CLASS : CC -AD

Revision Work-Sheet Chemical Kinetics

Single correct :

Q.1 For the gaseous phase reaction : $A(g) \rightarrow$ products, **occurring at constant volume** the **correct** relation between $\frac{dC_A}{dt}$, $\frac{dn_A}{dt}$ and $\frac{dP_A}{dt}$ is :

[$C_A \rightarrow$ Concentration of reactant A, $n_A \rightarrow$ Moles of reactant A, $P_A \rightarrow$ Partial pressure of reactant A]

(A) $\frac{dC_A}{dt} = \frac{dn_A}{dt} = \frac{dP_A}{dt}$

(B) $\frac{dC_A}{dt} = \left(\frac{dP_A}{dt}\right)RT = \frac{1}{V}\frac{dn_A}{dt}$

(C) $\frac{dC_A}{dt} = \frac{1}{RT}\frac{dP_A}{dt} = \frac{1}{V}\frac{dn_A}{dt}$

(D) $\frac{dC_A}{dt} = \frac{1}{V}\frac{dn_A}{dt} = \frac{1}{V}\frac{dP_A}{dt}$

Q.2 For a hypothetical reaction,

$A + 3B \longrightarrow P$ $\quad \Delta H = -2x$ kJ/mole of A

& $M \longrightarrow 2Q + R$ $\quad \Delta H = +x$ kJ/mole of M

If these reactions are carried simultaneously in a reactor such that temperature is not changing. If rate of disappearance of B is y M sec^{-1} then rate of formation (in M sec^{-1}) of Q is :

(A) $\frac{2}{3}y$ (B) $\frac{3}{2}y$ (C) $\frac{4}{3}y$ (D) $\frac{3}{4}y$

Q.3 Which of the following statement is incorrect for a photochemical reaction?

(A) Photochemical reactions are complex reactions.

(B) Overall order of photochemical reactions is always zero.

(C) Only the first step of such reactions follows zero order kinetics.

(D) The rate of such reactions depends on the intensity of radiations absorbed.

Q.4 During study of a liquid phase reaction A (aq) $\longrightarrow$ B (aq) + C (aq) the variation in concentration of B with time is given

t/min	0	10	20	30	....	∞
conc. (B) mole/L	0	0.1	0.19	0.271	....	1

The initial rate of reaction was?

(A) 1.76×10^{-4} M sec^{-1}

(B) 2.76×10^{-4} M sec^{-1}

(C) 3.86×10^{-4} M sec^{-1}

(D) 2×10^{-3} M sec^{-1}

Q.5 Reaction $A + B \longrightarrow C + D$ follow's following rate law : rate = $k = [A]^{+\frac{1}{2}}[B]^{\frac{1}{2}}$. Starting with initial conc. of one mole of A and B each, what is the time taken for amount of A of become 0.25 mole. Given $k = 2.31 \times 10^{-3}$ sec^{-1}.

(A) 300 sec. (B) 600 sec. (C) 900 sec. (D) none of these

Q.6 The activation energies of two reactions I and II are E_a and $2E_a$ respectively. If the temperature of the reacting systems is increased from T to T', predict which of the following alternative is correct?(k represent rate constant)

(A) $k'_I / k_I = k'_{II} / k_{II}$ (B) $k'_I / k_I > k'_{II} / k_{II}$ (C) $k'_I / k_I < k'_{II} / k_{II}$ (D) $k'_I / k_I = 2k'_{II} / k_{II}$

Q.7 For the first order reaction $A \longrightarrow B + C$, carried out at 27 ºC if 3.8×10^{-16} % of the reactant molecules exists in the activated state, the E_a (activation energy) of the reaction is [log 3.8 = 0.58]

(A) 12 kJ/mole (B) 831.4 kJ/mole (C) 100 kJ/mole (D) 88.57 kJ/mole

Q.8 Consider the following first order competing reactions:

$X \xrightarrow{k_1} A + B$ and $Y \xrightarrow{k_2} C + D$

if 50% of the reaction of X was completed when 96% of the reaction of Y was completed, the ratio of their rate constants (k_2/k_1) is

(A) 4.06 (B) 0.215 (C) 1.1 (D) 4.65

Q.9 A substance 'A' undergoes conversion by elementary step to 'B' and 'C' in aqueous phase as shown:

$$A_{(aq)} + H_2O \rightarrow B_{(aq)} + C_{(aq)}$$

If concentration of $A_{(aq)}$ initially and after 6.93 min. is 1M & $\frac{1}{4}$ M respectively then calculate rate constant in terms of $M^{-1}\,min^{-1}$.

(A) $\frac{1}{5}$ (B) $\frac{1}{10}$ (C) 3.6×10^{-3} (D) 1.8×10^{-3}

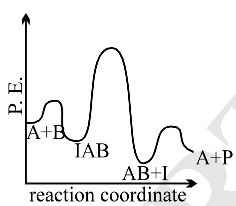
Q.10 The desorption of gas molecules from the adsorbent surface obeys Arrhenius equation. The average time upto which a N_2 molecule may remain adsorbed at Pt- surface at 400 K is
[**Given :** Pre-exponential factor, $A = 1.25 \times 10^8\ s^{-1}$; Activation energy of desorption = 16 Kcal ; $e^{20} = 5 \times 10^8$]

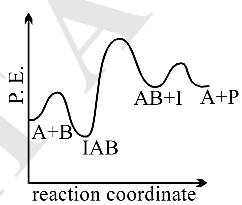
(A) 0.25 sec (B) 4 sec (C) 8 sec (D) 0.125 sec

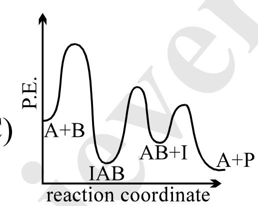
Q.11 The following mechanism has been proposed for the exothermic catalyzed complex reaction.

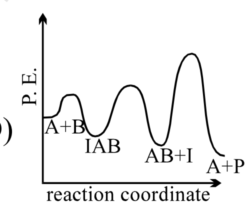
$$A + B \underset{}{\overset{fast}{\rightleftharpoons}} IAB \xrightarrow{k_1} AB + I \xrightarrow{k_2} P + A$$

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

(A) 

(B) 

(C) 

(D) 

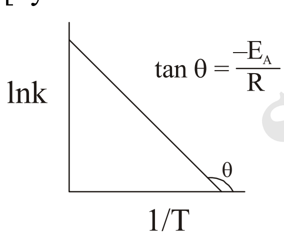
Q.12 For a two step reaction.

