CHEMICAL KINETICS
Weightage – 7 marks (2022-23)

GIST of the topics –

1. Rate of reaction: For a reaction R → P,

Rate of reaction = change of conc. of R or P / time interval

$$= \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

Unit of rate of reaction:- 1. **$MolL^{-1}s^{-1}$** **2. atm s^{-1}**

2. Unifying rate of reaction

For the reaction $2HI \rightarrow H_2 + I_2$

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

Similarly, for the reaction

$$5\,Br^-(aq) + BrO_3^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(l)$$

$$\text{Rate} = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

3. Differential rate law (Rate law)

a A + b B→ c C + d D

$$\text{Rate} \propto [A]^x\ [B]^y$$

$$\text{Rate} = k\,[A]^x\ [B]^y$$

$$-\frac{d[R]}{dt} = k[A]^x[B]^y$$

This is differential rate equation.

4) Order of reaction:-

For the reaction a A + b B→ c C + d D
Rate = $K[A]^x[B]^y$ x + y = order of reaction
(where x & y may or may not be equal to stoichiometric coefficient)

Note:

i. if x + y = 1, reaction is called **I order reaction**.

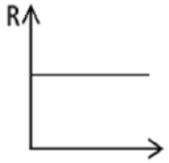
ii. if x + y = 2, reaction is called **II order reaction**.

iii. if x + y = 3, reaction is called **III order reaction**.

iv. if x + y = 0, reaction is called **zero order reaction**.

v. if x + y = fraction , reaction is called **fractional order reaction**.

5. Units of rate constants and graph between rate and conc. of reactant

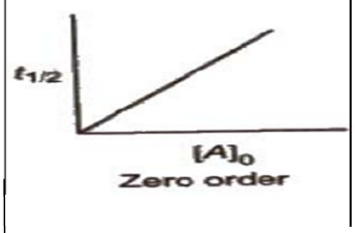
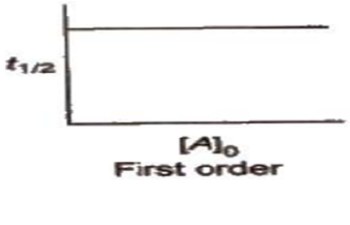
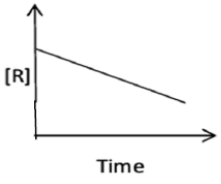
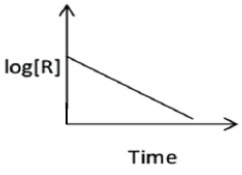
Order of reaction	zero	first	second	third
Unit of rate constt.	$MolL^{-1}s^{-1}$	s^{-1}	$Mol^{-1}L^{+1}s^{-1}$	$Mol^{-2}L^{+2}s^{-1}$
Relation b/w rate & conc of Reactant	$R \alpha [A]^0$	$R \alpha [A]^1$	$R \alpha [A]^2$	$R \alpha [A]^3$
Graph b/w rate & conc of Reactant				

6. Integrated rate equation for zero order and first order reaction

Note: 1. For zero order reaction $t_{1/2}$ α conc. of reactant.

2. For I order reaction $t_{1/2}$ is independent of conc. of reactant.

3. $t_{1/2} \alpha [conc]^{1-n}$ where n = order of reaction.

	for zero order reaction	for first order reaction
Integrated rate equation	$k = \frac{[R]_0 - [R]}{t}$	$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$
Half life	$t_{1/2} = [R]_0/2K$	$t_{1/2} = 0.693/K$
Graph b/w half-life & conc of Reactant		
Graph b/w conc .of reactant & time		

7. Arrhenius equation

$\log K = \log A - E_a/2.303RT$

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

- **IMPORTANT DEFINITIONS-**

1 Pseudo first order reaction:-A bimolecular reaction, in which one reactant is present in large excess and rate of reaction is independent of its concentration. Such a reaction is called pseudo first molecular reaction.

Eg. $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

molecularity of reaction is two and order of reaction is one.

