = $\dfrac{1}{2}$ Rate of formation of C

Rate of formation of C = 2 Rate of disappearance of A

= 2 10^{-2} mole/litre/second

Ex.2 A gaseous reaction : $2A(g) + B(g) \rightarrow 2C(g)$,

Show a decrease in pressure from 120 mm to 100 mm in 10 minutes. The rate of appearance of C is -

[A] 2 mm/min [B] 4 mm/min [C] 10 mm/min [D] 12 mm/min. **Ans. [B]**

Sol. Suppose 2p is the pressure of C after 10 min.

Fall in pressure of A = 2p ; Fall in pressure of B = p

Total fall in pressure = (2p + p) – 2p = p = 20 mm

Pressure of C = 2p = 40 mm

Rate of appearance of C = 40/10 = 4 mm/min

Ex.3 The term $\frac{dx}{dt}$ in the rate expression refers to the -

[A] concentration of the reactants [B] increase in concentration of the reactants

[C] instantaneous rate of the reaction [D] average rate of the reaction **Ans. [C]**

Sol. It is expression for instantaneous rate

Ex.4 Which of the following expression can be used to describe the instantaneous rate of the reaction ?

$2A + B \rightarrow A_2B$

[A] $-\frac{1}{2}\frac{d[A]}{dt}$ [B] $-\frac{d[A]}{dt}$ [C] $\frac{1}{2}\frac{d[A_2B]}{dt}$ [D] $-\frac{1}{2}\frac{d[A]}{dt}.\frac{d[B]}{dt}$ **Ans. [A]**

Sol. The instantaneous rate of the reaction can be expressed by any of the following expressions

$$-\frac{1}{2}\frac{d[A]}{dt} \quad \text{or} \quad -\frac{d[B]}{dt} \quad \text{or} \quad \frac{d[A_2B]}{dt}$$

Ex.5 Which of the following will react at the highest rate ?

[A] 1 mol of A and 1 mol of B in a 1 L vessel [B] 2 mol of A and 2 mol of B in a 2 L vessel

[C] 3 mol of A and 3 mol of B in a 3 L vessel [D] All would react at the same rate **Ans. [D]**

Sol. Since all have same conc. of reactants, all would react at same rate.

5. FACTORS AFFECTING THE RATE OF REACTION :

(i) **Concentration :** Law of mass action enunciates that greater is the conc. of the reactants, the more rapidly the reaction proceeds.

(ii) **Pressure (Gaseous reaction) :** On increasing the pressure, volume decreases and conc. increases and hence the rate increases.

(iii) **Temperature :** It is generally observed that rise in temperature increases the reaction rate.

(iv) **Nature of the reactants :** The rate depends upon specific bonds involved and hence on the nature of reactants.

$$\boxed{g > \ell > s}$$

(v) **Surface area of the reactants :** In heterogeneous reactions, more powdered is the form of reactants, more is the velocity. [as more active centres are provided]

(vi) **Catalyst :** Affects the rate immensely.

Ex.6 For the reaction :

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

Given : $\frac{d[NO]}{dt} = 3.6 \quad 10^{-3}$ mol L^{-1} s^{-1}

Calculate : (i) rate of disappearance of ammonia

(ii) rate of formation of water

Sol. From the eqn. it is clear that

Rate $= -\frac{1}{4}\frac{d[NH_3]}{dt} = \frac{1}{4}\frac{d[NO]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt}$ Thus : $-\frac{1}{4}\frac{d[NH_3]}{dt} = \frac{1}{4}\frac{d[NO]}{dt}$

or $-\frac{d[NH_3]}{dt} = \frac{d[NO]}{dt} = 3.6 \quad 10^{-3}\ \text{mol L}^{-1}\ \text{s}^{-1}$ Also $\frac{1}{4}\frac{d[NO]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt}$

$$\frac{3}{2}\frac{d[NO]}{dt} = \frac{d[H_2O]}{dt}$$

$$\frac{3}{2} \quad 3.6 \quad 10^{-3} = \frac{d[H_2O]}{dt}$$

$$\frac{d[H_2O]}{dt} = 5.4 \quad 10^{-3}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Ex.7 The following reaction was studied in a closed vessel.

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

It was found that concentration of NO_2 increases by $4.0 \quad 10^{-2}$ mol L^{-1} in five seconds, calculate

(a) the rate of reaction

(b) the rate of change of concentration N_2O_5.

Sol. (a) Rate $= \frac{1}{4}\frac{d[NO_2]}{dt}$

But $\frac{d[NO_2]}{dt} = \frac{4.0\times10^{-2}\,\text{mol}L^{-1}}{5\,\text{sec}} = 8 \quad 10^{-3}\ \text{mol L}^{-1}\ \text{s}^{-1}$

$\therefore$ Rate of reaction $= \frac{1}{4} \quad 8 \quad 10^{-3}\ \text{mol L}^{-1}\ \text{s}^{-1} = 2 \quad 10^{-3}\ \text{mol L}^{-1}\ \text{s}^{-1}$

(b) Rate of change of conc. of N_2O_5

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

$= -\frac{1}{2}\frac{[d[N_2O_5]]}{dt} = -\frac{1}{2} \quad 8 \quad 10^{-3} = 4 \quad 10^{-3}\ \text{mol L}^{-1}\text{s}^{-1}$

Ex.8 The rate of change in concentration of R in the reaction, $2P + Q \longrightarrow 2R + 3S$, was reported as 1.0 mol L^{-1} sec^{-1}. Calculate the reaction rate as well as rate of change of concentration of P, Q and S.

Sol. $\frac{-1}{2}\frac{d[P]}{dt} = -\frac{d[Q]}{dt} = \frac{1}{2}\frac{d[R]}{dt} = \frac{1}{3}\frac{d[S]}{dt} =$ Rate of reaction

$\because$ $\frac{d[R]}{dt} = 1.0\ \text{molL}^{-1}\ \text{s}^{-1}$

$\therefore$ $-\frac{d[P]}{dt} = \frac{d[R]}{dt} = 1.0\ \text{mol L}^{-1}\ \text{s}^{-1}$

$$\frac{-d[Q]}{dt} = \frac{1}{2}\frac{d[R]}{dt} = \frac{1}{2} = 0.5\ \text{molL}^{-1}\ \text{s}^{-1}$$

$$\frac{-d[S]}{dt} = \frac{3}{2}\frac{d[R]}{dt} = \frac{3}{2} \quad 1 = 1.5\ \text{molL}^{-1}\ \text{s}^{-1}$$

Rate of reaction $= \frac{1}{2}\frac{d[C]}{dt} = \frac{1}{2} \quad 1 = 0.5\ \text{mol L}^{-1}\text{s}^{-1}$

6. SPECIFIC REACTION RATE :

Applying law of mass action to the reaction :

$$m_1A + m_2B \rightarrow n_1C + n_2D$$

$$\text{Rate} \propto [A]^{m_1}\ [B]^{m_2}$$

or $$v = k[A]^{m_1}\ [B]^{m_2}$$

This equation is known as rate law. Where k is the proportionality constant and is called

(i) Velocity constant or (ii) Velocity coefficient or (iii) Specific reaction rate.

On putting [A] = [B] = 1, where have : v = k

Hence specific reaction rate is the rate of the reaction when the concentration of each reactant is taken as unit.

◆ **Unit of Specific Reaction Rate**

$$v = k\ [A]^{m_1} . [B]^{m_2}$$

$$\frac{\text{conc.}}{\text{time}} = k[\text{conc.}]^{m_1+m_2}$$

$$[\text{conc.}]^{[1-(m_1+m_2)]} \quad [\text{time}]^{-1} = k \quad \text{or} \quad k = \left[\frac{\text{mole}}{\text{litre}}\right]^{[1-(m_1+m_2)]} . [\text{second}^{-1}]$$

7. DISTINCTION BETWEEN UNIT OF RATE AND RATE CONSTANT :

- **Rate of a reaction :** Its units are always mole litre^{-1} time^{-1}.
- **Rate constant :** Its unit depends upon the order of reaction.

8. RATE LAW :

(a) It may also not depend upon the concentration of each reactant or product of the reaction.

Suppose, $mA + nB \rightarrow \text{Product}$

$$\boxed{R \propto [A]^m [B]^n}$$

(b) Rate of a chemical reaction is directly proportional to the product of the concentration of reactants raise to the power of their stoichiometric coffecient.

(c) The rate law represents the experimentally observed rate of reaction which depends upon the slowest step of the reaction.

(d) Rate law cannot be deduce from the equation for a given reaction. It can be find by experiments only.

(e) The rate law may not bear a simple relationship of the stoichiometric equation.

Ex.9 In the reaction, $A + 2B \rightarrow 6C + 2D$, if the initial rate $-\frac{d[A]}{dt}$ at t = 0 is 2.6 10^{-2} M sec^{-1}, what will be the value of $-\frac{d[B]}{dt}$ at t = 0 ?

[A] 8.5 10^{-2} M sec^{-1} [B] 2.5 10^{-2} M sec^{-1}

[C] 5.2 10^{-2} M sec^{-1} [D] 7.5 10^{-2} M sec^{-1} **Ans. [C]**

Sol. From the reaction it is evident that when a mole of A is reacting, 2 moles of B must react. Hence the decrease in the concentration of B must be twice that of A

$$\therefore \quad -\frac{d[B]}{dt} = 2\left[-\frac{d[A]}{dt}\right]$$

$$= 2 \quad 2.6 \quad 10^{-2} = 5.2 \quad 10^{-2} \text{ M sec}^{-1}$$

Ex.10 The dimensions of rate constant of a second order reaction involves :

[A] time and concentration [B] neither time nor concentration

[C] time only [D] concentration only **Ans. [A]**

Sol. $k = \frac{\text{Rate}}{[A]^2} = \frac{\text{mol}L^{-1}s^{-1}}{(\text{mol}L^{-1})^2} = \frac{s^{-1}}{\text{mol } L^{-1}} = (\text{mol } L^{-1})^{-1}\ s^{-1}$

Ex.11 The rate constant of a reaction has same units as the rate of reaction. The reaction is of

[A] zero order [B] first order [C] second order [D] none of these **Ans. [A]**

Sol. For a zero order reaction, $r = k[A]$. Thus the units of k are the same as that of rate of reaction.

Ex.12 The rate constant of n^{th} order reaction has units :

[A] $\text{litre}^{1-n}\text{mol}^{1-n}\text{sec}^{-1}$ [B] $\text{mol}^{1-n}\text{litre}^{1-n}\text{sec}$

[C] $\text{mol}^{1-n^2}\ \text{litre}^{n^2}\ \text{sec}^{-1}$ [D] $\text{mol}^{1-n}\text{litre}^{n-1}\text{sec}^{-1}$ **Ans. [D]**

Sol. For an n^{th} order reaction : rate = k $[\text{conc.}]^n$

$$k = \frac{\text{rate}}{[\text{conc.}]^n}$$

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

Ex.13 On which of the following factors, the rate constant does not depend ?

[A] Temperature [B] Concentration

[C] Presence of catalyst [D] Nature of reactants **Ans. [B]**

Sol. Rate constant is independent of the conc. of the reactants.

9. ORDER OF REACTION :

The sum of the power of the concentration terms on which the rate of reaction actually depends as observed experimentally is called the order of the reaction. For example,

Order of reaction = x + y

Thus, the order of reaction may also be defined as the sum of the exponents (powers) to which the concentration terms in the rate law equation are raised in order to express the observed rate of the reaction. Thus, reaction is said to be of the first order if its rate is given by the expression of the type,

$r = k_1C_A$

Second order if the rate is given by the expression of the type,

$r = k_2C^2{}_A$

or $r = k_2C_AC_B$

third order if the rate is given by the expression of the type

$r = k_3C_A{}^3$ or $r = k_3C_A^2C_B$ or $r = k_3C_AC_B{}^2$ or $k_3C_AC_BC_C$ and so on

For zero order reaction, the rate equation is written as $R = k_0$. It is to be noted that the order of reaction is essentially an experimental quantity.

Note: **Order may be zero, fractional, integer or negative.**

Example :

Reaction	Experimental rate equation	order
$H_2 + Cl_2 \rightarrow 2HCl$	$v = k$	zero
$H_2 + Br_2 \rightarrow 2HBr$	$v = k\ [H_2]\ [Br_2]^{1/2}$	one and half
$H_2 + I_2 \rightarrow 2HI$	$v = k\ [H_2]\ [I_2]$	two

◆ **Examples of fractional order reaction**

Reaction : $CO(g) + Cl_2(g) \rightarrow COCl_2(g)$

$v = k\,[CO]^2\,[Cl_2]^{1/2}$, order = 2.5

Reaction : $COCl_2(g) \rightarrow CO(g) + Cl_2(g)$

$v = k\,[COCl_2]^{3/2}$, order = 1.5

Ex.14 For the chemical reaction,

$$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$

Rate = $k\,[HBr]\,[O_2]$

What is the probable mechanism of the reaction ?

Sol. $HBr + O_2 \longrightarrow HOOBr$ (slow)

$HOOBr + HBr \longrightarrow 2HOBr$ (fast)

$HOBr + HBr \longrightarrow H_2O + [Br_2]\quad 2$ (fast)

Ex.15 Nitric oxide (NO) reacts with oxygen to produce nitrogen dioxide :

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

What is the predicted rate law, if the mechanism is :-

$NO\,(g) + O_2\,(g) \xrightleftharpoons{k} NO_3\,(g)$ (fast)

$NO_3\,(g) + NO\,(g) \xrightarrow{k_1} 2NO_2\,(g)$ (slow)

Sol. From the slow step,

Rate = $k_1\,[NO_3]\,[NO]$ ....(i)

From fast step :

Equilibrium constant (K) = $\dfrac{[NO_3]}{[NO][O_2]}$ ....(ii)

Substituting the value of $[NO_3]$ from equation (ii) into equation (i), we get

Rate= $k'[NO]^2\,[O_2]$

10. MOLECULARITY OF A REACTION :

"Molecularity is defined as the number of molecules, atoms, or radicals that must collide simultaneously in order for the reaction to take place." It is always a whole number and cannot be negative.

In the elementary processes :

Participating species		**Molecularity**
One species participates	.....	unimolecular, 1
Two species participates	.....	bimolecular, 2
Three species participates	.....	trimolecular, 3

◆ **Example :**

$N_2O_4 \rightarrow 2NO_2$	......	unimolecular
$H_2 + I_2 \rightarrow 2HI$	......	bimolecular
$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$	......	trimolecular

Note : If the reaction takes place in two or more steps then the overall molecularity of the reaction is monitored by the slow or rate determining step.

11. DIFFERENCE BETWEEN MOLECULARITY AND ORDER OF REACTION :

	Molecularity		Order of Reaction
1.	Molecularity can neither be zero nor fractional	1.	Order of a reaction can be zero, fractional or integer
2.	It is the number of molecules of reactants concentration terms taking part in elementary step of a reaction.	2.	It is sum of power raised or the rate expression.
3.	It can not have negative value.	3.	Order of a reaction may have negative value.
4.	Molecularity is a theoretical property.	4.	Order is an experimental property.
5.	Molecularity concerns with mechanism.	5.	Order concerns with kinetic (rate law).

Ex.

Reaction	Rate law	Order
$CH_3CHO \longrightarrow CH_4 + CO$	Rate $\propto [CH_3CHO]^{3/2}$	1.5
$NH_3 \longrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$	Rate $\propto [NH_3]^0$	0
$2HI \longrightarrow H_2 + I_2$	Rate $\propto [HI]^0$, i.e. Rate = k	0

Order may change with change in experimental conditions while molecularity can't.

Ex.

This reaction follows first order kinetics at high pressure and 2nd order kinetics at low pressure of cyclopropane.

12. PSEUDO UNIMOLECULAR REACTION :

Consider the reaction : $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

Since water is present in large excess, its concentration hardly changes during the course of the reaction. And as such rate depends only on the concentration of ester. The order is one but the molecularity is two. Such reactions are called **pseudo unimolecular reaction**.

Ex.16 For a chemical reaction, A → products, the rate of reaction doubles when the concentration of A is increased by 4 times. The order of reaction is

[A] 4 [B] 0 [C] 1/2 [D] 1 **Ans. [C]**

Ans. $r = k[A]^n$ .... (i) ; $2r = k\,[4A]^n$ .... (ii)

Dividing (ii) by (i) $\frac{2r}{r} = \frac{k}{k}\left[\frac{4A}{A}\right]^n$

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

Ex.17 For a hypothetical reaction

A + B → products, the rate law is, $r = k\,[B]\,[A]$, the order of reaction is :

[A] 0 [B] 1 [C] 2 [D] 3 **Ans. [B]**

Sol. 1 + 0 = 1

Ex.18 The slowest step of a particular reaction is found to be

$$\frac{1}{2}X_2 + Y_2 \rightarrow XY_2$$

The order of the reaction is

[A] 2 [B] 3 [C] 3.5 [D] 1.5 **Ans. [D]**

Sol. $r = k[X_2]^{1/2}\,[Y_2]^1$ $\therefore$ Order = 0.5 + 1 = 1.5

Ex.19 The rate of certain hypothetical reaction A + B + C → products, is given by

$$r = \frac{dA}{dt} = k\,[A]^{1/2}\,[B]^{1/3}\,[C]^{1/4}$$

The order of a reaction is given by

[A] 1 [B] 1/2 [C] 2 [D] 13/12 **Ans. [D]**

Sol. Order of reaction $= \frac{1}{2}+\frac{1}{3}+\frac{1}{4}=\frac{6+4+3}{12}=\frac{13}{12}$

13. ZERO ORDER REACTION :

Reaction whose rate is not affected by concentration said to be of zero order reaction.

Example :

(i) Reaction between Acetone and Bromine

(ii) Dissociation of HI on gold surface

(A) Unit of Rate Constant :

$\boxed{k = \text{mol L}^{-1}\,\text{sec}^{-1}}$ Unit of rate of reaction = Unit of rate constant.

(B) Rate Constant of Zero Order Reaction :

$\boxed{x = kt}$

The rate of reaction is independent of the concentration of the reaction substance.

(C) Determination of Half life Period of Zero Order Reaction :

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

$\boxed{t_{1/2} = \frac{a}{2k}}$ or $\boxed{t_{1/2} \propto a}$

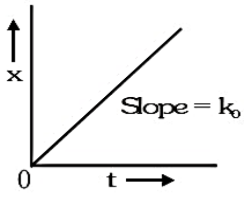
The half life period is directly proportional to the initial concentration of the reactants.

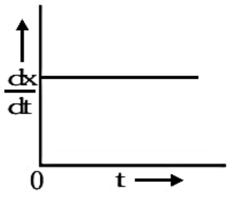
Ex.20 The rate equation of a reaction is $k[A]^{1/2}[B]^{1/2}[C]^{-1}$. What should be the order of the reaction ?

Sol. $n = \frac{1}{2} + \frac{1}{2} - 1 = 0$

∴ Order of the reaction is zero.

◆ **Graphical representation**





Example :

- Photochemical reactions, like $H_2 + Cl_2 \longrightarrow 2HCl$, are zero order reaction.
- Decomposition of NH_3 on platinum surface is also zero order reaction.

14. FIRST ORDER REACTION :

When the rate of reaction depends only on one concentration term of reactant.

A first order reaction is one whose rate varies as first power of the concentration of the reactant, i.e. the rate increases as number of times as the concentration of reactant is increased.

Let us, consider a unimolecular first order reaction represented by the general equation,

	$A \longrightarrow$	Product
At t =0	a	0
At t = t	a − x	x

The initial concentration of A is a mole L^{-1} and its concentration after time t is (a − x) mole L^{-1}. This means during the time interval t, x mole L^{-1} of A has reacted.

The rate of reaction at any time t is given by the following first order kinetics.

$$\frac{d(a-x)}{dt} \propto (a - x)$$

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

where k is the rate constant of the reaction.

$$\frac{dx}{a-x} = k dt$$

This is differential rate equation and can be solved by integration.

$$\int \frac{dx}{a-x} = k\int dt$$

or $- \ln (a - x) = k.t + C$ ....(1)

where C is integration constant.

The constant C can be evaluated by applying the initial condition of the reaction i.e. when t = 0, x = 0. Putting these in equation (1), we get

$C = - \ln a$

Putting the value of C in equation (1), we get

$- \ln (a - x) = k.t - \ln a$

or $k = \frac{1}{t} \ln \frac{a}{a-x} = \frac{2.303}{t} \log \frac{a}{a-x}$ ....(2)

Also, $k = \frac{2.303}{(t_2 - t_1)} \log \frac{(a-x_1)}{(a-x_2)}$

and $k = \frac{2.303}{(t_2 - t_1)} \log \frac{R_1}{R_2}$

where $(a - x_1)$ is concentration at time t_1 and $(a - x_2)$ is concentration after time t_2 and R_1 is rate at time t_1 and R_2 is rate at time t_2.

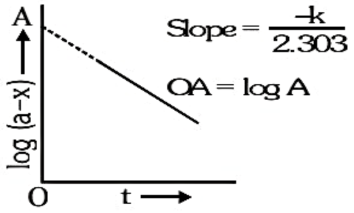
If $[A]_0$ and [A] be the concentrations of reactant at zero time and time t respectively, then Eq. (2) may be put as

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

Also, $[A] = [A]_0\, e^{-kt}$

This is the integrated rate expression for first order reaction.

