

4 ■ ■ ■ Chemical Kinetics

I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. The role of a catalyst is to change _____.

- (i) gibbs energy of reaction.
- (ii) enthalpy of reaction.
- (iii) activation energy of reaction.
- (iv) equilibrium constant

Ans. (iii)

Explanation: Catalyst can change the activation energy of the reaction by changing the path of the reaction.

2. In the presence of a catalyst, the heat evolved or absorbed during the reaction _____.

- (i) increases. (ii) decreases.
- (iii) remains unchanged. (iv) may increase or decrease.

Ans. (iii)

Explanation: Catalyst do not change the stability of the reaction and thus the heat remains constant.

3. Activation energy of a chemical reaction can be determined by _____.

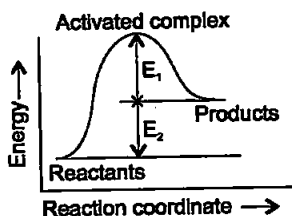
- (i) determining the rate constant at standard temperature.
- (ii) determining the rate constants at two temperatures.
- (iii) determining probability of collision.
- (iv) using catalyst.

Ans. (ii)

Explanation: $\log k_2/k_1 = E_a/2.303[T_2 - T_1/T_1T_2]$ this eq. can be used to calculate the activation energy of the reaction. k_2 and k_1 are the rate constant E_a = activation energy T_1 and T_2 are two different temperature.

4. Consider the figure and mark the correct option.

- (i) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.
- (ii) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant.
- (iii) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product.
- (iv) Activation energy of backward reaction is E_1 and product is more stable than reactant.



Ans. (i)

Explanation: The energy required to form the reaction intermediate is called activation energy. The energy gap between reactant and product molecule = $E_1 + E_2$ some energy is released when complex decomposes to form product.

5. Consider a first order gas phase decomposition reaction given below:



The initial pressure of the system before decomposition of A was p_i . After lapse of time 't', total pressure of the system increased by x units and became ' p_t '.

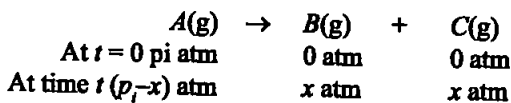
The rate constant k for the reaction is given as.

$$(i) k = \frac{2.303}{t} \log \frac{p_i}{p_i - x} \quad (ii) k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$$

$$(iii) k = \frac{2.303}{t} \log \frac{p_i}{2p_i + p_t} \quad (iv) k = \frac{2.303}{t} \log \frac{p_i}{2p_i + x}$$

Ans. (ii)

Explanation: Let p_A , p_B and p_C are the partial pressures of A, B and C respectively. If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.



where, p_i is the initial pressure at time $t = 0$.

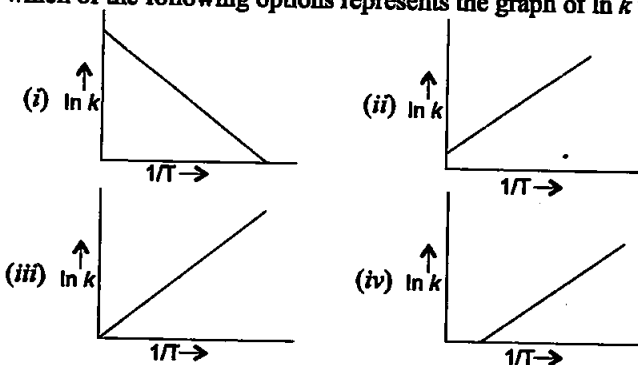
$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

where, $p_A = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$

According to the first order reaction rate constant $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$

6. According to Arrhenius equation rate constant k is equal to $k = Ae^{-E_a/RT}$, which of the following options represents the graph of $\ln k$ vs $1/T$?



Ans. (i)

Explanation: In the Arrhenius equation the factor $k = Ae^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a . Taking natural logarithm of both sides of equation

$$\ln k = \frac{E_a}{RT} + \ln A$$

The plot of $\ln k$ vs $1/T$ gives a straight line according to the equation. Thus, it has been found from Arrhenius equation that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

In graph, $\text{slope} = \frac{-E_a}{R}$

7. Consider the Arrhenius equation given below and mark the correct option.

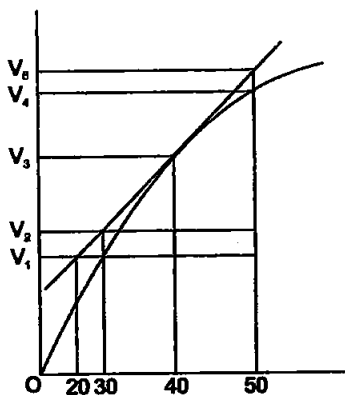
$$k = Ae^{-E_a/RT}$$

- (i) Rate constant increases exponentially with increasing activation energy and decreasing temperature.
- (ii) Rate constant decreases exponentially with increasing activation energy and decreasing temperature.
- (iii) Rate constant increases exponentially with decreasing activation energy and decreasing temperature.
- (iv) Rate constant increases exponentially with decreasing activation energy and increasing temperature.