2. Molecularity of reaction: The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

Types of reaction based on molecularity

Unimolecular reactions	Bimolecular reactions	Trimolecular or termolecular reactions
molecularity of reaction = 1	molecularity of reaction = 2	molecularity of reaction = 3
$NH_4NO_2 \rightarrow N_2 + 2H_2O$	$2HI \rightarrow H_2 + I_2$	$2NO + O_2 \rightarrow 2NO_2$

NOTE:

i. It is theoretical value.

ii. It cannot be zero or a non-integer.

iii. molecularity greater than three is not observed.

iv. molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning.

3. Order of reaction:-The power to which conc. term of a reactant is raised in rate law expression is called order w.r.t. that reactant. The sum of powers of conc. of all reactants in rate law expression is called overall order of reaction.

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

NOTE:-

Rate = $K[A]^x [B]^y$

x + y = order of reaction.

i. Order of a reaction is an experimental quantity

ii. It can be zero and even a fraction

iii. Order is applicable to elementary as well as complex reactions

4. Elementary step:-Many reactions complete in a number of steps. Each individual step of a reaction is called elementary step.

5. Activation energy: The additional energy which is required by the molecules of reactants to cause effective collision is called activation energy. It is denoted by E_a and is given as-

Activation energy = threshold energy – average energy of molecules of reactants

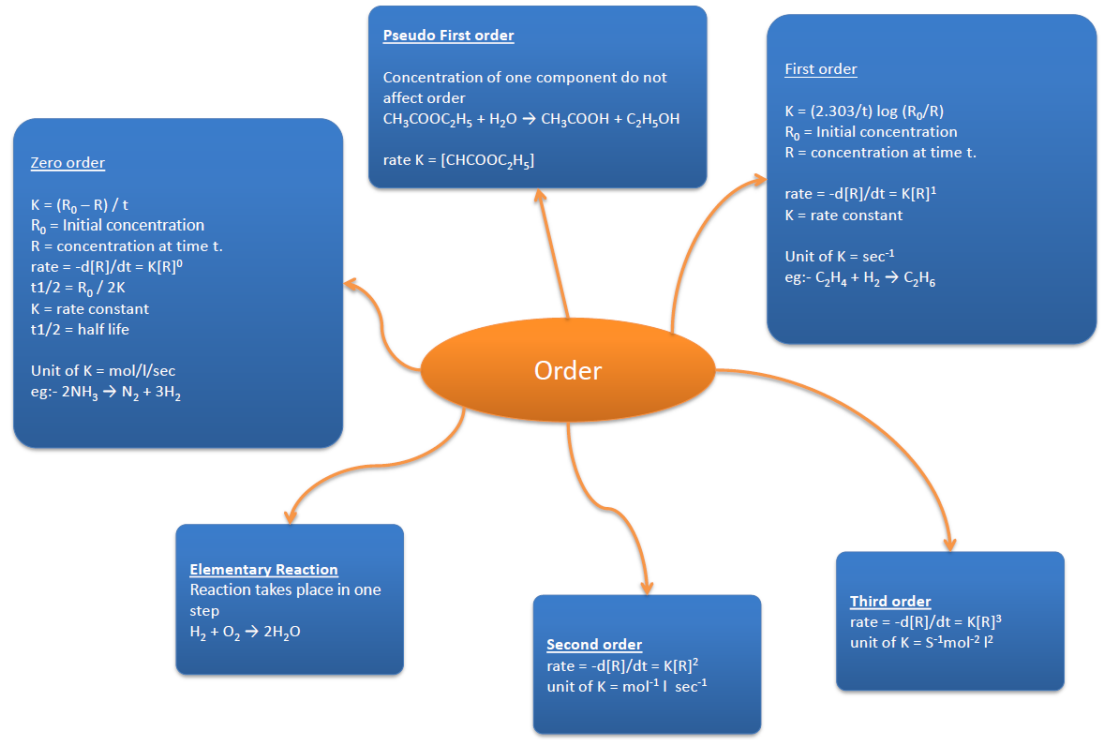
6. Threshold energy: The minimum energy which must be required by the molecules of reactants to cause effective collision is called threshold energy.