As, $k = \frac{1}{t} \ln \frac{a}{a-x} \Rightarrow \log(a-x) = \log(a) - \frac{kt}{2.303}$



$kt = \ln a - \ln(a-x)$

Also, $(a-x) = ae^{-kt}$

$x = a(1 - e^{-kt})$

$\therefore$ Degree of dissociation $\left(\frac{x}{a}\right) = (1 - e^{-kt})$

◆ **Unit of Rate constant**

The differential rate expression for nth order reaction is as follows :

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

or $\quad k = \frac{dx}{(a-x)^n dt} = \frac{(\text{concentration})}{(\text{concentration})^n \text{time}} = (\text{conc.})^{1-n}\ \text{time}^{-1}$

If concentration be expressed in mole L^{-1} and time in minutes, then

$k = (\text{mole } L^{-1})^{1-n} \min^{-1}$

For zero order reaction, n = 0 and hence, $k = \text{mole } L^{-1} \min^{-1}$

For first order reaction, n = 1 and hence,

$k = (\text{mole } L^{-1})^0 \min^{-1} = \min^{-1}$

For second order reaction, n = 2 and hence,

$k = (\text{mole } L^{-1})^{-1} \min^{-1} = \text{mole}^{-1} L \min^{-1}$

The rate constant of a first order reaction has only time in its unit. It has no concentration term in the unit. This means the numerical value of k for a first order reaction is independent of the unit in which concentration is expressed. If concentration unit is changed, the numerical value of k for a first order reaction will not change. However, it would change with change in time. Say, k is 6.0 10^{-3} min then it may also be written as 1 10^{-4} s^{-1}, i.e., numerical value of k will decrease 60 times if time unit is changed from hour to minute or from minute to second.

◆ **Half - time or half - life period of a first order reaction :**

The half - time of a reaction is defined as the time required to reduce the concentration of the reactant to half of its initial value. It is denoted by the symbol $t_{1/2}$. Thus,

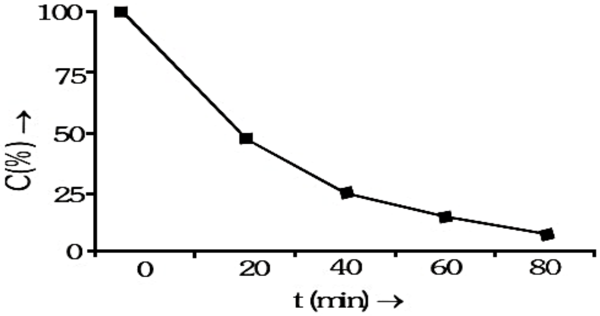
When $x = \frac{a}{2}$, $t = t_{1/2}$

Putting these values in Eq. (2), we get

$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - \frac{a}{2}} = \frac{2.303}{t_{1/2}} \log 2 = \frac{2.303}{t_{1/2}} \quad 0.30103$$

$(\because \log 2 = 0.30103)$

$$t_{1/2} = \frac{0.693}{k} \qquad ....(3)$$



Since k is a constant for a given reaction at a given temperature and the expression lacks any concentration term so from Eq. (3) it is evident that half-time of a first order reaction is a constant independent of initial concentration of reactant. This means if we start with 4 moles L^{-1} of a reactant reacting by first order kinetics, then after 20 minutes it is reduced to 2 moles L^{-1}. That is, after 20 minutes from the start of reaction the concentration of the reactant will be 2 moles L^{-1} after 40 minutes from the start of reaction, the concentration is 1 mole L^{-1}. After 60 minutes from the start of reaction, the concentration of the reactant will be reduced to 0.5 mol L^{-1}. In other words, if during 20 minutes 50% of the reaction completes, then in 40 minutes 75%, in 60 minutes 85.5% of the reaction and so on, will complete as shown in the figure above.

Thus, fraction left after n half-lives $=\left(\frac{1}{2}\right)^n$

Concentration left after n half-lives, $[A]=\left(\frac{1}{2}\right)^n[A]_0$

It is also to be noted that Eq. (3) helps to calculate $t_{1/2}$ or k.

A general expression for $t_{1/2}$ is as follows.

◆ **Half - life of a n^{th} order reaction**

Let us find out $t_{1/2}$ for n^{th} order reaction where $n \neq 1$.

$$\therefore \quad \frac{-d[A]}{dt}=k_n[A]^n \Rightarrow \frac{-d[A]}{[A]^n}=kdt \Rightarrow -\int_{[A]_0}^{[A]_0/2}\frac{d[A]}{[A]^n}=k\int_0^{t_{1/2}}dt$$

$$\int_{[A]_0/2}^{[A]_0}[A]^{-n}d[A]=k_nt_{1/2} \qquad \left[\frac{[A]^{1-n}}{1-n}\right]_{[A]_{0/2}}^{[A]_0}=k_nt_{1/2}$$

$$\Rightarrow \quad \frac{1}{1-n}\left([A]_0^{1-n}-\left[\frac{[A]_0}{2}\right]^{1-n}\right)=k_nt_{1/2} \Rightarrow \frac{[A]_0^{1-n}}{1-n}\left[1-\left(\frac{1}{2}\right)^{1-n}\right]=k_nt_{1/2}$$

$$\Rightarrow \quad \frac{1}{(1-n)[A]_0^{n-1}}[1-2^{n-1}]=k_nt_{1/2} \Rightarrow \frac{(2^{n-1}-1)}{k_n(n-1)[A]_0}=t_{1/2}\ \textbf{(order } n \neq 1\textbf{)}$$

Therefore, for n^{th} order reaction, the half-life is inversely related to the initial concentration raised to the power of (n − 1).

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

where n = order of reaction.

Example : **(i)** All radioactive reactions

(ii) A → Product

(iii) $2NO \rightleftharpoons 2N_2 + O_2$

(iv) $2Cl_2O_7 \rightarrow 2Cl_2 + 7O_2$

(A) **Unit of rate constant of first order reaction**

$K = (sec)^{-1} \qquad \Delta n = 1$

(B) **Velocity constant for first order reaction**

$$\boxed{k_1=\frac{2.303}{t}\log_{10}\frac{a}{(a-x)}} \quad \Rightarrow \quad \boxed{t=\frac{2.303}{k_1}\log_{10}\frac{a}{(a-x)}}$$

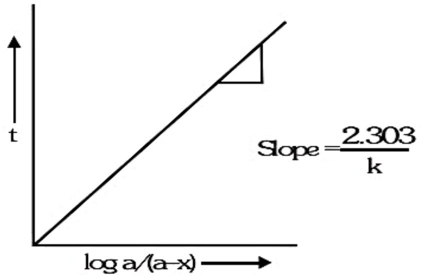
where t = time, a = initial concentration at t = 0

(a − x) = concentration after time t

K = Rate constant

(C) Graphical Representation

Graph between t v/s log $\frac{a}{(a-x)}$ is a straight line



Ex.21 A first order reaction gets 90% completed in 40 minute. Find out the half-life period of the reaction.

Sol. Suppose that the initial concentration of reactant (a) = 100 t = 40 minutes

90% of the reaction get completed in 40 minutes.

Therefore,

$$x = 90$$

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$= \frac{2.303}{40} \log \frac{100}{100-90} \Rightarrow k_1 = \frac{2.303}{40} \log 10$$

$$= \frac{2.303}{40} \quad 1 = 5.757 \quad 10^{-2} \text{ minutes}^{-1}$$

$$t_{½} = \frac{0.693}{5.757 \quad 10^{-2}} = 10.3 \text{ minutes}$$

Ex.22 Prove with the help of the following data that hydrolysis of H_2O_2 is a first order reaction. Initial concentration in the reaction 25.0.

Sol.

Time, t (in minutes)	10	20	30
V	20.0	15.7	12.5

For a first order reaction, $k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$; Here, a = 25

$$k_1 \text{ at } t = 10 \text{ minutes} = \frac{2.303}{10} \log \frac{25}{20} = \frac{2.303}{10} \quad 0.0969 = 2.23 \quad 10^{-2}$$

$$k_1 \text{ at } t = 20 \text{ minutes} = \frac{2.303}{20} \log \frac{25}{15.7} = \frac{2.303}{20} \quad 0.2020 = 2.32 \quad 10^{-2}$$

$$k_1 \text{ at } t = 30 \text{ minutes} = \frac{2.303}{30} \log \frac{25}{12.5} = \frac{2.303}{30} \quad 0.3010 = 2.31 \quad 10^{-2}$$

Constant value of k shows that hydrolysis of H_2O_2 in aqueous medium is a first order reaction.

Ex.23 The rate constant for an isomerization reaction, A $\longrightarrow$ B, is $2.5 \quad 10^{-3}$ min^{-1}. If the initial concentration of A is 1M, calculate the rate of reaction after 1 hr.

Sol. As, $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$, for first order reaction

$$\Rightarrow \quad 2.5 \quad 10^{-3} = \frac{2.303}{60} \log \frac{1}{(a-x)}$$

$\therefore \quad (a - x) = 0.8607$

The rate after 60 minutes = k (a – x) = $2.5 \quad 10^{-3} \quad 0.8607 = 2.1518 \quad 10^{-3}$

Ex.24 The rate of a first order reaction is 0.08 mol L^{-1} at 20 min. and 0.06 mol L^{-1} at 40 min. after start of reaction. Find the half-life of reaction.

Sol. As, rate = k[A]

$0.08 = k[A]_{10}$

$0.06 = k[A]_{20}$

$$\therefore \quad \frac{[A]_{10}}{[A]_{20}} = \frac{0.08}{0.06} = \frac{4}{3}$$

For first order reaction :

$$t = 2.303 \log \frac{[A]_{10}}{[A]_{20}}$$

when t = (40 – 20) = 20 min.

$$\therefore \quad 20 = \frac{2.303}{k} \log \frac{4}{3}$$

$$\therefore \quad k = \frac{2.303}{20} \log \frac{4}{3} = 0.0144 \ min^{-1}$$

$$\therefore \quad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0144} = 48.13 \ min$$

Ex.25 Radioactive decay of an atomic nucleus is a first order reaction. Half-life period of radium $[_{88}Ra^{226}]$ is 1590 years. Find out its decay constant.

Sol. $t_{½} = \frac{0.693}{k_1} = \frac{0.693}{t_{1/2}} = \frac{0.693}{1590} = 4.358 \quad 10^{-4} \ Y^{-1}$

☐ SECOND ORDER REACTION

	A	+	A	$\longrightarrow$	Product
	A	+	B	$\longrightarrow$	Product
At t = 0	a		a		0
At t = t	(a – x)		(a – x)		x
At $t = t_1$	$(a - x_1)$		$(a - x_1)$		x_1
At $t = t_2$	$(a - x_2)$		$(a - x_2)$		x_2

As per rate law, $\frac{dx}{dt} = k_2[A]^n = k_2[A]^2 = k_2 \ [A][B]$

$\therefore \quad \left(\frac{dx}{dt}\right) = k_2 \ (a - x)^2$ (k_2 = rate constant for second order reaction)

Also, $k_2 = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right] = \frac{1}{t}\frac{a}{a(a-x)}$ or $k_2 = \frac{1}{(t_2 - t_1)}\left[\frac{1}{(a-x_2)} - \frac{1}{(a-x_1)}\right]$

Where $(a - x_1)$ and $(a - x_2)$ are the concentration of the reactant A at time t_1 and t_2 respectively. If reactant A and B have different concentrations a and b, then $k_2 = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

when a >> b then (a − b) ≈ a

(a − x) ≈ a

Equation reduces to

$$k_2 = \frac{2.303}{t \times a} \log_{10} \frac{b}{a-x}$$

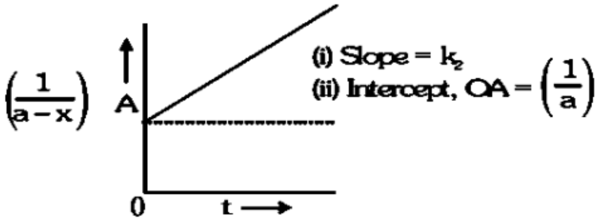
$$\Rightarrow \quad k_2' = k_2 \quad a = \frac{2.303}{t} \log_{10}\left(\frac{b}{b-x}\right) \quad \text{(equation for first order kinetics)}$$

This is an example of pseudo first order reaction.

Equation for second order reaction can be rewritten as

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

◆ **Graphical Representation**



In general for n^{th} order reaction,

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

In general for n^{th} order reaction,

$$t_{1/2(n)} = \frac{2^{n-1}-1}{(n-1)k_n(a)^{n-1}} \ (n \geq 2)$$

$$\Rightarrow \quad t_{1/2(n)} \propto \frac{1}{a^{(n-1)}}$$

$$\Rightarrow \quad t_{1/2(n)} \propto a^{(1-n)}$$

Ex.26 Initial concentrations of both the reactants of a second order reaction are equal and 60% of the reaction gets completed in 3000 seconds. How much time will be taken in 20% completion of the reaction ?

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

Suppose, a = 1 $\quad k_2 = \frac{1}{3000} \quad \frac{0.6}{1(1-0.6)} = \frac{1}{3000} \quad \frac{0.6}{0.4}$

Now, for 20% completion

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

$$\frac{1}{3000} \quad \frac{0.6}{0.4} = \frac{1}{t} \quad \frac{(0.2)}{1(1-0.2)}$$

$$\frac{1}{3000} \quad \frac{0.6}{0.4} = \frac{1}{t} \quad \frac{1}{4}$$

$$t = \frac{3000}{0.6} \quad \frac{0.4}{4}$$

t = 500 second

Ex.27 A second order reaction requires 70 minutes to change the concentration of reactants from 0.08 M to 0.01 M. How much time will it require to become 0.04 M.

Sol. For second order reaction

when, $(a - x) = 0.01$

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

$$k_2 = \frac{0.07}{70\ \ 0.08\ \ (0.01)} \qquad \text{......(1)}$$

$(a - x) = 0.04$

$$k_2 = \frac{0.04}{t\ \ 0.08\ \ (0.04)} \qquad \text{.......(2)}$$

From the equation (1) and (2)

$$\frac{0.07}{70\ \ 0.08\ \ (0.01)} = \frac{0.04}{t\ \ 0.08\ \ (0.04)}$$

$t = 10$ minutes

16. THIRD ORDER REACTION :

A reaction is said to be of third order if its rate is determined by the variation of three concentration terms. When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as

(i) $2NO + O_2 \rightleftharpoons 2NO_2$ (ii) $A + B + C \rightarrow \text{Product}$

Rate constant of third order reaction

$$\boxed{k_3 = \frac{1}{t}\cdot\frac{x(2a-x)}{2a^2(a-x)^2}}$$

Half life period $\boxed{t_{1/2} = \frac{3}{2ka^2}}$

Thus, half life is inversely proportional to the square of initial concentration.

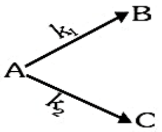
◆ **nth order reaction :**

$A \rightarrow \text{Product}$

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

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

◆ **Side or concurent reaction :**



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

◆ **Consecutive reaction :**

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \quad : \quad t_{max} = \frac{1}{k_1 - k_2}\ell n\left(\frac{k_1}{k_2}\right); \quad [B]_{max} = [A]_0\left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1-k_2}}$$

17. THRESHOLD ENERGY AND ACTIVATION ENERGY :

For a reaction to take place the reacting molecules must colloid together, but only those collisions, in which colliding molecules possess certain minimum energy is called threshold energy (E_T).

◆ **Activation energy (E_a) :**

The extra energy needed for the reactant molecules to be able to react chemically is known as Activation energy.

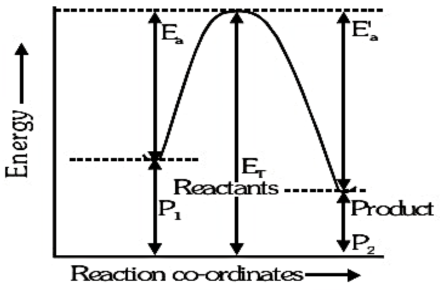
E_T = Threshold energy

E_a = Activation energy of forward reaction

E'_a = activation energy of backward reaction

P_1 = Potential energy of reactants

P_2 = Potential energy of products



18. EFFECT OF CATALYST :

A catalyst is a substance, which increases the rate of reaction without itself being consumed at the end of the reaction, and the phenomenon is called catalysis. There are some catalysts which decrease the rate of reaction and such catalysts are called negative catalyst. Obviously, the catalyst accelerating the rate will be positive catalyst. However, the term positive is seldom used and catalyst itself implies positive catalyst. Catalysts are generally foreign substances but sometimes one of the product formed may act as a catalyst and such a catalyst is called "auto catalyst" and the phenomenon is called **auto catalysis.**

Thermal decomposition of $KClO_3$ is found to be accelerated by the presence of MnO_2. Here, MnO_2 (foreign substance) act as a catalyst $2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2\uparrow + [MnO_2]$

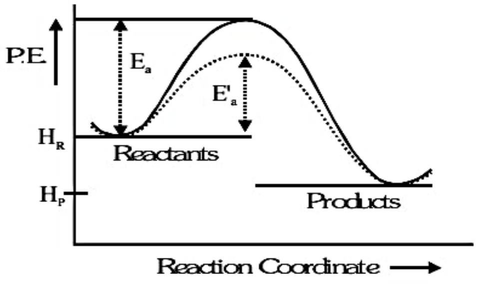
MnO_2 can be received in the same composition and mass at the end of the reaction.

In the permanganate titration of oxalic acid in the presence of bench H_2SO_4 (acid medium), it is found that there is slow discharge of the colour of permanganate solution in the beginning but after sometime the discharge of the colour becomes faster. This is due to the formation of $MnSO_4$ during the reaction which acts as a catalyst for the same reaction. Thus, $MnSO_4$ is an **"auto catalyst"** for this reaction. This is an example of auto catalyst.

$$2KMnO_4 + 4H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 8H_2O + 10CO_2$$

❑ **General Characteristic of Catalyst**

- ◆ A catalyst does not initiate the reaction, it simply fastens it.
- ◆ Only a small amount of catalyst can catalyse the reaction.
- ◆ A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant and hence ΔG . It simply lowers the time needed to attain equilibrium. This mean if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst also the reaction will go to 75% of completion before the attainment of equilibrium but the time needed for this will be less than 20 minutes.
- ◆ A catalyst drives the reaction through a different route for which energy barrier is of shortest height and Hence, E_a is of lower magnitude. That is, the function of the catalyst is to lower down the activation energy.



E_a = Energy of activation in absence of catalyst.

E'_a = Energy of activation in presence of catalyst.

$E_a - E'_a$ = Lowering of activation energy by catalyst.

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

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

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

Since E_a, E'_a is +ve, so $k_{cat} > k$. The ratio $\frac{k_{cat}}{k}$ gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature and this depends upon $E_a - E'_a$. Greater the value of $E_a - E'_a$, more number of times k_{cat} is greater than k.

The rate of reaction in the presence of catalyst at any temperature T_1 may be made equal to the rate of reaction in absence of catalyst but we will have to raise the temperature. Let, this temperature be T_2, then

$$e^{-E'_a/RT_1} = e^{-E_a/RT_2}$$

or $$\frac{E'_a}{T_1} = \frac{E_a}{T_2}$$

Ex.28 A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of catalyst at the same rate, the temperature required is 400K. Calculate the activation energy of the reaction if the catalyst lowers the activation energy barrier by 40 kJ/mol.

Sol. Let, E_a and E'_a be the energy of activation in absence and presence of catalyst for hydrogenation reaction,

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

$k_1 = Ae^{-E_a/R\times500}$ (In absence of catalyst)

$k_2 = Ae^{-E'_a/R\times400}$ (In presence of catalyst)

Given, $r_1 = r_2$; Hence $k_1 = k_2$

$$e^{-E_a/R\times500} = e^{-E'_a/R\times400}$$

$$\Rightarrow \quad \frac{E_a}{R\times500} = \frac{E'_a}{R\times400} \quad \text{or} \quad \frac{E_a}{500} = \frac{E_a - 40}{400} \quad (\text{As } E_a - E'_a = 40)$$

$\therefore$ E_a = 200 kJ/mol^{-1}

19. DETERMINATION OF ORDER OF REACTION :

◆ **Integration Method**

In this method, value of k is determined by putting values of initial concentration of reactants and change in concentration with time in kinetic equation of first, second and third order reactions. The equation by which constant value of k is obtained is called order of that reaction.

$$k_1 = \frac{2.303}{t}\log\frac{a}{a-x} \quad \text{(For first order reaction)}$$

$$k_2 = \frac{1}{t}\left[\frac{x}{a(a-x)}\right] \quad \text{(For second order reaction)}$$

$$k_3 = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right] \quad \text{(For third order reaction)}$$

Ex.29 For a reaction, A → B, it has been found that the order of the reaction is zero with respect to A. Which of the following expression correctly describes the reaction ?