Ans. (iv)

8. A graph of volume of hydrogen released vs time for the reaction between zinc and dil. HCl is given in the figure. On the basis of this mark the correct option.

- (i) Average rate upto 40 second is $\frac{V_3 - V_2}{40}$
- (ii) Average rate upto 40 seconds is $\frac{V_3 - V_2}{40 - 30}$
- (iii) Average rate upto 40 seconds is $\frac{V_3}{40}$
- (iv) Average rate upto 40 seconds is $\frac{V_3 - V_1}{40 - 20}$



Ans. (iii)

Explanation: Average rate for the reaction =

$$\frac{\text{Change in concentration of } H_2}{\text{Change in time}} = \frac{V_3 - 0}{40 - 0} = \frac{V_3}{40}$$

9. Which of the following statements is not correct about order of a reaction.
- The order of a reaction can be a fractional number.
 - Order of a reaction is experimentally determined quantity.
 - The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.
 - The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression

Ans. (iii)

Explanation: The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction. 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.

10. Consider the graph given in figure 4.2 (see question no. 8). Which of the following options does not show instantaneous rate of reaction at 40th second?

- | | |
|-----------------------------------|----------------------------------|
| (i) $\frac{V_5 - V_2}{50 - 30}$ | (ii) $\frac{V_3 - V_2}{40 - 30}$ |
| (iii) $\frac{V_3 - V_2}{40 - 30}$ | (iv) $\frac{V_3 - V_1}{40 - 20}$ |

Ans. (ii)

Explanation: The rate of a reaction at a particular moment of time. Average rate expression becomes instantaneous rate expression as $\Delta t \rightarrow 0$ (i), (iii) and (iv) are correct expression of instantaneous rate since small change in volume and small interval of time is taken

11. Which of the following statements is correct?

- The rate of a reaction decreases with passage of time as the concentration of reactants decreases.
- The rate of a reaction is same at any time during the reaction.
- The rate of a reaction is independent of temperature change.
- The rate of a reaction decreases with increase in concentration of reactant(s).

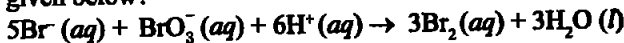
Ans. (i)

Explanation: The rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. To be more specific, it can be expressed in terms of:

- the rate of decrease in concentration of any one of the reactants, or
- the rate of increase in concentration of any one of the products.

Concentration of reactant decreases with the passage of time, we can say that the rate is also decreasing. $r = -dx/dt$ ($r = \text{rate}$)

12. Which of the following expressions is correct for the rate of reaction given below?



(i) $\frac{\Delta[\text{Br}^-]}{\Delta t} = 5 \frac{\Delta[\text{H}^+]}{\Delta t}$ (ii) $\frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{6 \Delta[\text{H}^+]}{5 \Delta t}$

(iii) $\frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{5 \Delta[\text{H}^+]}{6 \Delta t}$ (iv) $\frac{\Delta[\text{Br}^-]}{\Delta t} = 6 \frac{\Delta[\text{H}^+]}{\Delta t}$

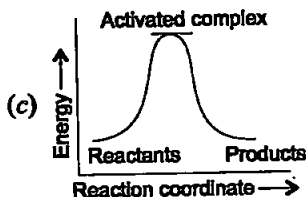
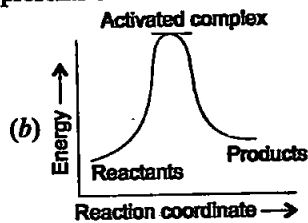
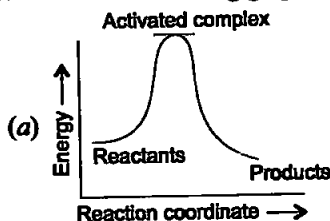
Ans. (iii)

Explanation: For the above equation rate of reaction can be written as

$$r = -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{[\text{BrO}_3^-]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

$$\Rightarrow -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} \text{ or } \frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{5 \Delta[\text{H}^+]}{6 \Delta t}$$

13. Which of the following graphs represents exothermic reaction?



(i) (a) only

(ii) (b) only

(iii) (c) only

(iv) (a) and (b)

Ans. (i) (a)

Explanation: For an exothermic reaction activation energy of product should be greater than the reactant.

14. Rate law for the reaction $\text{A} + 2\text{B} \rightarrow \text{C}$ is found to be

$$\text{Rate} = k[\text{A}][\text{B}]$$

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be _____.

(i) the same

(ii) doubled

(iii) quadrupled

(iv) halved

Ans. (ii)

Explanation: From the rate law expression it is clear that the rate w.r.t to B is of first order.

