UNIT 4

Chemical Kinetics

Points to Remember

RATE OF REACTION:-

For a reaction R→P

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

Rate = -Δ[R]/Δt = Δ [P]/ Δt , This is average rate of reaction.

For expressing the rate of such a reaction where stoichiometric coefficients of reactants or products are not equal to one, rate of disappearance of any of the reactants or the rate of appearance of products is divided by their respective stoichiometiric coefficients.

For e.g. for a chemical reaction: $N_2(g) + 3H_2(g) \rightarrow 2NH_3 (g)$

$r_{avg} = -\Delta [N_2] \Delta t = -1/3 (\Delta[H_2]/\Delta t) = ½(\Delta[NH_3]/\Delta t)$

Units of rate of a reaction:-

Concentration $time^{-1}$

- if concentration is in mol L^{-1} and time is in seconds then the units will be mol $L^{-1}s^{-1}$.
- In gaseous reaction, when the concentration of the gases is expressed in terms of their partial pressure, then the units will be atm s^{-1}.

INSTANTANEOUS RATE is defined as the rate of change in concentration of any one of reactant or product at a particular instant of time.

when $\Delta t \rightarrow 0$; $r_{inst} = - d[R]/dt = d [P]/dt$

Factors affecting rate of a reaction:

(a) **Nature of the reacting species:** Chemical reaction is a process in which new chemical bonds are formed and old bonds are broken. Therefore, the strength of these bonds affect the rate of the reaction.

(b) **Concentration of reactants:** The rate of reaction increases with increase in concentration of reactants.

(c) **Effect of temperature:** The rate of reaction is nearly double for every 10^0C rise in temperature.

(d) **Catalyst:** generally catalyst increases the rate of reaction.

(e) **Effect of radiations:** The rates of some reactions are enhanced due to absorption of radiation. These reactions are called photochemical reactions.

LAW OF MASS ACTION:

The rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants.

$aA+bB \rightarrow \text{Products}$

According to law of mass action $\quad$ Rate α $[A]^a[B]^b$,

Rate=$k[A]^a[B]^b$

- **RATE CONSTANT OF A REACTION**

  at a given temperature may be defined as rate of the reaction when the molar concentration of each of the reactants is unity.

- **CHARACTERISTICS OF RATE CONSTANT**

(i) Rate constant is a measure of the rate of the reaction.

(ii) Larger the value of k, faster is the reaction.

(iii) Different reactions have different values of k.

(iv) For a particular reaction, the rate constant is independent of concentration.

(v) At a particular temperature, the value of k is constant. However, it changes with temperature.

- **RATE LAW** is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation. It is determined experimentally.

- **ORDER OF A REACTION:** The sum of powers of the concentration of the reactants in the rate law expression is called the order of the chemical reaction.

  For the rate law expression

  Rate = $k[A]^x[b]^y$

  Order = $x+y$

- **UNITS OF RATE CONSTANTS:** Units of rate constant are different from reaction of different order : $(\text{moIL}^{-1})^{1-n}$ time^{-1} where 'n' is order of reaction. For gas phase reaction unit of rate constant is $(\text{atm of bar})^{1-n}\text{s}^{-1}$

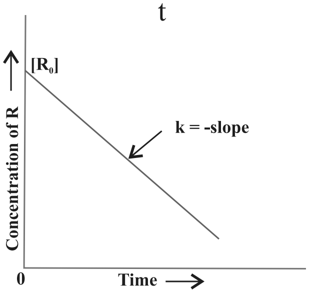
Reaction	Order (α+β)	Units of rate constant
Zero order reaction	0	$\frac{\text{molL}^{-1}}{\text{s}} \text{ x} \frac{1}{(\text{molL}^{-1})^{o}} = \text{molL}^{-1}\text{s}^{-1}$
First order reaction	1	$\frac{\text{molL}^{-1}}{\text{s}} \text{ x } \frac{1}{(\text{molL}^{-1})^{1}} = \text{s}^{-1}$
Second order reaction	2	$\frac{\text{molL}^{-1}}{\text{s}} \text{ x} \frac{1}{(\text{molL}^{-1})^{2}} = \text{mol L}^{-1}\text{s}^{-1}$

MECHANISM AND RATE LAW:

The reactions taking place in one step are called **elementary reactions.** When a sequence of elementary reactions, (called mechanism) gives us the products, the reactions are called **Complex reactions.** In complex reactions, the rate of the reaction is determined by the slowest step in the sequence. The slowest step is called **rate determining step** in the proposed mechanism.

ZERO ORDER REACTION

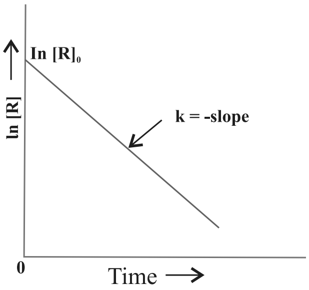
Integrated rate equation $k = \frac{[R]_0 - [R]}{t}$

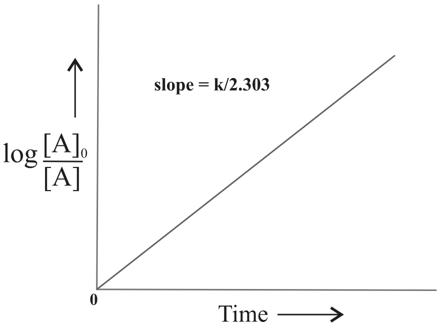


INTEGRATED RATE EQUATION FOR FIRST ORDER REACTION:

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

where $[R]_0$ is initial concentration of reactants and [R] is concentration at time t.