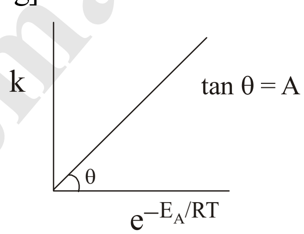
$A \rightleftharpoons R + B$ $R + C \xrightarrow{k_2} P$

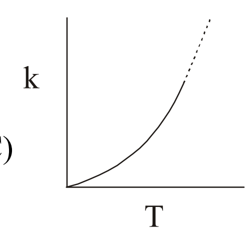
(Where, R is a reactive intermediate whose concentration is maintained at some low steady state throughout the reaction). If the concentration of C is very high then the order of reaction for formation of "P" is

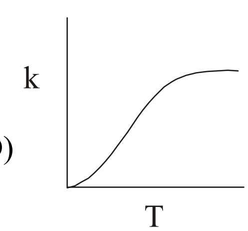
(A) 2 (B) 0 (C) 1 (D) 1/2 (E) 3

Q.13 Which of the following graphs is **incorrect** regarding rate constant (k) and absolute temperature? [Symbols have usual meaning]

(A) 

(B) 

(C) 

(D) 

Q.14 A substance undergoes a series of chemical reaction as shown

$A \xrightarrow{K_1} B \xrightarrow{K_2} C \xrightarrow{K_3} D$ with rate constant $K_1 = \frac{\ln 2}{2000}\ sec^{-1}$, $K_2 = \frac{\ln 2}{10}\ sec^{-1}$,

$K_3 = 20 \ln 2\ sec^{-1}$. What will be the value of $\frac{[A]}{[C]}$ once steady state is obtained.

{[ ] represents concentration}

(A) 40000 (B) 20000 (C) 200 (D) 400

Comprehension :

Paragraph for question nos. 15 to 17

Methane is an important green house gas since it absorbs infra-red radiations. In order to calculate its concentration in the atmosphere one needs to know the processes that release methane into the atmosphere and what happens to it in atmosphere.

While it is produced from a variety of natural and human related sources, it is mainly consumed by reaction with hydroxyl radical which is a **simple elementary reaction**

$$CH_4 + {}^{\bullet}OH \rightarrow CH_3^{\bullet} + H_2O$$ with a rate constant equal to $\mathbf{4 \times 10^6\ M^{-1}\ sec^{-1}}$.

It is also known that in atmosphere ${}^{\bullet}OH$ radicals are constantly produced and removed and so its concentration is **approximately constant** and is equal to $\mathbf{1 \times 10^{-15}\ M}$.

Similar to methane isoprene is also released in significant amount and has absorbing power. It is also removed in a similar manner with a rate constant equal to $\mathbf{2 \times 10^{11}\ M^{-1}\ sec^{-1}}$.

Also, the average life time of a reactant following **first order** kinetics is $\mathbf{t_{avg} = 1/K}$.

Using this information answer the question that follow.

Q.15 The average life time of methane in the atmosphere, is

(A) 250 sec (B) 25×10^7 sec (C) 10^{15} sec (D) 50 sec

Q.16 Which of the following gaseous molecules will travel to a longer distance in atmosphere.

(A) CH_4 (B) Isoprene

(C) Both will travel equally (D) Cannot be decided from the given data

Q.17 Methane is a better green house gas than isoprene because :

(A) CH_4 does not undergo any reaction where as isoprene undergoes chemical reaction.

(B) CH_4 is produced in a very large amount where as isoprene is produced in negligible amount.

(C) On an average CH_4 remains in atmosphere for a greater time as compared to isoprene.

(D) Isoprene does not absorb any infra-red radiation.

More than one may be correct :

Q.18 α-maltose ($C_{12}H_{22}O_{11}$) can be hydrolysed to glucose ($C_6H_{12}O_6$) according to the following reaction:

$$C_{12}H_{22}O_{11}(aq) + H_2O(\ell) \longrightarrow 2\,C_6H_{12}O_6(aq)$$

Given:

Standard enthalpies of formation of $C_{12}H_{22}O_{11}$ (aq) = –2238 kJ / mol

Standard enthalpies of formation of H_2O (ℓ) = –285 kJ / mol

Standard enthalpies of formation of $C_6H_{12}O_6$ (aq)= –1263 kJ / mol

Time (min.)	0	50	100
Conc. of α – maltose (M)	4.0	1.0	0.25

Which of the following statement(s) is / are true?

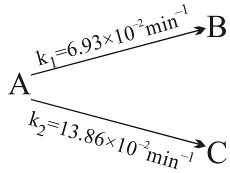
(A) The hydrolysis of α-maltose is exothermic

(B) Heat liberated in combustion of 1.0 mol of α-maltose is greater than the heat liberated in combustion of 2.0 mol of glucose.

(C) Increasing temperature will increase the degree of hydrolysis of α-maltose.

(D) The hydrolysis of α-maltose follow 1st order kinetics.

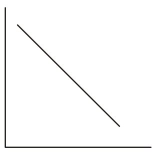
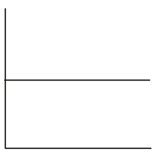
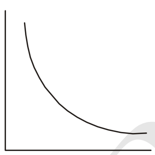
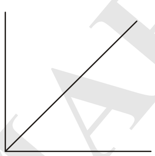
Q.19 Consider the reaction,



A, B and C all are optically active compound . If optical rotation per unit concentration of A, B and C are 60°, –72°, 42° and initial concentration of A is 2 M then select write statement(s).
(A) Solution will be optically active and dextro after very long time
(B) Solution will be optically active and levo after very long time
(C) Half life of reaction is 15 min
(D) After 75% conversion of A into B and C angle of rotation of solution will be 36°.

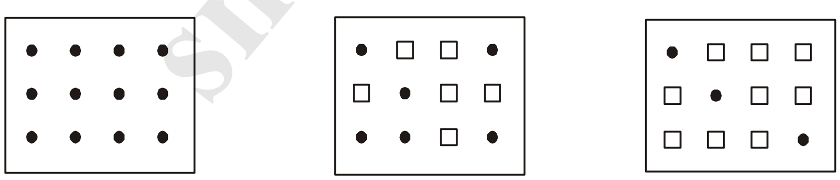
Match the Column

Q.20 **Column-I** and **column-II**. Entry of column-I are to be matched with **ONE OR MORE THAN ONE ENTRIES** of column-II and vice versa.