[A] $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$ [B] $[A]_0 - [A] = kt$ [C] $t_{1/2} = \frac{0.693}{k}$ [D] $t_{1/2} \propto \frac{1}{[A]_0}$ **Ans. [B]**

Sol. $-\frac{d[A]}{dt} = k[A]_0$, $-d[A] = kdt$

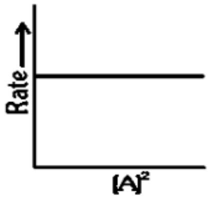
Integrating from t = 0 to t = t $[A]_0 - [A] = kt$

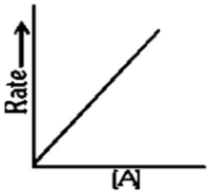
❑ Graphical Method

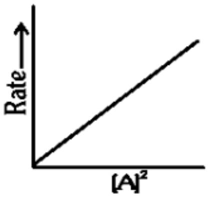
If a straight line is obtained on drawing a graph between log (a – x) and time then it is first order reaction.

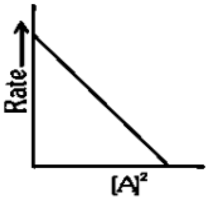
If a straight line is obtained on drawing a graph between $(a - x)^2$ and $\frac{dx}{dt}$, then it is second order reaction.

Ex.30 Which of the following graphs is for a second order reaction ?

[A] 

[B] 

[C] 

[D] 

Ans. [C]

Sol. For second order reaction rate vs $[A]^2$ is a straight line with slope equal to k rate = $k[A]^2$

If a straight line is obtained on drawing a graph between $(a - x)^3$ and $\frac{dx}{dt}$, then it is third order reaction.

❑ Half-life Method

Relation between half-life period of a reaction and initial concentration is as follows : $t^{1/2} \propto \frac{1}{a^{n-1}}$

For first order reaction	(Half life $\propto a^0$)
For second order reaction	(Half life $\propto 1/a$)
For third order reaction	(Half life $\propto 1/a^2$)

Ex.31 For a first order reaction, $t_{0.75}$ is 1386 seconds. Therefore, the specific rate constant is

[A] 10^{-1} s^{-1} [B] 10^{-3} s^{-1} [C] 10^{-2} s^{-1} [D] 10^{-4} s^{-1} **Ans. [B]**

Sol. $t_{0.75} = 1386$ s = 2 $t_{0.5}$; $t_{0.5} = \frac{1386}{2} = 693$ s ; $k = \frac{0.693}{693s} = 1 \;\; 10^{-3}$ s^{-1}

Ex.32 $t_{½}$ of first order reactions is given by $\frac{0.693}{k}$, $t_{3/4}$ would be equal to

[A] $\frac{0.693}{k}$ [B] $\frac{0.346}{k}$ [C] $\frac{1.386}{k}$ [D] $\frac{0.924}{k}$ **Ans. [C]**

Sol. $t_{3/4} = 2(t_{½}\ ) = \frac{2 \;\; 0.693}{k} = \frac{1.386}{k}$

Ex.33 The $t_{½}$ of a first order reaction is found to be 2 minutes. The percentage of the reactant left after 360 seconds is :

[A] 12.5 [B] 25 [C] 15 [D] 7.5 **Ans. [A]**

Sol. 360 seconds = 6 min = 3 half-lives

$$100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25 \xrightarrow{t_{1/2}} 12.5$$

❑ Ostwald Isolation Method

This method is used to find out the order of complex reactions. If nA, nB and nC molecules of substance A, B and C, respectively, are present in a reaction, then nA + nB + nC will be the order of reaction.

When B and C are in excess, the order of reaction will be nA.

When A and B are in excess, the order of reaction will be nC.

When A and C are in excess, the order of reaction will be nB.

Ex.34 When the initial concentration of a reaction was doubled, its half life become half, What should be the order of the reaction ?

Sol. Rate law for product of a reaction is as follows :

Rate = $k[A]^n$ and $\frac{t_{0.5}}{t_{\frac{0.5}{2}}} = \left[\frac{2a}{a}\right]^{n-1}$

$2 = [2]^{n-1}$; $n - 1 = 2$

$n = 2$

20. TEMPERATURE EFFECT :

The rate of reaction is dependent on temperature. This is expressed in terms of temperature coefficient which is a ratio of two rate constants differing by a temperature of 10 . Generally the temperature selected are 298K and 308K. It is mathematically expressed as,

$$\text{Temperature coefficient} = \frac{\text{rate constant at 308K}}{\text{rate constant at 298K}} = \frac{k_t + 10}{k_t}$$

The value of temperature coefficient for most of the reactions lies between 2 to 3.

21. ARRHENIUS EQUATION :

Arrhenius derived a mathematical expression to give a quantitative relationship between rate constant and temperature. The expression is

$$k = A.e^{-Ea/RT}$$

(Here, A = frequency factor; Ea = activation energy ; R = gas constant and T = temperature).

If k_1 and k_2 are rate constants at temperature T_1 and T_2 then

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

Ex.35 Ethylene oxide is decomposed into CH_4 and CO. Rate constant for this reaction may be described by the equation $\log k\ (s^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$

(i) What will be the energy of activation of this reaction ?

(ii) What will be the value of k at 670 K ?

(iii) At what temperature will its half-life period be 25.6 minutes ?

Sol. (i) We know, $\log_{10}k = \log_{10}A - \frac{E_a}{2.303RT}$ ....(i)

Given, $\log k\ (s^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$ ....(ii)

Comparing Eqs. (i) and (ii), we get

$$\frac{E_a}{2.303R} = 1.25 \quad 10^4$$

(ii) $E_a = 1.25 \quad 10^4 \quad 2.303 \quad 8.314 \quad 10^{-3}$

∴ $E_a = 239.339$ kJ/mol

Substituting the value of T (670 K) in Eq. (ii),

$$\log k\ (s^{-1}) = 14.34 - \frac{1.25 \times 10^4}{670} = 4.3167$$

∴ $k = 4.82 \quad 10^{-5}\ s^{-1}$

(iii) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{256 \times 60} = 0.000451\ sec^{-1}$

$\Rightarrow \log 0.000451\ sec^{-1}$

$= 14.34 - \frac{1.25 \times 10^4}{T} \Rightarrow T = 706.79\ K$

Ex.36 The rate constant of forward reaction a reaction increases by 6% when the temperature of the reaction is increased from 300 to 301 K, whereas equilibrium constant increases by 2%. Calculate the activation energy for the forward as well as backward reaction.

Sol. According to Arrhenius equation, $\log\frac{k_2}{k_1}=\frac{E_{a(f)}}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$

If k_1 = k at 300 K then at 301 K, k_2 = k + k $\frac{6}{100}$ = 1.06 k

$\therefore \quad \log_{10}\frac{1.06k}{k}=\frac{E_{a_{(f)}}}{2.303\times 8.314}\left[\frac{301-300}{300\times 301}\right]$

$\therefore \quad E_{a_{(f)}}$ = log (1.06)   2.303   8.314   300   301 = 43753 J/mol = 43.753 kJ/mol

According to van't Hoff equation, $\log\frac{k_2}{k_1}=\frac{\Delta H°}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$

If k_1 = k at 300 k, k_2 = k + $\frac{2}{100}$ = 1.02 k

$\log_{10}\frac{1.02k}{k}=\frac{\Delta H°}{2.303\times 8.314}\left(\frac{301-300}{300\times 301}\right)$

$\therefore \quad \Delta H$ = (log 1.02)   2.303   8.314   300   301 J/mol
= 14869 J mol^{-1} = 14.87 kJ/mol

Thus, reaction is endothermic.

For such a reaction, $\Delta H = E_{a(f)} - E_{a(b)}$

$\therefore \quad E_{a(b)} = E_{a(f)} - \Delta H$ = 43.753 – 14.87 kJ/mol = 28.883 kJ mol^{-1}

Ex.37 Value of rate constant for a first order reaction at 500 K is 1.60 10^{-5} $second^{-1}$, whereas at 600 K, it is 6.36 10^{-3} $second^{-1}$. Find out the activation energy of the reaction.

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

log 1.60 10^{-5} – log 6.36 10^{-3} = $\frac{-E_a}{2.303\times 8.314}\left[\frac{1}{500}-\frac{1}{600}\right]$

5.241 – 3.8035 = $\frac{E_a}{19.15}$ $\frac{1}{3000}$ E_a = 2.5999   19.15   3000

E_a = 1.49 10^5

Ex.38 An exothermic reaction, X → Y, has an activation energy 30 kJ mol^{-1}. If energy change (ΔE) during the reaction is – 20kJ, then the activation energy for the reverse reaction is

[A] –30kJ
[B] 20 kJ
[C] 50 kJ
[D] 10 kJ

Ans. [C]

Sol. $\Delta E = E_{a_{(f)}} - E_{a_{(b)}}$; $-20 = 30 - E_{a_{(b)}}$; $E_{a_{(b)}} = 50$ kJ

Ex.39 An endothermic reaction, A → B, has an activation energy as x kJ mol^{-1} of A. If energy change of the reaction is y kJ, the activation energy of reverse reaction is

[A] – x
[B] x – y
[C] x + y
[D] y – x

Ans. [B]

Sol. $\Delta E = E_{a_{(f)}} - E_{a_{(b)}}$; $y = x - E_{a_{(b)}}$; $E_{a_{(b)}} = x - y$

Ex.40 Which of the following relations is correct ?

[A] $k = A\ e^{Ea/RT}$
[B] $\ln k - \ln A = \frac{E_a}{RT}$
[C] $\ln A - \ln k = \frac{E_a}{RT}$
[D] $\ln A - \ln k = -\frac{E_a}{RT}$

Ans. [C]

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

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

Ex.41 Which of the following expression give the effect of temperature on the rate constant ?

[A] $\ln A = RT \ln E_a - \ln k$ [B] $\ln k = \ln A - E_a/RT$

[C] $k = AE_a/RT$ [D] None of these **Ans. [B]**

Sol. The effect of temperature on rate constant is quantitatively given by Arrhenius equation

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

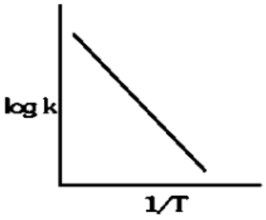
Ex.42 The plot of log k vs $\frac{1}{T}$ helps to calculate

[A] Energy of activation [B] Rate constant of the reaction

[C] Order of the reaction [D] Energy of activations as well as the frequency factor

Ans. [D]

Sol. According to Arrhenius equation : $\log k = \log A - \frac{E_a}{2.303} \cdot \frac{1}{T}$



Plot of log k vs. $\frac{1}{T}$ is straight line

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

Intercept = log A

Ex.43 The progress of the reaction given below, consider the reaction given below,

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

the reaction can be followed by measuring the concentration of acid (HCl acid used as catalyst plus acetic acid formed during the reaction) by means of alkali titration. Calculate the volume of alkali (NaOH) needed for the end point that will increase with time.

Sol.

	$CH_3COOC_2H_5$	$+ H_2O$	$\xrightarrow{H^+} CH_3COOH$	$+ C_2H_5OH$
At t = 0	a	excess	0	0
At t = t	a – x		x	x
At t = ∞	0		a	a

If V_0, V_t and V_∞ are the volumes of NaOH solution needed for the end point of titration of the reaction mixture at zero time, time t and at infinity, i.e. after completion of the reaction the condition being achieved by heating the reaction mixture for some time, then

$V_0 \propto$ [acid catalyst]

$V_t \propto$ [acid catalyst] + x

$V_\infty \propto$ [acid catalyst] + a

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

$\quad V_\infty - V_0 \propto a$

(since concentration of HCl acid acting as catalyst will remain constant).

The above reaction which is of first order (actually pseudo unimolecular) will, therefore, obey following equation.

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

Ex.44 $H_2O_2\ (aq.) \longrightarrow H_2O + \frac{1}{2}O_2\uparrow$

	H_2O_2	H_2O	O_2
At t = 0	a	0	0
At t = t	a − x	x	x

Since H_2O_2 acts as a reducing agent towards $KMnO_4$, so concentrations of H_2O_2 at various time intervals may be determined by the titration of the reaction mixture against standard $KMnO_4$ solution. The titre value will go on decreasing with time. If V_0 and V_t be the titre values at zero time and any time t then $V_0 \propto a$ and $V_t \propto a - x$

The above reaction being first order, its rate constant may be expressed as

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

Ex.45 The reaction mentioned below is first order w.r.t. sucrose and zero order w.r.t. water, since water is in large excess as compared to sucrose. That is, it is an example of pseudo unimolecular reaction. Sucrose, glucose and fructose all are optically active substances. Therefore, the progress of the reaction can be followed by measuring angle of rotations of the reaction mixture at various time intervals.

During the reaction, angle of rotation goes on decreasing and after sometime there is reversal of the direction of rotation, i.e. from dextro to laevo and Hence, the reaction is called **"inversion of cane sugar"** or inversion of sucrose.

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

	d-Sucrose		d-Glucose	ℓ-Fructose
Initially	a	Excess	0	0
After time t	a − x	Constant	x	x
At infinity	0	Constant	a	a

Angle of optical rotation is measured by means of an instrument called polarimeter. Optical rotation is mathematically expressed as,

$$R_{obs} = \ell.C.\ [\alpha]_D^t$$

where

ℓ = length of the polarimeter tube

C = concentration of test solution

$[\alpha]_D^t$ = specific rotation

For a given sample and polarimeter, ℓ and $[\alpha]_D^t$ are constant.

$R_{obs} \propto C$, or $R_{obs} = kC$,

If r_0, r_t and r_∞ be the observed angle of rotations of the sample at zero time, time t and infinity respectively, and k_1, k_2 and k_3 be proportionate in terms of sucrose, glucose and fructose, respectively.

Then,

$r_0 = k_1a$

$r_t = k_1(a - x) + k_2x + k_3x$

$r_\infty = k_2a + k_3a$

From these equations it can be shown that

$$\frac{a}{a-x} = \frac{r_0 - r_\infty}{r_t - r_\infty}$$

So, the expression for the rate constant of this reaction in terms of the optical rotational data may be put as $k = \dfrac{2.303}{t}\log\dfrac{r_0 - r_\infty}{r_t - r_\infty}$

Ex.46

	$2N_2O_5 \longrightarrow$	$4NO_2$ +	O_2
At t = 0	P_0	0	0
At t = t	$P_0 - 2x$	$4x$	x
At t =∞	0	$2P_0$	$\frac{1}{2}\ P_0$

The progress of the reaction can be followed by measuring the pressure of the gaseous mixture in a closed vessel, i.e. at constant volume. The expression for the rate constant in terms of pressure data will be as given below.

$$k = \frac{2.303}{t}\log\frac{P_0}{P_t}\text{, where } P_t = P_0 - 2x$$

If total pressure after any time t and at ∞ is given, then it is possible to find P_0 and x and hence, k may be calculated.

Ex.47 Consider a first order reaction,

$A \rightarrow B + C$

Assume that A, B and C are gases. The given data is

Time	0	T
Partial pressure of A	P_1	P_2

And we have to find the rate constant of the reaction.

Sol. Since A is a gas assuming it to be ideal, we can state that $P_A = [A]\ RT$ [From PV = nRT]

∴ At t = 0, $P_1 = [A]_0\ RT$ and at t =t, $P_2 = [A]_tRT$. Thus, the ratio of the concentration of A at two different time intervals is equal to the ratio of its partial pressure at those same time intervals.

$$\therefore \quad \frac{[A]_0}{[A]_t} = \frac{P_1}{P_2}$$

$$\therefore \quad k = \frac{1}{t}\ln\frac{P_1}{P_2}$$

Ex.48 $A \rightarrow B + C$

Time	0	t
Total pressure of A + B + C	P_1	P_2

Find k.

Sol. In this case, we are given total pressure of the system at these time intervals. The total pressure obviously includes the pressure of A, B and C. At t = 0, the system would only have A. Therefore, the total pressure at t = 0 would be the initial pressure of A.

∴ P_1 is the initial pressure of A. At time t, let us assume moles of A will decompose to give B and C because of which its pressure is reduced by an amount x while that of B and C is increased by x each. That is :

	$A \longrightarrow$	B +	C
Initial	P_1	0	0
At time t	$P_1 - x$	x	x

∴ Total pressure at time t = $P_1 + x = P_2$

$\Rightarrow \quad x = P_2 - P_1$

Now the pressure of A at time t would be $P_1 - x = P_1 - (P_2 - P_1) = 2P_1 - P_2$

$$\therefore \quad k = \ln\frac{[A]_0}{[A]_t} = \ln\frac{P_1}{(2P_1 - P_2)}$$

Ex.49 For the given following first order reaction,

$$A \longrightarrow B + C$$

Time	T	∞
Total pressure of A + B + C	P_2	P_3

Calculate k.

Sol. Here ∞ means that the reaction is complete. Now, we have

	A $\longrightarrow$	B +	C
At $t = 0$	P_1	0	0
At $t = t$	$(P_1 - x)$	x	x
At $t = \infty$	0	P_1	P_1

$\therefore \quad 2P_1 = P_3$

$$\Rightarrow \quad P_1 = \frac{P_3}{2}$$

At time t,

$P_1 + x = P_2$

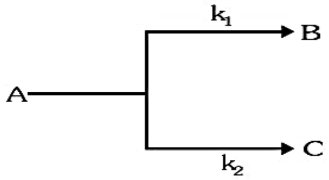
$$\Rightarrow \quad \frac{P_3}{2} + x = P_2 \quad \Rightarrow \quad x = P_2 - \frac{P_3}{2}$$

$$\Rightarrow \quad P_1 - x = \frac{P_3}{2} - \left(P_2 - \frac{P_3}{2}\right) = P_3 - P_2$$

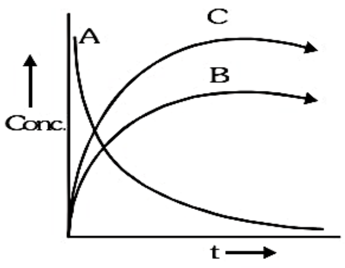
$$k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t} = \frac{1}{t}\ln\frac{P_3/2}{(P_3 - P_2)} = \frac{1}{t}\ln\frac{P_3}{2(P_3 - P_2)}$$

22. PARALLEL REACTIONS :

These are reactions in which reaction substances do not follow a particular path to give a particular set of products. It follows one or more paths to give different products, e.g.



The reactant A follows two different paths to form B and C as shown below :

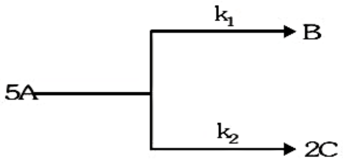


$$\text{Rate} = -\frac{d[A]}{dt} = k_1[A] + k_2[A]$$

$$= k[A] \; [\text{As, } (k_1 + k_2) = k]$$

$$\%\text{ yield of B} = \frac{k_1}{k_1 + k_2} \quad 100$$

Ex.50 A follows parallel path, first order reaction giving B and C as



If initial concentration of A is 0.25 M, calculate the concentration of C after 5 hours of reaction. [Given : $k_1 = 1.5 \quad 10^{-5}\ s^{-1}$, $k_2 = 5 \quad 10^{-6}\ s^{-1}$]

Sol. $k = \frac{2.303}{t}\log\frac{[A]}{[A]_t}$ $(k = k_1 + k_2 = 1.5 \quad 10^{-5} + 5 \quad 10^{-6} = 2 \quad 10^{-5}\ s^{-1})$

$\Rightarrow \quad 2 \quad 10^{-5} = \frac{2.303}{t}\log\frac{0.25}{[A]_t}$

$\therefore \quad [A]_t = 0.1744$ M

$\therefore \quad [A]_{\text{decomposed}} = [A]_0 - [A]_t = 0.25 - 0.1744 = 0.0756$ M

Fraction of C formed $= \frac{k_2}{(k_1+k_2)} \quad [A]_{\text{decomped}} \quad \frac{2}{5} = \frac{5\times10^{-6}}{2\times10^{-5}} \quad 0.0756 \quad \frac{2}{5} = 7.56 \quad 10^{-3}$ M

(5 moles of A are used to give 2 moles of C)

23. SEQUENTIAL REACTIONS :

These are reactions which proceed from reactants to product through one or more intermediate stages,

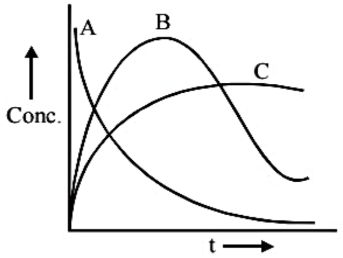
e.g. $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

◆ **Graphical representation**

$$\frac{-d[A]}{dt} = k_1[A] \qquad \text{.............(1)}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad \text{.............(2)}$$

$$\frac{d[C]}{dt} = k_2[B] \qquad \text{.............(3)}$$



Integrating Eq. (1), we get

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

Now, we shall integrate Eq. (2) and find the concentration of B related to time t.

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

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

$$\Rightarrow \quad \frac{d[B]}{dt} + k_2[B] = k_1[A]_0 e^{-k_1 t} \qquad \text{.............(4)}$$

Integration of the above equation is not possible as we are not able to separate the two variables, [B] and t. Therefore, we multiply Eq. (4) by integrating factor $e^{k_2 t}$, on both the sides of the equation.