When the concentration of A is kept constant and the concentration of B gets double than the rate will be twice.

$$\text{Rate} \rightarrow R_1 = k[A][B] \quad \dots(i)$$

$$\text{Rate} \rightarrow R_2 = k[A][2B] \quad \dots(ii)$$

$$\text{Dividing eq. (i) by eq. (ii)} = R_2 = 2R_1$$

15. Which of the following statements is incorrect about the collision theory of chemical reaction?

- (i) It considers reacting molecules or atoms to be hard spheres and ignores their structural features.
- (ii) Number of effective collisions determines the rate of reaction.
- (iii) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation.
- (iv) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective.

Ans. (iii)

16. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?

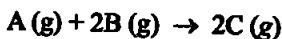
$$(i) 1.26 \times 10^{13} \text{ s} \quad (ii) 2.52 \times 10^{14} \text{ s}$$

$$(iii) 2.52 \times 10^{28} \text{ s} \quad (iv) \text{infinite}$$

Ans. (iv)

Explanation: It is impossible to perform 100% of the reaction, whole of the substance never react.

17. Compounds 'A' and 'B' react according to the following chemical equation.



Concentration of either 'A' or 'B' were changed keeping the concentrations of one of the reactants constant and rates were measured as a function of initial concentration. Following results were obtained. Choose the correct option for the rate equations for this reaction.

Experiment	Initial concentration of [A]/mol L ⁻¹	Initial concentration of [B]/mol L ⁻¹	Initial rate of formation of [C]/mol L ⁻¹ s ⁻¹
1.	0.30	0.30	0.10
2.	0.30	0.60	0.40
3.	0.60	0.30	0.20

$$(i) \text{Rate} = k[A]^2[B]$$

$$(ii) \text{Rate} = k[A][B]^2$$

$$(iii) \text{Rate} = k[A][B]$$

$$(iv) \text{Rate} = k[A]^2[B]^0$$

Ans. (ii)

Explanation: Rate of experiment = $k[A]^x[B]^y = k(0.30)^x(0.30)^y$

Rate of experiment = $k(0.30)^x(0.60)^y$

Dividing experiment (1) by (2)

$$\frac{k[0.30]^x [0.30]^y}{k[0.30]^x [0.60]^y} = \frac{0.10}{0.40}$$

$$[1/2]^y = 1/4 \text{ or } y = 2$$

Similarly, on dividing rate of experiment (1) by (3)

$$\frac{k[0.30]^x [0.30]^y}{k[0.60]^x [0.30]^y} = \frac{0.10}{0.20}$$

$$[1/2]^x = 1/2 \text{ or } x = 1$$

So the rate law expression is $\text{Rate} = k[A][B]^2$

18. Which of the following statement is not correct for the catalyst?

- (i) It catalyses the forward and backward reaction to the same extent.
- (ii) It alters ΔG of the reaction.
- (iii) It is a substance that does not change the equilibrium constant of a reaction.
- (iv) It provides an alternate mechanism by reducing activation energy between reactants and products

Ans. (ii)

Explanation: A catalyst does not alter Gibbs energy, (ΔG) of a reaction. It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.

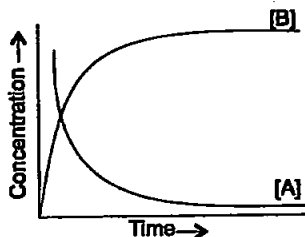
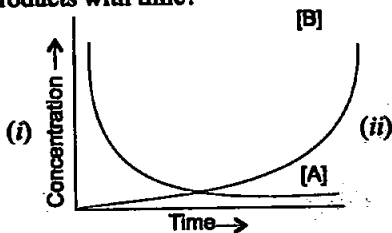
19. The value of rate constant of a pseudo first order reaction _____.

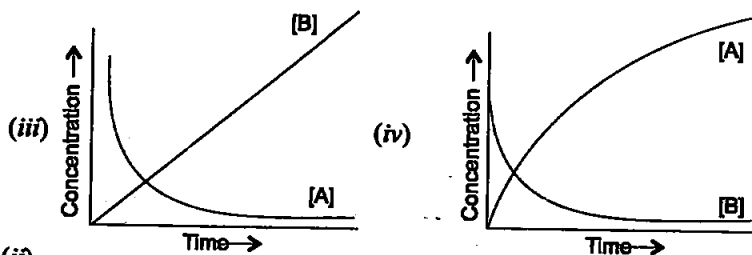
- (i) depends on the concentration of reactants present in small amount.
- (ii) depends on the concentration of reactants present in excess.
- (iii) is independent of the concentration of reactants.
- (iv) depends only on temperature

Ans. (ii)

Explanation: The concentration of the reactants that is present in excess does not get altered much during the course of the reaction. Due to this reaction behaves as first order reaction. Such reactions are called pseudo first order reactions. Hence, concentration of reactants present in excess determines rate constant of a pseudo first order reaction.

20. Consider the reaction $A \rightarrow B$. The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?





Ans. (ii)

Explanation: In graph (ii) concentration of reactant decreases exponentially with time and the concentration of product increases exponentially with time.

II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

Note : In the following questions two or more options may be correct.