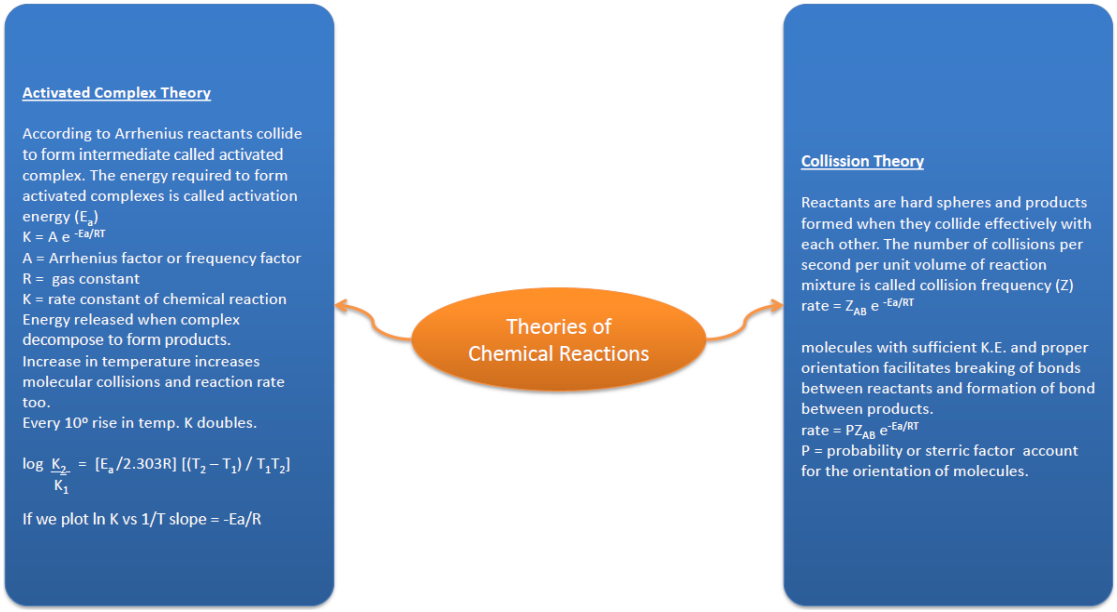
7. Collision frequency: The number of collision of reactant molecules per unit volume of reaction mixture per second is called collision frequency.

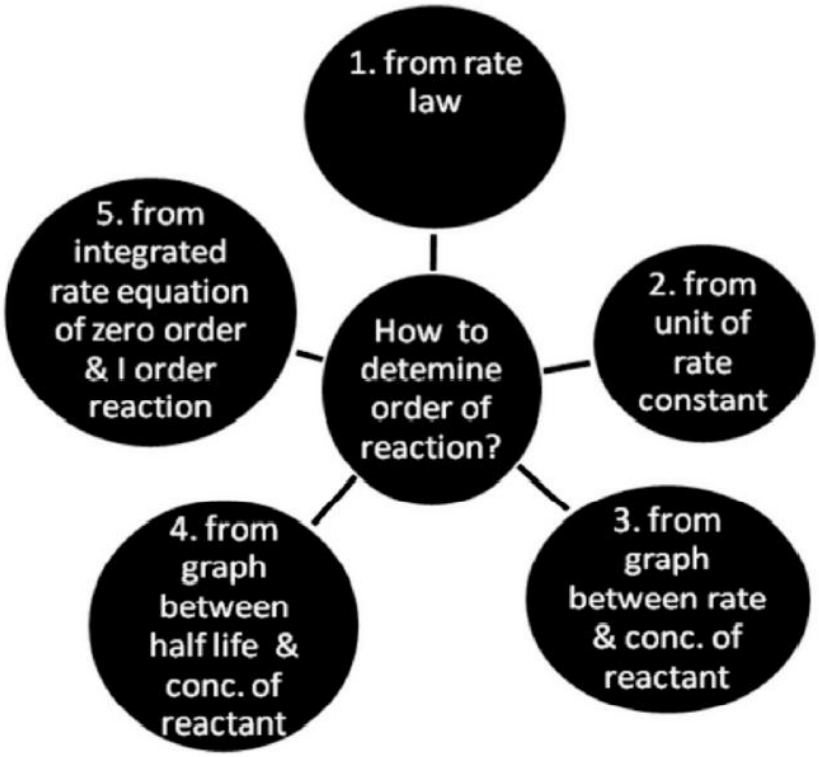
8. Examples- Zero order reaction: $H_2 + Cl_2 \rightarrow 2HCl$

I order reaction : All natural and artificial radioactive reactions.