For a typical first order gas phase reaction: $A(g) \rightarrow B(g) + C(g)$

Where p_i is the initial pressure of A and P_t the total pressure at time 't'.

- **HALF-LIFE PERIOD** ($t_{1/2}$): The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

$$k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_i)}$$

For zero order reaction : $t_{1/2} = [R]_0/2k$

For first order reaction : $t_{1/2} = 0.693/k$

For zero order reaction $t_{1/2}$ α $[R]_0$. For first order reaction $t_{1/2}$ is independent of $[R]_0$.

- **PSEUDO FIRST ORDER REACTIONS.** Chemical reactions which are not truly of the first order but under certain conditions become first order reactions e.g. A bimolecular reaction, in which one reactant is present in large excess and rate of reaction is independent of its concentration, the reaction follows first order kinetics.

  For example, ester hydrolysis, where water is taken in excess.

  $CH_3COOCH_2CH_3 + H_2O \rightarrow CH_3COOH + CH_3CH_2OH$ is a bimolecular but first order reaction.

- **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.

  Activation energy = Threshold energy - Kinetic energy

- **Temperature coefficient:** the ratio of rate constant at two temperatures having difference of 10 K is called temperature coefficient.

  Temperature coefficient = Rate constant at T + 10 K/Rate constant at TK

- **Arhenius Equation:**

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

  where , k = Rate constant

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

  E_a= Activation energy

  R= Rate constant

  T= Temperature

  $e^{-Ea/RT}$

  = Fraction of molecules having energy equal to or more than activation energy

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

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

  $$\log \frac{k_2}{k_1} = \frac{E_a}{2.303x\ 8.314} \left[\frac{T_2}{T_2} - \frac{T_1}{T_2}\right]$$ Where $R = 8.314\ JK^{-1}\ mol^{-1}$

OBJECTIVE TYPE QUESTIONS

I MULTIPLE CHOICE QUESTIONS

1. **The initial concentration of the reactant is doubled, the time for half reaction is also doubled. Then the order of the reaction is**

   (a) Zero (b) one (c) Fraction (d) none

2. **Which of the following statements is correct?**

   (a) The rate of a reaction decreases with passage of time as the concentration of reactants decreases

   (b) The rate of a reaction is same at any time during the reaction

   (c) The rate of a reaction is independent of temperature change

   (d) The rate of a reaction decreases with increase in concentration of reactants(s)

3. **The rate constant of a reaction is 5.8x $10^{-21}s^{-1}$. The order of the reaction is.**

   (a) First order (b) zero order (c) Second order (d) Third order

4. **A second order reaction between A and B is elementary reaction: A+B→Product rate law expression of this reaction will be:**

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

5. **Which of the following is pseudo first order reaction?**

   (a) $2H_2O_2 \rightarrow 2H_2O+O_2$

   (b) $2O_3 \rightarrow 3O_2$

   (c) $CH_3COOC_2H_5+NaOH \rightarrow CH_3COONa+C_2H_5OH$

   (d) $CH_3\,COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

6. **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.

7. **Radioactive decay is an example of:**

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

8. **For a zero order reaction, the plot of concentration of reactant vs time is (intercept refers to concentration axis)**

(a) linear with +ve slope and zero intercept

(b) linear with -ve slope and zero intercept

(c) linear with -ve slope and non-zero intercept

(d) linear with positive slope and non-zero inercept

9. **The rate constant of nth order has units**

(a) litre^{1-n}mol^{n}s^{-1} (b) mol^{1-n} litre^{1-n}s^{-1}

(c) mol^{1-n}litre^{n}s^{-1} (d) mol^{1-n}lire^{n-1}s^{-1}

10. **A hypothetical reaction $A_2 + B_2 \rightarrow 2\,AB$ follows the mechanism as given below:**

$A_2 \rightarrow A + A$ (fast)

$A + B_2 \rightarrow AB + B$ (slow)

$A + B \rightarrow AB$ (Fast)

The order of reaction is:

(a) 2 (b) 0 (c) 1½ (d) 1

11. **In a first order, the concentration of the reactant reduced to 1/4 in 60 minutes. What will be its half life?**

(a) 120 min (b) 40 min

(c) 30 min (d) 25 min

12. **For a complex reaction________________________**

(a) order of overall reaction is same as molecularity of the slowest step.

(b) order of overall reaction is less than the molecularity of the slowest step.

(c) order of overall reaction is greater than molecularity of the slowest step.

(d) molecularity of the slowest step is never zero or non integer.

13. **Which of the reaction ends in infinite time?**

(a) Zero order (b) First order

(c) Second order (d) Third order

14. **Which one is correct for first order reaction.**

(a) $t_{75\%}/t_{50\%}=1.5$ (b) $t_{75\%}/t_{50\%}=2$ (c) $t_{99.9\%}/t_{50\%}=10$ (d) $t_{99.9\%}/t_{50\%}=2$

15. The rate constant of a zero order reaction is :

(a) Independent upon initial concentration

(b) Inversely proportional to concentration

(c) Does not depend upon concentration

(d) None of these

16. For the elementary reaction M→N, the rate of dissappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is:

(a) 4 (b) 3 (c) 2 (d) 1

17. When initial concentration of a reactant is doubled in a reaction, its half life period is not affected. The order of the reaction is.

(a) Second (b) more than zero but less than first

(c) Zero (d) First

18. Which of the following influences the rate of reaction?

(a) Temperature (b) Concentration

(c) Light (d) All of these

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

(a) shifting of equilibrium towards reactants due to elastic collisions

(b) loss of active species on collisions

(c) low probability of simultaneous collision of all the reacting species

(d) increase in entropy and activation energy as more molecules are involved.