Column I **(Graphs reaction A→ Products)**		**Column II** **(Co-ordinates)**
(A) 	(P)	ln [A] (y-axis), t (x-axis) (order = 1)
(B) 	(Q)	$t_{1/2}$ (y-axis), $[A_0]$ (x-axis) (order = 1)
(C) 	(R)	r (y-axis), t (x-axis) (order = 0)
(D) 	(S)	$t_{1/2}$ (y-axis), $[A_0]$ (x-axis) (order > 1)
	(T)	r (y-axis), [A] (x-axis) (order = 1)

Subjective

Q.21 The following pictures represents the progress of the reaction : $A \rightarrow B$, where the circles represents moles of A and the squares represents moles of B. If the order of reaction is 'a' and the initial half life of the reaction **(in min)** is **'bcd'**, then the value of **'bcda'** is :


t = 0 t = 2 hrs t = 6 hrs

Q.22 $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

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

Assuming ideal gas condition. Calculate

(a) Order of reaction (b) Rate constant

(c) Time taken for 75% completion of reaction (d) Total pressure when $P_X = 700$ mm.

Q.23 A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as $CH_3OCH_3(g) \xrightarrow{1^{st}\text{ order}} CH_4(g) + CO(g) + H_2(g)$. The half life of decomposition is 175 min. Calculate the ratio of initial rate of diffusion to rate of diffusion after 350 min. of initiation of decomposition.

Given : $\sqrt{\dfrac{18.4}{46}} = \sqrt{0.4}$

Q.24 For the following first order gaseous reaction : $A(g) \xrightarrow{k_1} 2B(g)$; $A(g) \xrightarrow{k_2} C(g)$

The initial pressure in a container of capacity V litres is 1 atm. Pressure at time t = 10 sec is 1.4 atm and after infinite time it becomes 1.5 atmosphere. Find the rate constant k_1 and k_2 for the appropriate reactions. Assume initially only A is present.

Q.25 For the two parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, show that the activation energy E' for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by

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

Q.26 $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

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

Assuming ideal gas condition. Calculate

(a) Order of reaction (b) Rate constant

(c) Time taken for 75% completion of reaction (d) Total pressure when $P_X = 700$ mm.

Q.27 For the reaction: $A + B \rightarrow$ product

rate law is

rate = $k[A]^2 [B]$

where $k = 5 \times 10^{-5}$ (mol/lit)$^{-2}$ min^{-1}

Determine the **time (in minutes)** in which concentration of **'A'** becomes half of its initial concentration. If initial concentration of A and B are 0.2 M and 2×10^3 M respectively.

Q.28 0.01 moles of sulphuryl chloride $SO_2Cl_2(g)$ is taken in a sealed tube & heated to 400 K. It decomposes following 1st order kinetics according to reaction :

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

The tube is broken after 4 hours & gas passed through a 25 ml of an acidified 1 N iodine solution where all SO_2 is oxidised to SO_4^{2-}. The resulting solution required 10 ml of 1M Hypo solution. What is half life in hours.

REVISION FLOW CHART

CHEMICAL KINETICS

↓

Some basic concept

↓

1.Rate of reaction.
2.Average and instantaneous rate of reaction.
3.Rate law expression.
4.Order and molecularity of reaction.

↓

CHEMICAL KINETICS

Experimental Aspects

↓

1.Determination of order of reaction.
(a) Graphical method. (G)
(b) Initial rate method. (N)
(c) Half life method. (N)
2. Differential and integerated expressions for
(a) Zero order (N)
(b) First order (N)
(c) nth order reaction (N)
(d) $t_{1/2}$ of a reaction. (N+T)
(e) Rate constant expression in which conc. terms is replaced by other variables litre pressure, volume of reagent etc. (N)
(f) Parallel reaction (N)
(g) Consecutive or sequential reaction (N)
(h) Reversible reaction (N)

Theoretical Aspects

↓

1. Temperature depedence of rate of reaction (N)
2.Collision theory of rate of reaction (T)
3. Mechanism of reaction (T+N) and steady state approximation

(G) → represents topic of graphical importance

(T) → represents topic of theoretical importance

(N) → represents topic of numerical importance

LIST OF IMPORTANT FORMULAS

Characteristics of zero order reactions:

(i) Concentration of reactant decreases linearly with time.

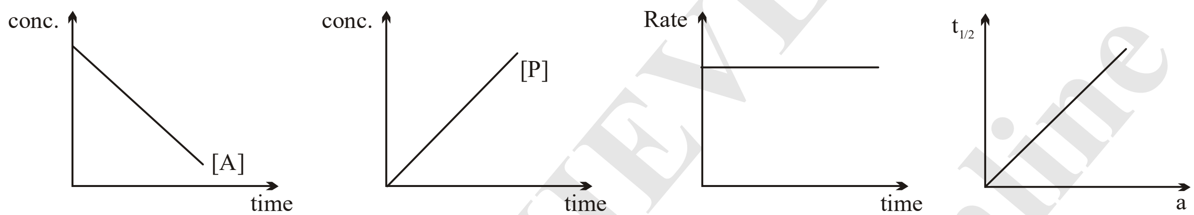
(ii) Units of k are **mol l^{-1} time^{-1}**.

(iii) Time required for the 100% completion of reaction is $\frac{[A]_0}{k}$

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

(v) Zero order reaction must be complex reaction

(vi) Graph related with zero order reactions.



Another term average life is defined as $\lambda = \frac{\int_0^{t_c} (dA) \times t}{A_0}$ where dA represent change in concentration in time t and t_c is time of completion.

