

UNIT 3

CHEMICAL KINETICS

CONCEPT

Chemical Kinetics : The branch of physical chemistry which deals with the study of rate of reaction and factors affecting rate.

Rate of chemical reaction : The change in concentration of any reactant or product per unit time is called rate of reaction.

Types of Rate of Reaction :

1. **Average rate of reaction :** The rate of reaction measured over the long time interval is called average rate of reaction.

$$\text{Avg rate } \Delta \frac{\Delta x}{\Delta t} = \frac{-\Delta[\text{R}]}{\Delta t} = \frac{\Delta[\text{P}]}{\Delta t}$$

2. **Instantaneous rate of reaction :** The rate of reaction measured at a particular time is called instantaneous rate of reaction.

$$(\text{Rate})_i = (\text{Instantaneous rate}) \frac{dx}{dt} = -\frac{d[\text{R}]}{dt} = +\frac{d[\text{P}]}{dt}$$

Factors affecting Rate of Reaction

1. Concentration of reactant
2. Surface area
3. Temperature
4. Nature of reactant
5. Presence of catalyst
6. Radiation in photochemical reaction

Rate constant (k) : It is equal to the rate of reaction when molar concentration of reactant is at unity.

Rate law : The rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to the equal to no of moles actually participating in the reaction.



$$\text{Rate law} = k[A]^p[B]^q$$

where powers p and q are determined experimentally.

Molecularity : The total number of reactants taking part in elementary chemical reaction is called molecularity.

Order of reaction : The sum of powers to which the concentration terms are raised in a rate law expression is called order of reaction.

For above case, $\text{Order} = P + Q$

Orders of reaction is determined experimentally.

Half-life period : The time during which the concentration of the reactant is reduced to half of its initial concentration is called half-life period.

Activation energy : The minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy is called activation energy.

$$\text{Activation energy} = \text{Threshold energy} - \text{Kinetic energy}$$

Temperature coefficient : The ratio of rate constant at two temperatures having difference of 10°C is called temperature coefficient.

$$\text{Temperature coefficient} = \frac{\text{Rate constant at } T + 10^\circ\text{C}}{\text{Rate constant at } T^\circ\text{C}}$$

Arrhenius Equation :

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

where, K = Rate constant

A = Arrhenius energy (Frequency factor or pre-exponential factor)

E_a = Activation energy

R = Rate constant

T = Temperature

$\frac{E_a}{RT}$ = Fraction of molecules having energy equal to or more than activation energy

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

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303 \times 8.314} \left[\frac{T_2 - T_1}{T_2 - T_1} \right] \quad \text{Where } R = 8.314 \text{ J M}^{-1} \text{ mol}^{-1}$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{19.147} \left[\frac{T_2 - T_1}{T_2 - T_1} \right] = 0.0522 E_a \left[\frac{T_2 - T_1}{T_2 - T_1} \right]$$

1. Integrated rate law equation for zero order reaction is given as below :

$$(a) \quad k = \frac{[R]_0 - [R]_t}{t}$$

Where k is rate constant and $[R]_0$ is initial molar concentration.

$$(b) \quad t_{1/2} = \frac{[R]_0}{2k}, \quad t_{1/2} \text{ is half-life period of zero order reaction.}$$

2. Integrated rate law equation for first order reaction :

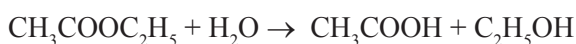
$$(a) \quad k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$$

where k is rate constant, $[R]_0$ is initial molar concentration and $[R]$, is final concentration at time ' t '.

(b) Half-life period ($t_{1/2}$) for first order reaction :

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

Pseudo chemical reaction : The chemical reaction which looks like higher order reaction but in real it follows lower order reaction.



