
Chemical Kinetics
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: $\log k_2 / k_1 = E_a / 2.303[T_2 - T_1 / T_1 T_2]$ 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.

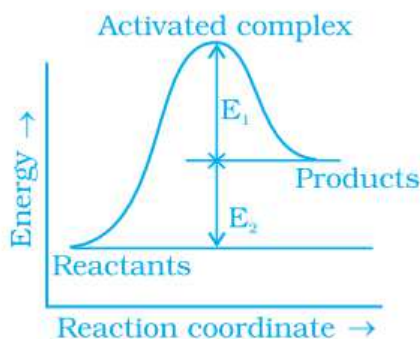


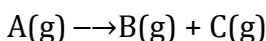
Fig. 4.1

- (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 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:



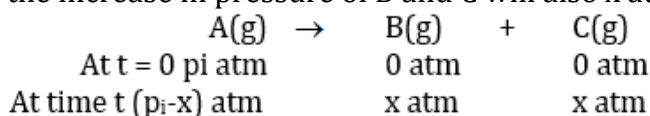
The initial pressure of the system before decomposition of A was p_i . After lapse of time 't', total pressure of the system increased by x units and became ' p_t '.

The rate constant k for the reaction is given as _____.

- (i) $k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$
- (ii) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$
- (iii) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i + p_t}$
- (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 x atm each.



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

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

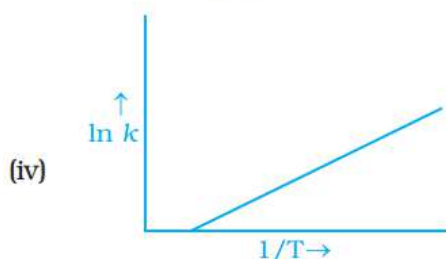
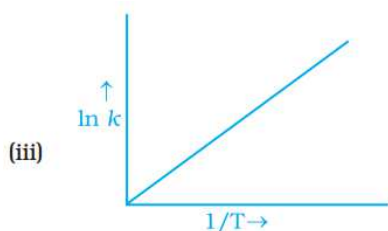
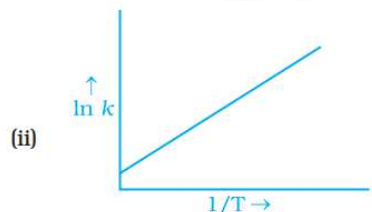
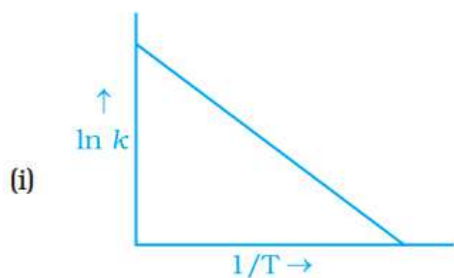
$$x = (p_t - p_i)$$

$$\text{where, } p_A = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$$

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

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.

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

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 Fig. 4.2. On the basis of this mark the correct option.

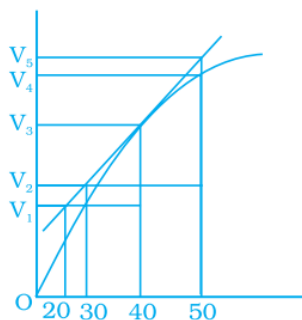


Fig. 4.2

(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.

(i) The order of a reaction can be a fractional number.

(ii) Order of a reaction is experimentally determined quantity.

(iii) 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.

(iv) 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 which 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 Fig. 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?

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

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

(iii) The rate of a reaction is independent of temperature change.

(iv) The rate of a reaction decreases with increase in concentration of reactant(s).