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

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

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

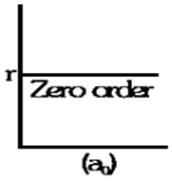
MEMORY TIPS

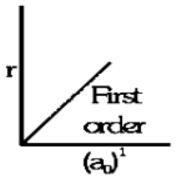
1. Expression for rate constants for reaction of different orders.

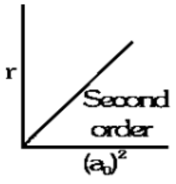
Type of reaction	Integrated rate equation	Unit of rate constant	Half-life period	$t^{3/4}$ life period
Zero order reaction	$-\frac{d[A]}{dt} = k_0[A]^0$ Differentiation form $\frac{dx}{dt}=k$	Concentration $time^{-1}$	$t_{\frac{1}{2}} = \frac{a}{2k_0}$	--
First order reaction	$k_1 = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$	$time^{-1}$	$t_{\frac{1}{2}} = \frac{0.693}{K_1}$	$t_{\frac{3}{4}}=2\ \frac{0.693}{k_1}=\frac{1.382}{k_1}$
Second order reaction	$k_2 = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}$ Differential form $\frac{dx}{dt} = k(a-x)^2$	$Mole^{-1} litre\ time^{-1}$	$t_{\frac{1}{2}} = \frac{1}{k_2 a}$	$t_{\frac{3}{4}} = \frac{3}{k_2 a}$
Third order reaction	$k_3 = \frac{x \times (2a-x)}{t 2a^2 (a-x)^2}$ Differential form $\frac{dx}{dt} = k(a-x)^3$	$Litre^2 mole^{-2} time^{-1}$	$t_{\frac{1}{2}} = \frac{3}{2k_3 a^2}$	---

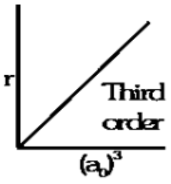
2. Some typical linear plots for reactions of different orders :

(i)

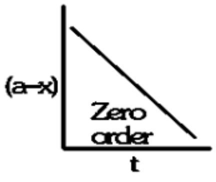


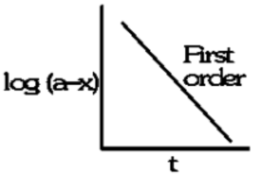


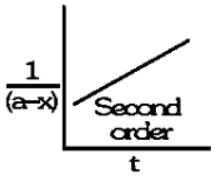


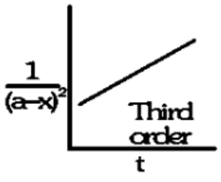


(ii)

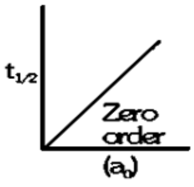


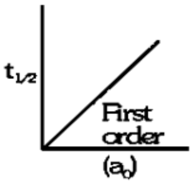


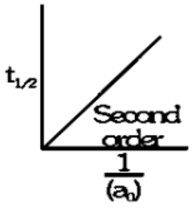


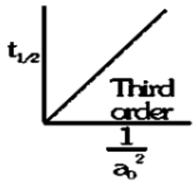


(iii)









3. Amount left after n half-lives $= \left(\frac{1}{2}\right)^n [A]_0$

No. of half-lives $= \frac{\text{Total time}}{t_{1/2}}$

4. Exponential form of expression for rate constant for reaction of 1st order : $[A] = [A]_0 e^{-kt}$ or $C_t = C_0 e^{-kt}$

5. $t_{1/2} \propto \dfrac{1}{[A]_0^{n-1}}$

6. Arrhenius equation for effect of temperature on rate constant,

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

$$\text{on } \log k = \log R - \frac{E_a}{2.303RT}$$

$$\text{Also, } \frac{d\ln k}{dT} = \frac{E_a}{RT^2}$$

If k_1 and k_2 are rate constants at temperature T_1 and T_2, then

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

7. Examples of reactions of 1st order and their formula for rate constants

(i) $2N_2O_5 \rightarrow 4NO_2 + O_2$; $k = \dfrac{2.303}{t}\log\dfrac{V_\infty}{V_\infty - V_t}$

where V_∞ = volume of O_2 gas collected at infinite time

V_t = volume of O_2 gas collected at time t

(ii) $NH_4NO_2 \rightarrow 2H_2O + N_2$; $k = \dfrac{2.303}{t}\log\dfrac{V_\infty}{V_\infty - V_t}$

where V_∞ and V_t are volumes of N_2 gas collected after infinity time and after time t respectively.

(iii) $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$; $k = \dfrac{2.303}{t}\log\dfrac{V_D}{V_t}$

where V_D and V_t are the volumes of $KMnO_4$ solution used for titrating a definite volume of the reaction mixture at t = D and at time t respectively.

(iv) $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

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

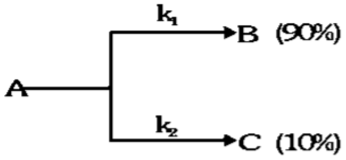
where V_D, V_t and V_∞ are the volume of NaOH solution used for titration mixture at zero time, after time t and after infinity respectively.

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

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

where r_0, r_t and r_∞ are the polarimetric reading at zero time, after time t and after infinity respectively.

8. Rate law equation for reactions involving parallel reaction



$$\text{Rate} = -\frac{d[A]}{[dt]} = k_1\,[A] + k_2\,[A] = [k_1 + k_2]\,[A]$$

9. Degree of dissociation at any time t = $(1 - e^{-kt})$

PRACTICE SET

A SINGLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

1. The concentration of the products in reaction I increases exponentially whereas in reaction II linearly with time. The respective orders are :

(a) 2 and 1 (b) 0 and 1
(c) 1 and 0 (d) 2 and 0

2. The differential rate law equation for the elementary reaction, $2A + B \rightarrow$ Products, is :

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

(b) $-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A]^{1/2}[B]$

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

(d) $-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A^2][B]$

3. The chemical reaction $2O_3 \rightarrow 3O_2$ involves two elementary steps :

$O_3 \xrightarrow{\text{fast}} O_2 + O; \quad O + O_3 \xrightarrow{\text{slow}} 2O_2$

The differential rate law expression will be:

(a) rate $= k[O_3]^2$ (b) rate $= k[O_3]^2[O_2]$
(c) rate $= k[O_3]^2[O_2]^{-1}$ (d) rate $= k[O_3]^2[O_2]^{-3}$

4. For the reaction : $4KClO_3 \rightarrow 3KClO_4 + KCl$

if $\frac{-d[KClO_3]}{dt} = k_1[KClO_3]^4$

$\frac{d[KClO_4]}{dt} = k_2[KClO_3]^4$

$\frac{d[KCl]}{dt} = k_3[KClO_3]^4$, the correct relation between k_1, k_2 and k_3 is

(a) $k_1 = k_2 = k_3$ (b) $4k_1 = 3k_2 = k_1$
(c) $3k_1 = 4k_2 = 12k_3$ (d) none of these

5. The rate of disappearance of $Cr_2O_7^{2-}$ ion at any instant in the following reaction :

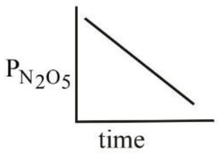
$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$ is 1.55×10^{-2} mol L^{-1} s^{-1}. The rate of formation of iodine is :

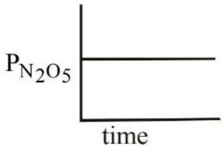
(a) 9.3×10^{-2} Ms^{-1} (b) 4.65×10^{-2} M s^{-1}
(c) 5.0×10^{-3} M s^{-1} (d) 2.50×10^{-3} M s^{-1}

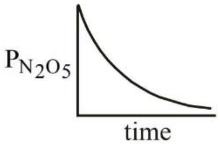
6. For the reaction : $aA + bB \rightarrow$ Products, the rate law is given by Rate $= k[A]^m[B]^n$. On making the concentration of A two fold and halving that of B, the ratio of the new rate to the earlier rate of the reaction would be :

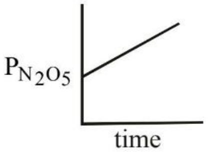
(a) $n - 1$ (b) $m + n$
(c) $2^{-(m+n)}$ (d) 2^{m-n}

7. Which of the following graphs does show the variation of partial pressure of N_2O_5 decomposing into NO_2 and O_2 following the first order kinetics?

(a)


(b)


(c)


(d)


8. Half-lives of decomposition of NH_3 on the surface of a catalyst for different initial pressures are given as:

p(torr)	200	300	500
$t_{1/2}$*(min)*	10	15	25

The order of the reaction is :

(a) 2 (b) 0
(c) 1 (d) 0.5

MARK YOUR RESPONSE					
	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ		

9. Decomposition of HI : $2HI \rightarrow H_2 + I_2$, is a second order reaction. At what initial concentration of HI, the initial rate will represent the rate constant of the reaction ?

(a) $0.1\,M$ (b) $2.0\,M$
(c) $1.0\,M$ (d) $1.0 \times 10^{-2}\,M$

10. In the reaction $A + B \rightarrow$ Products, initial concentration of both A and B equal to 0.1 M, each is reduced to 1.0×10^{-2} M. The half-life is increased to ten fold. The rate of the reaction is :

(a) proportional to first power of concentration
(b) proportional to second power of concentration
(c) independent of concentration
(d) insufficient information

11. In the elementary reaction $aA + bB \rightarrow$ Products, doubling the concentration of A the rate is doubled whereas doubling the concentration of B the rate is made eight times. Which of the following relates the rate of disappearance of A to that of B.

(a) $-\dfrac{d[A]}{dt} = -\dfrac{d[B]}{dt}$ (b) $-\dfrac{d[A]}{dt} = -\dfrac{3d[B]}{dt}$

(c) $-\dfrac{3d[A]}{dt} = -\dfrac{d[B]}{dt}$ (d) $-\dfrac{3d[A]}{dt} = -\dfrac{d[B]}{dt}$

12. In the reaction $A \rightarrow$ Products, time required to complete 50% reaction was found to increase 9 times when the concentration of the reactant was decreased to one-third. The rate law equation is :

(a) $-\dfrac{d[A]}{dt} = k[A]^{1/2}$ (b) $-\dfrac{d[A]}{dt} = k[A]$

(c) $-\dfrac{d[A]}{dt} = k[A]^2$ (d) $-\dfrac{d[A]}{dt} = k[A]^3$

13. In the reaction : $CO + Cl_2 \rightarrow COCl_2$; the rate increases by factor of 4 on doubling the concentration of CO, and by a factor of two on making the concentration of Cl_2 four fold. If the initial concentrations of CO and Cl_2 are x and y, then what respective values of their concentrations would cause the rate to increase by a factor of eight ?

(a) $2x, 2y$ (b) $4x, y$
(c) $x, 4y$ (d) $2x, 4y$

14. Time required for 99.9% completion of a first order reaction is nearly

(a) 10 times that required for 25% of the reaction
(b) 10 times that required for 50% of the reaction
(c) 20 times that required for 50% of the reaction
(d) 100 times that required for 90% of the reaction

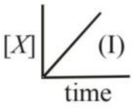
15. Select the rate law that conforms to the following data for the reaction : $A + B \rightarrow$ Products

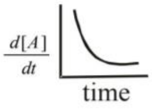
Exp No.	$[A]$ (mol L^{-1})	$[B]$(mol L^{-1})	Initial rate(mol L^{-1}s^{-1})
1	0.0012	0.0035	1×10^{-4}
2	0.024	0.070	8×10^{-3}
3	0.024	0.035	1×10^{-3}
4	0.012	0.070	8×10^{-3}

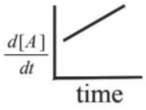
(a) $-\dfrac{d[A]}{dt} = k[A][B]^2$ (b) $-\dfrac{d[A]}{dt} = k[A]^2[B]$

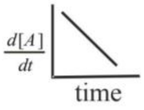
(c) $-\dfrac{d[A]}{dt} = k[A][B]^3$ (d) $-\dfrac{d[A]}{dt} = k[B]^3$

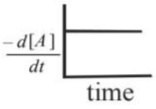
16. Variation of concentration of the product (X) with time in the reaction $A \rightarrow X$ is shown in graph (I). Hence, the graph between $-\dfrac{d[A]}{dt}$ and time will be of the type :



(a)


(b)


(c)


(d)


17. The rate constant of the reaction : $A \rightarrow 2B$, is 1.0×10^{-3} mol L^{-1} min^{-1}. If the initial concentration of A is 1.0 mol L^{-1}, what would be the concentration of B after 100 minutes:

(a) 0.1 mol L^{-1} (b) 0.2 mol L^{-1}
(c) 0.9 mol L^{-1} (d) 1.8 mol L^{-1}

18. The rate constant of a reaction is 6.93×10^{-3} min^{-1}. If initial concentration of the reactant is 2.0 M, the rate after 100 min will be:

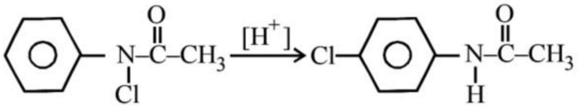
(a) 6.93×10^{-3} mol L^{-1} min^{-1}
(b) 6.93×10^{-5} mol L^{-1} min^{-1}
(c) $6.93 \times 10^{-3} \times 2$ mol L^{-1} min^{-1}
(d) $6.93 \times 10^{-3} \times 0.5$ mol L^{-1} min^{-1}

19. At 227°C, the presence of catalyst causes the activation energy of a reaction to decrease by 4.606 k cal. The rate of the reaction will be increased by :

(a) 2 times (b) 10 times
(c) 100 times (d) 1000 times

MARK YOUR RESPONSE	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ
	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ
	19. ⓐⓑⓒⓓ				

20. N- chloroacetanilide isomerizes into p–chloroacetaanilide in presence of H^+ ions as catalyst.



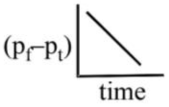
N- chloro isomer oxidizes I^- ion to I_2 whereas the p-chloro isomer does not. The kinetics can be studied by adding excess of KI to a fixed volume of the reaction mixture at different intervals of time and titrating the liberated I_2 with hypo solution. If the plot of log (titre) *vs* time (abscissa) is a straight line, which of the following is correct?

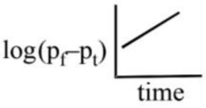
(a) order = 1, slope = $k/2.303$
(b) order = 1, slope = $-k/2.303$
(c) order = 0, slope = $-k/2.303$
(c) order = 2, slope = k

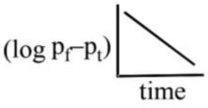
21. Benzene diazonium chloride in aqueous solution decomposes as :

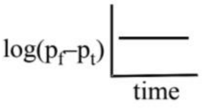
$$C_6H_5{-}N{=}N^+Cl^-_{(aq)} + H_2O_{(\ell)} \rightarrow C_6H_5OH_{(aq)} + HCl_{(aq)} + N_{2(g)}$$

The reaction follows first order kinetics. If p_t is the pressure of N_2 at constant volume and temperature corresponding to different intervals of time t and p_f that after completion of the reaction, then which of the following graphs conforms to the kinetics of the reaction?

(a) 

(b) 

(c) 

(d) 

22. The following data pertains to reaction between A and B :

S. No.	$[A]$ mol L^{-1}	$[B]$ mol L^{-1}	Rate (mol L^{-1} time^{-1})
1	1.0×10^{-2}	2.0×10^{-2}	2.0×10^{-4}
2	2.0×10^{-2}	2.0×10^{-2}	4.0×10^{-4}
3	2.0×10^{-2}	4.0×10^{-2}	8.0×10^{-4}

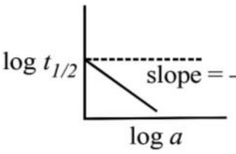
Which of the following inference(s) can be drawn from the above data ?

1. Rate constant of the reaction is 1.0×10^{-4}.
2. Rate law of the reaction is : rate = $k[A][B]$
3. Rate of reaction increases four times on doubling the concentration of both the reactants.

Select the correct answer using the codes given below :

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

23. A graph between log $t_{1/2}$ and log a (abscissa), a being the initial concentration of A in the reaction, $A \rightarrow$ Products ,is depicted in the figure. The rate law is :



(a) $-\frac{d[A]}{dt} = k$ (b) $-\frac{d[A]}{dt} = k[A]$

(c) $-\frac{d[A]}{dt} = k[A]^2$ (d) $-\frac{d[A]}{dt} = k[A]^3$

24. Half-life of the reaction : $H_2O_{2(aq)} \rightarrow H_2O_{(\ell)} + ½O_{2(g)}$ is independent of initial concentration of H_2O_2. Volume of O_2 gas after 20 minutes is 5L at 1 atm and 27°C, and after completion of the reaction 50L. The rate constant is :

(a) $\frac{1}{20}\log 10\ \text{min}^{-1}$ (b) $\frac{2.303}{20}\log 10\ \text{min}^{-1}$

(c) $\frac{2.303}{20}\log\frac{50}{45}\ \text{min}^{-1}$ (d) $\frac{2.303}{20}\log\frac{45}{50}\ \text{min}^{-1}$

25. In most cases, for a rise of 10K temperature the rate constant is doubled to tribled. This is due to the reason that

(a) collision frequency increases by a factor of 2 to 3.
(b) fraction of molecules possessing threshold energy increases by a factor of 2 to 3
(c) Activation energy is lowered by a factor of 2 to 3.
(d) none of these

26. The activation energies of two reactions are E_a and E_a', $E_a > E_a'$. If the temperature of reaction systems is increased from T_1 to T_2, predict which of the following alternatives is correct ? (k's are the rate constants)

(a) $\frac{k_1'}{k_1} = \frac{k_2'}{k_2}$ (b) $\frac{k_1'}{k_1} < \frac{k_2'}{k_2}$

(c) $\frac{k_1'}{k_1} > \frac{k_2'}{k_2}$ (d) $\frac{k_1'}{k_1} = 2\frac{k_2'}{k_2}$

MARK YOUR RESPONSE	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ
	25. ⓐⓑⓒⓓ	26. ⓐⓑⓒⓓ			

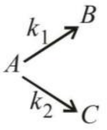
27. For the formation of SO_3 in the following reaction, it is given that

$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$ E_a = activation energy

$SO_{2(g)} + ½O_{2(g)} \rightarrow SO_{3(g)}$ E_a' = activation energy

(a) $E_a > E_a'$ (b) $E_a < E_a'$
(c) $E_a' = E_a^{1/2}$ (d) $E_a = E_a'$

28. A substance undergoes first order decomposition involving two parallel first order reactions as :



$k_1 = 1.25 \times 10^{-4} s^{-1}$
$k_2 = 3.80 \times 10^{-5} s^{-1}$

The mol percent of B in the products is :

(a) 23.17 (b) 76.83
(c) 30.16 (d) 69.84

29. For the first order reaction $C_2H_4O_{(g)} \rightarrow CH_{4(g)} + CO_{(g)}$, the initial pressure of $C_2H_4O_{(g)}$ is 80 torr and total pressure at the end of 20 minutes is 120 torr. The time needed for 75% decomposition of C_2H_4O would be :

(a) 20 minutes (b) 40 minutes
(c) 80 minutes (d) 120 minutes

30. A reaction : $A_2 + B \rightarrow$ Products, involves the following mechanism :

$A_2 \rightleftharpoons 2A$ (fast) (A being the intermediate)

$A + B \xrightarrow[k_2]{}$ Products (slow). The rate law consistent to this mechanism is :

(a) rate = $k[A_2][B]$ (b) rate = $k[A_2]^2[B]$
(c) rate = $k[A_2]^{1/2}[B]$ (d) rate = $k[A_2][B]^2$

31. For the second order reaction $A + B \rightarrow$ Products the rate constant k is given by :

$k = \dfrac{2.303}{(a-b)t}\log\dfrac{b(a-x)}{a(b-x)}$, a and b are the initial concentrations of A & B and x is the change after time t.

If $b >> a$, the reaction reduces to

(a) first order w.r.t. A (b) zero order w.r.t. A
(c) first order w.r.t. B (d) overall zero order

32. A gaseous substance undergoes decomposition that involves two parallel reactions having rate constants to be 2.0×10^{-3} L mol^{-1} s^{-1} and 5×10^{-3} L mol^{-1} s^{-1}, and corresponding energies of activation to be 50.0 and 78.0 kJ mol^{-1} respectively. The apparent overall energy of activation of the reaction will be :

(a) 128. 0 kJ mol^{-1} (b) 28.0 kJ mol^{-1}
(c) 70.0 kJ mol^{-1} (d) 64.0 kJ mol^{-1}

33. In a reaction $A \rightarrow$ Products, when start is made from 8.0×10^{-2} M of A, half-life is found to be 120 minute. For the initial concentration 4.0×10^{-2} M, the half-life of the reaction becomes 240 minute. The order of the reaction is :

(a) zero (b) one
(c) two (d) 0.5

34. Which of the following statements is correct for a reaction of first order ?

(a) A plot of concentration of the reactant against time is linear.
(b) Half life varies directly with the concentration of the reactant.
(c) A plot of $[A]_0/[A]$ against time is a straight line.
(d) Fractional change is equal to $1-e^{-kt}$.