20. Half life period of a first order reaction is:

(a) directly proportional to the initial concentration of the reactant

(b) half of the rate constant

(c) same for all reactions

(d) independent of initial concentration of reactants

21. The half-life for a zero order reaction equals:

(a) $\frac{2k}{R}$ (b) $\frac{1}{2}\frac{k}{R^2}$

(c) $\frac{R^2}{2k}$ (d) $\frac{R}{2k}$

Where R is the initial concentration.

II FILL IN THE BLANKS

1. Hydrolysis of ethyl acetate in an acidic solution is an example of .... order reaction.

2. If the activation energy of the reaction is low, it proceeds at .... rate.

3. In a multi step reaction, the .... step determines the rate of reaction.

4. For a first order reaction, the half life period is equal to ....

5. The order and molecularity of a complex reaction............................be same.

6. The inversion of cane sugar is a .... order reaction though its molecularity is..........

7. The difference of energy between activated complex and that of the reactants is called.....................................

8. The unit of first order rate constant when concentration is Measured in terms of pressure and time in minutes is..................................

9. A first order reaction has t½ = 6.93min. The rate constant is ....

10. Increase in temperature increases the number of ....

III ASSERTION REASON TYPE QUESTIONS

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is wrong statement.

(d) Assertion is wrong, but reason is correct statement.

1. **Assertion:** Hydrolysis of methyl ethanoate is a pseudo first order reaction.

Reason: Water is present in large excess and therefore its concentration remains constant throughout the reaction.

2. **Assertion:** The slowest elementary step in a complex reaction decides the rate of the reaction.
   Reason: The slowest elementary step always has the smallest molecularity.
3. **Assertion:** A catalyst increases the rate of a reaction.
   Reason: The catalyst increases the activation energy which in turn increases the rate of the reaction.
4. **Assertion:** Activation complex for the forward reaction reaction will have lower energy than that for the backward reaction in an exothermic reaction.
   Reason: Reactants have greater energy than products for an exothermic reaction.
5. **Assertion:** Increase in temperature increases rate of reaction.
   Reason: More colliding molecules will have energy greater than threshold energy.
6. **Assertion:** Unit of rate constant is independent of order of reaction.
   Reason: The power of concentration terms in the rate equation keep changing with change in order.
7. **Assertion:** In zero order reaction , the concentration. versus time graph is a straight line.
   Reason: The rate of change of concentration per unit time in zero order reaction remains constant
8. **Assertion:** Half-life period is always independent of initial concentration
   Reason: Half-life period is inversely proportional to rate constant
9. **Assertion:** The rate of reaction is the rate of change of concentration of a reactant or a product.
   Reason: Rate of reaction remains constant during the course of reaction.
10. **Assertion:** Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex reactions.
    Reason: Reactant molecules undergo chemical change irrespective of their orientation during collision

IV ONE WORD ANSWER TYPE QUESTIONS

1. For reactions of which order the units of rate constant and rate of reaction are same?
2. What is the difference in energy between the energy of activated complex and the average energy of reactants called?
3. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction?
4. What is the effect of catalyst on activation energy of reaction?
5. For a reaction half-life is observed to be independent of the initial concentration of the reactants. What is the order of reaction?
6. What is the effect of catalyst on Gibb's energy change (ΔG) of a reaction?
7. For which type of reaction, order and molecularity have the same value?
8. Identify the order of reaction from the following unit of rate constant: $L mol^{-1} s^{-1}$
9. What is the effect of increase in surface area of reactants on rate of reaction?
10. E_1 and E_2 are the activation energies of the reactant and product respectively. If $E_2 > E_1$, predict the nature of reaction (Exothermic or Endothermic)?

11. The reaction, A + 2B→C obeys the rate equation.
    Rate = $K[A]^{1/2}[B]^{3/2}$
    What is the order of a reaction?
12. Express the rate of the following reaction in terms of disapperance of hydrogen in the reaction.
    $3H_2(g)+N_2(g) \rightarrow 2\,NH_3(g)$
13. For the reaction, A→B, the rate of reaction becomes twenty seven times when the concentration of A is increased three times. What is the order of the reaction ?
14. The decomposition reaction of ammonia gas on platinum surface has a rate constant = 2.5×10^{-4} mol L^{-1} s^{-1}. What is the order of the reaction?
15. An endothermic reaction A→ B has an activation energy of 15 kcal/mole and the energy of the reactant is 5 kcal/mol. What is the activation energy for the reaction B → A ?

VERY SHORT ANSWER TYPE QUESTIONS (1 MARK)

1. The rate law for a reaction is 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.

2. For the reaction $3H_2 + N_2 \rightarrow 2NH_3$, how are the rate of reaction expression - $d[H_2]/dt$ and $d[NH_3]/dt$ **inter-related?**

Ans.-$1/3\ d[H_2]/dt = 1/2\ d[NH_3]/dt$

3. Identify the order of a reaction from the following rate constant :
=2.3×10^{-5} L mol^{-1} s^{-1}

Ans. Second order

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

Ans. 1/32

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

Ans. No change in ΔG.

6. What value of k is predicted for the rate constant by Arrhenius equation is T→∞ ? Is this value physically reasonable?

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

7. Determine the roder of reaction?
Step 1. $2NO+H_2 \rightarrow N_2+ H_2O_2$ (Slow)
Step 2. $H_2O_2+H_2 \rightarrow 2H_2O$ (Fast)

Ans. Rate = $k[NO]^2[H_2]$
Order = 2+1
= 3

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

Ans. Zero order

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

Ans. 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.

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 10^0C.

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.

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.