21. Rate law cannot be determined from balanced chemical equation if _____.

- (i) reverse reaction is involved.
- (ii) it is an elementary reaction.
- (iii) it is a sequence of elementary reactions.
- (iv) any of the reactants is in excess

Ans. (i), (iii) and (iv)

Explanation: Rate law can be determined from balanced chemical equation if it is an elementary reaction.

22. Which of the following statements are applicable to a balanced chemical equation of an elementary reaction?

- (i) Order is same as molecularity.
- (ii) Order is less than the molecularity.
- (iii) Order is greater than the molecularity.
- (iv) Molecularity can never be zero.

Ans. (i), (iv)

Explanation: For a single step reactions, the order and molecularity will be the same.

23. In any unimolecular reaction _____.

- (i) only one reacting species is involved in the rate determining step.
- (ii) the order and the molecularity of slowest step are equal to one.
- (iii) the molecularity of the reaction is one and order is zero.
- (iv) both molecularity and order of the reaction are one.

Ans. (i) and (ii)

Explanation: In an unimolecular reaction only one reacting species are involved in the slowest step or rate determining step.

24. For a complex reaction _____.

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

- (ii) order of overall reaction is less than the molecularity of the slowest step.
- (iii) order of overall reaction is greater than molecularity of the slowest step.
- (iv) molecularity of the slowest step is never zero or non interger.

Ans. (i) and (iv)

Explanation: Order of a complex reaction can be determined experimentally by the slowest step. Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.

25. At high pressure the following reaction is zero order.



Which of the following options are correct for this reaction?

- (i) Rate of reaction = Rate constant
- (ii) Rate of the reaction depends on concentration of ammonia.
- (iii) Rate of decomposition of ammonia will remain constant until ammonia disappears completely.
- (iv) Further increase in pressure will change the rate of reaction.

Ans. (i), (iii) and (iv)

Explanation: Rate = $k[\text{NH}_3]^0$ or rate of reaction = rate constant

At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of catalyst making rate of the reaction independent of its concentration.

26. During decomposition of an activated complex

- (i) energy is always released
- (ii) energy is always absorbed
- (iii) energy does not change
- (iv) reactants may be formed

Ans. (i) and (iv)

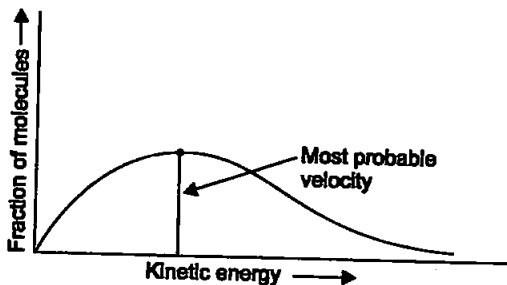
Explanation: Energy required to form an intermediate, called activated complex (C), is known as activation energy (E_a). Some energy is released when the complex decomposes to form product. the entire concentration of activated complex do not convert into product some activated complex may give reactant also.

27. According to Maxwell Boltzmann distribution of energy, _____.

- (i) the fraction of molecules with most probable kinetic energy decreases at higher temperatures.
- (ii) the fraction of molecules with most probable kinetic energy increases at higher temperatures.
- (iii) most probable kinetic energy increases at higher temperatures.
- (iv) most probable kinetic energy decreases at higher temperatures.

Ans. (i) and (iii)

Explanation: Maxwell Boltzmann distribution of energy can be explained by fig.

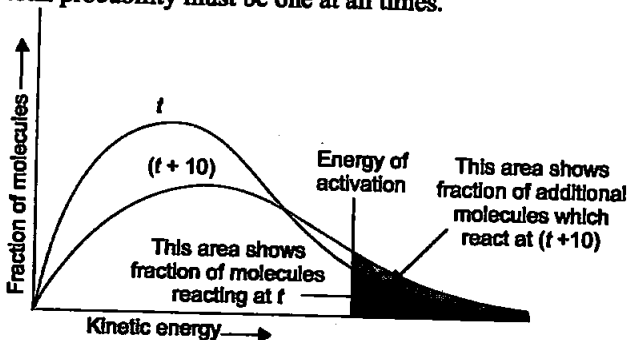


28. In the graph showing Maxwell Boltzmann distribution of energy,

- (i) area under the curve must not change with increase in temperature.
- (ii) area under the curve increases with increase in temperature.
- (iii) area under the curve decreases with increase in temperature.
- (iv) with increase in temperature curve broadens and shifts to the right hand side.

Ans. (i) and (iv)

Explanation: When the temperature is raised, the maximum of the curve moves to the higher energy value and the curve broadens out, i.e., spreads to the right such that there is a greater proportion of molecules with much higher energies. The area under the curve must be constant since total probability must be one at all times.



29. Which of the following statements are in accordance with the Arrhenius equation?

- (i) Rate of a reaction increases with increase in temperature.
- (ii) Rate of a reaction increases with decrease in activation energy.
- (iii) Rate constant decreases exponentially with increase in temperature.
- (iv) Rate of reaction decreases with decrease in activation energy.