FIRST ORDER REACTIONS

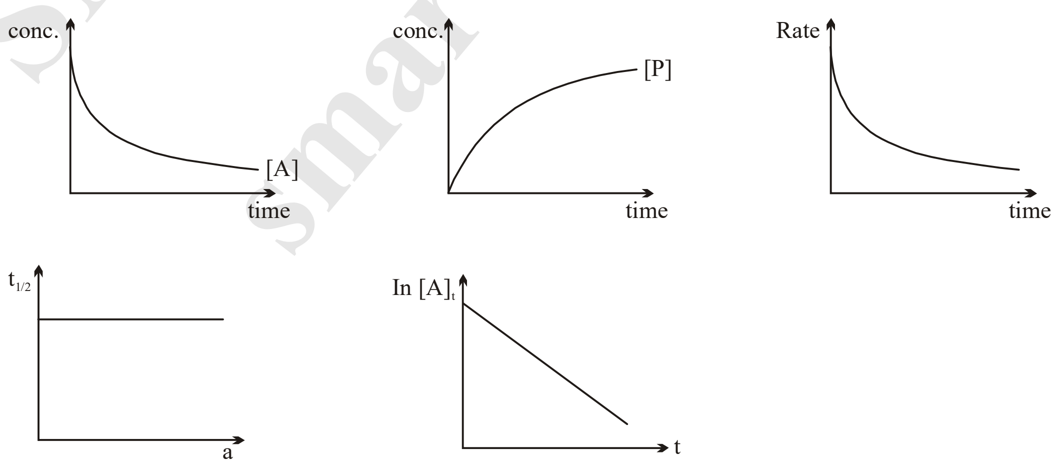
Characteristics of First Order Reaction :

(i) Unit of rate constant is time^{-1}.

(ii) $t_{1/2} = \frac{0.693}{k}$ (Half-life)

(iii) **log (a – x)** v/s **t** is a straight line with slope $-\frac{k}{2.303}$.

(iv) Graph related with first order reactions.



SECOND ORDER REACTION :

Integrated rate equation $k = \frac{1}{t}.\frac{x}{a(a-x)}$ or $kt = \frac{1}{a-x} - \frac{1}{a}$.

(For reaction nA $\rightarrow$ Products)

Integrated rate equation $k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

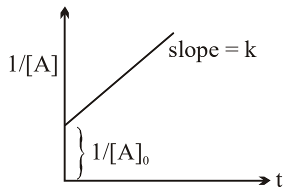
(For reaction A + B $\rightarrow$ Products)

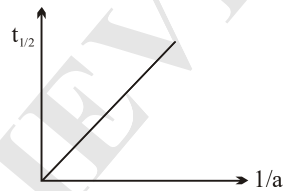
Characteristics of Second Order Reaction :

(i) Unit of rate constant L mol^{-1} $time^{-1}$.

(ii) $t_{1/2} \propto a^{-1}$ (In general $t_{1/2} \propto a^{(1-n)}$; n = order of reactions).

(iii) 2^{nd} order reaction conforms to first order when one of the reactant is in excess.

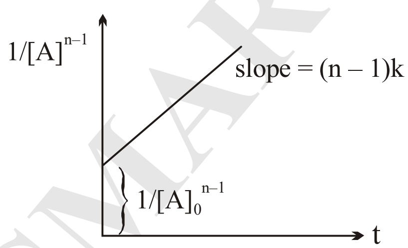


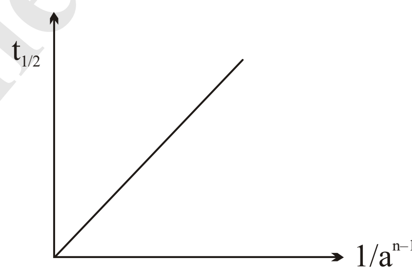


n^{th} ORDER REACTION

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

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



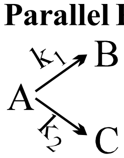


DEPENDENCE OF HALF LIFE ON INITIAL CONCENTRATION

$$n = 1 + \frac{\log(t_{1/2})_2 - \log(t_{1/2})_1}{\log(a_0)_1 - \log(a_0)_2}$$

MISCELLENEOUS REACTIONS

(i) **Parallel Reactions**



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

$$[A] = [A_0]\,e^{-kt} \qquad [B] = \frac{k_1[A_0]}{k_1+k_2}(1-e^{-kt}) \qquad [C] = \frac{k_2[A_0]}{k_1+k_2}(1-e^{-kt})$$

where $k = k_1 + k_2$ {Initial concentration of [B] and [C] is taken zero}

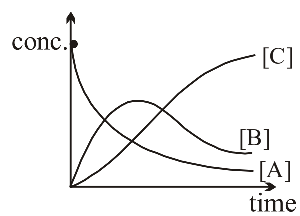
(ii) **Consecutive Reaction**

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

{at t = 0 $[A] = [A_0]$, $[B] = 0$, $[C] = 0$}

$$[A]_t = [A]_0 e^{-k_1 t}\ ,\ [B]_t = \frac{k_1[A]_0}{(k_2-k_1)}\left[e^{-k_1 t} - e^{-k_2 t}\right]\ ,\ \ [C]_t = [A_0] - ([A]_t + [B]_t)$$

$$t_{max} = \frac{1}{(k_1-k_2)}\,ln\left(\frac{k_1}{k_2}\right); \qquad [B]_{max} = [A_0].\left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2-k_1}}$$



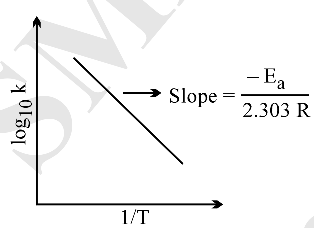
(iii) **Reversible reaction**

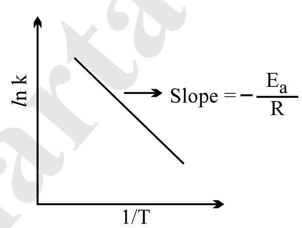
$$ln\left(\frac{x_{eq}}{x_{eq}-x}\right) = (k_f + k_b)\,t \qquad ; \qquad \frac{x_{eq}}{a - x_{eq}} = \frac{k_f}{k_b}$$

Arrhenius Equation :

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

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





Rate = Collision frequency × fraction of effective collision
= Collision frequency × fraction of collisions with sufficient energy × fraction of molecules in proper orientation

or , $r = (Z_{11} \text{ or } Z_{12}) \times e^{-E_a/RT} \times P$

$k = A\,.\,e^{-E_a/RT}$

LAST MOMENT REVIEW

CHEMICAL KINETICS

Theory : ....

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Exercise - 1 : Question ....

Exercise - 2 : Question ....

Exercise - 3 : Question ....

Exercise - 4 : Question ....

DPPs : ....

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Other Sources : ....

....