13. The rate constant of a reaction is $3x10^2$ min^{-1}. What is its order of reaction ?(On the basis of units of rate constant)

Ans. First order reaction.

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

Ans. 16 minutes.

15. What is meant by an elementary reaction?

Ans. A reaction which takes place in one step is called an elementary reaction. For example: $H_2+I_2\rightarrow 2HI$.

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

Ans. $2HI\rightarrow H_2+I_2$ (Order = Molecularity = 2)

17. For a reaction R→P, the rate becomes 2 time when the concentration of the reactant A is increased 4 times. What is the order of reaction ?

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

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

Ans. $t=[R]_0-[R]/k=0.10-0.075/0.003=8.3$ second

19. In a reaction 2A → Products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval.

Ans. Average rate: $-\Delta[A]/2\Delta t=-½(0.4-0.5/10)=5x10^{-3}M\ min^{-1}$

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

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

Ans. Decomposition of acetaldehyde (order = 1.5)

$CH_3CHO\rightarrow CH_4+CO$

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

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

23. What is order of radioactive decay?

Ans. First order

24. For a reaction A+B → product, the rate law is given by $r=k[A]^{1/2}[B]^2$. **What is the order of the reaction ?**

Ans. Order of reaction = 1/2 + 2 = 2.5

25. For a chemical reaction half life period cannot depend on concentration of solution. What is order of reaction?

Ans. First order reaction

SHORT ANSWER TYPE QUESTIONS (2 or 3 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

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

follows a first order kinetics.

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

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

Ans. (a) Rate $= k[N_2O_5]$

$$k = \frac{\text{Rate}}{[N_2O_5]} = \frac{1.5\times10^{-6}}{0.05}$$

$$k = 3.0 \times 10^{-5}\text{ s}^{-1}$$

(b) Rate $= 2.45 \times 10^{-5}\text{ mol L}^{-1}\text{ s}^{-1}$

(b)

$$[N_2O_5] = \frac{\text{Rate}}{k} = \frac{2.45\times10^{-5}}{3.0\times10^{-5}} = 0.82\text{ M}$$

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 :

$$2H_2O_2 \xrightarrow{OH^-/I^-} 2H_2O + O_2$$

This reaction takes place in two steps as given below :

Step 1. $H_2O_2 + I^- \rightarrow H_2O + IO^-$ **(slow)**

Step 2. $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$ **(fast)**

(a) Determine rate law expression.

(b) Determine the order of reaction.

Ans. (a) Rate = $k[H_2O_2][I^-]$ because first step is rate determining step.

(b) Order = 1 + 1 = 2

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

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

Comparing the equation with Arrhenius equation,

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

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

$$E_a = 28000 \times 8.314$$

$$= 232192\ J\ mol^{-1}$$

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 or rate constant for such a reaction?

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

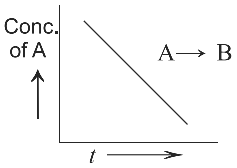
New rate will be 1/4 of initial rate

$k = mol^{-1}\ Ls^{-1}$

Q.7. For a first order reaction time taken for half of the reaction to complete is t_1 and ¾ of the reaction to complete is t_2. How are t_1 and t_2 related ?

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

Q.8.



(A) Why is the order of the reaction ?
(b) What is the slope of the curve ?

Ans. (a) Zero order reaction.

(b) $[R] = [R]_o - kt$ $\therefore$ 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

$$\therefore \quad kt = [R]_0 \qquad t = \frac{[R]_0}{k}$$

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

Q.10. 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) → Products

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

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

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

Dividing equation (i) by equation (ii),

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

Q.11. A reaction which is first order with respect to A has rate constant 6 min^{-1}. If we start with [A] = 0.5 mol L^{-1}, when would [A] reach the value of 0.05 mol L^{-1}

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

$k = 6$ 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.12. 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.13. A first order reaction has a rate constant 1.15×10^{-3} s^{-1}. How long will 5 gram of this reactant take to reduce to 3 grams ?

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

$$t=\frac{2.303}{(1.15\times10^{-3})s^{-1}}\log\left(\frac{5}{3}\right)$$

$$=\frac{2.303}{(1.15\times10^{-3})s^{-1}}[\log5-\log3]$$

$=444$s

Q.14. Distinguish between rate expression and rate constant of a reaction.

Ans. Rate expression is the way to express rate of reaction in terms of concentration of reactants. for a chemical reaction $aA+bB\rightarrow cC+dD$ Rate $= k\,[A]^x\,[B]^y$

Rate constant (k) is defined as the rate of reaction when the concentration of reactants are taken as unity.

Q.15. Consider a certain reaction A → Product with k = 2.0×10^{-2} s^{-1}. Calculate the concentration of A remaining after 100 s, if the initial concentration of A is 1.0 mol L^{-1}.

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

$$2 \text{ x } 10^{-2}=\frac{2.303}{100}\log\frac{1}{[R]}$$

$$\log\frac{1}{[R]}=\frac{2}{2.303}=0.8684$$

$$\frac{1}{[R]}=\text{Antilog }(0.8684)$$

$=7.3853$

$$[R]=\frac{1}{7.3853}=0.135\text{M}$$

Q.16. **For the reaction $NO_2 + CO \longrightarrow CO_2 + NO$, the experimentally determined rate expression below 400K is rate= $k[NO_2]^2$. What mechanism can be proposed for this reaction?**

Ans. $NO_2 + NO_2 \xrightarrow{\text{Slow}} NO + NO_3$

$NO_3 + CO \xrightarrow{\text{Fast}} NO_2 + CO_2$

Q.17. **The half life period of a first order reaction is 60 min. What % will be after 240 mins?**

Hint: No. of half lives (n) = 240/60 = 4

$\% \text{ of A left} = \frac{[A]_\circ}{2^n} = \frac{[A]_\circ}{2^n} = 6.25\%$

Q.18. **Time for half change for a first order reaction is 40 min. What % will be left after 240 mins. ?**

Ans.