Ans. (i)

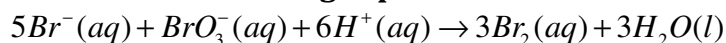
Explanation: The rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. To be more specific, it can be expressed in term of:

(i) The rate of decrease in concentration of any one of the reactants, or

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

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

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

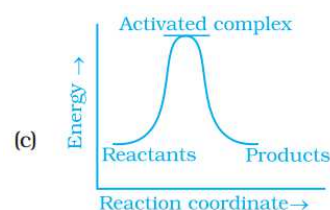
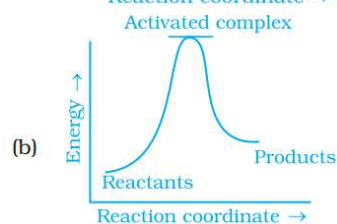
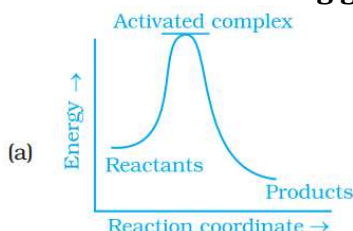
Ans. (iii)

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

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

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

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) only

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

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

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

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.

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

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

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

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)

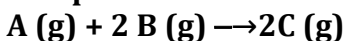
16. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?

- (i) 1.26×10^{15} s
- (ii) 2.52×10^{14} s
- (iii) 2.52×10^{28} s
- (iv) 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]/mole 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) Rate = $k[A]^2[B]$
- (ii) Rate = $k[A][B]^2$
- (iii) Rate = $k[A][B]$
- (iv) 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)

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

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

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.

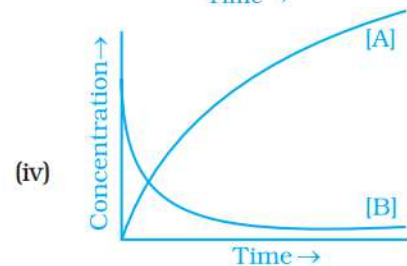
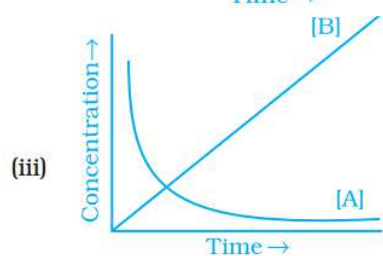
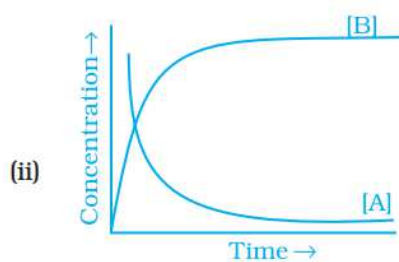
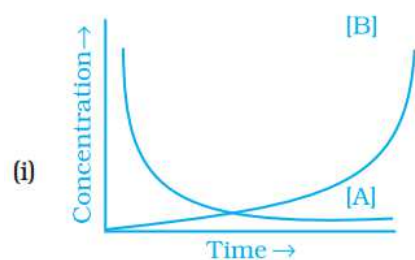
19. The value of rate constant of a pseudo first order reaction _____.

- (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.

Chemical Kinetics
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), (ii) 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 reaction, 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.

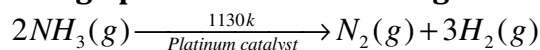
24. For a complex reaction ____.

- (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-integer.

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 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)

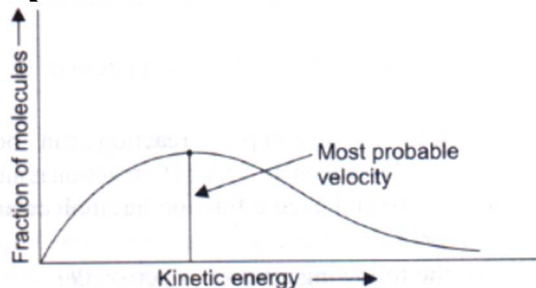
Explanation: Energy required to form an intermediate, called activated complex (C), is known as activation energy (E_a). Some energy is released when the complex decomposes to form product. The entire concentration of activated complex do not convert into product some activated complex may give reactant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



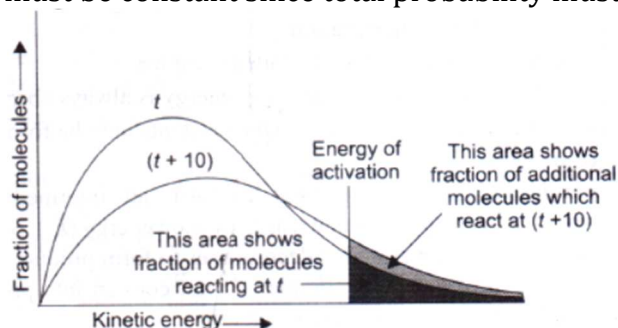
28. In the graph showing Maxwell Boltzmann distribution of energy, _____.

