

Chemical Kinetics

A Quick Recapitulation of the Chapter

1. **Chemical kinetics** It is the branch of chemistry which deals with the study of rates of the chemical reactions and their mechanism. It also describes the conditions in which rates can be altered.

2. **Rate of chemical reaction** It is the change in molar concentration of the species taking part in the chemical reaction per unit time.

Rate of reaction

$$= \frac{\text{Decrease in concentration of reactant}}{\text{Time taken}} = \frac{-\Delta[A]}{\Delta t}$$

$$= \frac{\text{Increase in concentration of product}}{\text{Time taken}} = \frac{\Delta[B]}{\Delta t}$$

Units of rate = $\text{mol L}^{-1} \text{s}^{-1}$ or atm s^{-1} (in gaseous state)

3. **Instantaneous rate of reaction** It is the rate of change of concentration of any one of the species involved in the reaction at a particular instant of time.

For a general reaction, $aA + bB \longrightarrow cC + dD$

Instantaneous rate

$$= -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

4. **Rate of reaction** It is affected by some factors like temperature, concentration of reactants/products, catalyst, surface area of the reactants etc.

5. **Rate law** It is the representation of rate of reaction in terms of concentration of the reactants.

Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e. theoretically but must be determined experimentally.

6. **Order of a chemical reaction** It is the sum of coefficients of reacting species that are involved in the rate equation for the reaction.

Order of a reaction = $x + y$; if rate = $k[A]^x[B]^y$

Reaction occurring only in one step are called

elementary reactions, while that involving a sequence of elementary reactions, are called

complex reactions. In case of complex reactions, the slowest step is called **rate determining step**.

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

For 1st order reaction, $k = \text{s}^{-1}$

2nd order reaction, $k = \text{mol}^{-1} \text{L s}^{-1}$

3rd order reaction, $k = \text{mol}^{-2} \text{L}^2 \text{s}^{-1}$

Zero order reaction $k = \text{mol L}^{-1} \text{s}^{-1}$

7. **Molecularity of a reaction** is the number of the reacting species that collide simultaneously to bring about a chemical reaction.

8. **Integrated rate equation for zero order reaction**,

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

Half-life period $(t_{1/2}) = \frac{[A]_0}{2k}$

[Half-life period is that time in which a substance remain half of its available or initial amount]

9. **Integrated rate equation for 1st order reaction**,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

For gaseous reaction, $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$

Half-life period for 1st order reaction $(t_{1/2}) = \frac{0.693}{k}$

For a chemical reaction, a 10° rise in temperature, results in nearly double the rate constant.

10. Arrhenius gave the following relationship between rate constant and temperature, i.e. $k = Ae^{-E_a/RT}$
 here, A = Arrhenius factor, E_a = activation energy, R = gas constant and T = temperature.
11. Activation energy is the extra amount of energy which has to be supplied to the reacting species in their normal energy state to make their energy equal to threshold energy. Arrhenius equation for activation energy is

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

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

A catalyst increases the rate of reaction by decreasing activation energy.

12. **Collision frequency (Z)** It is the number of collisions per second per unit volume of the reaction mixture. It is related with rate as

$$\text{rate} = Z_{AB}e^{-E_a/RT}$$

13. **Effective collisions** These are the collisions in which molecules collide with sufficient kinetic energy (threshold energy) and with proper orientation.

For showing effective collision, probability or steric factor, P is introduced and rate becomes,

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

Objective Questions Based on NCERT Text

Topic 1

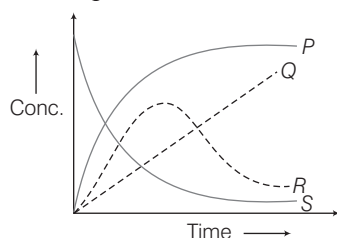
Rate of Reaction

1. Rate of which of the following reactions can be determined easily?
- Rusting of iron in the presence of air and moisture
 - Hydrolysis of starch
 - Reaction of silver nitrate with sodium chloride
 - All of the above
2. Consider the reaction,
- $$R \longrightarrow P + Q$$
- its rate can be defined as
- rate of decrease in concentration of R per unit time
 - rate of increase in concentration of R per unit time
 - rate of increase in concentration of P and Q collectively per unit time
 - rate of decrease in concentration of R in 5 min

3. For a reaction,

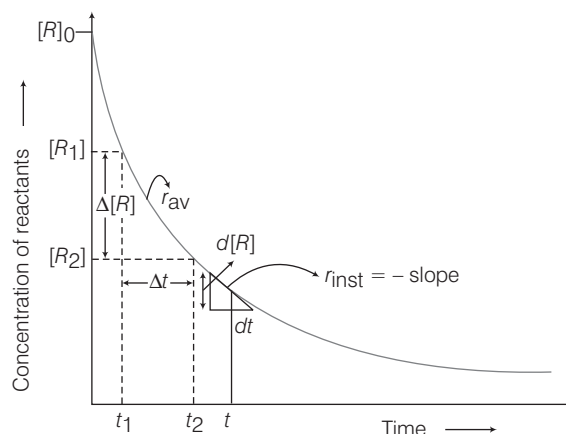


The curve which depicts the variation of the concentration of products is



- (a) P (b) Q (c) R (d) S

4. Find the value of r_{av} from the graph shown below.



- (a) $r_{av} = \frac{+\Delta[R]}{\Delta t}$ (b) $r_{av} = \frac{-[R_2] - [R_1]}{(t_1 - t_2)}$
- (c) $r_{av} = \frac{-d[R]}{dt}$ (d) $r_{av} = \frac{-\{[R_2] - [R_1]\}}{(t_2 - t_1)}$

5. For a hypothetical reaction, $R \longrightarrow$ products;

rate $= -k[R]$. The negative sign used in the rate expression indicates.