II order reaction : $H_2 + I_2 \rightarrow 2HI$.


Order
Pseudo First order
Concentration of one component do not affect order
$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$
rate K = $[CHCOOC_2H_5]$
First order
K = (2.303/t) log (R_0/R)
R_0 = Initial concentration
R = concentration at time t.
rate = -d[R]/dt = $K[R]^1$
K = rate constant
Unit of K = sec^{-1}
eg:- $C_2H_4 + H_2 \rightarrow C_2H_6$
Zero order
K = (R_0 – R) / t
R_0 = Initial concentration
R = concentration at time t.
rate = -d[R]/dt = $K[R]^0$
t1/2 = R_0 / 2K
K = rate constant
t1/2 = half life
Unit of K = mol/l/sec
eg:- $2NH_3 \rightarrow N_2 + 3H_2$
Elementary Reaction
Reaction takes place in one step
$H_2 + O_2 \rightarrow 2H_2O$
Second order
rate = -d[R]/dt = $K[R]^2$
unit of K = mol^{-1} l sec^{-1}
Third order
rate = -d[R]/dt = $K[R]^3$
unit of K = $S^{-1}mol^{-2}$ l^2


Theories of Chemical Reactions
Activated Complex Theory
According to Arrhenius reactants collide to form intermediate called activated complex. The energy required to form activated complexes is called activation energy (E_a)
$K = A e^{-Ea/RT}$
A = Arrhenius factor or frequency factor
R = gas constant
K = rate constant of chemical reaction
Energy released when complex decompose to form products.
Increase in temperature increases molecular collisions and reaction rate too.
Every 10° rise in temp. K doubles.
$\log \frac{K_2}{K_1} = [E_a/2.303R][(T_2 - T_1) / T_1T_2]$
If we plot ln K vs 1/T slope = -Ea/R
Collission Theory
Reactants are hard spheres and products formed when they collide effectively with each other. The number of collisions per second per unit volume of reaction mixture is called collision frequency (Z)
rate = $Z_{AB} e^{-Ea/RT}$
molecules with sufficient K.E. and proper orientation facilitates breaking of bonds between reactants and formation of bond between products.
rate = $PZ_{AB} e^{-Ea/RT}$
P = probability or sterric factor account for the orientation of molecules.



Multiple Choice Questions –

1. The slope in Arrhenius plot, is equal to:

(a) $-\frac{E_a}{2.303R}$	(b) $\frac{E_a}{R}$	(c) $-\frac{R}{2.303E_a}$	(d) None of these

2. The term – dx/dt in a rate equation refers to :
(a) the conc. of a reactant (b) the decrease in conc. of the reactant with time
(c) the velocity constant of reaction (d) None of these

3. Instantaneous rate of a chemical reaction is
(a) rate of reaction in the beginning (b) rate of reaction at the end
(c) rate of reaction at a given instant (d) rate of reaction between two specific time intervals

4. Order of reaction is decided by
(a) temperature (b) mechanism of reaction as well as relative concentration of reactants
(c) molecularity (d) pressure

5. A zero order reaction is one whose rate is independent of

(a) the concentration of the reactants (b) the temperature of reaction
(c) the concentration of the product
(d) the material of the vessel in which reaction is carried out

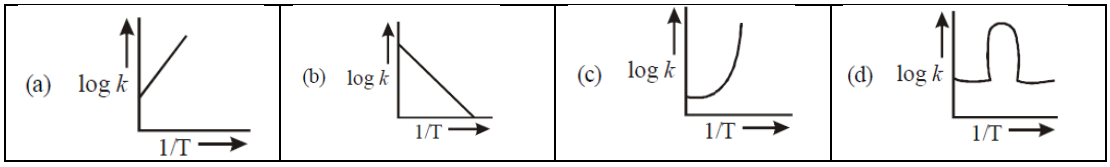
6. For the reaction $A + 2B \rightarrow C$, rate is given by $R = [A]\,[B]^2$ then the order of the reaction is
(a) 3 (b) 6 (c) 5 (d) 7