$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]^1$$

Order = 1

MULTIPLE CHOICE QUESTIONS (1 Mark)

1. The half life period of a first order reaction is 100° seconds. Its rate constant is:

- (a) 0.693 sec^{-1} (b) $6.93 \times 10^{-3} \text{ sec}^{-1}$
 (c) $6.93 \times 10^{-2} \text{ sec}^{-1}$ (d) None of these

2. In Arrhenius equation if a graph is plotted between $\log K$ and $1/T$, the slope of the curve will be:

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

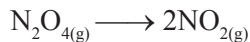
3. The rate law for a reaction $2C + D \longrightarrow A + E$ is

$$\frac{-d[D]}{dt} = K[C]^2[D]$$

if C is present in large excess, the order of the reaction will be:

- (a) zero (b) first
(c) second (d) third

4. What is the activation energy for the reverse of this reaction?



Data for the given reaction is $\Delta H = 54 \text{ KJ/mol}$ and $\epsilon_a = 57.2 \text{ KJ}$.

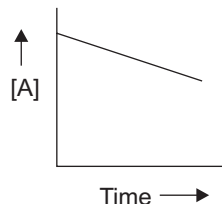
- (a) -54 KJ (b) 3.2 KJ
(c) 60.2 KJ (d) 111.2 KJ

5. The rate constant of a reaction becomes equal to the pre exponential factor when:

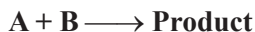
- (a) the absolute temperature is zero
(b) the activation energy is infinity
(c) the absolute temperature is infinity
(d) the activation energy is zero

6. The following graph show that the reaction is:

- (a) zero order
(b) first order
(c) second order
(d) fractional order



7. A second order reaction between A and B is elementary reaction:



rate law expression of this reaction will be:

- (a) $\text{Rate} = K[A][B]$ (b) $\text{Rate} = K[A]^0[B]^2$
(c) $\text{Rate} = K[A]^2[B]^0$ (d) $\text{Rate} = K[A]^{3/2}[B]^{1/2}$

8. The order and molecularity of the chain reaction, $H_{2(g)} + Cl_{2(g)} \xrightarrow{h\nu} HCl$

- (a) 2, 0 (b) 0, 2
(c) 1, 1 (d) 3, 0

9. Which of the following is pseudo first order reaction?

- (a) $2H_2O_2 \longrightarrow 2H_2O + O_2$
(b) $2O_3 \longrightarrow 3O_2$
(c) $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$
(d) $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

10. A large increase in the rate of reaction for rise in temperature is due to:

- (a) Increase in the number of collisions
- (b) Increase in the number of activated molecules
- (c) Lowering of activation energy
- (d) Shortening of the mean free path.

11. For a reaction, the following data were obtained:

Concentration (mol/L)	0.1	0.05	0.025	0.0125
Half life in (sec)	30	29.9	30.1	30

the order of reaction is:

- (a) 2
- (b) 1
- (c) 0
- (d) fractional

12. For the formation of SO_3 in the following reaction, it is given that



- (a) $E_a > E'_a$
- (b) $E_a < E'_a$
- (c) $E_a = E'_a$
- (d) $E_a = E'_a$

13. A first order reaction is 20% complete in one hour. At the end of 3 hrs the extent of the reaction is:

- (a) 60%
- (b) 52.2%
- (c) 48.8%
- (d) 44.4%

14. Radioactive decay is an example of:

- (a) first order
- (b) second order
- (c) zero order
- (d) 0.5 order

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

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

16. The decomposition of N_2O_5 occurs as, $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$ and follows first order kinetics, hence:

- (a) the reaction is bimolecular
- (b) the reaction is unimolecular
- (c) $t_{yz} \propto a^\circ$
- (d) unit of $K = \frac{\text{mol}}{\text{L}} \text{sec}^{-1}$

17. Rate of which reactions increases with temperature:

- (a) of any reaction
- (b) of exothermic reaction
- (c) of endothermic reaction
- (d) of none

18. For the reaction, $\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \text{O}_2$; Given

$$-\frac{d}{dt}[\text{N}_2\text{O}_5] = K_1[\text{N}_2\text{O}_5]$$

$$\frac{d}{dt}[\text{NO}_2] = K_2[\text{N}_2\text{O}_5]$$

$$\frac{d}{dt}[\text{O}_2] = K_3[\text{N}_2\text{O}_5], \text{ the relation in between of } K_1, K_2, K_3 \text{ is}$$