$\text{No. of half lives} = \frac{240}{40} = 6$

$\% \text{ of A left} = \frac{[A]_\circ}{2^n} = \frac{[A]_\circ}{2^6}$

$= 1.56\%$

Q.19. **The following data were obtained during the first order thermal decomposition of N_2O_5 at constant volume :**

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

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

Calculate rate constant.

Ans.

	N_2O_5	N_2O_4	$+ 1/2O_2$
Initial	0.5	0	0
Final	(0.5-x)	x	x/2

$P_t = 0.5 - x + x + x/2 = 0.5 + x/2$

$0.5 + x/2 = 0.512$

$x = 0.024$

$$k = \frac{2.303}{t} \log \frac{p_i}{p_{N_2O_5}}$$

$$k = \frac{2.303}{100} \log \frac{0.5}{0.5 - 0.0240}$$

$$k = 4.92 \times 10^{-4} s^{-1}$$

Q.20. The decomposition of A into product has value of k as 4.5 x$10^3$$s^{-1}$ at 10^{o}C and energy of activation 60 KJ mol. At what temperature would k be 1.5 × 10^4 sec^{-1}.

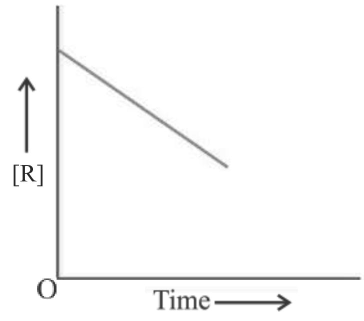
Ans.

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2\text{-}T_1}{T_1T_2}\right)$$

$$\log\left(\frac{1.5\text{-}10^4}{4.5\times 10^3}\right) = \frac{60000}{2.303\times 8.314}\left[\frac{T_2\text{-}283}{283\ T_2}\right]$$

T_2= 297K

Q.21. For a chemical reaction R → 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?

Ans. (a) Zero

(b) Rate = $k[R]^0$

(c) Slope = - k

Q.22. (a)Write rate law and order of the following reaction:

$AB+C_2 \rightarrow AB_2C+C$ (slow)

$AB_2+C \rightarrow AB_2C$ (fast)

(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

(b) Refer ' points to remember"

(c) $k=Ae^{-Ea/RT}$

Q.23. 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.

$$t = \frac{2.303}{K} \log \frac{[R]_0}{[R]}$$

$$t = \frac{2.303}{60} \log \frac{[R]_0}{[R]_0/10}$$

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

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

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

Q.24. The rate of most of reaction double when their temperature is raised from 298K to 308K. Calculate the activation energy of such a reaction .

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

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

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

Q.25. A first order reaction takes 69.3 min for 50% completion. Set up on equation for determining the time needed for 80% completion

$$k = \frac{0.693}{t1/2} = \frac{0.693}{69.3} \text{ min}$$

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

$$T = \frac{2.303}{T} \log \frac{[R]_0}{[R]}$$

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

$$= 160.9 \text{ min}$$

Q.26. The activation energy of a reaction is 94.14 KJ/mol and the value of rate constant at 40° C is 1.8 X 10^{-1} sec^{-1}. Calculate the frequency factor A.

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

By using, $k = Ae^{-Ea/RT}$ $\quad$ $\text{In } k = \text{In } A - \frac{E_a}{RT}$

Or $\log k = \log A - \frac{Ea}{2.303RT}$

Or $\log(1.8x10^{-1}) + \dfrac{94.19\times10^{3}}{2.303\times8.314\times313} = \log A$

Or $A = \text{antilog}(10.9635) = 9.194\times10^{10}\ S^{-1}$

Q.27. The rate constant of a reaction at 700 K and 760 k are 0.011 $M^{-1}S^{-1}$ and 0.105 $M^{-1}\ S^{-1}$ respectively. Calculate the value of arrhenius parameters

Ans. 2.824×10^{10}

Q.28. The initial concentration of N_2O_5 in the first order reaction $N_2O_5 \rightarrow 2NO_2 + ½O_2$ was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.

Ans.

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]} = \frac{2.303}{t}\log\frac{[N_2O_5]_0}{[N_2O_5]_t} = \frac{2.303}{60}\log\frac{1.24\times10^{-2}}{0.2\times10^{-2}}$$

$$= \frac{2.303}{60}\log 6.2 = \frac{2.303}{60}\times0.7924\ \text{min}^{-1}$$

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

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q.1. (a) Define order or 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 to conc. terms are raised in rate law expression.

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

Here, $T_1 = 298$ K, $T_2 = 308$ K, R = 8.314 JK^{-1} Mol^{-1}

$$\frac{k_2}{k_1} = 2$$

$$\log 2 = \frac{E_a}{2.303\times8.314}\left[\frac{1}{298} - \frac{1}{308}\right]$$

$$0.3010 = \frac{E_a}{2.303\times8.314}\left[\frac{10}{298\times308}\right]$$

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

$$= 52898 \text{ Jmol}^{-1}$$

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

Q. 2. (a) What are pseudo order reaction ? Give example.

(b) Rate constant K of a reaction varies with temperature 'T' according to the equation :

$$\log K = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

where E_a is the activation energy. When a graph is plotted for log K vs 1/T, a straight line with a slope of – 4250 K is obtained. Calculate E_a for the reaction.

Ans. (a) The chemical reaction which look like higher order reaction but in real they follow lower order kinetics.