7. Which of the following influences the reaction rate performed in a solution?
(a) Temperature (b) Activation energy (c) Catalyst (d) All of the above

8. A catalyst increases the reaction rate by:
(a) decreasing enthalpy (b) increasing internal energy
(c) decreasing activation enthalpy (d) increasing activation enthalpy

9. In a reaction, the threshold energy is equal to
(a) activation energy + normal energy of reactants
(b) activation energy - normal energy of reactants
(c) normal energy of reactants - activation energy
(d) average kinetic energy of molecules of reactants

10. A graph plotted between log k vs 1/T for calculating activation energy is shown by



Assertion Reason Questions –

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:
(a) Both assertion and reason are true and reason is the correct explanation of assertion.
(b) Both assertion and reason are true but reason is not the correct explanation of assertion.
(c) Assertion is true but reason is false.
(d) Assertion is false but reason is true.

1. Assertion : Order of a reaction with respect to any reactant or product can be zero, positive, negative and fractional.
Reason : Rate of a reaction cannot decrease with increase in concentration of a reactant or product. (Ans - c)

2. Assertion : The rate of a reaction sometimes does not depend on concentration.
Reason : Lower the activation energy faster is the reaction. (Ans - b)

3. Assertion – Order and molecularity of a reaction is always same.
Reason – Order is determined experimentally whereas molecularity by a balanced elementary reaction.

4. Assertion – In a first order reaction, if the concentration of the reactant is doubled, its half-life is also doubled.
Reason – Half-life of a reaction does not depend upon initial concentration of the reactant in a first order reaction.

5. Assertion – Average rate and instantaneous rate of a reaction has the same unit. Reason – Average rate becomes instantaneous rate when time interval is too small.

Two Marks Questions –

1. (a) How does catalyst alter rate of a reaction?
   (b) A reaction is 50% complete in 2 hours and 75% completes in 4 hours. What is the order of the reaction?

2. (a)What is the unit of rate constant for a Pseudo first order reaction?
(b) What is the overall order of reaction which has the rate expression r= k $[A]^2[B]^0$?

3. What is the effect of adding a catalyst on :
(a) Activation energy (Ea) and (b) Gibbs energy (ΔG) of a reaction.

4. A first order reaction takes 30 minutes for 75% decomposition. Calculate $t_{1/2}$.

Given : [log 2 = 0.3, log 3 = 0.48, log 4 = 0.6, log 5 = 0.7]

5. The decomposition of NH_3 on Pt surface is a zero order reaction. What are the rate of formations of N_2& H_2 if k= 2.5 x 10^{-4} mol $L^{-1}s^{-1}$.

Three Marks Questions –

1. A reaction is first order in A and second order in B.
(i) Write the differential rate equation.
(ii) How is the rate affected on increasing the concentration of B three times?
(iii) How is the rate affected when the concentrations of both A and B are doubled?
2. A 1st order reaction is 40% complete in 50 minutes. Calculate the value of rate constant. At what time will the reaction be 80% completed?
3. In the given reaction A + 3B → 2C,the rate of formation of C is 2.5 x 10^{-4} mol$L^{-1}s^{-1}$.

Calculate the i) rate of reaction ii) rate of disappearance of B

4. Give three important differences between rate of reaction and rate constant of reaction.5. Give four important differences between order of reaction molecularity of reaction.

Five Marks Questions –

1. (i) For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

t/s	0	20	40
$[CH_3COOCH_3]$/mol L^{-1}	0.40	0.20	0.10

a) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

b) Calculate the average rate of reaction between the time interval 20 to 40 seconds.

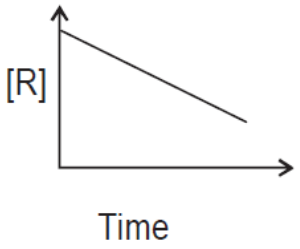
(ii) Why does the rate constant is nearly doubled for every 10° C rise in temperature?