- (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 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.

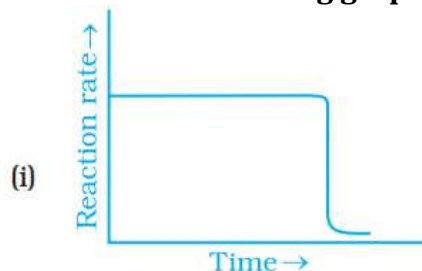
30. Mark the incorrect statements.

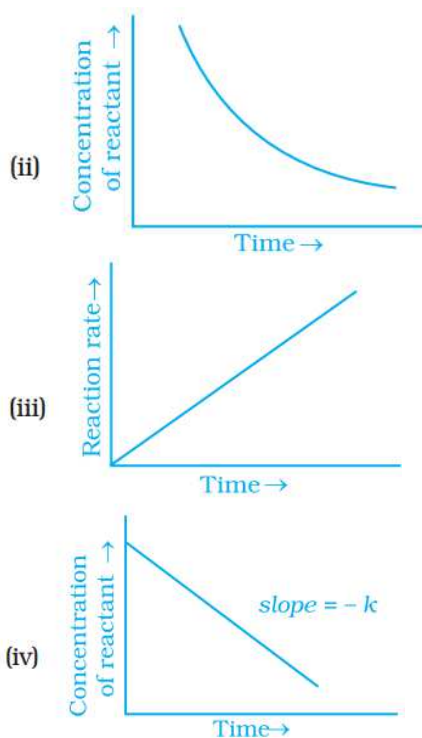
- (i) Catalyst provides an alternative pathway to reaction mechanism.
- (ii) Catalyst raises the activation energy.
- (iii) Catalyst lowers the activation energy.
- (iv) Catalyst alters enthalpy change of the reaction.

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?





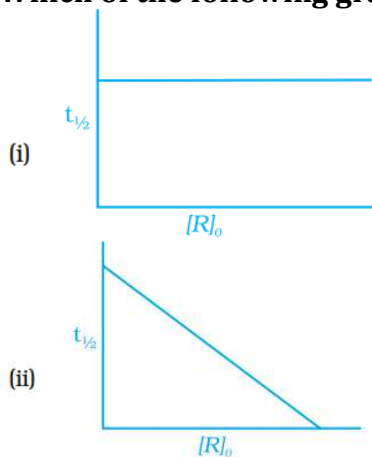
Ans. (i) and (iv)

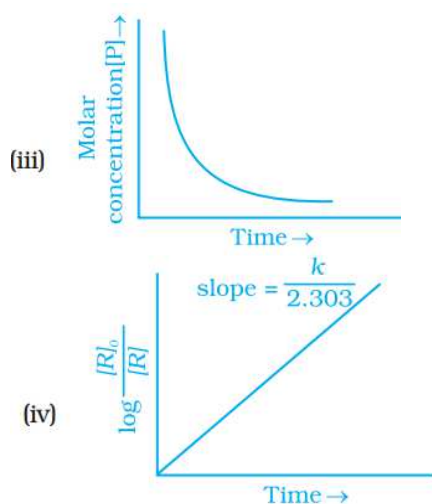
Explanation: $k = \frac{[R]_0 - [R]}{t}$ where, k = rate constant for zero order reaction

$[R]_0$ = 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 $k = 2.303/t \log [R]_0/[R]$

Slope = $-k/2.303$

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

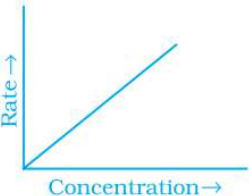
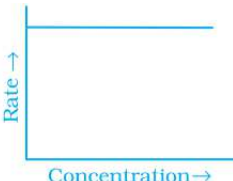
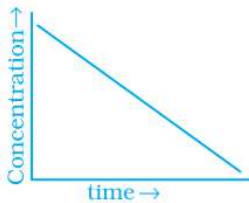
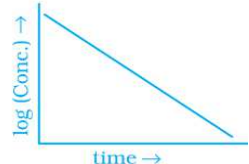
Therefore $t_{1/2}$ for first order reaction is independent of the concentration of the reactant.