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Revision Work-Sheet Chemical Kinetics

Single correct :

Q.1 For the gaseous phase reaction : A(g) $\rightarrow$ products, **occurring at constant volume** the **correct** relation between $\frac{dC_A}{dt}$, $\frac{dn_A}{dt}$ and $\frac{dP_A}{dt}$ is :

[$C_A \rightarrow$ Concentration of reactant A, $n_A \rightarrow$ Moles of reactant A, $P_A \rightarrow$ Partial pressure of reactant A]

(A) $\frac{dC_A}{dt} = \frac{dn_A}{dt} = \frac{dP_A}{dt}$

(B) $\frac{dC_A}{dt} = \left(\frac{dP_A}{dt}\right)RT = \frac{1}{V}\frac{dn_A}{dt}$

(C*) $\frac{dC_A}{dt} = \frac{1}{RT}\frac{dP_A}{dt} = \frac{1}{V}\frac{dn_A}{dt}$

(D) $\frac{dC_A}{dt} = \frac{1}{V}\frac{dn_A}{dt} = \frac{1}{V}\frac{dP_A}{dt}$

Q.2 For a hypothetical reaction,

$A + 3B \longrightarrow P$ $\quad \Delta H = -2x$ kJ/mole of A

& $M \longrightarrow 2Q + R$ $\quad \Delta H = +x$ kJ/mole of M

If these reactions are carried simultaneously in a reactor such that temperature is not changing. If rate of disappearance of B is y M sec^{-1} then rate of formation (in M sec^{-1}) of Q is :

(A) $\frac{2}{3}y$ (B) $\frac{3}{2}y$ (C*) $\frac{4}{3}y$ (D) $\frac{3}{4}y$

Q.3 Which of the following statement is incorrect for a photochemical reaction?

(A) Photochemical reactions are complex reactions.

(B*) Overall order of photochemical reactions is always zero.

(C) Only the first step of such reactions follows zero order kinetics.

(D) The rate of such reactions depends on the intensity of radiations absorbed.

Q.4 During study of a liquid phase reaction A (aq) $\longrightarrow$ B (aq) + C (aq) the variation in concentration of B with time is given

t/min	0	10	20	30	....	∞
conc. (B) mole/L	0	0.1	0.19	0.271	....	1

The initial rate of reaction was?

(A*) 1.76×10^{-4} M sec^{-1} (B) 2.76×10^{-4} M sec^{-1}

(C) 3.86×10^{-4} M sec^{-1} (D) 2×10^{-3} M sec^{-1}

Q.5 Reaction A + B $\longrightarrow$ C + D follow's following rate law : rate = $k = [A]^{+\frac{1}{2}}[B]^{\frac{1}{2}}$. Starting with initial conc. of one mole of A and B each, what is the time taken for amount of A of become 0.25 mole. Given $k = 2.31 \times 10^{-3}$ sec^{-1}.

(A) 300 sec. (B*) 600 sec. (C) 900 sec. (D) none of these

Q.6 The activation energies of two reactions I and II are E_a and $2E_a$ respectively. If the temperature of the reacting systems is increased from T to T', predict which of the following alternative is correct?(k represent rate constant)

(A) $k_I'/k_I = k_{II}'/k_{II}$ (B) $k_I'/k_I > k_{II}'/k_{II}$ (C*) $k_I'/k_I < k_{II}'/k_{II}$ (D) $k_I'/k_I = 2k_{II}'/k_{II}$

Q.7 For the first order reaction $A \longrightarrow B + C$, carried out at 27 ºC if 3.8×10^{-16} % of the reactant molecules exists in the activated state, the E_a (activation energy) of the reaction is [log 3.8 = 0.58]
(A) 12 kJ/mole (B) 831.4 kJ/mole
(C*) 100 kJ/mole (D) 88.57 kJ/mole

Q.8 Consider the following first order competing reactions:

$X \xrightarrow{k_1} A + B$ and $Y \xrightarrow{k_2} C + D$

if 50% of the reaction of X was completed when 96% of the reaction of Y was completed, the ratio of their rate constants (k_2/k_1) is
(A) 4.06 (B) 0.215 (C) 1.1 (D*) 4.65

Q.9 A substance 'A' undergoes conversion by elementary step to 'B' and 'C' in aqueous phase as shown:

$$A_{(aq)} + H_2O \rightarrow B_{(aq)} + C_{(aq)}$$

If concentration of $A_{(aq)}$ initially and after 6.93 min. is 1M & $\frac{1}{4}$ M respectively then calculate rate constant in terms of $M^{-1}\,min^{-1}$.

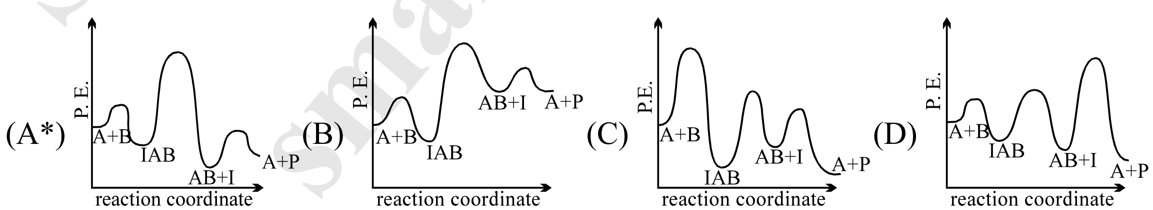
(A) $\frac{1}{5}$ (B) $\frac{1}{10}$ (C*) 3.6×10^{-3} (D) 1.8×10^{-3}

Q.10 The desorption of gas molecules from the adsorbent surface obeys Arrhenius equation. The average time upto which a N_2 molecule may remain adsorbed at Pt- surface at 400 K is
[**Given :** Pre-exponential factor, $A = 1.25 \times 10^8\ s^{-1}$; Activation energy of desorption = 16 Kcal ; $e^{20} = 5 \times 10^8$]
(A) 0.25 sec (B*) 4 sec (C) 8 sec (D) 0.125 sec

Q.11 The following mechanism has been proposed for the exothermic catalyzed complex reaction.

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

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

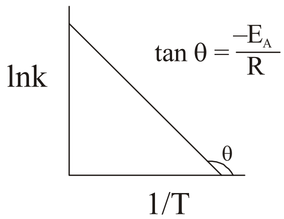


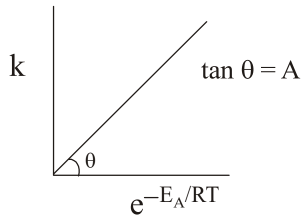
Q.12 For a two step reaction.