- (a) $2K_1 = K_2 = 4K_3$ (b) $K_1 = K_2 = K_3$
 (c) $2K_1 = 4K_2 = K_3$ (d) $2K_1 = 2K_2 = 3K_3$

19. Which of the following statement is/are correct about order of reaction:

- (a) order of reaction is determined experimentally
 (b) order of reaction can not have fractional value
 (c) it does not necessarily depend on stoichiometric coefficients.
 (d) it is the sum of power of concentration terms in rate law expression

20. Which one is correct for first order reaction.

- (a) $\frac{t_{75\%}}{t_{50\%}} = 1.5$ (b) $\frac{t_{75\%}}{t_{50\%}} = 3$
 (c) $\frac{t_{99.9\%}}{t_{50\%}} = 10$ (d) $\frac{t_{87.5\%}}{50\%} = 3$

21. Match the column and found out correct option.

- | | |
|---------------------------|---|
| (A) zero order reaction | P. unit of K is $\frac{\text{L}}{\text{mol}} \cdot \text{sec}^{-1}$ |
| (B) first order reaction | Q. unit of K is $\frac{\text{mol}}{\text{L}} \cdot \text{sec}^{-1}$ |
| (C) second order reaction | R. unit of K is sec^{-1} |
| (a) A-R, B-Q, C-P | (b) A-P, B-Q, C-R |
| (c) A-Q, B-R, C-P | (d) A-R, B-P, C-Q |

Assertion and Reasoning:

22. (a) Statement 1: is true, Statement 2 is true, and Statement 2 is a correct explanation of statement 1
 (b) Both statement are true but statement 2 is not a correct explanation for statement 1
 (c) Statement 1 is true and statement 2 is false
 (d) Statement 1 is false and Statement 2 is true
 (e) Statement 1 the rate of reaction is accelerated by the presence of catalyst.
 (f) Statement 2 The presence of catalyst makes the value of ΔG° more negative.

23. **Statement 1: Lower the activation energy, faster is the reaction.**

Statement 2 : Catalyst does not affect activation energy of the reaction.

24. Integer type Question:

For first order reaction: $\frac{t_{99.9}}{t_{50}} = x$, Here x is

- (a) 3 (b) 5
(c) 7 (d) 10

Fill in the blanks type Questions

25. The reactions taking place in one step is called reactions.

26. The order of reaction is determined.

Answers

1. (b) 2. (b) 3. (b) 4. (b) 5. (c) 6. (a) 7. (a) 8. (b) 9. (d) 10. (b)
11. (b) 12. (d) 13. (c) 14. (a) 15. (c) 16. (c) 17. (a) 18. (a)
19. (a, c, d) 20. (c, d) 21. (c) 22. (c) 23. (c) 24. (d)
25. elementary 26. experimentally

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. The rate law for a reaction is

$$\text{Rate} = K [A] [B]^{3/2}$$

Can the reaction be an elementary process ? Explain.

Ans. No, an elementary process would have a rate law with orders equal to its molecularities and therefore must be in integral form.

Q. 2. For the reaction $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$, how are the rate of reaction expressions

$-\frac{d[\text{H}_2]}{dt}$ and $\frac{d[\text{NH}_3]}{dt}$ inter-related ?

$$\text{Ans. } -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

Q. 3. Identify the order of a reaction from the following rate constant :

$$k = 2.3 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$$

Ans. Second order

Q. 4. After five half-life periods for a first order reaction, what fraction of reactant remains ?

$$\text{Ans. } \frac{1}{32}$$

Q. 5. What is the effect of adding catalyst on the free energy of a reaction ?

Ans. No change in ΔG .

Q.6. What value of k is predicted for the rate constant by Arrhenius equation is $T \rightarrow \infty$? Is this value physically reasonable ?

Ans. From the equation $k = Ae^{-E_a/RT}$ if $T \rightarrow \infty$ $k \rightarrow A$ so that $E_a = 0$. This is not feasible.