For example,

$$\underset{\text{excess}}{CH_3COOC_2H_5 + H_2O} \xrightarrow{H^+} CH_5COOH + C_2H_5OH$$

$$\text{Rate} = K[CH_3COOC_2H_5]$$

$$\text{Order} = 1$$

(b) $$\text{Slope} = \frac{E_a}{2.303R} = -4250 \text{ K}$$

So, $$E_a = -2.303 \times R \times \text{Slope}$$

$$= -2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 4250$$

$$= 81375.3 \text{ J mol}^{-1}$$

$$= 81.375 \text{ KJ mol}^{-1}$$

Q.3. **(a) Determine the units of rate constant for first and zero order reaction.**

(b) Show that time required for the completion of 99% of the first order reaction is twice the 90% of completion of the reaction.

Ans. (a) $k = (\text{mol})^{1-n}\, L^{n-1}\, s^{-1}$

For zero order, $n = 0$

So, $k = (\text{mol})^{1-0}\, L^{0-1}\, s^{-1} = s^{-1}\ \text{mol}\, L^{-1}$

For first order, $n = 1$

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

So, $k = (\text{mol})^{1-1}\, L^{1-1}\, s^{-1}$

$= s^{-1}$

(b) For a first order reaction,

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

$$[A]_0 = a,\ [A] = a - \frac{a \times 99}{100} = 0.01\, a$$

$$t_{99\%} = \frac{2.303}{k} \log \frac{a}{0.01a} \qquad = \frac{2.303}{k} \log 100 \qquad = \frac{2.303}{k} \times 2$$

...(i)

For 90% completion of reaction,

$$[A] = a - \frac{a \times 99}{100} = 0.1a$$

$$t_{99\%} = \frac{2.303}{k} \log \frac{a}{0.1a} \qquad = \frac{2.303}{k} \times 1$$

...(ii)

Dividing equation (i) by equation (ii), we get

$$t_{99\%} = 2 \times t_{90\%}$$

Q.4. **(a) Define rate constant of reaction.**

(b) A first order reaction takes 40 mins for 30% decomposition. Calculate $t_{1/2}$.

Ans. (a) **Rate constant :** It is the rate of chemical reaction when the concentration of reactant taken as unity at a given temperature.

(b) Let initial conc. $= a$

$$\text{Conc. after 40 mins.} = a - \frac{a \times 30}{100} = 0.70\,a$$

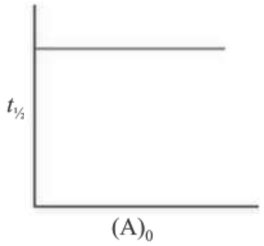
$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

$$= \frac{2.303}{40}\log\frac{a}{0.70a} \quad = \frac{2.303}{40}\log\frac{1}{0.70}$$

$$= \frac{2.303}{40} \times 0.1549 = 8.92 \times 10^{-3}\ \text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.92 \times 10^{-3}} = 77.7\ \text{min}$$

Q. 5. **(a) Determine the order of reaction and also determine the units of rate constant.**



(b) The following data were given for thermal decomposition of SO_2Cl_2 at a constant volume :

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

Exp.	Time/s	Total p/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

Ans. (a) First order reaction

$$k = \text{mol}^{1-n}\,\text{L}^{n-1}\,\text{s}^{-1}$$

$$n = 1$$

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

$$= \text{s}^{-1}$$

(b)
$$k = \frac{2.303}{t}\log\frac{P_i}{(2P_i - P_t)}$$

$$= \frac{2.303}{100}\log\frac{0.5}{\left(2\times 0.5 - 0.6\right)}$$

$$= \frac{2.303}{100}\log\frac{0.5}{0..4}$$

$$= \frac{2.303}{100}\times 0.969 = 2.23\times 10^{-3}\text{s}^{-1}$$

Now, Rate $= P_{SO_2Cl_2}$

Pressure of SO_2Cl_2 when total pressure = 0.65 atm

$$P_{SO_2Cl_2} = 2P_i - P_t$$

$$= 2\times 0.5 - 0.65 \quad = 0.35 \text{ atm}$$

$$\text{Rate} = 2.23\times 10^{-3}\times 0.35 \quad = 7.8\times 10^{-4}\text{ atm s}^{-1}$$

Q.6. **(a)The activation energy of a reaction is 100 kJ/mol. In the presence of catalyst the activation energy is decreased by 75%. What is the effect on rate constant of the reaction at 20°C ?**

(b) $A+2B \rightarrow 3C+2D$

The rate of disappearance of B is 1×10^{-2} mol L^{-1} sec^{-1}. What will be

(i) rate of reaction (ii) rate of change in the concentration of A and C ?

Ans. (a) 2.35×10^{10} times

(b) $(5\times10^{-3}, 5\times10^{-3}, 15\times10^{-3})$ mol L^{-1} s^{-1}

Q.7. **(a)A reaction is of first order in A and of second order in B. Write the differential rate equation for this reaction. How will its initial rate be affected if the concentration of both A and B are together doubled ?**

(b) The rate constant k of a reaction increases four fold when the temperature changes from 300 K to 320 K. Calculate the activation energy for the reaction. ($R=8.314$ J K^{-1} mol^{-1})

Ans. (a) $r=k[A]^1$ .... (1)

$r=k[B]^2$ .... (2)

Differential rate equation is

$r=k[A]^1 \quad [B]^2$ .... (3)

When conc. of both A and B is doubled

$r'=k[2A]^1 \quad [2B]^2$ .... (4)

Divide (4) by (3),

$r'/r=8$

Thus , rate becomes 8 times.