(iii) Write the equation of temperature dependence rate of a chemical reaction.

2. (i) The rate constant of a first order reaction increases from 4 x 10^{-2} to 24 x 10^{-2} when the temperature changes from 300 K to 350 K. Calculate the energy of activation.

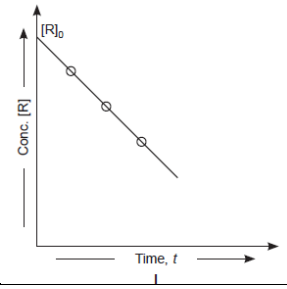
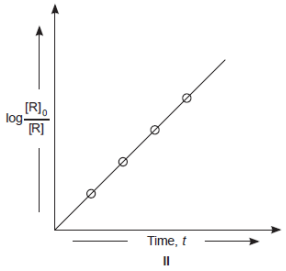
(log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021, log 6 = 0.7782)

(ii) Consider the reaction R → P. the change in concentration of R with time is shown in the following plot :

	a) Predict the order of reaction b)What does the slope of the above line indicate?

Passage/Case based questions –

1. Observe the following graphs and answer the questions based on these graphs.

(*a*) What is order of reaction shown in graph I?

(*b*) What is slope in graph II?

(*c*) How does $t_{1/2}$ varies with initial concentration in zero order reaction?

OR

If $t_{1/2}$of first order reaction is 40 minute, what will be $t_{99.9\%}$for first order reaction?

2. Read given passage and answer the questions that follow:

Chemical kinetics deals with rate of chemical reactions, how fast reactants get used up or how fast products are formed in the reaction. Different chemical reactions have different speed. Rate of reaction depends upon concentration of reactants, temperature, pressure especially in gaseous reactions and presence of catalyst. Chemical reaction takes place as a results of collision between reacting molecules. The rate of reaction does not depend upon total number of collisions rather it depends upon number of effective collisions. In a redox reaction, if $E°_{cell}$ is +ve, $\Delta G°$ will be –ve and 'K' equilibrium constant will be high i.e. products formed will be more than the reactants.

(*a*) What is meant by activation energy?

(*b*) What does $e^{-Ea/RT}$ represent?

(*c*) If $Fe^{3+} + 2I^- \rightarrow Fe^{2+} + I_2$ has E° = 0.24V, what is the value of log K? What does value of 'K' indicate?

OR

What type of molecules undergo effective collisions?

LAST THREE YEARS BOARD QUESTIONS

1. In a reaction $2N_2O_5\ (g) \rightarrow 4NO_2(g) + O_2(g)$, the concentration of N_2O_5 decreases from 0.5 mol/L to 0.4 mol/L in 10 minutes. Calculate the average rate of this reaction and rate of production of NO_2 during this period.

2. A first order reaction takes 30 minutes for 75% decomposition. Calculate $t_{1/2}$.

Given : [log 2 = 0.3, log 3 = 0.48, log 4 = 0.6, log 5 = 0.7]

3. a) Draw the plot of *ln* k vs 1/T for a chemical reaction. What does the intercept represent? What is the relationship between slope and Ea?

b) A first order reaction takes 30 minutes for 20% decomposition. Calculate $t_{1/2}$.[log 2 = 0.3010]

4. In the given reaction, A + 3B → 2C, the rate of formation of C is 2.5 x 10^{-4} $molL^{-1}s^{-1}$.

Calculate the i) rate of reaction ii) rate of disappearance of B.

5. A first order reaction is 40% complete in 80 minutes. Calculate the value of rate constant (k). In what time will the reaction be 90% completed.

6. The rate of a reaction quadruples when the temperature changes from293 K to 313 K. Calculate the energy of activation of the reaction assumingthat it does not change with temperature.

7. For the reaction : $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

The rate of formation of $NO_2(g)$ is 2.8 x 10^{-3} M s^{-1}. Calculate the rate of disappearance of $N_2O_5(g)$.

8. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction.