35. A drop of solution (volume = 0.050 mL) contains 6×10^{-7} mol of H_3O^+ ions. If H_3O^+ ions disappear at a constant rate of 6.0×10^5 mol L^{-1} s^{-1}, how long will it take for the H_3O^+ ions in the drop to disappear?

(a) 2.0×10^{-2} s (b) 6.0×10^{-6} s
(c) 2.0×10^{-8} s (d) 8.0×10^{-8} s

36. In an exothermic reaction $A \rightarrow B$, the activation energy of reverse reaction is twice that of forward reaction. If enthalpy of the reaction is – 80 k J mol^{-1}, the activation energy of the reverse reaction is :

(a) 80.0 kJ mol^{-1} (b) 60.0 kJ mol^{-1}
(c) 40.0 kJ mol^{-1} (d) 160.0 kJ mol^{-1}

37. Activation energy and pre-exponential factor of a chemical reaction are 2×10^2 kJ mol^{-1} and 3.0×10^{15} s^{-1} respectively. If the rate constant of the reaction at 298 is 5.0×10^{-1}, its value when $T \rightarrow \infty$ is :

(a) 2.0×10^5 s^{-1} (b) 1.5×10^{11} s^{-1}
(c) 3.0×10^{15} s^{-1} (d) 2×10^2 s^{-1}

38. The reaction $2\,FeCl_{3(aq)} + SnCl_{2(aq)} \rightarrow 2\,FeCl_{2(aq)} + SnCl_{4(aq)}$ is an elementary process. If the reaction system contains 1.2 M $FeCl_3$ and 0.8 M $SnCl_2$ at the start, what would be the rate of the reaction relative to the initial one when 0.4 M $FeCl_2$ is formed ?

(a) 3 (b) 1/3
(c) 1/2 (d) 1/12

MARK YOUR RESPONSE	27. ⓐⓑⓒⓓ	28. ⓐⓑⓒⓓ	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ	31. ⓐⓑⓒⓓ
	32. ⓐⓑⓒⓓ	33. ⓐⓑⓒⓓ	34. ⓐⓑⓒⓓ	35. ⓐⓑⓒⓓ	36. ⓐⓑⓒⓓ
	37. ⓐⓑⓒⓓ	38. ⓐⓑⓒⓓ			

39. $A \rightarrow B,\ k_1 = 10^{11} e^{-3000/T}$

$X \rightarrow Y,\ k_2 = 10^{10} e^{-2000/T}$

If the two reactions have all the reactants at unit molarity each, at what temperature their initial rates will be equal?

(a) 2000 K
(b) 3000 K
(c) 1000 K
(d) 1000/2.303 K

40. During the study of dehydrogenation of 2 -propanol $CH_3CHOHCH_{3(\ell)} \rightarrow CH_3COCH_{3(\ell)} + H_{2(g)}$, the following data were obtained.

Time (min)	0	10	20	30
[Acetone] mol L^{-1}	0	0.2	0.4	0.6

The initial rate of the reaction was :

(a) zero
(b) 0.02 mol L^{-1} min^{-1}
(c) 0.04 mol L^{-1} min^{-1}
(d) 0.06 mol L^{-1} min^{-1}

41. Which of the following statements is incorrect ?

(a) On raising the temperature, rate constant increases in most cases
(b) The collision frequency increases
(c) Fraction of molecules possessing energy less than threshold energy increases
(d) Molecules acquire greater kinetic energy

42. The rate constant of a reaction at 27ºC is 2.3×10^{-3} min^{-1} and at this temperature 0.001% of the reactant molecules are able to cross over the energy barrier existing between the reactants and the products. What can the maximum value of rate constant be achieved on raising the temperature ?

(a) 23.0 min^{-1}
(b) 2.3×10^{-2}
(c) 115.0 min^{-1}
(d) 230.0 min^{-1}

43. A catalyst lowers the energy of activation by 25%. Temperature at which rate of uncatalysed reaction will be equal to that of the catalysed one at 27ºC is :

(a) 400ºC
(b) 127ºC
(c) 300ºC
(d) 227ºC

44. Consider the two hypothetical reactions given below :

I $a\,A \rightarrow$ Products, $k = x$ mol^{-1} L min^{-1}
II $b\,B \rightarrow$ Products, $k = y$ min^{-1}

The half-lives of both the reactions are the same, equal to 1 hr when molar concentration of the reactant is 1.0 *M* in each case. If these reactions are started at the same time taking 1*M* of the reactant in each case, the ratio [*A*]/[*B*] after 3 hr will be :

(a) 0.5
(b) 4
(c) 1
(d) 2

45. In a reaction at 27ºC, 10^{-3}% reactant molecules manage to cross over the barrier of transition state. The energy of these molecules in excess of the average value will be (R = 2 cal K^{-1} mol^{-1}) :

(a) 6.91 *k* cal mol^{-1}
(b) 3.00 *k* cal mol^{-1}
(c) 4.15 *k* cal mol^{-1}
(d) 5.10 *k* cal mol^{-1}

46. For the reaction $R - X + OH^- \rightarrow ROH + X^-$, the rate is given as :

Rate $= 5.0 \times 10^{-5}[R–X][OH^-] + 0.20 \times 10^{-5}[R–X]$.

What percentage of R–X react by S_N2 mechanism when $[OH^-] = 1.0 \times 10^{-2}$ *M*?

(a) 96.1%
(b) 3.9%
(c) 80%
(d) 20%

47. Consider the consecutive reactions :

$$A \xrightarrow{k=2\times10^{-5}s^{-1}} B \xrightarrow{k=8\times10^{-6}s^{-1}} C \xrightarrow{k=3\times10^{-3}s^{-1}} D.$$

The rate determining step of the reaction is :

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

48. In a reaction $aA \rightarrow$ products, the rate is doubled when the concentration of *A* is increased 4 times. If 50% of the reaction occurs in 1414 *s*, how long would it take for the completion of 75% reaction ?

(a) 4242 s
(b) 2828 s
(c) 2414 s
(d) 2121 s

49. Consider the reaction $A \rightarrow 2B + C, \Delta H = -15$ k cal. The energy of activation of backward reaction is 20 k cal mol^{-1}. In presence of catalyst the energy of activation of forward reaction is 3 k cal mol^{-1}. At 400 K the catalyst causes the rate of the reaction to increase by the number of times equal to

(a) $e^{3.5}$
(b) $e^{2.5}$
(c) $e^{-2.5}$
(d) $e^{2.303}$

50. 16.0 g of a radioactive substance is reduced to 0.50 g after 1 hour. The half-life of the radioactive substance is:

(a) 15 minutes
(b) 10 minutes
(c) 12 minutes
(d) 20 minutes

51. Half-life of a first order reaction is 69.3 minutes. Time required to complete 99.9% of the reaction will be:

(a) 693 minutes
(b) 999 minutes
(c) 99.9 minutes
(d) 691 minutes

52. The following data were obtained at certain temperature for the decomposition of NH_3 over tungsten.

p_{NH_3} (torr)	50	100	200
$t_{1/2}$ (minutes)	5.64	2.82	1.41

Units of rate constant of the reaction would be :

(a) mol L^{-1} min^{-1}
(b) min^{-1}
(c) L mol^{-1} min^{-1}
(d) L^2 mol^{-2} min^{-1}

MARK YOUR RESPONSE					
	39. ⓐⓑⓒⓓ	40. ⓐⓑⓒⓓ	41. ⓐⓑⓒⓓ	42. ⓐⓑⓒⓓ	43. ⓐⓑⓒⓓ
	44. ⓐⓑⓒⓓ	45. ⓐⓑⓒⓓ	46. ⓐⓑⓒⓓ	47. ⓐⓑⓒⓓ	48. ⓐⓑⓒⓓ
	49. ⓐⓑⓒⓓ	50. ⓐⓑⓒⓓ	51. ⓐⓑⓒⓓ	52. ⓐⓑⓒⓓ	

53. Gaseous cyclobutane isomerizes to butadiene following first order process which has half-life of 150.5 minutes at certain temperature. How long will take for the process to occur to the extent of 40% at the same temperature ?

(a) 103 minutes (b) 121 minutes
(c) 111 minutes (d) None of these

54. At certain temperature, the first order rate constant k_1 is found to be smaller than the second order rate constant k_2. If the energy of activation, $E_{a(1)}$, for the first order reaction is greater than the energy of activation, $E_{a(2)}$ for the second order reaction, then on raising the temperature

(a) k_1 will increase faster than k_2 and become equal to k_2
(b) k_1 will increase faster than k_2 and exceed k_2
(c) k_1 will increase faster than k_2 but will always remain less than k_2
(d) k_2 will increase faster than k_1

55. For a first order reaction $A \longrightarrow$ Products; the rate of reaction at $[A] = 0.2\ M$ is 1.0×10^{-3} mol $L^{-1}\ s^{-1}$. The reaction will occur to 75% completion in

(a) 138.6 s (b) 277.2 s
(c) 442 s (d) 822 s

56. (A) follows first order reaction : $A \longrightarrow$ Products; concentration of A changes from 0.1 M to 0.025 M in 40 minutes. Find the rate of reaction of A when its concentration is 0.01 M.

(a) $1.73\times10^{-4}\ M\ \text{min}^{-1}$ (b) $1.73\times10^{-5}\ M\ \text{min}^{-1}$
(c) $3.47\times10^{-4}\ M\ \text{min}^{-1}$ (d) $3.47\times10^{-5}\ M\ \text{min}^{-1}$

57. If I is the intensity of absorbed light and C mol L^{-1} is the concentration of AB for the photochemical process $AB + h\upsilon \longrightarrow AB^*$, the rate of formation of AB^* (activated AB molecules) varies proportionally to

(a) CI (b) I^2
(c) C (d) I

58. The rate constant for the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$ is $3.0\times10^{-4}\ s^{-1}$. If start made with 1.0 mol L^{-1} of N_2O_5, calculate the rate of formation of NO_2 at the moment of the reaction when concentration of O_2 is 0.1 mol L^{-1}.

(a) $2.7\times10^{-4}\ \text{mol}\,L^{-1}s^{-1}$ (b) $2.4\times10^{-4}\ \text{mol}\,L^{-1}s^{-1}$
(c) $4.8\times10^{-4}\ \text{mol}\,L^{-1}s^{-1}$ (d) $9.6\times10^{-4}\ \text{mol}\,L^{-1}s^{-1}$

59. A first order reaction is 20% complete in one hour. At the end of three hours the extent of the reaction is

(a) 60% (b) 52.2%
(c) 48.8% (d) 44.4%

60. The decomposition of N_2O into N_2 and O_2 in presence of gaseous argon follows second order kinetics with rate constant, $k = 5.0\times10^{11}\,e^{-29000\,K/T}\ \text{L}\,\text{mol}^{-1}\text{s}^{-1}$. The pre-exponential factor and the energy of activation are respectively ($R = 2$ cal $K^{-1}\text{mol}^{-1}$)

(a) $5.0\times10^{8}\ \text{L}\,\text{mol}^{-1}\text{s}^{-1}$; 29 kcal mol^{-1}
(b) $5.0\times10^{8}\ \text{L}\,\text{mol}^{-1}\text{s}^{-1}$; 58 kcal mol^{-1}
(c) $5.0\times10^{11}\ \text{L}\,\text{mol}^{-1}\text{s}^{-1}$; 58 kcal mol^{-1}
(d) None of these

61. For a gaseous reaction $A + B \longrightarrow$ Products, occurring under the conditions

I. 1 mol of A and B each in 1 L vessel
II. 2 mol of A and B each in 2 L vessel
III. 0.2 mol of A and B each in 0.1 L vessel

The fastest formation of products and the highest rate of the reaction will be in the case

(a) *III*-Both fastest and greatest rate
(b) *II*-Fastest, *III*-Greatest
(c) *III*-Fastest, *II* - greatest
(d) *I* and *II*-Fastest, *III*-Greatest

62. In the first order reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$, if a mol L^{-1} is the initial concentration of N_2O_5, the concentration of NO_2 at time t will be

(a) $a\,e^{-kt}$ (b) $a\,(1-e^{-kt})$
(c) $2a\,(e^{-kt}-1)$ (d) $2a\,(1-e^{-kt})$

63. If n_A and n_B are the number of moles at any instant in the reaction : $2A_{(g)} \longrightarrow 3B_{(g)}$ carried out in a vessel of VL, the rate of the reaction at that instant is given by

(a) $-\frac{1}{2}\frac{dn_A}{dt} = \frac{1}{3}\frac{dn_B}{dt}$ (b) $-\frac{1}{V}\frac{dn_A}{dt} = \frac{1}{V}\frac{dn_B}{dt}$
(c) $-\frac{1}{2V}\frac{dn_A}{dt} = \frac{1}{3V}\frac{dn_B}{dt}$ (d) $-\frac{1}{V}\frac{n_A}{t} = \frac{1}{V}\frac{n_B}{t}$

MARK YOUR RESPONSE					
	53. ⓐⓑⓒⓓ	54. ⓐⓑⓒⓓ	55. ⓐⓑⓒⓓ	56. ⓐⓑⓒⓓ	57. ⓐⓑⓒⓓ
	58. ⓐⓑⓒⓓ	59. ⓐⓑⓒⓓ	60. ⓐⓑⓒⓓ	61. ⓐⓑⓒⓓ	62. ⓐⓑⓒⓓ
	63. ⓐⓑⓒⓓ				

64. In a spontaneous process $X + 2Y \rightarrow Z$,the activation energy of forward and reverse reaction is the same, then

(a) $\Delta G = 0, \Delta S = 0, \Delta U > 0$

(b) $\Delta G < 0, \Delta S < 0, \Delta U = 0$

(c) $\Delta G < 0, \Delta S > 0, \Delta U = 0$

(d) $\Delta G < 0, \Delta S > 0, \Delta U < 0$

65. For the reaction $H_2 + I_2 \rightarrow 2HI$, log k values at temperatures 769 K and 667 K are 2.9 and 1.1 respectively. Estimate the activation energy for the reaction.

$$\left(\frac{1}{769}=1.3\times10^{-3}\,K^{-1};\ \frac{1}{667}=1.5\times10^{-3}\,K^{-1}\right)$$

(a) 41.4 cal mol^{-1} (b) 41.4 k cal mol^{-1}

(c) 18 cal mol^{-1} (d) 18 k cal mol^{-1}

66. For a consecutive reaction

$$R_1 \xrightarrow{k_1} R_2 \xrightarrow{k_2} R_3$$

If the initial concentration of R_1 is 100M,
and $k_1 : k_2 = 1.0 : 0.15$
The value of $[R_2]_{max}$ is [Given : $k_1 = 4.0 \times 10^{-2}$ min^{-1}]

(a) 71.55 M (b) 55.71 M

(c) 7.155 M (d) 5.571 M

67. For a consecutive reaction

$$R_1 \xrightarrow{k_1} R_2 \xrightarrow{k_2} R_3$$

If initial concentration of R_1 is 100 M and $k_1 : k_2 = 1 : 0.15$
the value of t_{max} is [Given = $k_1 = 4.0 \times 10^{-2}$ min^{-1}]

(a) 80.55 min (b) 55.80 min

(c) 58.50 min (c) 85.0 min

68. On the top of a certain mountain where atmospheric pressure is 535 mm Hg, pure water shows a b.p. of 360 K and it takes 3×10^2 min to boil at the top of mountain as against 3 min taken to boil egg at 370K. The ratio of rate constants K_{370}/K_{360} is

(a) 10 (b) 1

(c) 100 (d) $\frac{1}{10}$

69. The following data were obtained for a given reaction at 300 K.

	Reaction	Energy of activation (kJ mol^{-1})
(i)	uncatalysed	76
(ii)	catalysed	57

The factor by which rate of catalysed reaction is increased, is

(a) 21 (b) 2100

(c) 2000 (d) 1200

70. At certain temperature, the half-life periods for the decomposition of ammonia in contact with tungsten were as follows :

Pressure (mm of Hg)	50	100	200
$t_{1/2}$ (sec)	3.52	1.82	0.93

The order of reaction is

(a) 1 (b) 2

(c) 3 (2) zero

71. If the half-life of C–14 is 5600 years, the atoms of C–14 required to produce an average of five β-emissions per minute is

(a) 2.95×10^9 atom (b) 2.13×10^{10} atoms

(c) 0.693 atoms (c) none of these

MARK YOUR RESPONSE					
	64. ⓐⓑⓒⓓ	65. ⓐⓑⓒⓓ	66. ⓐⓑⓒⓓ	67. ⓐⓑⓒⓓ	68. ⓐⓑⓒⓓ
	69. ⓐⓑⓒⓓ	70. ⓐⓑⓒⓓ	71. ⓐⓑⓒⓓ		

B COMPREHENSION TYPE

This section contains groups of questions. Each group is followed by some multiple choice questions based on a paragraph. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

PASSAGE-1

Several techniques have been developed to determine the order of reaction. The rate of a reaction cannot be predicted on the basis of the overall equation, but it can be predicted on the basis of the rate-determining step. For instance, the following reaction can be broken down into three steps.

$$A + D \xrightarrow{k} F + G \qquad \text{(Reaction - 1)}$$

Step - 1 : $A \xrightarrow{k_1} B + C$ (slow)

Step - 2 : $B + D \xrightarrow{k_2} E + F$ (fast)

Step - 3 : $E + C \xrightarrow{k_3} G$ (fast)

In this case, the first step in the reaction pathway is the rate-determining step. Therefore, the overall rate of the reaction must be equal to the rate of the first step, $k_1[A]$ where k's are the rate constants of different steps.

In some cases, it is desirable to measure the rate of a reaction in relation to only one species. In a second-order reaction involving two reacting substances for instance, a large excess of one substance is included in the reaction vessel. Since a relatively small amount of this large concentration is reacted, we assume that the concentration or this substance essentially remains unchanged. Such a reaction is called a pseudo first-order reaction. A new rate constant, K', is established, equal to the product of the rate constant of the original reaction, k, and the concentration of the species in excess.

1. In a test of the rate of Step - 3 of Reaction - 1, a solution is prepared containing a 0.1 M concentration of E and a 50 M concentration of C. The rate is calculated after the reaction has gone 50% to completion. By what percent will the calculated rate differ from the true rate if we treat the reaction as pseudo first-order?

(a) 0.02% (b) 0.05%
(c) 0.1% (d) 0.2%

2. What is the molecularty of the Reaction - 1?

(a) One (b) Two
(c) Three (d) Unpredictable

3. The differential rate law of reaction -1 is given by

(a) Rate $= k[A][D]$ (b) Rate $= k_3[E][C]$
(c) Rate $= k_2[B][D]$ (d) Rate $= k_1[A]$

PASSAGE-2

Measurement of rate of reactions provides an insight into the series of elementary steps by which a reaction takes place. In most cases, the rate depends on the concentrations of the reactants which decreases with the progress of the reaction. In consequence, the rate invariably decreases with time. In chemical kinetics, the rate at any instant of time i.e., instantaneous rate is expressed as $\frac{-d[R]}{dt}$ or $\frac{d[P]}{dt}$, where R and P are the reactants and products respectively. For example, for the reaction

$$A + 2B \longrightarrow 3C + D \quad \text{.....................(i)}$$

The rates w.r.t A, B, C and D would be $\frac{-d[A]}{dt}, \frac{-d[B]}{dt}, \frac{d[C]}{dt}$ and $\frac{d[D]}{dt}$ respectively. Obviously, these rates will be different.

However, the unique or rationalized rate of reaction is defined as the rate of change of extent of reaction as :

$$\text{Rate (unique) of reaction} = \frac{-d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = \frac{d[D]}{dt}$$

The dependence of rate on concentrations of reactants is expressed in terms of rate law, which is established experimentally.

$$\text{Rate} = k[A]^a[B]^b \qquad \text{(Rate law)} \quad \text{.....................(ii)}$$

The exponents a, b, etc. (determined experimentally) may or may not be equal to the respective stoichiometric coefficients. k is the velocity constant of the reaction.