Ans. (i) and (ii)

Explanation: It has been found from Arrhenius equation that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant.

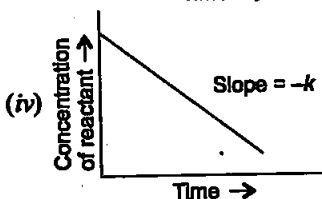
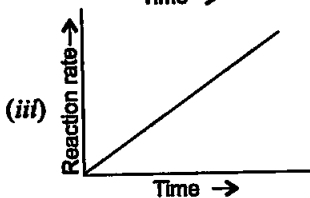
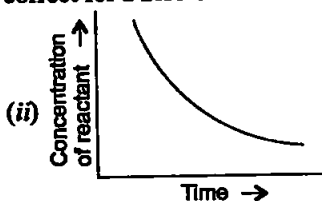
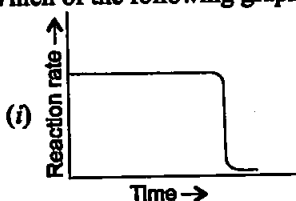
30. Mark the **Incorrect** statements.

- (i) Catalyst provides an alternative pathway to reaction mechanism.
- (ii) Catalyst raises the activation energy.
- (iii) Catalyst lowers the activation energy.
- (iv) Catalyst alters enthalpy change of the reaction

Ans. (ii) and (iv)

Explanation: Catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier.

31. Which of the following graphs is correct for a zero order reaction?



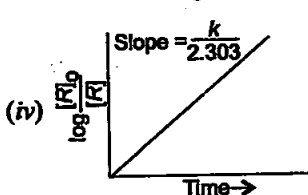
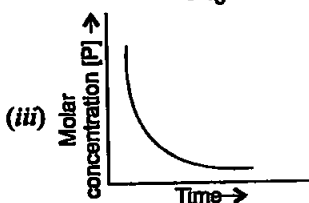
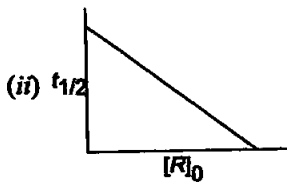
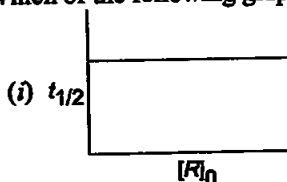
Ans. (i) and (iv)

Explanation: $k = \frac{[R]_0 - [R]}{t}$ where, k = rate constant for zero order reaction

$[R]_0$ = initial concentration of the reactant

$[R]$ = concentration of the reactant at time t

32. Which of the following graphs is correct for a first order reaction?



Ans. (i) and (iv)

Explanation: For first order reaction $K = 2.303/t \log [R]_0/[R]$

$$\text{Slope} = -k/2.303$$

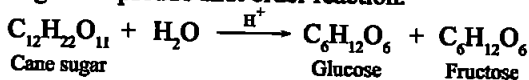
For first order reaction $t_{1/2} = 0.693/k$

Therefore $t_{1/2}$ for first order reaction is independent of the concentration of the reactant.

III. SHORT ANSWER TYPE

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

Ans. Bimolecular reaction becomes kinetically first order or pseudo first order reaction when one of the reactant is in excess w.r.t to other, the rate of reaction depends on one of the reactant only. For example, inversion of cane sugar is a pseudo first order reaction.

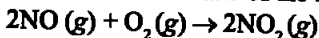


34. Write the rate equation for the reaction $2A + B \rightarrow C$ if the order of the reaction is zero.

Ans. The rate law for the above reaction is

$$\text{Rate} = k[A]^0[B]^0$$

35. How can you determine the rate law of the following reaction?



Ans. 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.

We can measure the rate of this reaction as a function of initial concentrations either by keeping the concentration of one of the reactants constant and changing the concentration of the other reactant or by changing the concentration of both the reactants.

36. For which type of reactions, order and molecularity have the same value?

Ans. For an elementary reaction order and molecularity have same value.

37. In a reaction if the concentration of reactant A is tripled, the rate of reaction becomes twenty seven times. What is the order of the reaction?

Ans. $\text{rate } r = k[A]^x \quad \dots(i)$

according to equation $27r = k[3A]^x \quad \dots(ii)$

Dividing eq. (i) by eq. (ii)

$$\frac{r}{27r} = \frac{k[A]^x}{k[3A]^x}$$

$$1/27 = [1/3]^x$$

$$[1/3]^3 = [1/3]^x \quad x = 3$$

Thus the order of reaction = 3.

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

Ans. $R \rightarrow P$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

As any quantity raised to power zero is unity

$$\text{Rate} = \frac{-d[R]}{dt} = k \times 1$$

$$d[R] = -k dt$$

Integrating both sides

$$[R] = -k t + I \quad \dots(i)$$

where, I is the constant of integration.

At $t = 0$, the concentration of the reactant $R = [R]_0$, where $[R]_0$ is initial concentration of the reactant.