(Given : log 2 = 0.3010, log 4 = 0.6021, R = 8.314 JK^{-1} mol^{-1})

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ANSWERS -

Multiple Choice Questions –

1. (a) 2. (b) 3. (c) 4. (b) 5. (a) 6. (a) 7. (d)

8. (c) 9. (a) 10. (b)

Assertion Reason Questions – 1. (c) 2. (b) 3. (d) 4. (d) 5. (b)

Two Marks Questions –

Ans.1. (a) It increases rate of reaction by providing a new path having low activation energy.
(b) Since half-life remains constant so it is a first order reaction.

Ans. 2 (a) s^{-1} (b) 2

Ans –3 (a) Ea decreases (b) Gibbs energy doesn't change.

Ans. 4. 15 minutes

Ans. 5. – rate of formation of $N_2 = 2.5 \times 10^{-4}$ mol $L^{-1}s^{-1}$&

rate of formation of $H_2 = 7.5 \times 10^{-4}$ mol $L^{-1}s^{-1}$

Three Marks Questions –

Ans. 1. (i) Rate = $K[A]^1 [B]^2$
(ii) Rate = $K[A]^1 [3B]^2 = 9K[A]^1 [B]^2$ hence, it becomes 9 times.
(iii)Rate = $K[2A]^1 2[B]^2 = 8K[A]^1 [B]^2$ hence, it becomes 8 times.
Ans. 2 – find k by taking values a = 100 & a-x = 60 i.e. = 0.01028 min^{-1} and then using

this value of k, find the time when the reaction will complete 80%, i.e. =156.52 min.

Ans. 3. (i) 2.5×10^{-4} mol$L^{-1}s^{-1}$ ii) $7.5 \times$ mol$L^{-1}s^{-1}$

Ans. 4.

S.No.	Rate of reaction	Rate constant of reaction
1	It is the change in concentration of reactant or product in a unit interval of time.	It is the rate of reaction when molar conc. of each of the reactants is unity.
2	Its unit is mol$L^{-1}s^{-1}$	Its unit depends upon the order of reaction.

3	The rate of reaction at any instant of time depends upon the molar conc. of the reactants at that time.	The rate constant does not depend upon the molar conc. of the reactants.

Ans. 5.

S.No.	order of reaction	molecularity of reaction
1	It is sum of the powers of the concentration of the reactants in the rate law expression	The number of reacting species taking part in an elementary reaction, which must collide to give products is called molecularity of a reaction.
2	Order of a reaction is an experimental quantity.	It is theoretical value.
3	It can be zero and even a fraction.	It cannot be zero or a non integer.
4	Order is applicable to elementary as well as complex reactions.	molecularity is applicable only for elementary reactions.

Five Marks Questions –

Ans.1.(i) (a)Value of rate constant (k) remains constant at time 20 and 40 sec

(b) 0.005 mol $L^{-1}s^{-1}$

(ii) An increase in temperature will raise the average kinetic energy of the reactant molecules. Therefore, a greater proportion of molecules will have the minimum energy necessary for an effective collision.

(iii) Arrhenius equation, $k = A\, e^{-Ea/RT}$

Ans. 2. (i) By using the formula, $\log k_2/k_1 = Ea/2.303\ R\ [T_2-T_1]/T_1.T_2$

Ea = 24125 J

(ii) a) Zero order reaction b) Concentration of the reactant decreases with time.

Passage/Case based questions –

Ans. 1. (a) Zero order reaction.

Ans. (b) k/2 303 where '*k*' is rate constant.

Ans. (c) $t_{1/2}$ is directly proportional to initial concentration.

OR

Ans. $t_{99.9\%} = 10\ t_{1/2} = 10 \times 40 = 400$ minutes

2. Ans. (a) The extra energy which must be supplied to reactants in order to undergo effective

collision to form products.

Ans. (b) It represents fraction of molecules possessing activation energy (Ea) or more than Ea.

Ans. (c) $\log K = nE°/0.0591 = 2 \times 0.24/0.0591V = 8.122$

The value indicates that products are formed 10^8, times than reactants.

OR

Ans: Those molecules which possess activation energy and collide in proper orientation undergo effective collisions.

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