The determination of rate law is simplified by the isolation method in which the concentration of all the reactants except one are in large excess. The concentrations of the reactants in large excess remain practically constant throughout the reaction. If B is in large excess, we can approximate $[B]$ by $[B]_0$

Hence, Rate $= k[A]^a[B]^b = k[A]^a[B]_0^b = k'[A]^a$

$(k' = k[B]_0^b)$

or $\quad \log(\text{initial rate}) = \log\upsilon_0 = \log k' + a\log[A]$ .... (iii)

A plot of log (rate) against log $[A]$ values will be a straight line which enables to calculate both k' and a. Similarly orders with respect to other reactants, taken in much smaller concentrations turn by turn, can be determined. Consider the reaction :

$$2I_{(g)} + Ar_{(g)} \longrightarrow I_{2(g)} + Ar_{(g)}$$

The following figures show the variation of log υ_0 against (a) $\log I_0$ for a given $[Ar]_0$ and (b) $\log[Ar]_0$ for a given $[I]_0$

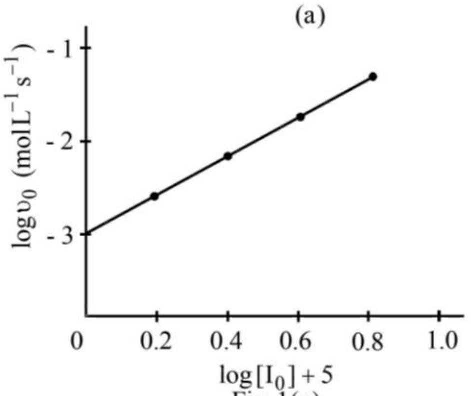


Fig. 1(a)

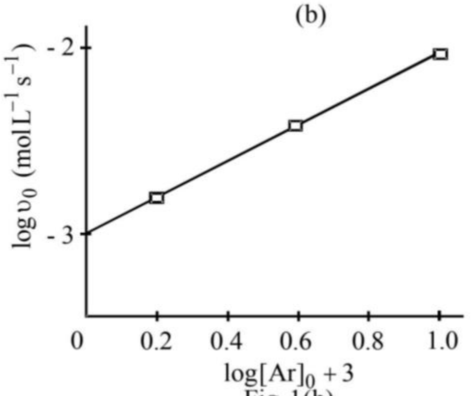


Fig. 1(b)

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ		

4. The rate of change of molar concentration of C in Reaction - 1, is found to be 3.0×10^{-3} mol $L^{-1}s^{-1}$. The rate of reaction and rate of disappearance of the reactant B are respectively

(a) 3.0×10^{-3} mol $L^{-1}s^{-1}$ each

(b) 1.0×10^{-3} mol $L^{-1}s^{-1}$ each

(c) 1.0×10^{-3} mol $L^{-1}s^{-1}$ and 2.0×10^{-3} mol $L^{-1}s^{-1}$

(d) None of these

5. According to the Fig -1 (a) and 1 (b), the rate law for the reaction

$$2I_{(g)} + Ar_{(g)} \longrightarrow I_{2(g)} + Ar_{(g)} \text{ is given by}$$

(a) Rate $= k[I][Ar]$ (b) Rate $= k[I]^2$

(c) Rate $= k[I]^2[Ar]^2$ (d) Rate $= k[I]^2[Ar]$

6. The greater slope of the plot of $\ln k$ against $1/T$ for a reaction shows the rate constant to be

(a) Independent of temperature

(b) Strongly dependent on temperature

(c) Poorly dependent on temperature

(d) Insufficient information to predict

7. Which of the following statements is *not* correct?

(a) Rate of effective collisions between reacting molecules is equal to A

(b) Rate of the effective collisions between reacting molecules is $Ae^{-Ea/RT}$

(c) Rate of total collisions between reacting molecules is equal to A

(d) Fraction of collisions between reacting molecules having energy in excess of activation energy $= e^{-Ea/RT}$

PASSAGE-3

Chemical reactions such as

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

proceed from reactants to products through one or more intermediate steps are called consecutive reactions. In these reactions each stage has its own rate and own rate constants.

The simplest case is one in which there are only two consecutive stages and the two reactions are of first order with specific reaction rates k_1 and k_2.

The rate equation for A is readily integrated to obtain

$$[A]_t = [A]_0.e^{-k_1.t}; \text{ and } [B] = \frac{k_1[A]_0}{k_2 - k_1}(e^{-k_1.t} - e^{-k_2.t})$$

8. The above equation shows that

(a) concentration of A falls exponentially and the amount of C will rise until it approaches that of B.

(b) concentration of A falls exponentially but the concentration of B slowly goes on increasing till it becomes constant at certain concentrations.

(c) The concentration of B will first increase and rises to a maximum and then decreases.

(d) all the above are correct.

9. The time (t) when B is present in maximum concentration is given by

(a) $t = \frac{k_1}{k_2 - k_1}$ (b) $t = \frac{1}{k_1 - k_2}\ln\frac{k_1}{k_2}$

(c) $\frac{1}{k_2 - k_1}\ln\frac{k_1}{k_2}$ (c) none of these

10. If C_0 is the initial concentration of A and C_1, C_2 and C_3 are concentrations of A, B and C respectively at any time t, then the values of k_1 and k_2 can be determined using the equations

(a) $C_2 = \frac{k_1.C_0.}{k_2 - k_1}[e^{-k_1.t} - e^{-k_2t}]$

(b) $C_2 = \frac{k_1.C_1.}{k_2 - k_1}[e^{-k_1.t} - e^{-k_2.t}]$

(c) $C_2 = \frac{k_1.C_0.}{k_1 - k_2}[e^{-k_1.t} - e^{-k_2.t}]$

(d) none of these

PASSAGE-4

In case of photochemical reactions the Einstein's law of equivalence is strictly applicable to primary processes, whereas for secondary processes some complicating factors step in. Hence, a simple one to one relationship between number of quanta absorbed and the number of new molecules is seldom realized. The over all result of photochemical reaction is thus expressed in terms of Quantum efficiency or Quantum yield (ϕ).

$$\phi = \frac{\text{moles of substance reacted in a given time}}{\text{moles of photons absorbed in the same time}}$$

11. A certain system absorbed 3.0×10^{16} quanta of light per second. On irradiations for 10 minutes, 0.002 moles of the reactants was found to have reacted. The quantum efficiency of the process is

(a) 50 (b) 60

(c) 67 (d) 76

MARK YOUR RESPONSE	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ
	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ		

12. Acetone decomposes as follows :

$$(CH_3)_2CO \xrightarrow{hv} C_2H_6 + CO$$

If ϕ for above reaction at 330 nm is 0.3 and a sample of acetone absorbs monochromatic radiations at 330 nm at the rate of 7.2×10^{-3} Js^{-1}, the rate of formation of CO is

(a) 6×10^{-10} mol/s (b) 6×10^{-9} mol/s
(c) 6×10^{-8} mol/s (d) 6×10^{-7} mol/s

13. If the quantum yield is 0.6, then rate of formation of C_2H_6 (mol/s) is

(a) 1×10^{-8} (b) 1.2×10^{-9}
(c) 1.8×10^{-9} (d) 12×10^{-9}

MARK YOUR RESPONSE	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ			

C REASONING TYPE

In the following questions two Statement-1 (Assertion) and Statement-2 (Reason) are provided. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct. Mark your responses from the following options:

(a) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(b) Both Statement-1 and Statement-2 are true and Statement-2 is not the correct explanation of Statement-1.
(c) Statement-1 is true but Statement-2 is false.
(d) Statement-1 is false but Statement-2 is true.

1. **Statement-1** : The rate of the reaction is the rate of change of concentration of a reactant or a product.
Statement-2 : Rate of reaction remains constant during the course of reaction.

2. **Statement-1** : If in a zero order reaction, the concentration of the reactant is doubled, the half-life period is also doubled.
Statement-2 : For a zero order reaction, the rate of reaction is independent of initial concentration.

3. **Statement-1** : If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.
Statement-2 : Lower the activation energy, faster is the reaction.

4. **Statement-1** : According to steady state hypothesis, in a multistep reaction, the change in concentration with time for reactive intermediates is zero.
Statement-2 : The intermediates are so reactive that after a brief initial period their concentrations rise from zero to a small value and remains constant for most of the duration of the reaction.

5. **Statement-1** : For the reaction

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

Rate $= k[N_2O_5]$.

Statement-2 : Rate of decomposition of N_2O_5 is determined by slow step.

6. **Statement-1** : The order of a reaction may be negative.
Statement-2 : In some cases, the rate of reaction decreases as the concentration of the reactant increases.

7. **Statement-1** : The rate of reaction is always negative.
Statement-2 : Minus sign used in expressing the rate shows that concentration of reactant is decreasing.

8. **Statement-1** : Hydrolysis of cane sugar is a first order reaction.
Statement-2 : Water is present in large excesss during hydrolysis.

9. **Statement-1** : The kinetics of the reaction –

$$mA + nB + pC \longrightarrow m'X + n'Y + p'Z$$

obey the rate expression as

$$\frac{dX}{dt} = k[A]^m[B]^n.$$

Statement-2 : The rate of the reaction does not depend upon the concentrations of C.

10. **Statement-1** : For each ten degree rise of temperature the specific rate constant is nearly doubled.
Statement-2 : Energy-wise distribution of molecules in a gas is an experimental function of temperature.

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ

11. **Statement-1** : In most of the homogeneous gaseous reaction the values of temperature coefficient lies between 2 and 3. The average value of temperature coefficient is 3.

Statement-2 : For change of temperature by 100°C, the rate of reaction is found to change by $3^{10} (\simeq 59049)$ times

12. **Statement-1** : The combination of hydrogen and oxygen to form water at ordinary temperature in presence of platinum is an example of negative catalysis.

Statement-2 : A catalyst can increase or decrease the rate of reaction.

13. **Statement-1** : Assuming the reaction to occur through molecular collisions, molecularity of a reaction is defined as the number of atoms or molecules which colloide together at one and the same time for reaction to occur.

Statement-2 : Molecularity is defined as equal to the number of molecules, atoms or ions of the reactants used in forming the activated complex.

MARK YOUR RESPONSE	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ		

D MULTIPLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE OR MORE is/are correct.

1. For a first order reaction
(a) The extent of reaction is equal to $(1 - e^{-kt})$
(b) Concentration of the reactant decreases exponentially with time
(c) Concentration of the product increases exponentially with time
(d) A plot of logarithm of concentration of the product *versus* time is linear with negative slope

2. Which of the following is/are pseudo first order reactions
(a) The basic hydrolysis of ethyl acetate
(b) The inversion of sucrose in the presence of an acid
(c) The acidic hydrolysis of ethyl acetate
(d) The decomposition of ammonium nitrite in aqueous solution.

3. Which of the following statement(s) about the Arrhenius equation is/are correct?
(a) The pre-exponential factor becomes equal to the rate constant of the reaction at extremely high temperature.
(b) When the activation energy of the reaction is zero, the rate becomes independent of temperature
(c) The term $e^{-E_a/RT}$ represents the fraction of the molecules having energy in excess of threshold value
(d) On raising temperature, rate constant of the reaction of greater activation energy increases less rapidly than that of the reaction of smaller activation energy.

4. What happens when the temperature of a reaction system is increased by 10°C?
(a) The total number of collisions between reacting molecules increases atleast by 100%
(b) The effective number of collisions between the molecules possessing certain threshold energy increases atleast by 100%
(c) The total number of collisions between reacting molecules increases merely by 1-2%
(d) The activation energy of the reaction is lowered

5. In Arrhenius equation : $k = A\,e^{-E_a/RT}$
(a) The pre-exponential factor has the units of rate of the reaction
(b) The pre-exponential factor has the units of rate constant of the reaction
(c) The exponential factor is a dimensionless quantity
(d) The exponential factor has the units of reciprocal of temperature

6. Pick out the correct statement(s) of the following
(a) An unstable intermediate in a reaction has the maximum potential energy and normal bond orders for its atoms
(b) Activated complex is a postulated species which has maximum energy during the conversion of reactants into products
(c) The transition state in a reaction has no independent existence but has greater vibrational character than unstable intermediate
(d) An unstable intermediate is an actual chemical species which can be stabilized under different reaction conditions

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ				

7. Hydrolysis of an ester is catalysed by H^+ ion. Using equimolar concentrations of two acids *HX* and *HY*, both being strong acids, the rate constants of the reaction are found to be $3 \times 10^{-3}\ min^{-1}$ and $5 \times 10^{-3}\ min^{-1}$ respectively at a fixed temperature. It can be concluded that

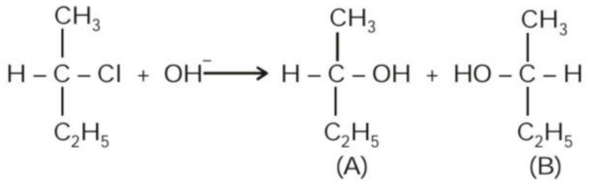
(a) Rate constant may be taken as the measure of degree of ionization of the acid used as catalyst

(b) *HX* is a stronger acid than *HY*, their relative strength being 1.7

(c) *HX* is a weaker acid than *HY*, their relative strength being 0.6

(d) none is correct

8. Consider the substitution reaction :



$$H-\underset{C_2H_5}{\overset{CH_3}{C}}-Cl + OH^- \longrightarrow \underset{(A)}{H-\underset{C_2H_5}{\overset{CH_3}{C}}-OH} + \underset{(B)}{HO-\underset{C_2H_5}{\overset{CH_3}{C}}-H}$$

Select the correct statements of the following :

(a) It is unimolecular substitution reaction (S_N1) if either (A) or (B) is formed

(b) It is bimolecular substitution reaction (S_N2) if either (A) or (B) is formed

(c) It is S_N1 reaction if both (A) and (B) are formed to give racemic mixture

(d) It is S_N2 reaction if (B) is formed

9. Which of the following statements are correct?

(a) Time required for 75% completion is 1.5 times of half-life for zero order reaction

(b) Time needed for a definite fraction of first order reaction does not vary with the initial concentration

(c) Time for 25% reaction is one-third of half-life in second order process

(d) Rate of zero order reaction gets doubled if the concentration of the reactant is increased to a two fold value

10. Hydrolysis of a sugar is catalysed by H^+ ion. Half-life of the reaction is independent of initial concentration of sugar at a particular pH. At a constant concentration of sugar rate increases 10 times when pH is decreased by one unit. Pick out the correct statements of the following :

(a) Rate α [sugar]

(b) Rate α $[H^+]$

(c) Rate law : rate = *k* [sugar]

(d) Rate law : rate = *k* [sugar] $[H^+]$

11. Estrification of acetic anhydride by ethanol takes place as

$$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$

Select the correct statements of the following :

(a) When reaction is carried out in dilute hexane solution, the rate law is given by *k* [Anhydride] [Alcohol]

(b) When ethanol is the solvent, the rate law is given by *k* [Anhydride]

(c) The values of *k* in the two cases are the same

(d) Using ethanol as the solvent, its concentration changes significantly during the course of the reaction

12. The rate law of gaseous reaction : $A_{(g)} + B_{(g)} \rightarrow$ Products is given by $k[A]^2[B]$. If the volume of the reaction vessel is suddenly doubled, which of the following will happen?

(a) The rate w.r.t. *A* will decrease two times

(b) The rate w.r.t. *A* will decrease four times

(c) The rate w.r.t. *B* will decrease two times

(d) The overall rate will decrease 8 times of the original value

13. When the temperature of a reaction is changed from T_1 to T_2 half-life is found to decrease. Thus :

(a) $T_2 > T_1$

(b) The reaction is exothermic

(c) The reaction is endothermic

(d) The reaction can be exothermic or endothermic

14. Choose the correct statements.

(a) The units of zero order rate constant (*k*) is that of concentration × $time^{-1}$.

(b) In zero order reaction the concentration of product increases linearly with time.

(c) The photochemical reaction of H_2 and Cl_2 over water surface is of zero order.

(d) The thermal decomposition of HI on gold surface is of zero order.

15. The reaction $2A + B \longrightarrow C + D$

goes to completion and follows the following rate law

$$-\frac{d}{dt}[A] = k[A]^2[B]$$

For this reaction the values of *x* and *y* in the following table are

Set	$[A]_0 \times 10^6$ (moledm^{-3})	$[B]_0 \times 10^6$(moledm^{-3})	Half-life ($t_{1/2}$)(sec)
1	300	40	62.6
2	300	60	*x*
3	5	300	625
4	10	300	*y*

(a) 62.6 and 625 (b) 62.6 and 312.5

(c) 31.3 and 625 (d) 31.3 and 312.5

MARK YOUR RESPONSE	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ
	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	

16. Choose the correct statements.

(a) Dimensions of the zero-order rate constant (k) are concentration × $(\text{time})^{-1}$.

(b) For a zero order reaction the time required for the completion of any fraction of change is inversely proportional to initial concentration.

(c) The rate constant depends on the unit in which concentration is expressed.

(d) None of these are correct.

17. Rate constant k varies with temperature by the equation

$$\log k\,(\text{min}^{-1}) = 7 - \frac{3000\,K}{T},$$

From the above equation we may conclude that

(a) Pre-exponential factor A is 7.

(b) E_a is 3000 k cal.

(c) E_a is 9.212 k cal.

(d) pre-exponential factor A is 10^7.

18. Choose the correct statements :

(a) Rate equation for a fractional order reaction is

$$\left(\frac{2n-1}{2}\right)A \longrightarrow \text{products} \; ; \; k = \frac{2}{t}\left[\frac{a}{(a-x)^{\frac{1}{2}}} - \frac{1}{a^{\frac{1}{2}}}\right]$$

(b) The unit of k for fractional order reaction could be expressed in terms of $(\text{conc.})^{-\frac{2n-1}{2}}.\text{time}^{-1}$ units.

(c) Half-life values for fractional order reaction is inversely proportional to the odd under-root of the initial concentration.

(d) none of these is correct.

19. Choose the method that can be used to determine the rate of fast reactions

(a) Shock tubes technique

(b) Flash photolysis technique

(c) Linear flow technique

(d) Stopped flow technique

MARK YOUR RESPONSE	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	

E

MATRIX-MATCH TYPE

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labeled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column -I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:
If the correct matches are A–p, s and t; B–q and r; C–p and q; and D–s then the correct darkening of bubbles will look like the given.

	p	q	r	s	t
A	●	ⓠ	ⓡ	●	●
B	ⓟ	●	●	ⓢ	ⓣ
C	●	●	ⓡ	ⓢ	ⓣ
D	ⓟ	ⓠ	ⓡ	●	●

1. Match the appropriate experimental methods used to study the kinetics of the following reactions :

Reactions		**Experimental Methods**
(A)	$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$	p. Measurement of optical activity
(B)	$CH_3COOC_2H_5(aq) + H_2O \xrightarrow{[H^+]} CH_3COOH(aq) + C_2H_5OH(aq)$	q. Measurement of volume of gas at constant P and T
(C)	$C_6H_5N = N - Cl(aq) \rightarrow C_6H_5Cl(\ell) + N_2(g)$	r. Titration of an aliquot of reaction mixture with alkali
(D)	$C_{12}H_{22}O_{11}(aq) + H_2O \xrightarrow{[H^+]} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$	s. Measurement of pressure of reaction mixture at constant V and T

MARK YOUR RESPONSE

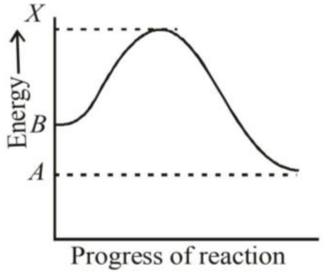
1.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

2. Kinetics of hydrolysis of ethyl acetate catalysed by an acid is followed by titrating a fixed volume of reaction mixture with a standard alkali solution at different intervals of time. If V_o, V_t and V_∞ are the titre values at zero, t and ∞ time, then match the following :

Column 1		**Column II**
(A) $V_0 \propto$	p.	[Acid] initially present and that formed at time t
(B) $V_t \propto$	q.	[Acid] present as catalyst
(C) $(V_\infty - V_t) \propto$	r.	[Acid] formed after completion of reaction
(D) $(V_\infty - V_o) \propto$	s.	[Acid] formed after time t

3. Consider the energy diagram of a reaction : $B \rightarrow A$, as shown in the figure and match the following



Column 1		**Column II**
(A) $X - A$	p.	Enthalpy of reaction
(B) $X - B$	q.	Energy of transition state
(C) $A - B$	r.	Activation energy of forward reaction
(D) X	s.	Activation energy of backward reaction

4. C_o = Intital concentration of reactant; C = Concentration of reactant at any time t; k = rate constant. Match the following :

Plots		**Slopes**
(A) C Vs t (abscissa) for zero order	p.	Unity
(B) $\log C$ Vs t (abscissa) for first order	q.	Zero
(C) $\left(-\frac{dc}{dt}\right)$ Vs C for zero order	r.	$-k$
(D) $\ln(-dc/dt)$ Vs $\ln C$ for first order	s.	$-k/2.303$

5.

Column A (Reaction)		**Column B** (Reaction characteristics or order of reaction)
(A) Hydrodysis of an ester	p.	Pseuo-first order
(B) Saponification of ester	q.	$t_{1/2} = \frac{0.693}{k}$
(C) Inversion of cane sugar	r.	$t_{1/2} \propto \frac{1}{\text{initial conc.}}$
(D) Decomposition of N_2O_5 in CCl_4 solution	s.	Rate constant k is expressed in units of litre mol^{-1} sec^{-1}.

MARK YOUR RESPONSE

	2. p q r s	3. p q r s	4. p q r s	5. p q r s
A	ⓟⓠⓡⓢ	ⓟⓠⓡⓢ	ⓟⓠⓡⓢ	ⓟⓠⓡⓢ
B	ⓟⓠⓡⓢ	ⓟⓠⓡⓢ	ⓟⓠⓡⓢ	ⓟⓠⓡⓢ
C	ⓟⓠⓡⓢ	ⓟⓠⓡⓢ	ⓟⓠⓡⓢ	ⓟⓠⓡⓢ
D	ⓟⓠⓡⓢ	ⓟⓠⓡⓢ	ⓟⓠⓡⓢ	ⓟⓠⓡⓢ

F

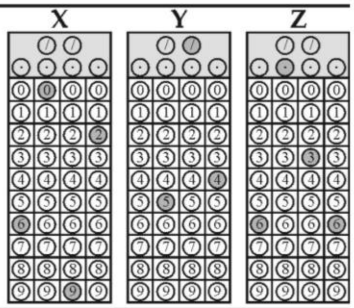
NUMERIC/INTEGER ANSWER TYPE

The answer to each of the questions is either numeric (eg. 304, 40, 3010, 3 etc.) or a fraction (2/3, 23/7) or a decimal (2.35, 0.546).