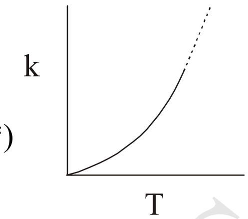
$A \rightleftharpoons R + B$ $R + C \xrightarrow{k_2} P$

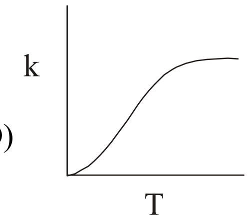
(Where, R is a reactive intermediate whose concentration is maintained at some low steady state throughout the reaction). If the concentration of C is very high then the order of reaction for formation of "P" is
(A) 2 (B) 0 (C*) 1 (D) 1/2 (E) 3

Q.13 Which of the following graphs is **incorrect** regarding rate constant (k) and absolute temperature? [Symbols have usual meaning]

(A) 

(B) 

(C*) 

(D) 

Q.14 A substance undergoes a series of chemical reaction as shown

$A \xrightarrow{K_1} B \xrightarrow{K_2} C \xrightarrow{K_3} D$ with rate constant $K_1 = \dfrac{\ln 2}{2000}\ \text{sec}^{-1}$, $K_2 = \dfrac{\ln 2}{10}\ \text{sec}^{-1}$,

$K_3 = 20 \ln 2\ \text{sec}^{-1}$. What will be the value of $\dfrac{[A]}{[C]}$ once steady state is obtained.

{[ ] represents concentration}

(A*) 40000 (B) 20000 (C) 200 (D) 400

Comprehension :

Paragraph for question nos. 15 to 17

Methane is an important green house gas since it absorbs infra-red radiations. In order to calculate its concentration in the atmosphere one needs to know the processes that release methane into the atmosphere and what happens to it in atmosphere.

While it is produced from a variety of natural and human related sources, it is mainly consumed by reaction with hydroxyl radical which is a **simple elementary reaction**

$$CH_4 + {}^{\bullet}OH \rightarrow CH_3^{\bullet} + H_2O$$ with a rate constant equal to $\mathbf{4 \times 10^{6}\ M^{-1}\ sec^{-1}}$.

It is also known that in atmosphere ${}^{\bullet}OH$ radicals are constantly produced and removed and so its concentration is **approximately constant** and is equal to $\mathbf{1 \times 10^{-15}\ M}$.

Similar to methane isoprene is also released in significant amount and has absorbing power. It is also removed in a similar manner with a rate constant equal to $\mathbf{2 \times 10^{11}\ M^{-1}\ sec^{-1}}$.

Also, the average life time of a reactant following **first order** kinetics is $\mathbf{t_{avg} = 1/K}$.

Using this information answer the question that follow.

Q.15 The average life time of methane in the atmosphere, is

(A) 250 sec (B*) 25×10^{7} sec (C) 10^{15} sec (D) 50 sec

Q.16 Which of the following gaseous molecules will travel to a longer distance in atmosphere.

(A*) CH_4 (B) Isoprene
(C) Both will travel equally (D) Cannot be decided from the given data

Q.17 Methane is a better green house gas than isoprene because :

(A) CH_4 does not undergo any reaction where as isoprene undergoes chemical reaction.
(B) CH_4 is produced in a very large amount where as isoprene is produced in negligible amount.
(C*) On an average CH_4 remains in atmosphere for a greater time as compared to isoprene.
(D) Isoprene does not absorb any infra-red radiation.

More than one may be correct :

Q.18 α-maltose ($C_{12}H_{22}O_{11}$) can be hydrolysed to glucose ($C_6H_{12}O_6$) according to the following reaction:

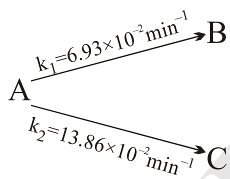
$$C_{12}H_{22}O_{11}(aq) + H_2O\ (\ell) \longrightarrow 2\ C_6H_{12}O_6\ (aq)$$

Given:

Standard enthalpies of formation of $C_{12}H_{22}O_{11}$ (aq) = –2238 kJ / mol
Standard enthalpies of formation of H_2O (ℓ) = –285 kJ / mol
Standard enthalpies of formation of $C_6H_{12}O_6$ (aq)= –1263 kJ / mol

Time (min.)	0	50	100
Conc. of α – maltose (M)	4.0	1.0	0.25

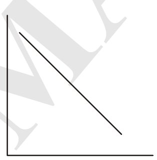
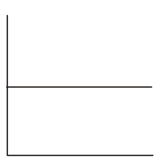
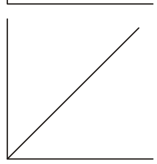
Which of the following statement(s) is / are true?
(A*) The hydrolysis of α-maltose is exothermic
(B*) Heat liberated in combustion of 1.0 mol of α-maltose is greater than the heat liberated in combustion of 2.0 mol of glucose.
(C) Increasing temperature will increase the degree of hydrolysis of α-maltose.
(D*) The hydrolysis of α-maltose follow 1st order kinetics.

Q.19 Consider the reaction, 

A, B and C all are optically active compound . If optical rotation per unit concentration of A, B and C are 60°, –72°, 42° and initial concentration of A is 2 M then select write statement(s).
(A*) Solution will be optically active and dextro after very long time
(B) Solution will be optically active and levo after very long time
(C) Half life of reaction is 15 min
(D*) After 75% conversion of A into B and C angle of rotation of solution will be 36°.

Match the Column

Q.20 **Column-I** and **column-II**. Entry of column-I are to be matched with **ONE OR MORE THAN ONE ENTRIES** of column-II and vice versa.

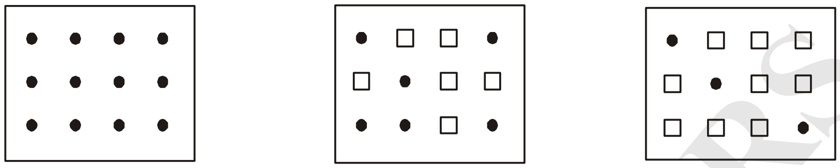
Column I (Graphs reaction A→ Products)		**Column II** (Co-ordinates)
(A)		(P) ln [A] (y-axis), t (x-axis) (order = 1)
(B)		(Q) $t_{1/2}$ (y-axis), [A_0] (x-axis) (order = 1)
(C)		(R) r (y-axis), t (x-axis) (order = 0)
(D)		(S) $t_{1/2}$ (y-axis), [A_0] (x-axis) (order > 1)

(T) r (y-axis), [A] (x-axis) (order = 1)

[Ans.(A) P (B) Q,R (C) S (D) T]

Subjective

Q.21 The following pictures represents the progress of the reaction : $A \rightarrow B$, where the circles represents moles of A and the squares represents moles of B. If the order of reaction is 'a' and the initial half life of the reaction **(in min)** is **'bcd'**, then the value of **'bcda'** is :



t = 0 t = 2 hrs t = 6 hrs

[Ans. 1202 or 0240]

Q.22 $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

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

Assuming ideal gas condition. Calculate

(a) Order of reaction (b) Rate constant

(c) Time taken for 75% completion of reaction (d) Total pressure when $P_X = 700$ mm.