Q.7. Determine the order of reaction :



Ans. Rate = $k [\text{NO}]^2 [\text{H}_2]$

$$\text{Order} = 2 + 1$$

$$= 3$$

Q.8. What is the order of reaction whose rate constant has the same units as the rate of reaction ?

Ans. Zero order

Q.9. Why are reactions of higher order less in number ?

Ans. A reaction takes place due to collide of molecules. The chances for a large number of molecules or ions to collide simultaneously are less. Hence, the reactions of higher order are less.

Q.10. What will be the effect of temperature on rate constant ?

Ans. Rate constant of a reaction is nearly doubled with rise in temperature by 10° .

Q.11. State a condition under which a bimolecular reaction is kinetically first order reaction.

Ans. A bimolecular reaction becomes first order reaction when one of the reactants is in excess.

Q.12. Why can't molecularity of any reaction be equal to zero ?

Ans. Molecularity of a reaction means the number of molecules of the reactants taking place in an elementary reaction. Since at least one molecule must be present, so that molecularity will be atleast one.

Q.13. The rate constant of a reaction is $3 \times 10^2 \text{ min}^{-1}$. What is its order of reaction ? (On the basis of units of rate constant)

Ans. First order reaction.

Q.14. Three-fourth of a reaction is completed in 32 minutes. What is the half life period of this reaction ?

Ans. 16 minutes.

Q.15. What is meant by an elementary reaction ?

Ans. A reaction which takes place in one step is called an elementary reaction. For example : $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$.

Q.16. Give one example of a reaction where order and molecularity are equal ?

Ans. $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ (Order = Molecularity = 2)

Q.17. For a reaction $\text{R} \rightarrow \text{P}$, the rate becomes 2 times when the concentration of the reactant A is increased 4 times. What is the order of reaction ?

Ans. $r = k(a)^n \Rightarrow 2r = k(4a)^n \Rightarrow 2 = 4^n \Rightarrow n = 0.5$

Q.18. The rate constant of a zero order reaction in A is $0.003 \text{ mol L}^{-1} \text{ sec}^{-1}$. How long will it take for the initial concentration of A to fall from 0.10M to 0.075 M ?

Ans. $t = \frac{[\text{A}]_0 - [\text{A}]}{k} = \frac{0.10 - 0.075}{0.003} = 8.3 \text{ sec}$

Q.19. In a reaction $2\text{A} \rightarrow \text{Products}$, the concentration of A decreases from 0.5 mol L^{-1} in 10 minutes. Calculate the rate during this interval.

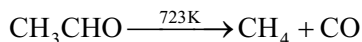
Ans. Average rate = $\frac{-\Delta[\text{A}]}{2\Delta t} = -\frac{1}{2} \left(\frac{0.4 - 0.5}{10} \right) = 5 \times 10^{-3} \text{ M min}^{-1}$

Q.20. In some cases large number of colliding reactant molecules have energy more than threshold energy even then the reaction is slow. Why ?

Ans. Because resultant molecules do not collide in proper orientation.

Q.21. Give an example of a reaction having fractional order.

Ans. Decomposition of acetaldehyde (order = 1.5).



Q.22. Decomposition reaction of ammonia on Pt surface has rate constant = $2.5 \times 10^{-1} \text{ mol L}^{-1} \text{ sec}^{-1}$. What is order of reaction ?

Ans. Unit of k explain that it is zero order reaction.

Q.23. What is order of radioactive decay ?

Ans. First order

Q.24. For a reaction $\text{A} + \text{B} \rightarrow \text{Product}$, the rate law is given by $r = k[\text{A}]^{1/2} [\text{B}]^2$. What is the order of the reaction ?

Ans. Order of reaction = $\frac{1}{2} + 2 = 2.5$

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. The rate of a particular reaction quadruples when the temperature changes from 293 K to 313 K. Calculate activation energy.