(b) $\dfrac{k_2}{k_1} = 4$, $T^1 = 300K$, $T_2 = 320$ K

$R=8.314J\ K^{-1}\ mol^{-1}$

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

$$\Rightarrow \qquad \log 4 = \frac{E_a}{2.303\times8.314JK^{-1}\ mol^{-1}} \times \left[\frac{320-300}{300\times320}\right] K^{-1}$$

$$\Rightarrow \qquad 0.6020 = \frac{E_a}{2.303\times8.314JK^{-1}\ mol^{-1}} \left[\frac{20\ K^{-1}}{96\times10^{3}}\right]$$

E_a= 55327.6 J mol^{-1} = 55.33 kJ mol^{-1}

Q.8. **(a)What are the factors on which rate of the reaction depends ? Discuss each factor in brief.**

(b) The following results have been obtained during the kinetics studies of the reaction:

$2A+B \rightarrow C+D$

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}**

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

(a) Refer "Points to Remember"

(b) For the reaction $2A+B \rightarrow C+D$

Assume rate law expression as Rate $= k[A]^a [B]^b$

According to question,

$$6.0 \times 10^{-3} = k(0.1)^a (0.1)^b \quad .....(i)$$
$$7.2 \times 10^{-2} = k(0.3)^a (0.2)^b \quad .....(ii)$$
$$2.88 \times 10^{-1} = k(0.3)^a (0.4)^b \quad .....(iii)$$
$$2.40 \times 10^{-2} = k(0.4)^a (0.1)^b \quad .....(iv)$$

Divide eqn. (iv) by (i), we get

$$4=(4)^a \quad \therefore a=1$$

Divide eqn. (iii) by (ii), we get

$$4=(2)^b$$
$$(2)^2=(2)^b \quad \therefore b=2$$

Order with respect to A = 1

Order with respect to B = 2

$\therefore$ Rate Law $= k[A][B]^2$

On putting the value of 'a' and 'b' into any equation say (i)

$$\therefore \quad 6.0 \times 10^{-3}\,M\,min^{-1} = k(0.1M)(0.1M)^2$$
$$k = 6\,M^{-2}\,min^{-1}$$

Q.9. (a) Derive the general from of the expression for the half life of a first order reaction.

(b) The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rates of production of N_2 and H_2 if $k=2.5x10^{-4}$ mol^{-1} Ls^{-1}?

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

When $[R] = \frac{[R]_0}{2}$, then $t = t_{1/2}$

$$\therefore \quad t_{1/2} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_{0/2}} = \frac{2.303}{k} \log 2$$

or $t_{1/2} = \frac{2.303}{k}$ x 0.3010

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

(b)

$$2NH_3 \longrightarrow N_2 + 3H_2$$

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

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

$$\frac{d[N_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{1}{2} \text{x } 2.5 \text{ x } 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$d[H_2] = -\frac{3}{2}\frac{d[NH_3]}{dt} = \frac{3}{2} \text{x } 2.5 \text{ x } 10^{-4} = 3.75 \text{ x } 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$= -\frac{d[NH_3]}{dt} = k \text{x} [NH_3]^0 = 2.5 \text{ x } 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

Rate of production of N_2 = 2.5 x 10^{-4} mol L^{-1} sec^{-1}

Q.10. (i) What is rate constant ?
(ii) On what factors it depends ?
(iii)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. (i) rate constant(k) of a chemical reaction is rate of reaction when the concentration of the reactants is unity .
(ii) Rate constant (k) depends upon (i) temperature (ii) order of reaction
(iii)

(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)

$$k_{30} = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{30} \log \frac{0.55}{0.31}$$

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

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

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

CASE STUDY BASED QUESTIONS

1. **Read the passage given below and answer the questions that follow:**

The rate of reaction is the change of concentration of reactant or product with time. The rate law for the reaction $aA+bB \rightarrow cC+dD$ the rate law is rate=$k[A]^a[B]^b$. The rate of reaction is calculated by knowing *k, a* and *b*. The rate laws are determined experimentally. During the collisions among two A and two B molecules, doubling the number of either type of molecule increases the number of collisions to eight. The species temporarily formed by the reactant molecules as a result of the collision before they form the product is called the *activated complex*. The temperatare-dependent rate constant is given by the Arrhenius equation. In many cases, the sum of a series of simple reactions are called elementary steps or elementary reactions because they represent the progress of the overall reaction at the molecular level. The sequence of elementary steps that leads to product formation is called the reaction mechanism. The number of molecules reacting in an elementary step determines the molecularity of a reaction.

(A) **On which of the following quantities does the rate constant of a reaction depend?**

(a) Concentrations of reactants (b) Nature of reactant

(c) Temperature (d) All the above

(B) **Instantaneous rate of reaction is measured from the:**

(a) graph of time versus concentration (b) molecularity of reaction

(c) integration method (d) reaction mechanism of a reaction

(C) **The order of reaction is always defined in terms of:**

(a) product concentration (b) rate constant of a reaction

(c) reactant concentration (d) ratio of the product concentration to the reactant concentration

(D) **The number of molecules reacting in an elementary step of a reaction may be:**

(a) 1 (b) 1/2 (c) 12 (d) 5

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

The integrated rate equations can be fitted with kinetic data to determine the order of a reaction. The integrated rate equations for zero and first order reaction are:

Zero order : $[A] = -kt + [A]_o$

First order : $\log [A] = \frac{-kt}{2.303} + \log [A]_o$

These equations can also be used to calculate the half life periods of different reactions, which give the time during which the concentration of a reactant is reduced to half of its initial concentration i.e. at time $t_{1/2}$; $[A] = [A]_o$

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

(A) **ASSERTION:** For the first order reaction the units of rate constant are time^{-1}.