The appropriate bubbles below the respective question numbers in the response grid have to be darkened.

For example, if the correct answers to question X, Y & Z are 6092, 5/4 & 6.36 respectively then the correct darkening of bubbles will look like the following.

For single digit integer answer darken the extreme right bubble only.

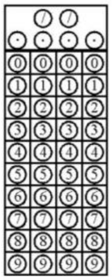


1. A reaction $A + B \rightarrow$ Products is first order w.r.t. each reactant, k being $5.0 \times 10^{-3}\ M^{-1}\ s^{-1}$. If start is made with initial concentration of A to be 0.1 M acid that of $B = 5.0\ M$, calculate the concentration of A (in M) remaining after 100 s.

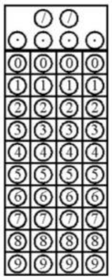
2. Substances A and B react to form C and D and the reaction is found to be second order overall and second order in A. The rate constant at 300 K is $0.500\ \text{L mol}^{-1}\ \text{min}^{-1}$. What is the half-life of A (in min.) when $4.0 \times 10^{-2}\ M$ of A is mixed with excess of B ?

MARK YOUR RESPONSE

1.



2.



Answerkey

A SINGLE CORRECT CHOICE TYPE

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

B COMPREHENSION TYPE

1	(c)	**4**	(c)	**7**	(a)	**10**	(a)	**13**	(d)
2	(a)	**5**	(d)	**8**	(c)	**11**	(c)		
3	(d)	**6**	(b)	**9**	(c)	**12**	(b)		

C REASONING TYPE

1	(c)	**4**	(a)	**7**	(c)	**10**	(a)	**13**	(b)
2	(b)	**5**	(a)	**8**	(a)	**11**	(b)		
3	(b)	**6**	(a)	**9**	(a)	**12**	(d)		

D MULTIPLE CORRECT CHOICE TYPE

1.	a,b,c	**2.**	b,c	**3.**	a,b,c	**4.**	b,c	**5.**	b,c	**6.**	b,c,d	**7.**	a,c	**8.**	c,d	**9.**	a,b,c	**10.**	a,b,c
11.	a,b	**12.**	d	**13.**	a,b	**14.**	a,b,c	**15.**	b	**16.**	a,c	**17.**	d	**18.**	a,b,c	**19.**	a,b		

E MATRIX-MATCH TYPE

1. A - s; B - r; C - q; D - p
2. A - q; B - p; C - s; D - r
3. A - s; B - r; C - p; D - q
4. A - r; B - s; C - q; D - p
5. A - p, q ; B - r, s ; C - p, q ; D - p, q

F NUMERIC/INTEGER ANSWER TYPE

1	0.008	**2**	50

Solutions

A SINGLE CORRECT CHOICE TYPE

2. **(d)** For elementary reaction, molecularity = order

3. **(c)** From the slow step, rate = $k'[O][O_3]$............(i)

From the fast reaction, $K = \dfrac{[O_2][O]}{[O_3]}$

or $[O] = \dfrac{K[O_3]}{[O_2]}$ ....(ii)

From (i) & (ii), rate $= k'\,K = \dfrac{[O_3]^2}{[O_2]} = k\dfrac{[O_3]^2}{[O_2]}$

4. **(c)** Rate $= -\dfrac{1}{4}\dfrac{d[KClO_3]}{dt} = \dfrac{1}{3}\dfrac{d[KClO_4]}{dt} = \dfrac{d[KCl]}{dt}$

or $\dfrac{k_1}{4}[KClO_3]^4 = \dfrac{k_2}{3}[KClO_3]^4 = k_3[KClO_3]^4$

or $3k_1 = 4\,k_2 = 12\,k_3$

5. **(b)** The rate $= -\dfrac{d[Cr_2O_7^{2-}]}{dt} = \dfrac{1}{3}\dfrac{d[I_2]}{dt}$

or, $\dfrac{d[I_2]}{dt} = 3 \times 1.55 \times 10^{-2}\,M\,s^{-1}$

6. **(d)** $(\text{Rate})_1 = k[A]^m[B]^n$; $(\text{Rate})_2 = k(2[A])^m([B]/2)^n$

Hence, $\dfrac{(\text{rate})_2}{(\text{rate})_1} = 2^m \times \left(\dfrac{1}{2}\right)^n = 2^{m-n}$

7. **(c)** For first order, $(a - x) = a\,e^{-kt}$; partial pressure or conc. of the reactant decreases exponentially with time.

8. **(b)** $\dfrac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\dfrac{a_2}{a_1}\right)^{n-1}$; $\dfrac{10}{15} = \left(\dfrac{300}{200}\right)^{n-1}$

or, $\left(\dfrac{2}{3}\right)^1 = \left(\dfrac{3}{2}\right)^{n-1} = \left(\dfrac{2}{3}\right)^{1-n}$; $1-n = 1$, $n = 0$

9. **(c)** Rate $= k[HI]^2$; rate $= k$ $[HI] = 1M$

10. **(b)** $\dfrac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\dfrac{a_1}{a_2}\right)^{n-1}$; $10 = \left(\dfrac{0.1}{0.01}\right)^{n-1}$; $\Rightarrow$ $n = 2$

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

11. **(c)** When concentration is made m times, the rate becomes m^n times, n = order

On doubling conc. of A, the rate is doubled : $2^n = 2$, $n = 1$

On doubling conc of B, rate becomes 8 times: $2^n = 8 = 2^3$, $n = 3$

For elementary reaction, $A + 3\,B \to$ Products

$$-\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} \quad \text{or} \quad -\frac{3d[A]}{dt} = -\frac{d[B]}{dt}$$

12. **(d)** $\dfrac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\dfrac{a_1}{a_2}\right)^{n-1}$; $9 = \left(\dfrac{1}{1/3}\right)^{n-1} = 3^{n-1}$; $3^2 = 3^{n-1}$

$n = 3$; $-\dfrac{d[A]}{dt} = k[A]^3$

13. **(d)** Making conc. m times, rate becomes m^n times, n = order. For CO, $2^n = 4 = 2^2$, $n = 2$.

For Cl_2, $4^n = 2$, $n = \dfrac{1}{2}$

14. **(b)** For first order reaction, $t = \dfrac{2.303}{k}\log\dfrac{a}{a-x}$

$$t_{99.9} = \frac{2.303}{k}\log\frac{100}{100-99.9} = \frac{2.303}{k}\times 3$$

$$t_{50} = \frac{2.303}{k}\log\frac{100}{50} = \frac{2.303}{k}\log 2 = \frac{2.303}{k}\times 0.301$$

$t_{99.9}/t_{50} = 10$ approx.

15. **(d)** Rate $= k[A]^x[B]^y$; From exp 2 & 3,

$$\frac{(\text{rate})_2}{(\text{rate})_3} = k\frac{[0.024]^x[0.070]^y}{[0.024]^x[0.035]^y} = \frac{8\times10^{-3}}{1\times10^{-3}} = 8$$

or $2^y = 8 = 2^3$, $y = 3$

From exp 2 and 4,

$$\frac{(\text{rate})_2}{(\text{rate})_1} = \frac{8\times10^{-3}}{8\times10^{-3}} = \frac{k[0.024]^x[0.070]^y}{k[0.012]^x[0.070]^y} = 2^x$$

or $2^x = 1 \Rightarrow x = 0$

or, $-\dfrac{d[A]}{dt} = k[B]^3$

16. **(d)** Concentration of the product increases linearly with time t, hence order = 0, and $-\dfrac{d[A]}{dt}$ = constant

17. **(c)** Units of k show zero order; rate = k = constant

$[A]$ reacted after 100 min = $100 \times k = 100 \times 1.0 \times 10^{-3}$ $= 0.1$ mol L^{-1}. $[B]$ after 100 min $= 2 \times 0.1 = 0.2$ mol L^{-1}

18. **(a)** Units of k show first order.

Hence, $t_{1/2}=\dfrac{0.693}{k}=\dfrac{0.693}{6.93\times10^{-3}}=100\,\text{min}$

[reactant] after $t_{1/2}$ = ½ × 2 = 1 M;
Rate = k[reactant] = $6.93\times10^{-3}\times1\ M\,\text{min}^{-1}$

19. **(c)** $\log\dfrac{k_2}{k_1}=-\dfrac{\Delta E_a}{2.303\,RT}=-\dfrac{(-4.606\times10^3)}{2.303\times2\times500}=2$

Thus, $k_2/k_1=10^2=100$

20. **(b)** The titre ∝ residual conc. of N-chloro isomer at time t. For first order reaction, $\log[A]$ *vs* t is a straight line. Hence slope = $-k/2.303$

21. **(c)** $x\ \alpha\ p_t$; $a\ \alpha\ p_f$; $(a-x)\ \alpha\ (p_f-p_t)$

$$\log(a-x)=\log a-\frac{kt}{2.303},$$

$$\text{or } \log(p_f-p_t)=\log p_f-\frac{k}{2.303}t$$

22. **(c)** Rate law : $-\dfrac{d[A]}{dt}=k[A]^x[B]^y$

Doubling $[A]$, rate is doubled. Hence $2^x=2, x=1$

Similarly $y=1$; $-\dfrac{d[A]}{dt}=k[A][B]$

$$k=\frac{\text{rate}}{[A][B]}=\frac{2.0\times10^{-4}}{1\times10^{-2}\times2\times10^{-2}}=1$$

$$\frac{(\text{rate})_2}{(\text{rate})_1}=\frac{k(2[A])(2[b])}{k[A][B]}=4$$

23. **(d)** $t_{1/2}=k\,a^{1-n}$, n being order, k = rate constant
$\log t_{1/2}=\log k+(1-n)\log a$
Slope = $(1-n)=-2, n=3$

24. **(c)** $t_{1/2}$ is independent of initial concentration, a, for first order reaction.
$x\ \alpha\ V_t$ (= 5L at t = 20 minutes)
$a\ \alpha\ V_\infty$ (= 50 L at completion)

$$k=\frac{2.303}{t}\log\frac{a}{a-x}=\frac{2.303}{20}\log\frac{50}{45}$$

25. **(b)** For a 10 K rise in temperature, collision frequency increases merely by 1 to 2% but the number of effective collisions increases by 100 to 200%.

26. **(c)** Greater E_a, lower k and greater will be the increase in its magnitude with rise in temperature.

27. **(b)** E_a is independent of stoichiometry of the reaction.

28. **(b)** $\dfrac{k_1\times100}{k_1+k_2}=\dfrac{1.26\times10^{-4}\times100}{1.25\times10^{-4}+3.80\times10^{-5}}=76.83$

29. **(b)** Let x torr of C_2H_4O decompose after 20 min. Then, $80-x+2x=120$; $x=40$ torr = 50% of initial pressure. Hence $t_{1/2}$ = 20 min. For 75% reaction, fraction left =

$$\frac{25}{100}=\frac{1}{4}=\left(\frac{1}{2}\right)^2$$

No. of half lives = 2. Time needed for 75% reaction., 2 × 20 = 40 min

30. **(c)** From the slow step : rate = $k_2[A][B]$ ....(i)
From fast step :

$$K_e=\frac{[A]^2}{[A_2]}\text{ or }[A]=K_e^{1/2}[A]^{1/2}\quad\text{..........................(ii)}$$

From (i) and (ii) rate = $k_2k_e^{1/2}[A_2]^{1/2}[B]=k[A_2]^{1/2}[B]$

31. **(a)** $[B]$ (= b), being present in large excess, does not change practically. The rate becomes independent of $[B]$, i.e., order = 0 w.r.t. B.

32. **(c)** Overall activation energy

$$=\frac{k_1E_{a(1)}+k_2E_{a(2)}}{k_1+k_2}=\frac{2\times10^{-3}\times50+5\times10^{-3}\times78}{2\times10^{-3}+5\times10^{-3}}$$

$$=70\text{kJ mol}^{-1}$$

33. **(c)** $\dfrac{(t_{1/2})_1}{(t_{1/2})_2}=\left(\dfrac{a_2}{a_1}\right)^{n-1}$; $\dfrac{120}{240}=\left(\dfrac{4\times10^{-2}}{8\times10^{-2}}\right)^{n-1}$; $n=2$

34. **(d)** For Ist order reaction : $(a-x)=a\,e^{-kt}$; $x/a=1-e^{-kt}$

35. **(c)** $|H_3O^+|=\dfrac{6\times10^{-7}\times10^3}{0.05}$; $\quad t=\dfrac{|H_3O^+|}{\text{rate}}$

$$=\frac{6\times10^{-4}}{0.05}/6.0\times10^5=2.0\times10^{-8}\text{s}$$

36. **(d)** E_a = activation energy for forward reaction, $E_a^{'}$ that for reverse reaction. Then, $E_a-E_a^{'}=\Delta H$

or, $E_a-2E_a=-80$, $E_a=80$ kJ, $E_a^{'}=2\times80$ kJ

37. **(c)** $k=Ae^{-E_a/RT}$; when $T\to\infty, k=A$

38. **(c)** Rate = $k\,[FeCl_3]^2\,[SnCl_2]$ [reaction being elementary]

	$2\,FeCl_3$ +	$SnCl_2$ →	$2\,FeCl_2$ +	$SnCl_4$
$t=0$	1.2 M	0.8 M	0	0
time = t	0.8 M	0.6 M	0.4 M	0.2 M

$$\frac{(\text{Rate})_2}{(\text{Rate})_1}=\frac{k(0.8)^2\times0.6}{k(1.2)^2\times0.8}=\frac{1}{3}$$

39. **(d)** Under the given condition, $k_1=k_2$
$10^{11}\,e^{-3000/T}=10^{10}\,e^{-2000/T}$; $10=e^{1000/T}$
$\ln 10=1000/T$, $2.303\log10=1000/T$;
$\Rightarrow T=1000/2.303$ K

40. **(b)** [Product] α time; order = zero, rate remains constant throughout. Rate = 0.2/10 = 0.02 mol L^{-1} min^{-1}.

42. **(d)** $k = Ae^{-E_a/RT}$, $k = 2.3 \times 10^{-3}$ min^{-1}

$e^{-E_a/RT}$ = fraction of molecules crossing over energy barrier $= \frac{0.001}{100} = 1.0 \times 10^{-5}$

Hence, $2.3 \times 10^{-3} = A \times 1.0 \times 10^{-5}$; $A = 230$ min^{-1}

$k_{max} = A$ when $T \rightarrow \infty$, hence $k_{max} = 230$ min^{-1}

43. **(b)** $\frac{E_a}{T_1} = \frac{E_a^c}{T_2} \Rightarrow \frac{T_2}{T_1} = \frac{E_a^c}{E_a} = \frac{75}{100} = 0.75$

$\frac{300}{T_1} = 0.75 \Rightarrow T_1 = \frac{300}{0.75} = 400\,K = 127°C$

44. **(d)** Units of k indicate that reaction I is of second order and reaction II is first order.
For I reaction, $t_{1/2} \propto 1/a$,
first $t_{1/2} =$ 1 hr, second $t_{1/2} = 2$ hr

$[A] = 1M \xrightarrow{1\,hr} 0.5M \xrightarrow{2\,hr} 0.25M$

$[B] = 1M \xrightarrow{1\,hr} 0.5M \xrightarrow{1\,hr} 0.25M \xrightarrow{1\,hr} 0.125M$

$\frac{[A]}{[B]} = \frac{0.25\,M}{0.125\,M} = 2$

45. **(a)** $e^{-E_a/RT} = 10^{-3}\% = 10^{-5}$;
$E_a = 2.303 \times 2 \times 300 \times 5$ cal $= 6.91$ $k\,cal$ mol^{-1}

46. **(d)** Rate $(S_{N^2}) = 5.0 \times 10^{-5} \times 10^{-2}[R-X]$

$= 5.0 \times 10^{-7}[R-X]$

Rate $(S_{N^1}) = 0.20 \times 10^{-5}[R-X]$

$$\% \; of \; S_{N^2} = \frac{5 \times 10^{-7}[R-X] \times 100}{5 \times 10^{-7}[R-X] + 0.20 \times 10^{-5}[R-X]} = 20$$

47. **(c)** The slowest step determines the rate.

48. **(c)** Since the rate becomes two fold on increasing $[A]$ four times, the order = 0.5
First $t_{1/2} = 1414\,s$

Second $t_{1/2} = 1414 \times \left(\frac{a}{a/2}\right)^{0.5-1} = 1414 \times 2^{-0.5}$

$= \frac{1414}{\sqrt{2}} = \frac{1414}{1.414} = 1000$ s

Total time for 75% reaction = 1414 + 1000 s = 2414 s

49. **(b)** $E_{a(f)} - E_{a(b)} = \Delta H = -15$ $k\,cal$
$\Rightarrow E_{a(f)} = -15 + 20 = 5$ $k\,cal$

$$\frac{k\text{ (catalyst)}}{k} = e^{\frac{E_a - E_{a(\text{catalyst})}}{RT}} = e^{\frac{(5-3)\times 10^3}{2\times 400}} = e^{2.5}$$

50. **(c)** Fraction left $= \frac{0.5}{16} = \frac{1}{32} = \left(\frac{1}{2}\right)^5$; number of $t_{1/2} = 5$

Hence, $5 \times t_{1/2} = 1$ hr = 60 min $\Rightarrow t_{1/2} = 12$ min

51. **(d)** $t = \frac{2.303 \times t_{1/2}}{0.693} \log \frac{100}{100 - 99.9}$

$= \frac{2.303 \times 69.3}{0.693} \log 1000 = 691\,min$

52. **(c)** Data show that $t_{1/2}$ is inversely proportional to the initial pressure of the reactant. Hence, second order reaction.

53. **(c)** $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{150.5} min^{-1}$;

$t = \frac{2.303}{k} \log \frac{100}{100-40} = \frac{2.303 \times 150.5}{0.693} \log \frac{100}{60}$

$= 111$ minutes

55. **(b)** $k = \frac{\text{rate}}{[A]} = \frac{1.0 \times 10^{-3}}{0.2} = 5 \times 10^{-3} s^{-1}$;

$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5 \times 10^{-3}} = 138.6\,s$

Fraction remaining ,

$\left(\frac{1}{2}\right)^n = \left(\frac{100-75}{100}\right) = \frac{25}{100} = \frac{1}{4} = \left(\frac{1}{2}\right)^2$;

Hence, $n = 2$ half-lives, $t = 2 \times 138.6 = 277.2$ s

56. **(c)** Fraction remaining after 40 minutes

$= \frac{0.025}{0.1} = \frac{1}{4} = \left(\frac{1}{2}\right)^2$;

Hence $2 \times t_{1/2} = 40 \Rightarrow t_{1/2} = 20$ minutes

Rate $= k\,[A] = \frac{0.693}{20} \times 0.01 = 3.47 \times 10^{-4}$ mol L^{-1} min^{-1}

57. **(d)** Each molecule of AB gets activated after absorption of one quantum of light. Hence, rate of formation of AB^* is proportional to the rate of quanta absorbed i.e., the intensity of light I.

58. **(d)** Mol L^{-1} of N_2O_5 reacted $= 2 \times 0.1 = 0.2$

$[N_2O_5]$ left $= 1.0 - 0.2 = 0.8$ mol L^{-1}

Rate of reaction $= k \times [N_2O_5]$

$= 3.0 \times 10^{-4} \times 0.8 = 2.4 \times 10^{-4}$ mol $L^{-1}s^{-1}$

Rate of formation of NO_2

$= 4 \times 2.4 \times 10^{-4} = 9.6 \times 10^{-4}$ $mol\,L^{-1}s^{-1}$

59. **(c)** Fraction left after 3 hours $=\left(\frac{100-20}{100}\right)^3=0.512$

Extent of reaction $=1-0.512=0.488$ or 48.8 %

60. **(c)** Pre-exponential factor $A = 5.0\times10^{11}\,\text{L mol}^{-1}\text{s}^{-1}$;

$$-\frac{E_a}{R}=-29000$$

$$\Rightarrow E_a=2\times29000\text{ cal}=58\text{ k cal mol}^{-1}$$

61. **(b)** (II) Fastest : Since there are more reactants present, there will be more product produced per unit time.

(III) Highest rate : Greatest concentrations $C=\frac{0.2}{0.1}$

$=2\text{ mol L}^{-1}$ each,

So greatest change in concentration per unit time.

64. **(c)** For equal $E_{a(f)}$ and $E_{a(r)}$, the reactant and product molecules have equal energies. Hence, $\Delta U=0$; $\Delta G=\Delta U-T\Delta S$ or $-\Delta G=T\Delta S$. For spontaneity ΔG must be negative and hence $\Delta S>0$.