Ans. $K_2/K_1 = 4$

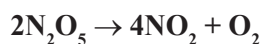
$$T_1 = 293 \text{ K}, T_2 = 313 \text{ K}$$

$$\log \frac{K_2}{K_1} = -\frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Thus, on calculating and substituting values, we get :

$$E_a = 52.86 \text{ KJ mol}^{-1}$$

Q. 2. If the decomposition of nitrogen oxide as



follows a first order kinetics.

(a) Calculate the rate constant for a 0.05M solution if the instantaneous rate is $1.5 \times 10^{-6} \text{ mol/l/s}$?

Ans. $\text{Rate} = K[\text{N}_2\text{O}_5]$

$$K = \frac{\text{Rate}}{[\text{N}_2\text{O}_5]}$$

$$= \frac{1.5 \times 10^{-6}}{0.05}$$

$$K = 3.0 \times 10^{-5}$$

(b) What concentration of N_2O_5 would give a rate of $2.45 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$?

Ans. $\text{Rate} = 2.45 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$

$$[\text{N}_2\text{O}_5] = \frac{\text{Rate}}{K} = \frac{2.45 \times 10^{-5}}{3.0 \times 10^{-5}}$$

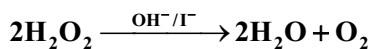
$$= 0.82 \text{ M}$$

Q. 3. Write the difference between order and molecularity of reaction.

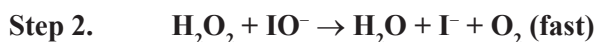
Ans.

Order	Molecularity
1. It is the sum of the powers of concentration terms in the rate law expression.	It is the number of reacting species undergoing simultaneously collision in a reaction.
2. It is determined experimentally.	2. It is a theoretical concept.
3. Order of reaction need not to be a whole number.	3. It is whole number only.
4. Order of reaction can be zero.	4. It can't be zero or fractional.

Q. 4. Consider the decomposition reaction :



This reaction takes place in two steps as given below :



(a) Determine rate law expression.

(b) Determine the order of reaction.

Ans. (a) Rate = $K[\text{H}_2\text{O}_2][\text{I}^-]$ because second step is rate determining step.

(b) Order = 1 + 1 = 2

Q. 5. The decomposition of hydrocarbon follows the equation $K = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000\text{k}/T}$. Calculate E_a .

Ans. $K = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000\text{k}/T}$

Comparing the equation with Arrhenius equation,

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

$$-\frac{E_a}{R} = -28000 \text{ K}$$

$$\begin{aligned} E_a &= 28000 \times 8.314 \\ &= 232192 \text{ J mol}^{-1} \end{aligned}$$

Q. 6. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the conc. of the reactant is reduced to half. What is the unit of rate constant for such a reaction ?

Ans. Rate = $k[A]^2$

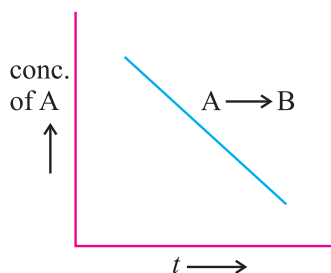
$$\text{Unit of } k = \frac{\text{mol L}^{-1}}{\text{S}} = k(\text{mol}^{-1})^2$$

$$k = \text{mol}^{-1} \text{ L S}^{-1}$$

Q.7. For a first order reaction time taken for half of the reaction to complete is t_1 and $3/4$ of the reaction to complete is t_2 . How are t_1 and t_2 related ?

Ans. $t_2 = 2t_1$ because for $3/4$ th of the reaction to complete time required is equal to two half lives.

Q. 8.



(a) What is the order of the reaction ?

(b) What is the slope of the curve ?

Ans. (a) Zero order reaction.

(b) $[R] = [R_0] - kt$ \therefore Slope = $-k$

Q.9. Derive an expression to calculate time required for completion of zero order reaction.

Ans. For a zero order reaction,

$$R = [R]_0 - kt$$

For completion of the reaction $[R] = 0$

$$\therefore kt = [R]_0$$

$$\text{Or } t = \frac{[R]_0}{k}$$

Q.10. For the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

How is the rate of formation of ammonia related to the rate of disappearance of H_2 ?