Substituting in equation (i)

$$[R]_0 = -k \times 0 + I$$

$$[R]_0 = I$$

Substituting the value of I in the equation (i)

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

For completion $[R] = 0$

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

39. For a reaction $A + B \rightarrow \text{Products}$, the rate law is — $\text{Rate} = k[A][B]^{3/2}$. Can the reaction be an elementary reaction? Explain.

Ans. From the rate law expression it is clear that w.r.t to B is $3/2$ and w.r.t to A it is 1.

Thus the order of reaction is $5/2$ for an elementary reaction order and molecularity should be same.

Therefore the above reaction cannot be an elementary reaction.

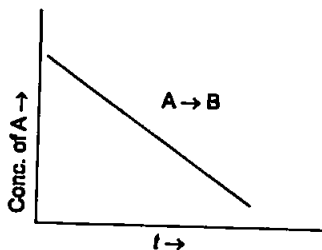
40. For a certain reaction large fraction of molecules has energy more than the threshold energy, yet the rate of reaction is very slow. Why?

Ans. If in a reaction large fraction of molecules has energy more than the threshold energy and still the rate of reaction is slow it means there is lack of proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collision.

41. For a zero order reaction will the molecularity be equal to zero? Explain.

Ans. Molecularity shows the no. of reactants taking part in a chemical reaction. It can never be zero or a fractional number.

42. For a general reaction $A \rightarrow B$, plot of concentration of A vs time is given in the figure. Answer the following question on the basis of this graph.



- (i) What is the order of the reaction?
 (ii) What is the slope of the curve?
 (iii) What are the units of rate constant?

Ans. (i) The graph shows that it is a zero order reaction.

(ii) $[R] = -kt + [R]^0$ (mathematical expressions of zero order reaction)
 slope = $-k$

(iii) Rate = k [reactant]⁰

Or, rate = k

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

43. The reaction between $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ is highly feasible yet allowing the gases to stand at room temperature in the same vessel does not lead to the formation of water. Explain.

Ans. This is because activation energy for the above reaction is very high at room temperature. For the reaction to be feasible it requires breaking of H—H and O—O bonds which is not possible at room temperature.

44. Why does the rate of a reaction increase with rise in temperature?

Ans. Increasing the temperature of the substance increases the fraction of molecules, which collide with energies greater than E_a and leads to faster rate.

45. Oxygen is available in plenty in air yet fuels do not burn by themselves at room temperature. Explain.

Ans. Activation energy for combustion of any fuel is very high that is why it could not be possible at room temperature.

46. Why is the probability of reaction with molecularity higher than three very rare?

Ans. Because it is very difficult for more than three molecules to collide effectively with proper orientation.

47. Why does the rate of any reaction generally decreases during the course of the reaction?

Ans. Rate of reaction directly depends on the molar concentration of the reactant with the progress of the reaction concentration of the reactant start decreasing that is why the rate also decreases.

48. Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of one example.

Ans. Thermodynamically the conversion of diamond into graphite is highly feasible but the reaction is very slow because the activation energy is very high.

49. Why in the redox titration of KMnO_4 vs oxalic acid, we heat oxalic acid solution before starting the titration?

Ans. In a mixture of potassium permanganate (KMnO_4) and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), potassium permanganate gets decolourised faster at a higher temperature than that at a lower temperature. Because the rate of reaction increases at high temperature.

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

Ans. Molecularity can be defined as the no. of reactant molecule taking part in a chemical reaction. Without any reactant no product will be formed that is why it cannot be zero.

51. Why molecularity is applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?

Ans. A complex reaction involves a number of steps that is why molecularity is meaningless for complex reaction. Order of a complex reaction is determined by the slowest step in the reaction mechanism. In elementary reaction number of reactant molecule decide the molecularity of the reaction.

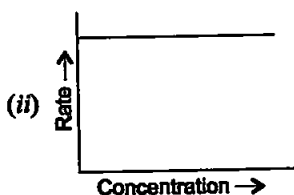
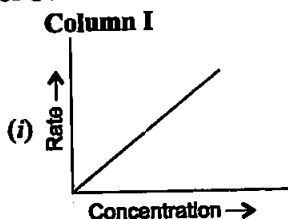
52. Why can we not determine the order of a reaction by taking into consideration the balanced chemical equation?

Ans. In a complex reaction order can not be predicted by balanced chemical equation because the reaction takes place in several steps Which step controls the rate of the overall reaction can be decide by the overall mechanism of the reaction thus the order of a reaction is an experimental quantity.

IV. MATCHING TYPE

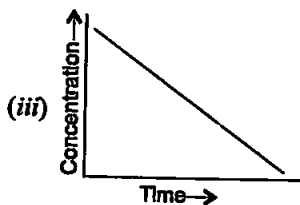
Note : In the following questions match the items of Column I with appropriate item given in Column II.

53. Match the graph given in Column I with the order of reaction given in Column II. More than one item in Column I may link to the same item of Column II.