Chemical Kinetics

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 I	Column II
(i) 	
(ii) 	(a) 1st order
(iii) 	(b) Zero order
(iv) 	

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 $\text{rate} = k[R]^0$. 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 show	(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 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)- (b)
(ii)- (a)
(iii)- (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)- (b)
(ii)- (a)
(iii)- (d)
(iv)- (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.

Chemical Kinetics
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 difference 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)

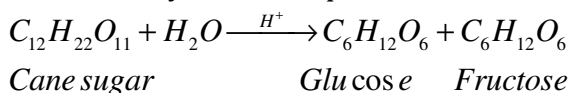
Explanation: $Rate = PZ e^{E_a/RT}$

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.

Chemical Kinetics
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 $2A + B \longrightarrow C$ if the order of the reaction is zero.

Ans. The rate law for the above reaction is
Rate = $k[A]^0[B]^0$

**35. How can you determine the rate law of the following reaction?
 $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$**

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. Three, because rate = $k[A]^3$

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

Ans. $[R] = [R]_0 - kt$
for completion $[R] = 0$
 $\therefore t = \frac{[R]_0}{k}$

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

Ans. During an elementary reaction, the number of atoms or ions colliding to react is referred to as molecularity. Had this been an elementary reaction the order of reaction with

respect to B would have been 1, but in the given rate law it is $\frac{3}{2}$. This indicates that the reaction is not 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. Apart from the energy considerations, the colliding molecules should also have proper orientation for effective collision. This condition might not be getting fulfilled in the reaction.

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

Ans. No, the molecularity can never be zero or a fractional number.

42. For a general reaction, $A \longrightarrow B$, plot of concentration of A vs time is given in Fig. 4.3. Answer the following question on the basis of this graph.

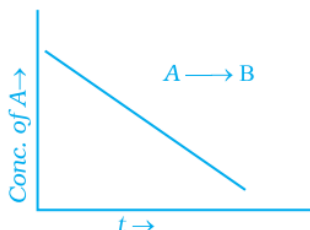


Fig. 4.3

(i) What is the order of the reaction?

Ans. Zero

(ii) What is the slope of the curve?

Ans. -k

(iii) What are the units of rate constant?

Ans. $\text{mol L}^{-1} \text{s}^{-1}$

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 reaction is very high at room temperature.

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

Ans. At higher temperatures, larger fraction of colliding particles can cross the energy barrier (i.e. the activation energy), which leads to faster rate.

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

Ans. The activation energy for combustion reactions of fuels is very high at room temperature

therefore they do not burn by themselves.

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

Ans. The probability of more than three molecules colliding simultaneously is very small. Hence possibility of molecularity being three is very low.

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

Ans. The rate of a reaction depends on the concentration of reactants. As the reaction progresses, reactants start getting converted to products so the concentration of reactants decreases hence the rate 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 to graphite is highly feasible but this reaction is very slow because its activation energy is high.

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

Ans. The reaction between KMnO_4 and oxalic acid is very slow. By raising the temperature, we can enhance the rate of reaction.

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

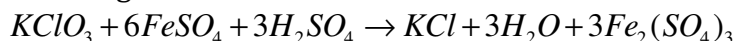
Ans. Molecularity is the number of molecules taking part in an elementary step. For this we require at least a single molecule leading to the value of minimum molecularity of one.

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

Ans. A complex reaction proceeds through several elementary reactions. Numbers of molecules involved in each elementary reaction may be different i.e., the molecularity of each step may be different. Therefore, discussion of molecularity of overall complex reaction is meaningless. On the other hand, order of a complex reaction is determined by the slowest step in its mechanism and is not meaningless even in the case of complex reactions.