Ans. Rate of reaction = $-\frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t}$ Or $\frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{2}{3} \frac{\Delta[\text{H}_2]}{\Delta t}$

Q.11. The rate of a gaseous reaction becomes half when volume of the vessel is doubled. What is the order of reaction ?

Ans. Suppose, order of reaction is n and the reaction is $A(g) \rightarrow \text{Products}$

$$\text{Rate} = k[A]^n \quad \dots(i)$$

When volume is doubled, molar conc. becomes half and rate of reaction gets halved.

$$\frac{\text{Rate}}{2} = k \left(\frac{A}{2} \right)^n \quad \dots(ii)$$

Dividing equation (i) by equation (ii),

$$(2)^1 = (2)^n$$

Or $n = 1$

Q.12. A reaction which is first order with respect to A has rate constant 6 min^{-1} . If we start with $[A] = 0.5 \text{ mol L}^{-1}$, when would $[A]$ reach the value of 0.05 ML^{-1} ?

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

$$k = 6 \text{ min}^{-1}, [A]_0 = 0.5, [A] = 0.05, t = ?$$

$$t = \frac{2.303}{6} \log \frac{0.5}{0.05} = \frac{2.303}{6} \log 10 = 0.3838 \text{ min}$$

Q.13. The conversion of the molecules X to Y follows second order kinetics. If the concentration of X is increased to three times, how will it affect the rate of formation of Y ?

Ans. 9 times

Q.14. A first order reaction has a rate constant $1.15 \times 10^{-3} \text{ s}^{-1}$. How long will 5 gram of this reactant take to reduce to 3 grams ?

Ans. $t = 444$ seconds

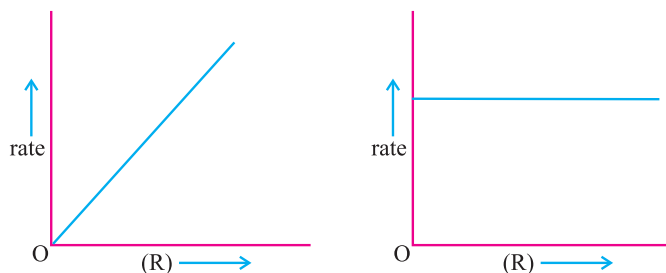
Q.17. $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$. If rate of formation of NO is $6 \times 10^{-4} \text{ atm min}^{-1}$, calculate the rate of formation of H_2O .

Ans. $9.0 \times 10^{-4} \text{ atm min}^{-1}$

Q.18. Consider a certain reaction $A \rightarrow \text{Product}$ with $K = 2.0 \times 10^{-2} \text{ s}^{-1}$. Calculate the concentration of A remaining after 100 s, if the initial concentration of A is 1.0 mol L^{-1} .

Ans. $[A] = 0.135 \text{ M}$

Q.19. Explain with an example, what is a pseudo first order reaction ? The graphs (A and B) given below are plots of rate of reaction Vs concentration of the reactant. Predict the order from the graphs.



Q.20. Differentiate between :

- Average rate and instantaneous rate of a chemical reaction.
- Molecularity and order of reaction.

Q.21. Show that in case of first order reaction, the time required for 99.9% of the reaction to take place is about ten times than that required for half the reaction.

Q.22. For the reaction $\text{NO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{NO}$, the experimentally determined rate expression below 400 K is $\text{rate} = k[\text{NO}_2]^2$. What mechanism can be proposed for this reaction ?

Q.23. The half life period of a first order reaction is 60 min. What % will be left after 240 mins. ?

Ans. 6.25%

Q.24. Time for half change for a first order reaction is 25 min. What time will be required for 99% reaction ?

Ans. 166.16 mins.

SHORT ANSWER TYPE-II QUESTIONS

Q. 1. The rate constant for first order reaction is 60/s. How much time will it take to reduce the concentration of the reaction to 1/10 of its initial value ?