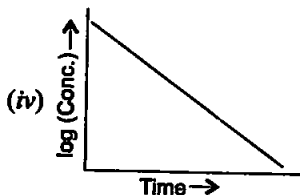


Column II

(a) 1st order



(b) Zero order



Ans. (i) → (a) (ii) → (b) (iii) → (b) (iv) → (a)

Explanation: For the first order reaction rate of reaction is directly proportional to the concentration of the reactant.

$$d[R]/dt \propto [R]$$

Hence the graph (i) will be a straight line.

Modifying the integrated rate equation for first order reaction

$$k = 2.303/t \log [R_0]/[R] \text{ graph (iv) is of first order reaction.}$$

For zero order reaction rate = $k[R]_0$. Therefore rate is independent of the concentration of reactant.

Therefore graph (ii) is of zero order reaction.

From integrated rate equation of zero order reaction $k = [R_0] - [R]$ thus graph (iii) of zero order reaction.

54. Match the statements given in Column I and Column II.

Column I	Column II
(i) Catalyst alters the rate of reaction	(a) cannot be fraction or zero
(ii) Molecularity	(b) proper orientation is not there always
(iii) Second half life of first order reaction	(c) by lowering the activation energy
(iv) $e^{-E_a/RT}$	(d) is same as the first
(v) Energetically favourable reactions are sometimes slow	(e) total probability is one
(vi) Area under the Maxwell Boltzman curve is constant	(f) refers to the fraction of molecules with energy equal to or greater than activation energy

Ans. (i) → (c) (ii) → (a) (iii) → (d)
 (iv) → (f) (v) → (b) (vi) → (e)

Explanation:

- (i) Catalyst can alter the rate of reaction by lowering the activation energy.
- (ii) Molecularity is always a whole number it cannot be zero or fraction.
- (iii) Second half life of first order reaction is also temperature dependent.
- (iv) In the Arrhenius equation the factor $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a .
- (v) In collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.
- (vi) The area under the Maxwell Boltzmann distribution curve must be constant since total probability must be one at all times.

55. Match the items of Column I and Column II.

Column I	Column II
(i) Diamond	(a) short interval of time
(ii) Instantaneous rate	(b) ordinarily rate of conversion is imperceptible
(iii) Average rate	(c) long duration of time

Ans. (i) \rightarrow (b) (ii) \rightarrow (a) (iii) \rightarrow (c)

Explanation: (i) Rate of conversion of diamond is imperceptible because it requires high activation energy. (ii) Instantaneous rate of a reaction is rate of a reaction at a particular moment of time. (iii) Average rate is obtained by dividing the change in concentration of any one of the reactant or product by the time taken for the change i.e., $\Delta x/\Delta t$.

56. Match the items of Column I and Column II.

Column I	Column II
(i) Mathematical expression for rate of reaction	(a) rate constant
(ii) Rate of reaction for zero order reaction is equal to	(b) rate law
(iii) Units of rate constant for zero order reaction is same as that of	(c) order of slowest step
(iv) Order of a complex reaction is determined by	(d) rate of a reaction

Ans. (i) \rightarrow (b) (ii) \rightarrow (a)
 (iii) \rightarrow (d) (iv) \rightarrow (c)

Explanation:

- (i) Mathematical expressions for rate of a reaction can be given by rate law.
- (ii) Rate for zero order reaction : $\text{rate} = k [\text{reactant}]^0 = k$ (rate constant).
- (iii) It is very clear from above that unit of rate constant = rate of reaction.
- (iv) Order of a complex reaction is determined by the slowest step which is known as rate determining step.

V. ASSERTION AND REASON TYPE

Note: 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.

- (i) Both assertion and reason are correct and the reason is correct explanation of assertion.
 - (ii) Both assertion and reason are correct but reason does not explain assertion.
 - (iii) Assertion is correct but reason is incorrect.
 - (iv) Both assertion and reason are incorrect.
 - (v) Assertion is incorrect but reason is correct.
57. **Assertion** : Order of the reaction can be zero or fractional.
Reason : We cannot determine order from balanced chemical equation.

Ans. (ii)

Explanation: Assertion is correct as order can be zero or fraction but it can be determined experimentally.

58. **Assertion** : Order and molecularity are same.

Reason : Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step.

Ans. (v)

Explanation: Order and molecularity can be same only for elementary reaction and it is different for complex reaction.

59. **Assertion** : The enthalpy of reaction remains constant in the presence of a catalyst.

Reason : A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy but the different in energy of reactant and product remains the same.

Ans. (i)

Explanation: It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier but the enthalpy of reaction remains constant.

60. Assertion : All collision of reactant molecules lead to product formation.

Reason : Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

Ans. (v)

Explanation: The collisions in which molecules collide with sufficient kinetic energy (called threshold energy) and proper orientation, leads to the formation of product.

61. Assertion : Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.

Reason : Reactant molecules undergo chemical change irrespective of their orientation during collision.