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

Q.23 A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as $CH_3OCH_3(g) \xrightarrow{1^{st} \text{ order}} CH_4(g) + CO(g) + H_2(g)$. The half life of decomposition is 175 min. Calculate the ratio of initial rate of diffusion to rate of diffusion after 350 min. of initiation of decomposition.

Given : $\sqrt{\dfrac{18.4}{46}} = \sqrt{0.4}$

Ans. $(0.4)^{3/2} = 0.253$

Q.24 For the following first order gaseous reaction : $A(g) \begin{cases} \xrightarrow{k_1} 2B(g) \\ \xrightarrow{k_2} C(g) \end{cases}$

The initial pressure in a container of capacity V litres is 1 atm. Pressure at time t = 10 sec is 1.4 atm and after infinite time it becomes 1.5 atmosphere. Find the rate constant k_1 and k_2 for the appropriate reactions. Assume initially only A is present.

Ans. 0.0805

Q.25 For the two parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, show that the activation energy E′ for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by

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

Q.26 $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

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

Assuming ideal gas condition. Calculate

(a) Order of reaction (b) Rate constant

(c) Time taken for 75% completion of reaction (d) Total pressure when $P_X = 700$ mm.

[Ans. (a) 1, (b) $6.93 \times 10^{-3}\ min^{-1}$, (c) 200, (d) 950 mm**]**

Q.27 For the reaction: $A + B \rightarrow$ product

rate law is

rate = $k[A]^2 [B]$

where $k = 5 \times 10^{-5}\ (mol/lit)^{-2}\ min^{-1}$

Determine the **time (in minutes)** in which concentration of **'A'** becomes half of its initial concentration. If initial concentration of A and B are 0.2 M and 2×10^3 M respectively. [Ans. 0050.00]

Q.28 0.01 moles of sulphuryl chloride $SO_2Cl_2(g)$ is taken in a sealed tube & heated to 400 K. It decomposes following 1st order kinetics according to reaction :

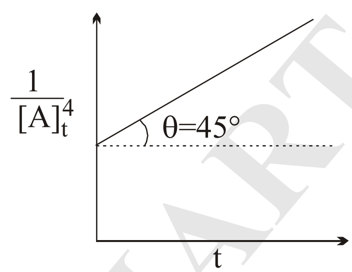
$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

The tube is broken after 4 hours & gas passed through a 25 ml of an acidified 1 N iodine solution where all SO_2 is oxidised to SO_4^{2-}. The resulting solution required 10 ml of 1M Hypo solution. What is half life in hours. [Ans. 2]

Q.29 A catalyst changes the activation energy of a first order reaction by 0.693 Kcal without affecting Arhenius parameter. If its half life without catalyst is 6 min at 500K. What will be time **(in min)** for 75% completion in presence of catalyst at same temperature. [Ans. 0006]

Q.30 For the reaction

$2A \rightarrow 3B$, following graph was obtained.



where $[A]_t$ is concentration of A at a time t. [in M] & t is in sec.

From the graph calculate rate of reaction **M sec^{-1}** at a concentration of [A] = 2 M.

[Ans. 4]

REVISION FLOW CHART

CHEMICAL KINETICS

↓

Some basic concept

↓

1. Rate of reaction.
2. Average and instantaneous rate of reaction.
3. Rate law expression.
4. Order and molecularity of reaction.

↓

CHEMICAL KINETICS

Experimental Aspects

↓

1. Determination of order of reaction.
   - (a) Graphical method. (G)
   - (b) Initial rate method. (N)
   - (c) Half life method. (N)
2. Differential and integerated expressions for
   - (a) Zero order (N)
   - (b) First order (N)
   - (c) nth order reaction (N)
   - (d) $t_{1/2}$ of a reaction. (N+T)
   - (e) Rate constant expression in which conc. terms is replaced by other variables litre pressure, volume of reagent etc. (N)
   - (f) Parallel reaction (N)
   - (g) Consecutive or sequential reaction (N)
   - (h) Reversible reaction (N)

Theoretical Aspects

↓

1. Temperature depedence of rate of reaction (N)
2. Collision theory of rate of reaction (T)
3. Mechanism of reaction (T+N) and steady state approximation

(G) → represents topic of graphical importance

(T) → represents topic of theoretical importance

(N) → represents topic of numerical importance

LIST OF IMPORTANT FORMULAS

Characteristics of zero order reactions:

(i) Concentration of reactant decreases linearly with time.

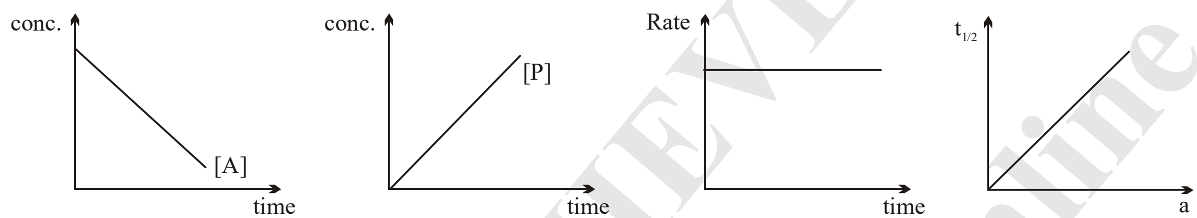
(ii) Units of k are **mol l^{-1} time^{-1}**.

(iii) Time required for the 100% completion of reaction is $\frac{[A]_0}{k}$

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

(v) Zero order reaction must be complex reaction

(vi) Graph related with zero order reactions.



Another term average life is defined as $\lambda = \frac{\int_0^{t_c} (dA) \times t}{A_0}$ where dA represent change in concentration in time t and t_c is time of completion.