Ans.

$$t = \frac{2.303}{K} \log \frac{[R_0]}{[R]}$$

$$t = \frac{2.303}{\frac{1}{10}} \log \frac{[R_0]}{[R]}$$

$$t = \frac{2.303}{60} \log 10$$

$$t = \frac{2.303}{60}$$

$$= 3.38 \times 10^{-2} \text{ s}^{-1}$$

Q. 2. The rate of most of reaction double when their temperature is raised from 298 K to 308 K. Calculate the activation energy of such a reaction.

Ans.

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times 0.3010}{1000}$$

$$E_a = 52.89 \text{ KJ/mol}$$

Q. 3. A first order reaction takes 69.3 min for 50% completion. Set up an equation for determining the time needed for 80% completion.

Ans.

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} \text{ min}^{-1}$$

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

$$T = \frac{2.303}{K} \log \frac{[R_0]}{[R]}$$

$$= \frac{2.303}{10^{-2}} \log 5$$

$$= 160.9 \text{ min}$$

Q. 4. The activation energy of a reaction is 94.14 KJ/mol and the value of rate constant at 40° C is $1.8 \times 10^{-1} \text{ sec}^{-1}$. Calculate the frequency factor A.

Ans. Given, $E_a = 94.14 \times 10^3 \text{ J mol}^{-1}$, $T = 40 + 273 = 313 \text{ K}$, $K = 1.8 \times 10^{-1} \text{ sec}^{-1}$

By using, $K = Ae^{-E_a/RT} \Rightarrow \ln K = \ln A - \frac{E_a}{RT}$

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

Or $\log (1.8 \times 10^{-1}) + \frac{94.19 \times 10^3}{2.303 \times 8.314 \times 313} = \log A$

Or $A = \text{antilog} (10.9635) = 9.194 \times 10^{10} \text{ sec}^{-1}$

Q. 5. The rate constant of a reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} respectively. Calculate the value of E_a and A.

Ans. $18.23 \text{ KJ mol}^{-1}$, 1.603

Q. 6. The rate constant of a reaction at 700 K and 760 K are $0.011 \text{ M}^{-1} \text{ s}^{-1}$ and $0.105 \text{ M}^{-1} \text{ s}^{-1}$ respectively. Calculate the value of Arrhenius parameters.

Ans. 2.824×10^{10}

Q. 7. The initial concentration of N_2O_5 in the first order reaction $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ was $1.24 \times 10^{-2} \text{ mol L}^{-1}$ at 318 K. The concentration of N_2O_5 after 60 minutes was $0.20 \times 10^{-2} \text{ mol L}^{-1}$. Calculate the rate constant of the reaction at 318 K.

Ans.

$$K = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{t} \log \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} = \frac{2.303}{60} \log \frac{1.24 \times 10^{-2}}{0.2 \times 10^{-2}}$$

$$= \frac{2.303}{60} \log 6.2 = \frac{2.303}{60} \times 0.7924 \text{ min}^{-1}$$

$$= 0.0304 \text{ min}^{-1}$$

Q. 8. The following data were obtained during the first order thermal decomposition of N_2O_5 at constant volume :



S. No.	Time per second	Total pressure (atm)
1	0	0.5
2	100	0.512

Calculate rate constant.

Ans. $4.98 \times 10^{-4} \text{ sec}^{-1}$

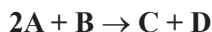
Q. 9. A first order reaction is 20% complete in 20 minutes. Calculate the time taken for the reaction to go to 80% completion.

Ans. 144.3 minutes

Q. 10. For a first order reaction, calculate the ratio between the time taken to complete $\frac{3}{4}$ of the reaction and the time taken to complete half of the reaction.

Ans. Two

Q. 11. The following results have been obtained during the kinetics studies of the reaction :



Experiment	[A] mol L ⁻¹	[B] mol L ⁻¹	Initial rate of formation of D mol L ⁻¹ min ⁻¹
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-1}

Determine the rate law and the rate constant for the reaction.