65. **(b)** $\log k_2-\log k_1=\frac{E_a}{2.303\,R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$

$$=\frac{E_a}{2.303\times2}(1.5\times10^{-3}-1.3\times10^{-3})$$

or $E_a=\frac{2.303\times2\times(2.9-1.1)}{0.2\times10^{-3}}=41.4\text{ k cal mol}^{-1}$

66. **(a)** The values of $[R_2]_{\max}$ is given by the relation

$$[R_2]_{\max}=[R_1]_0\left[\frac{k_2}{k_1}\right]^{k_2/(k_2-k_1)}$$

$$\therefore\quad [R_2]_{\max}=100\left[\frac{0.15\times10^{-2}}{1.0\times10^{-2}}\right]^{\frac{0.15\times10^{-2}}{(1-0.15)\times10^{-2}}}$$

$$=100\left[\frac{0.15}{1}\right]^{\frac{0.15}{0.85}}=71.55\text{ M.}$$

67. **(b)** The value of $t_{\max}$ is given by the relation

$$t_{\max}=\frac{2.303}{(k_1-k_2)}\log\left(\frac{k_1}{k_2}\right)$$

$$=\frac{2.303}{(1.0-0.15)\times10^{-2}}\log\frac{1\times10^{-2}}{0.15\times10^{-2}}$$

$$=\frac{2.303}{0.85\times10^{-2}}\log110.15=55.80\text{ min}$$

68. **(c)** From the problem it is evident that

Rate of boiling egg $\propto\frac{1}{\text{time}}=\frac{K}{t}$

or $K=t\times$ rate of boiling

Hence $K_{370}=3\times10^2\times$ rate of boiling
$K_{360}=3\times$ rate of boiling

$$\therefore\quad \frac{K_{370}}{K_{360}}=\frac{3\times10^2}{3}=10^2\text{ or }100$$

69. **(c)** Using Arrhenius equation,

$$K=A.e^{-\frac{E_a}{Rt}},\quad\text{we get}$$

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

$$\therefore\quad \log k_1=\log A-\frac{E_{a(1)}}{2.303RT}\qquad\text{....(i)}$$

$$\text{and}\quad \log k_2=\log A-\frac{E_{a(2)}}{2.303RT}\qquad\text{...(ii)}$$

$$\text{or}\quad \log\frac{k_2}{k_1}=\frac{1}{2.303RT}[E_{a(1)}-E_{a(2)}]$$

(from (i) and (ii))

$$=\frac{1}{2.303\times8.314\times300}(76000-57000)$$

$$\text{or}\quad \log\frac{k_2}{k_1}=\frac{19000}{2.303\times8.314\times300}$$

$$=\frac{190}{6.9\times8.314}$$

or $\frac{k_2}{k_1}=2000$ [taking antilog]

70. **(b)** The order of reaction (n) can be calculated using the relation

$$n=1+\frac{\log[t_{1/2}]_1-\log[t_{1/2}]_2}{\log a_2-\log a_1}$$

Thus

(i) $n=1+\frac{\log3.52-\log1.82}{\log100-\log50}=1.95$

(ii) $n=1+\frac{\log1.82-\log0.93}{\log200-\log100}=1.97$

Thus $n=2$

71. **(b)** It is radioactive decay and so of first order.
For such a reaction

$$k=\frac{2.303}{t_{1/2}}\log\frac{a}{a-\left(\frac{a}{2}\right)}$$

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

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

For the given reaction

$$t_{1/2} = 5600\times365\times24\times60\,\text{min}$$

∴ $$k = \frac{0.693}{5600\times365\times24\times60}\text{min}^{-1}$$

$$= \frac{0.693}{2.95\times10^{9}}\text{min}^{-1} \text{ or } 2.35\times10^{-10}\,\text{min}^{-1}$$

If $-\frac{\Delta n}{\Delta t} = 5\,\text{min}^{-1}$, then using the relation

$\frac{-dn}{dt} = k_1 n$, we get

$$n = \frac{-\left(\frac{\Delta n}{\Delta T}\right)}{k} = \frac{5.00}{2.35\times10^{-10}}\text{atoms}$$

$$= 2.13\times10^{10}\,\text{atoms}$$

B Comprehension Type

1.(c) The reactant C is present in large excess and its concentration during the reaction remains practically constant. So the step 3 may be treated as pseudo first order reaction with respect to E. However, the rate calculated in this way will be slightly larger than the true value because the true concentration of C is reduced slightly.

$[C]$ left $= \frac{0.1}{2} = 0.05$ M; $[E]$ left $= 50.0 - 0.05 = 49.95\,M$

Calculated rate $= k\,[C]\,[E] = k\times0.05\times50\,M\,\text{s}^{-1}$

True rate $= k\times0.05\times49.95\ \text{mol L}^{-1}\text{s}^{-1}$

The difference of the two rates

$$= k\times0.05\,[50-49.95] = k\times0.05\times0.05$$

Percent error $= \frac{k\times0.05\times0.05\times100}{k\times0.05\times49.95} = 0.1$

2.(a) The molecularty of overall reaction is equal to the molecularty of slowest step taking place in the reaction.

3.(d) The rate law equation is determined by the slowest step of the reaction and molecularty of the slowest step is equal to the order of the reaction.

4.(c) Rate of reaction $= \frac{1}{3}\frac{d[C]}{dt}$

$$= \frac{1}{3}\times3.0\times10^{-3} = 1.0\times10^{-3}\ \text{mol L}^{-1}\text{s}^{-1}$$

Rate of disappearance of B = 2 × Rate of reaction

$$= 2\times1.0\times10^{-3}\ \text{mol L}^{-1}\text{s}^{-1}$$

5.(d) The slope of the straight line graph in Fig. 1(a) gives the order

w.r.t. $I_{(g)}$ Slope $= \frac{-1.5-(-3)}{(0.8-0)} = \frac{1.5}{0.8} = 1.9 \approx 2$

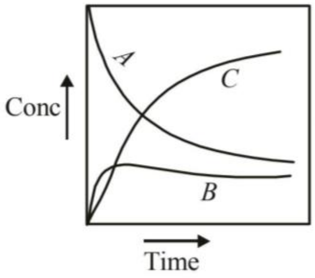
The slope of the straight line in Fig - 2 (a) gives the order

w.r.t. $Ar_{(g)}$ Slope $= \frac{-2-(-3)}{1.0-0} = 1$

Hence, rate $= k[I]^2[Ar]$ (Rate law)

8. **(c)** The concentration of A falls exponentially, whereas the amount of C will rise until it approaches that of A (not of B), thus (a) is incorrect.

The concentration of B will first increase and then it will decrease showing a maxima. (see figure below). Thus (b) is incorrect and (c) is correct.



9. **(c)** For maximum conc. of B;

$$\frac{d}{dt}[B] = 0,$$

Thus the time (t) when conc. of B is maximum is

$$t = \frac{1}{k_1-k_2}\ell n\frac{k_1}{k_2}$$

10. **(a)** We have

$$C_0 = C_1 + C_2 + C_3$$

The rate of disappearance of A is

$$-\frac{dC_1}{dt} = k_1 C_1 \qquad \text{...(i)}$$

Rearranging and integrating the above equation

$$C_1 = C_0 e^{-k_1 t}$$

Since rate of formation of B is given by $k_1.C_1$ and the rate of decomposition of B into C is given by $k_2.C_2$, the rate at which B accumulates in the system is given by

$$\frac{dC_2}{dt} = k_1C_1 - k_2C_2$$

or $$\frac{dC_2}{dt} + k_2C_1 = k_1C_1$$

Putting the values of C_1 from equation (i)

$$\frac{dC_2}{dt} + k_2C_2 = k_1.C_0.e^{-k_1.t}$$

Multiplying both sides by e^{k_2t}, we get

$$e^{k_2.t}.\frac{dC_2}{dt} + e^{k_2.t}.k_2C_2 = k_1.C_0.e^{(k_2-k_1)t}$$

On integration under the condition, $t = 0$ at $C_2 = 0$

$$C_2 = \frac{k_1C_0}{k_2-k_1}[e^{-k_1.t} - e^{-k_2.t}]$$

From this equation values of k_1 and k_2 can be determined.

11. (c) Amount of energy absorbed in 10 min
$= 3.0 \times 10^{16} \times 60 \times 10$ Quanta
Number of molecules reacted in 10 min
$= 0.002 \times 6.023 \times 10^{23}$

$$\therefore \quad \phi = \frac{0.002 \times 6.023 \times 10^{23}}{3.0 \times 10^{16} \times 60 \times 10} = 67$$

12. (b) Energy of 1 mole of photon = $Nh\nu$

$$= \frac{6.02 \times 10^{23} \times 6.6 \times 10^{-34} \times 3 \times 10^8}{330 \times 10^{-9}} \text{ J.} = 3.6 \times 10^5 \text{ J.}$$

Energy absorbed/sec = 7.2×10^{-3} J (given)

$$\therefore \quad \text{Number of moles of photons absorbed/sec} = \frac{7.2 \times 10^{-3}}{3.6 \times 10^5}$$
$$= 2 \times 10^{-8}$$

$$\text{Now, } \phi = \frac{\text{mole of substance reacted in given time}}{\text{moles of photons absorbed in same time}}$$

$$0.3 = \frac{\text{mole of substance reacted}}{2 \times 10^{-8}}$$

or moles of substance reacted/sec $= 0.3 \times 2 \times 10^{-8}$
$= 0.6 \times 10^{-8}$
$= 6 \times 10^{-9}$

Moles of CO formed/sec
= moles of $(CH_3)_2CO$ reacting/sec
$\therefore$ $= 6 \times 10^{-9}$

13. (d) Proceeding as in question 2

$$\therefore \quad 0.6 = \frac{\text{moles of substance reacted}}{2 \times 10^{-8}}$$

Moles of acetone reacted $= 0.6 \times 2 \times 10^{-8}$
$= 1.2 \times 10^{-8}$
$= 12 \times 10^{-9}$

Moles of C_2H_6 formed/sec = moles of acetone reacting/sec
Moles of C_2H_6 formed/sec $= 12 \times 10^{-9}$

C REASONING TYPE

1.(c) Rate of reaction does not remain constant during the complete reaction because rate depends upon the concentration of reactants which decreases with time.

2.(b) For a zero order reaction, $t_{1/2} = [A_0]/2K$.

3.(b) According to Arrhenius equation, $k = Ae^{-E_aRT}$
when $E_a = 0$, $k = A$

4.(a) Reason is the correct explanation of Assertion.

5.(a) $N_2O_5 \xrightarrow{\text{Slow}} NO_2 + NO_3$

$N_2O_5 \xrightarrow{\text{Fast}} 3NO_2 + O_2$

First step is the rate determining step.

6.(a) The negative order with respect to a substance indicates that the rate of reaction decreases as the concentration of that substance increases.

7.(c) The rate of reaction is never negative. Minus sign used in expressing the rate only shows that the concentration of the reactant is decreasing.

8.(a) If a reactant is present in excess, order with respect to that reactant is zero.

9.(a) Rate expression $\frac{dX}{dt} = k[A]^m[B]^n$ shows that the total order of reaction is $m + n + 0 = m + n$

As the rate of reaction is independent of concentration of C, i.e., the order with respect to C is zero. This is the reason that C does not figure in the rate expression.

10.(a) Assertion is correct as for every 10ºC rise in temperature, the specific rate constant, k nearly doubles. (Although it is not correct for all reactions. For some reactions K even gets tripled for 10ºC rise). The statement is clearly true and it explains the assertion, as the rate of collision among the molecules doubles for 10º rise in temperature. So the answer is (a).

11.(b) Both assertion and reason are correct. Reason is not correct explanation of assertion.

12.(d) Assertion is false, reason is true.
The combination of hydrogen and oxygen to form water at ordinary temperature is a slow reaction but it proceeds rapidly in presence of platinum. Thus it is an example of positive catalysis.
Some times the reaction slows down in presence of certain external substance. Such a substance is called a negative catalyst, e.g. the oxidation of sodium sulphite to sodium sulphate by atmospheric oxygen becomes slow in presence of ethyl alcohol.

13.(b) Both assertion and reason are correct. Reason is not the correct explanation of assertion.

D MULTIPLE CORRECT CHOICE TYPE

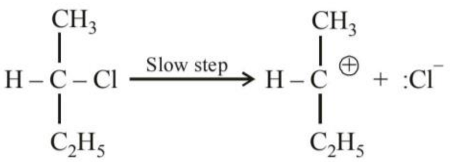
3. **(a,b,c)** In Arrhenius equation $k = Ae^{-E_a/RT}$, $A = k$ when $T \longrightarrow \infty$ and $E_a = 0$

7. **(a,c)** In acid catalysed reaction, the rate constant is directly proportional to the extent of ionization of the acid and hence the strength of the acid.

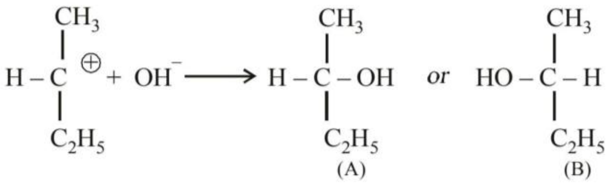
Relative strength of (I)HX and (II)HY

$$= \frac{\alpha_{\text{I}}}{\alpha_{\text{II}}} = \frac{k_{\text{I}}}{k_{\text{II}}} = \frac{3\times10^{-3}}{5\times10^{-3}} = 0.6$$

8. **(c,d)** In case of S_N1 reactions, the rate depends only on the concentration of the substrate, the reaction is first order. The substrate undergoes heterolytic fission forming a carbocation (a slow process)



The carbocation is planar and sp² hybridised. The nucleophile (OH⁻) can attack the planar carbocation from either side.



In case of S_N2 reactions, the rate depends on the concentration of both substrate and the nucleophile. In this case the alkyl halide is attacked by OH⁻ nucleophile from the opposite side of the Cl⁻ atom, a transition state results in which both OH and Cl are partially bonded to carbon atom.

9. **(a,b,c)** (a) For zero order reaction rate remains constant, independent of concentration.

$$\text{Time for 75\% reaction} = \frac{t_{½}}{50} \times 75 = 1.5\, t_{½}$$

(b) For first order reaction time for any fractional change is independent of initial concentration.

(c) For 2nd order reaction, $t = \frac{1}{k}\left[\frac{1}{C} - \frac{1}{C_0}\right]$

$$t_{½} = \frac{1}{k}\left[\frac{1}{C_0/2} - \frac{1}{C_0}\right] = \frac{1}{kC_0};$$

$$t_{¼} = \frac{1}{k}\left[\frac{1}{\frac{3}{4}C_0} - \frac{1}{C_0}\right] = \frac{1}{3kC_0}$$

10. **(a,b,c)** Since $t_{½}$ is independent of initial concentration of sugar, the reaction is first order w.r.t. sugar. The rate increases ten fold on increasing H⁺ ion concentration 10 times (decreasing pH by unity), the reaction is also first order in H⁺ ion.

Since [H⁺] in a particular run remains constant (H⁺ ion being catalyst), the rate is independent of [H⁺]. Hence, rate = k[sugar] (Pseudo first order reaction).

11. **(a,b)** (a) In dilute hexane solution, concentration of both anhydride and ethanol change with the progress of the reaction and the rate depends upon the concentrations of both the reactants.

(b,c) When solvent (ethanol) is also a reactant, its concentration is so large in comparison of anhydride that it remains practically constant. So, the rate does not depend on [ethanol].

(d) The values of k are not the same in the two cases.

12. **(d)** On doubling the volume of the vessel, all the concentrations are halved at that moment.

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k\left(\frac{[A]}{2}\right)^2\left(\frac{[B]}{2}\right)}{k\,[A]^2\,[B]} = \frac{1}{8}$$

13. **(a,b)** Half-life of a reaction will decrease only when rate constant increases. Rate constants of all reactions (endothermic or exothermic) increase on increasing temperature (except the reaction $2NO + O_2 \rightarrow 2NO_2$).

14. **(a, b, c)** The thermal decomposition of HI on gold surface obey first order kinetics and not a zero order reaction.

15. **(b)** In more than one reactant system, the half-life time ($t_{1/2}$) is the time for half of the reactant present in small amount.

For set (1) and (2), B is in small amount and according to rate law, the reaction is of first order w.r.t B. So in these sets the half-life is independent of initial concentration and so the $t_{1/2}$ for set (2) will be same as that for set (1) i.e. 62.6 sec.

In set (3) and (4), A is present in small quantity and $t_{1/2}$ will depend on [A]. According to rate law expression the order w.r.t. A is 2.

$$\therefore\ t_{1/2} = \frac{1}{k.a} = \frac{1}{k[A]_0} \quad \text{or} \quad \frac{(t_{1/2})_3}{(t_{1/2})_4} = \frac{[A_0]_4}{[A_0]_3}$$

$$\text{or} \quad \frac{625}{(t_{1/2})_4} = \frac{10}{5} \text{ or } 2$$

$$\therefore\ (t_{1/2})_4 = \frac{625}{2} = 312.5 \text{ sec.}$$

i.e. $y = 312.5$ sec.

16. **(a, c)** For a zero order reaction the time required for completion of any fraction of change is proportional (not inversely) to initial concentration.

17. **(d)** All other statements are incorrect.

19. **(a, b)** These method can be used for the determination of rate of fast reactions.

E MATRIX-MATCH TYPE

1. **A - s; B - r; C - q; D - p**

(A) 2 moles of gaseous reactant gives 5 moles of gaseous products. Hence, pressure of the reaction system at constant volume and temperature will increase with the progress of the reaction.

(B) With the progress of the reaction, more and more CH_3COOH will be formed and total acid concentration would increase as the reaction proceeds. Hence, kinetics can be followed by titrimetric method.

(C) Volume of N_2 gas (at constant temperature and pressure) will increase with the progress of the reaction.

(D) Dextro rotatory sucrose on hydrolysis gives laevo rotatory equimolar mixture of glucose and fructose. Hence, measurement of optical rotation of the reaction mixture can be used to study the kinetics of the reaction. Optical rotation would decrease with time.

2. **A - q; B - p; C - s; D - r**

(A) At the start of the reaction the acid catalyst is only the acid, concentration of which remains constant throughout. Hence $V_0 \propto [\text{Acid}]_{\text{catalyst}}$

(B) At time t, concentration of acid includes the acid as catalyst and the acid that formed after time t.

(C) $V_\infty \propto \{[\text{Acid}]_{\text{catalyst}} + [\text{Acid}]_{t=\infty}\}$

$V_t \propto \{[\text{Acid}]_{\text{catalyst}} + [\text{Acid}]_{t=t}\}$

$(V_\infty - V_t) \propto \{[\text{Acid}]_{t=\infty} - [\text{Acid}]_{t=t}\} \propto \{[\text{Acid}]$ formed after time t.

(D) From (A) and (C), $(V_\infty - V_0) \propto [\text{Acid}]_{t=\infty}$

4. **A - r; B - s; C - q; D - p**

(A) For zero order reaction, $C = C_0 - kt$

(B) For first order reaction $\log C = \log C_0 - \dfrac{k}{2.303} \times t$

(C) For zero order reaction $= -\dfrac{dc}{dt} = kC^\circ = k$ (constant)

Hence slope of $-\dfrac{dc}{dt} Vs\ C = 0$

(D) For first order reaction $-\dfrac{dc}{dt} = kC$,

$$\log\left(\frac{-dc}{dt}\right) = \log k + \log C.$$

Hence, plot of $\log\left(\dfrac{-dc}{dt}\right)$ against $\log C$ (abscissa) will have slope equal to unity.

5. **A - p, q ; B - r, s ; C - p, q ; D - p, q**

Hydrolysis of an ester is pseudo-first order reaction.
For first order reaction

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

Inversion of cane sugar and decomposition of N_2O_5 also follow first order kinetics.
Saponification of an ester is a second order reaction.
For a second order reaction units of rate constant are litre mol^{-1} sec^{-1}.

F NUMERIC/INTEGER ANSWER TYPE

1. Since $[B] >>> [A]$, $[B]$ remains practically constant and the rate is dependent only on $[A]$. The reaction is pseudo first order w.r.t. A.

$$\text{Rate} = k[A][B] = k[A] \times 5 = 5k[A] = k'[A]$$

$$k' = \frac{2.303}{t}\log\frac{C_o}{C_t} = \frac{2.303}{100}\log\frac{C_o}{C_t}$$

$$\log\frac{C_o}{C_t} = \frac{100\,k'}{2.303} = \frac{100\times 5k}{2.303} = \frac{100\times5\times5\times10^{-3}}{2.303} = 1.0855$$

$$\frac{C_o}{C_t} = 12.17,\ C_t = \frac{C_o}{12.17} = \frac{0.1}{12.17} = 0.008M$$

Hence, concentration of the reactant A remaining after 100 s $=$ **0.008 *M***

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

Since the reaction is second order in A and second order overall, so

$$\frac{-dc}{dt} = k[A]^x[B]^y = k[A]^2 = kC^2$$

$$k = \frac{1}{t}\left[\frac{1}{C} - \frac{1}{C_o}\right]$$

(C_o = inital concentration; C = concentration after time t)

$$t = t_{1/2} = \frac{1}{k}\left[\frac{1}{C_o/2} - \frac{1}{C_o}\right] = \frac{1}{kC_o} = \frac{1}{0.500\times4\times10^{-2}}\text{min}$$

$$= \mathbf{50.0\ min.}$$