FIRST ORDER REACTIONS

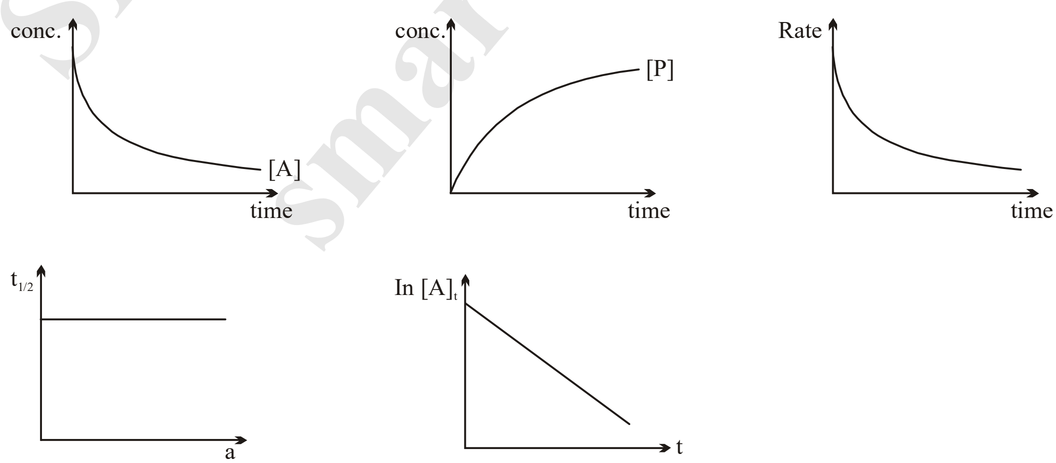
Characteristics of First Order Reaction :

(i) Unit of rate constant is time^{-1}.

(ii) $t_{1/2} = \frac{0.693}{k}$ (Half-life)

(iii) **log (a – x)** v/s **t** is a straight line with slope $-\frac{k}{2.303}$.

(iv) Graph related with first order reactions.



SECOND ORDER REACTION :

Integrated rate equation $k = \frac{1}{t}.\frac{x}{a(a-x)}$ or $kt = \frac{1}{a-x} - \frac{1}{a}$.

(For reaction $nA \rightarrow$ Products)

Integrated rate equation $k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

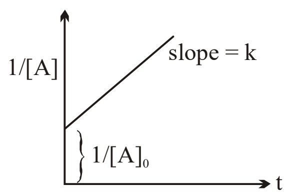
(For reaction $A + B \rightarrow$ Products)

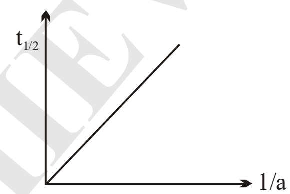
Characteristics of Second Order Reaction :

(i) Unit of rate constant L mol^{-1} $time^{-1}$.

(ii) $t_{1/2} \propto a^{-1}$ (In general $t_{1/2} \propto a^{(1-n)}$; n = order of reactions).

(iii) 2^{nd} order reaction conforms to first order when one of the reactant is in excess.

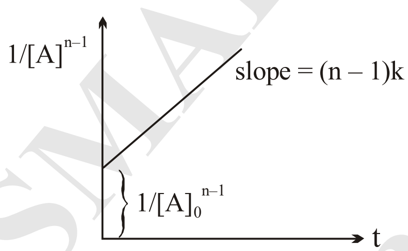


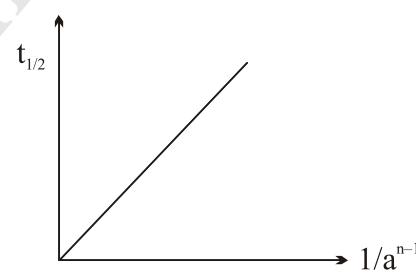


nth ORDER REACTION

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

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



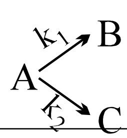


DEPENDENCE OF HALF LIFE ON INITIAL CONCENTRATION

$$n = 1 + \frac{\log(t_{1/2})_2 - \log(t_{1/2})_1}{\log(a_0)_1 - \log(a_0)_2}$$

MISCELLENEOUS REACTIONS

(i) **Parallel Reactions**



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

$[A] = [A_0]\, e^{-kt}$ $\qquad [B] = \dfrac{k_1[A_0]}{k_1+k_2}(1-e^{-kt})$ $\qquad [C] = \dfrac{k_2[A_0]}{k_1+k_2}(1-e^{-kt})$

where $k = k_1 + k_2$

{Initial concentration of [B] and [C] is taken zero}

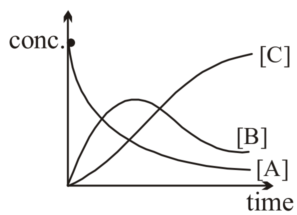
(ii) **Consecutive Reaction**

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

{at t = 0 $[A] = [A_0]$, $[B] = 0$, $[C] = 0$}

$[A]_t = [A]_0 e^{-k_1 t}$, $[B]_t = \dfrac{k_1[A]_0}{(k_2-k_1)}\left[e^{-k_1 t} - e^{-k_2 t}\right]$, $[C]_t = [A_0] - ([A]_t + [B]_t)$

$$t_{max} = \frac{1}{(k_1-k_2)}\, ln\left(\frac{k_1}{k_2}\right) \quad ; \quad [B]_{max} = [A_0].\left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2-k_1}}$$



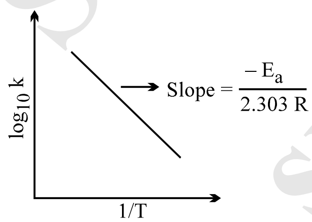
(iii) **Reversible reaction**

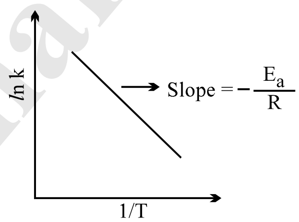
$$ln\left(\frac{x_{eq}}{x_{eq}-x}\right) = (k_f + k_b)\,t \quad ; \quad \frac{x_{eq}}{a-x_{eq}} = \frac{k_f}{k_b}$$

Arrhenius Equation :

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

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





Rate = Collision frequency × fraction of effective collision

= Collision frequency × fraction of collisions with sufficient energy × fraction of molecules in proper orientation

or , $r = (Z_{11} \text{ or } Z_{12}) \times e^{-E_a/RT} \times P$

LAST MOMENT REVIEW

CHEMICAL KINETICS

Theory : ....

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Exercise - 1 : Question ....

Exercise - 2 : Question ....

Exercise - 3 : Question ....

Exercise - 4 : Question ....

DPPs : ....

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Other Sources : ....

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