REASON: The rate of first order reaction remains constant throughout.

(B) **ASSERTION:** In zero order reaction, the concentration versus time graph is a straight line.

REASON: The rate of change of concentration per unit time in zero order reaction remains constant.

(C) **ASSERTION:** Half-life period is always independent of initial concentration.

REASON: Half-life period is inversely proportional to rate constant.

(D) **ASSERTION**: The slowest step in the reaction is rate determining step.

REASON: Order of a reaction is given by rate law expression.

ANSWERS

I MULTIPLE CHOICE QUESTION:

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

II FILL IN THE BLANKS:

1. Pseudo first
2. Fast
3. Slowest
4. 0.693/k
5. Cannot
6. First, two
7. Activation energy
8. min^{-1}
9. $0.1\ min^{-1}$
10. Effective collisions

III ASSERTION REASON TYPE QUESTIONS:

1. (a) 2. (c) 3. (c) 4. (d) 5. (a) 6. (d) 7. (a) 8. (d) 9. (c) 10. (c)

IV ONE WORD ANSWER TYPE QUESTIONS:

1. Zero order
2. Activation energy
3. First order reaction
4. Decrease
5. First order
6. No effect
7. Elementary reaction
8. Second order
9. Increase
10. Endothermic
11. Two
12. Rate of Disappearence of $H_2 = -\frac{d[H_2]}{dt}$
13. 3
14. Zero
15. 10 Kcal/mol

CASE STUDY BASED QUESTIONS:

1: (A) c (B) a (C) c (D) a
2: (A) c (B) a (C) d (D) b

UNIT TEST-1
CHAPTER - 4
CHEMICAL KINETICS

TIME ALLOWED : 1 HR **M.M. : 20**

1. Which of the following statements is not correct for the catalyst? 1
   - (a) It catalyses the forward and backward reaction to the same extent.
   - (b) It alters ΔG of the reaction.
   - (c) It is a substance that does not change the equilibrium constant of a reaction.
   - (d) It provides an alternate mechanism by reducing activation energy between reactants and products.
2. For the reaction: $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$ 1

   Which of the following expression is correct for the rate of the reaction?
   - (a) $\Delta[Br^-]/\Delta t = 5\Delta[H^+]/\Delta t$ (b) $\Delta[Br^-]/\Delta t = 6\Delta[H^+]/5\Delta t$
   - (c) $\Delta[Br^-]/\Delta t = 5\Delta[H^+]/6\Delta t$ (d) $\Delta[Br^-]/\Delta t = 6\Delta[H^+]/\Delta t$
3. For a zero order reaction will the molecularity be equal to zero? Explain. 1

ASSERTION REASON TYPE QUESTIONS

- (a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.
- (b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.
- (c) Assertion is correct, but reason is wrong statement.
- (d) Assertion is wrong, but reason is correct statement.

4. **ASSERTION:** The rate of reaction is the rate of change of concentration of a reaction or a product. 1

   REASON: Rate of reaction remains constant during the course of reaction.
5. **ASSERTION:** Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex reactions. 1

   REASON: Reactant molecules undergo chemical change irrespective of their orientation during collision.
6. (i) Why does the rate of a reaction increase with increase in temperature? 2

   (ii) Why is the probability of reaction with molecularity higher than three very rare?

7. After 24 hours, only 0.125 g out of the initial quantity of 1g of a radioactive isotope remains behind. What is its half-life period? 3

8. A first order reaction is 50% completed in 40 minutes at 300K and in 20 minutes at 320K. Calculate the activation energy of the reaction. 3

   (Given: log2= 0.3010, log4=0.6021, R= 8.314JK^{-1}mol^{-1})

9. (i) Define order of reaction. How does order of a reaction differ from molecularity for a complex reaction? 5

   (ii) Define instantaneous rate of reaction

   (iii) Why H_2 and O_2 do not react at room temperature?

   (iv) For which type of reactions, order and molecularity have the same value?

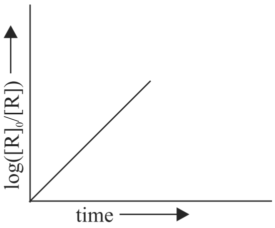
UNIT TEST-2

CHAPTER - 4

CHEMICAL KINETICS

TIME ALLOWED : 1 HR **M.M. : 20**

1. Identify the order of reaction from the following unit for its rate constant: $Lmol^{-1}s^{-1}$ (1)
2. for the reaction, $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ If rate of formation of NO is $6X10^{-4}$ atm min^{-1}, calculate the rate of formation of H_2O (1)
3. Write the relationship between k and $t_{1/2}$ (half life period) for first order reaction. (1)
4. Explain with an example, what is a pseudo first order reaction? (1)
5. For the chemical reaction, what is the effect of a catalyst on the rate constant of the reaction? (1)
6. Differentiate between: Average rate and instantaneous rate of a chemical reaction. (2)
7. Observe the graph shown in figure and answer the following question. (2)
   (a) What is the order of the reaction ?
   (b) What is the slope of the curve ?



8. 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. (3)
9. The rate constant of a reaction at 500K and 700 K are 0.02 s^{-1} and 0.07s^{-1} respectively. Calculate the value of Ea and A. (3)
10. (i) Answer the following questions (3)
    (a) The conversion of molecules A to B follow second order kinetics. If concentration of A is increased to three times, how will it affect the rate of formation of B ?
    (b) Write the expression of integrated rate equation for zero order reaction.
    (ii) A first order reaction is 20% complete in 20 minutes. Calculate the time taken for the reaction to go to 80% completion (5)