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

Ans. Balanced chemical equation often leads to incorrect order or rate law. For example, the following reaction seems to be a tenth order reaction.



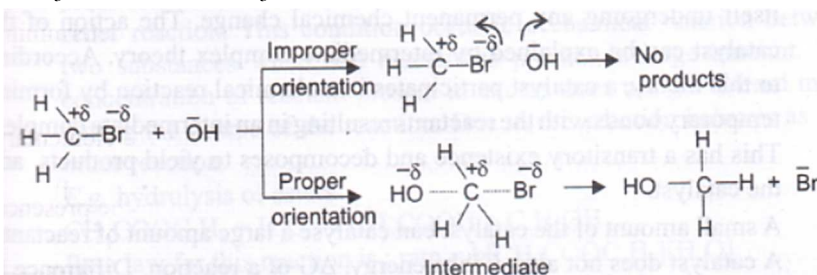
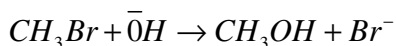
This is actually a second order reaction. Actually, the reaction is complex and occurs in several steps. The order of such reaction is determined by the slowest step in the reaction mechanism. Order is determined experimentally and is confined to the dependence of observed rate of reaction on the concentration of reactants.

Chemical Kinetics

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:



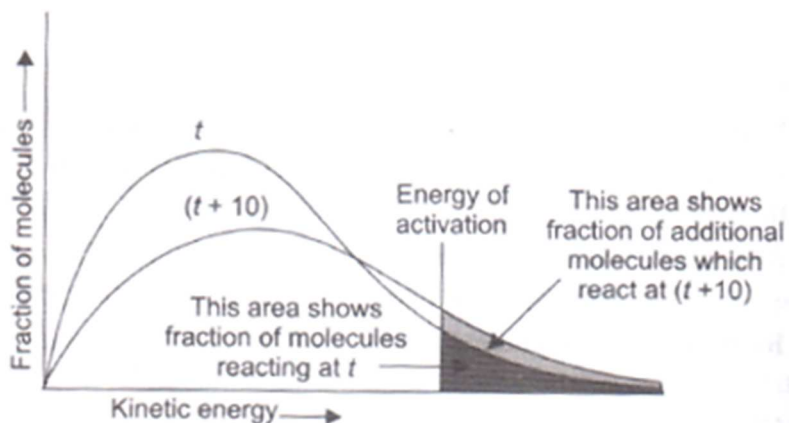
The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed

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?

Ans.



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

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

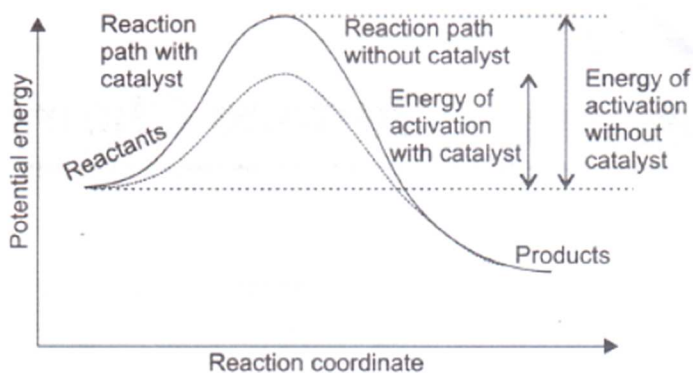
Thus, it also shows an increase with rise in temperature.

64. Describe how does the enthalpy of reaction remain unchanged when a catalyst is used in the reaction.

Ans. A catalyst is 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 transitory existence and decomposes to yield products and the catalyst.

A small amount of the catalyst can catalyze 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 catalyzes 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 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

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

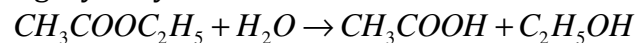
$$\text{Instantaneous rate } r_{inst} = dx / dt$$

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; $\text{rate} = k[CH_3COOC_2H_5][H_2O]$

But the concentration of water does not change during the course of the reaction. So; $[H_2O]$ is constant.

Therefore $\text{rate} = k_1[CH_3COOC_2H_5]$. Where $k = k[H_2O]$.

The reaction behaves as a first order reaction.