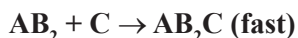
Ans. Rate = $K[A][B]^2$

Q. 12. The rate of reaction triples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Q. 13. The decomposition of A into product has value of K as $4.5 \times 10^3 \text{ sec}^{-1}$ at 10° C and energy of activation 60 kJ/mol. At what temperature would K be $1.5 \times 10^4 \text{ sec}^{-1}$.

Ans. 24° C

Q. 14. (a) Write rate law and order of the following reaction :



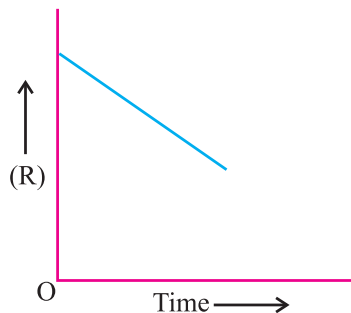
(b) Define energy of activation of a reaction.

(c) What is the relationship between rate constant and activation energy of a reaction ?

Ans. (a) Rate = $K[AB][C_2]$, Order = 1 + 1 = 2

(c) $K = Ae^{-E_a/RT}$

Q. 15. For a chemical reaction $R \rightarrow P$, the variation in the concentration (R) vs time (t) plot is given :



(a) Predict the order of reaction.

(b) Write down its rate law.

(c) What is the slope of the curve ?

- Q. 17. What do you understand by a first order reaction ? Show that for a first order reaction time required to complete a definite fraction of the reaction is independent of initial concentration.
- Q. 18. In a pseudo first order reaction of hydrolysis of an ester in H_2O , the following results were obtained :

t/s	0	30	60	90
Ester (M/L)	0.55	0.31	0.17	0.085

- (a) Calculate the average rate of reaction between the time interval 30 to 60 sec.
- (b) Calculate the pseudo first order rate constant for the hydrolysis of ester.

Ans. (a) Average rate during 30-60 sec. $= \frac{0.17 - 0.31}{60 - 30} = 4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1}$

(b)
$$K_{30} = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{30} \log \frac{0.55}{0.31}$$

$$K_{60} = \frac{2.303}{60} \log \frac{0.55}{0.17}$$

$$K_{90} = \frac{2.303}{90} \log \frac{0.55}{0.085}$$

$$\text{Average } K = 1.98 \times 10^{-2} \text{ sec}^{-1}$$

- Q. 19. The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rate of production of N_2 and H_2 ? [$K = 2.5 \times 10^{-4}$]



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

$$\begin{aligned} \frac{d[NH_3]}{dt} &= \text{rate} = k \times [NH_3]^0 \\ &= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1} \end{aligned}$$

$$\frac{d[N_2]}{dt} = -\frac{1}{2} \frac{d[NH_3]}{dt}$$

$$= \frac{1}{2} \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$d[\text{H}_2] = -\frac{3}{2} \frac{d[\text{NH}_3]}{dt} = \frac{3}{2} \times 2.5 \times 10^{-4}$$

$$= 3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\text{Rate} = -\frac{d[\text{NH}_3]}{dt} = k \times [\text{NH}_3]^0$$

$$= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\text{Rate of production of N}_2 = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

LONG ANSWER TYPE QUESTIONS

Q. 1. (a) Define order of reaction.

(b) Rates of reaction double with every 10° rise in temperature. If this generalization holds for a reaction in the temperature ranges 298 K to 308 K, what would be the value of activation energy for their reaction ?
R = 8.314 J K⁻¹ mol⁻¹.

Ans. (a) Order of Reaction : It is the sum of powers to which the conc. terms are raised in rate law expression.

$$(b) \quad \log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\text{Here, } T_1 = 298 \text{ K, } T_2 = 308 \text{ K, } R = \text{K}^{-1} \text{ mol}^{-1}$$

$$\frac{K_2}{K_1} = 2$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \left[\frac{1}{298} - \frac{1}{308} \right]$$

$$0.3010 = \frac{E_a}{2.303 \times 8.314} \left[\frac{10}{298 \times 308} \right]$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 298 \times 308}{10}$$

$$= 52898 \text{ J mol}^{-1}$$

$$= 52.898 \text{ KJ mol}^{-1}$$