Ans. (iii)

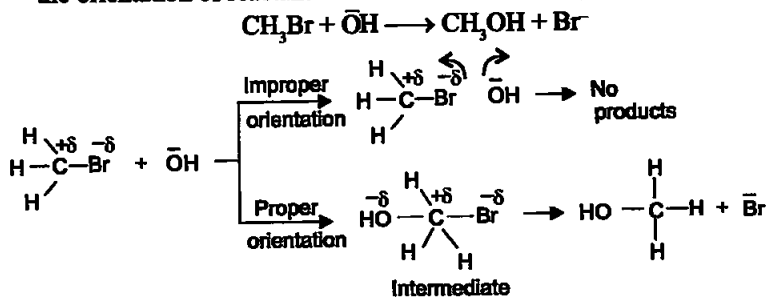
Explanation: Rate = $PZ e^{-E_d/RT}$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

VI. LONG ANSWER TYPE

62. All energetically effective collisions do not result in a chemical change. Explain with the help of an example.

Ans. All energetically effective collisions do not result in a chemical change. For example, formation of methanol from bromoethane depends upon the orientation of reactant molecules as shown below:

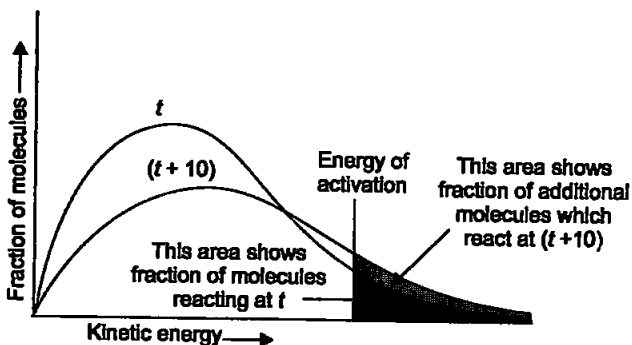


The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

To account for effective collisions, another factor P, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

$$\text{Rate} = PZ_{AB} e^{-E_a/RT}$$

63. What happens to most probable kinetic energy and the energy of activation with increase in temperature?



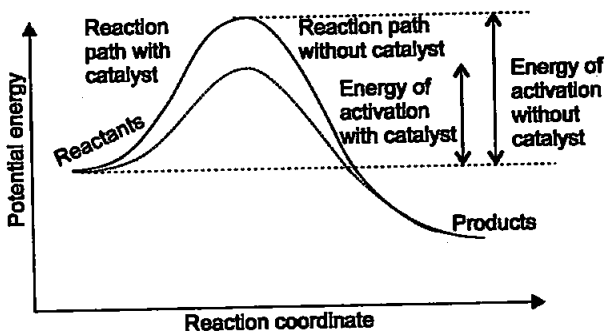
Kinetic energy is directly proportional to the absolute temperature and the number of molecules possessing higher energies increases with increase in temperature, i.e., most probable kinetic energy increases with increase in temperature.

Energy of activation is related to temperature by the following Arrhenius equation

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

Thus, it also shows an increase with rise in temperature.

64. Describe how does the enthalpy of reaction remain unchanged when a catalyst is used in the reaction.
- Ans. A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change. The action of the catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.
- A small amount of the catalyst can catalyse a large amount of reactants. A catalyst does not alter Gibbs energy, ΔG of a reaction. Difference in energy between reactants and product is constant.
- It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same enthalpy of reaction means difference in energy between reactant and product it will also remain unchanged. It can be shown by



65. Explain the difference between instantaneous rate of a reaction and average rate of a reaction.

Ans. Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur. However, average rate cannot be used to predict the rate of a reaction at a particular instant as it would be constant for the time interval for which it is calculated. So, to express the rate at a particular moment of time we determine the instantaneous rate. It is obtained when we consider the average rate at the smallest time interval say dt (i.e. when Δt approaches zero). Hence, mathematically for an infinitesimally small dt instantaneous rate is given by

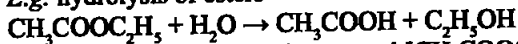
$$\text{Average } r_{av} = \Delta x / \Delta t$$

$$\text{Instantaneous rate } r_{inst} = dx/dt$$

66. With the help of an example explain what is meant by pseudo first order reaction.

Ans. **Pseudo first order reaction:** Reaction which appears to be a second order reaction, but actually is first order reaction is called pseudo first order reaction. This condition occurs in a chemical reaction between two substances when one reactant is present in large amount. The concentration of reactant present in excess does not get altered much during the course of the reaction. Due to this reaction behaves as first order reaction.

E.g. hydrolysis of esters



Rate law for this reaction is ; rate = $k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$

But the concentration of water does not change during the course of the reaction. So; $[\text{H}_2\text{O}]$ is constant.

Therefore rate = $k_1[\text{CH}_3\text{COOC}_2\text{H}_5]$. Where $k = k[\text{H}_2\text{O}]$.

The reaction behaves as a first order reaction.

□□□