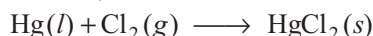
- decrease in the concentration of reactants with time
- decrease in the rate with time
- reaction is reversible
- None of the above

6. During a chemical reaction with increase in time, rate of a reaction

(a) decreases (b) increases
(c) remains constant (d) show irregular trends

7. The correct statement among the following is
(a) square brackets in the expression $\Delta[R]$ shows the equivalent concentration
(b) units of rate of reaction are concentration time⁻¹
(c) units of rate in terms of partial pressure is atmosphere L⁻¹
(d) rate at a given time interval is called instantaneous rate

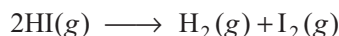
8. For the reaction,



The rate of reaction is given as

- (a) $\frac{\Delta[\text{HgCl}_2]}{\Delta t}$ (b) $-\frac{\Delta[\text{Hg}]}{\Delta t}$
(c) $-\frac{\Delta[\text{Cl}_2]}{\Delta t}$ (d) Either (a) or (b) or (c)

9. In the reaction given below,



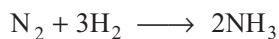
Choose the correct alternative.

- (a) Rate of reaction $= -\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$
(b) Stoichiometric coefficients of HI (reactant) and H₂ and I₂ (products) are not same
(c) Rate of consumption of HI = 2 (rate of formation of H₂ or I₂)
(d) All of the above statements are true
10. For the reaction, $2X + Y \longrightarrow X_2Y$

What will be the expression for instantaneous rate of the reaction?

- (a) $\frac{-d[X]}{2dt}$ (b) $+\frac{1}{2} \frac{d[Y]}{dt}$
(c) $-\frac{1}{2} \frac{d[X_2Y]}{dt}$ (d) None of these

11. Choose the correct value of $\frac{d[\text{NH}_3]}{dt}$ for the reaction,

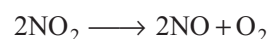


- (a) $-\frac{2}{3} \frac{d[\text{H}_2]}{dt}$ (b) $\frac{2}{3} \frac{d[\text{H}_2]}{dt}$
(c) $\frac{3}{2} \frac{d[\text{N}_2]}{dt}$ (d) $-\frac{3}{2} \frac{d[\text{N}_2]}{dt}$

12. In a reaction, $2x \rightarrow y$, the concentration of x decreases from 3.0 M to 1.5 M in 4 min. The rate of the reaction is

(a) 0.187 M min⁻¹
(b) 1.87 M min⁻¹
(c) 3.75×10^{-1} M min⁻¹
(d) 0.75 M min⁻¹

13. Consider the following reaction,



If rate of disappearance of NO₂ is

6.0×10^{-12} mol L⁻¹ s⁻¹ then the rate of appearance of O₂ is

(a) 3×10^{-12} mol L⁻¹ s⁻¹
(b) 6×10^{-12} mol L⁻¹ s⁻¹
(c) 1×10^{-12} mol L⁻¹ s⁻¹
(d) 1.5×10^{-12} mol L⁻¹ s⁻¹

14. For the reaction,

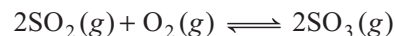


if $-\frac{d[\text{Br}^-]}{dt} = k_1[\text{Br}^-]$, $-\frac{d[\text{BrO}_3^-]}{dt} = k_2[\text{Br}^-]$,

$\frac{d[\text{Br}_2]}{dt} = k_3[\text{Br}^-]$ then k_1 , k_2 and k_3 are related as

(a) $k_1 = 5k_2 = 1.66k_3$
(b) $3k_1 = k_2 = 5k_3$
(c) $5k_1 = 3k_2 = k_3$
(d) $k_1 = k_2 = k_3$

15. Contact process is used in the formation of sulphur trioxide,



The rate of reaction can be expressed as

$\frac{-\Delta[\text{O}_2]}{\Delta t} = 2.5 \times 10^{-4}$ mol L⁻¹ s⁻¹.

Then rate of disappearance of [SO₂] will be

(a) 50.0×10^{-5} mol L⁻¹ s⁻¹
(b) 3.75×10^{-4} mol L⁻¹ s⁻¹
(c) 2.5×10^{-4} mol L⁻¹ s⁻¹
(d) 4.12×10^{-4} mol L⁻¹ s⁻¹

Topic 2

Factors Influencing Rate Reaction

16. The factors affecting the rate of a reaction are

- I. temperature
- II. pressure
- III. concentration of reactant or product
- IV. catalyst

Choose the correct option from the alternatives given below.

- (a) I, II and III
- (b) I, III and IV
- (c) II, III and IV
- (d) All of these

17. Select the correct statement.

- (a) Rate of reaction increases with decrease in concentration of reactants
- (b) Rate law or rate equation shows rate of reaction in terms of concentration
- (c) Units of rate constant are $\text{mol L}^{-1}\text{s}^{-1}$
- (d) For the reaction, $aA + bB \longrightarrow \text{product}$, if rate = $[A]^x$ and $[B]^y$, a and b are always equal to x and y

18. In acidic medium, the rate of reaction between $[\text{BrO}_3]^-$ and Br^- ions is given as

$$-\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

It means that

- (a) the change in pH of the solution will not affect the rate of reaction
- (b) rate constant of the reaction is 2 s^{-1}
- (c) the reaction rate increases by 4 times on doubling the concentration of H^+ ions
- (d) All of the above

19. For the elementary reaction $M \rightarrow N$, the rate or disappearance of M increases by a factor of 8 upon doubling the concentration of M . The order of the reaction with respect to M is (JEE Main 2014)

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

20. In a reaction, $A + B \longrightarrow \text{Product}$, rate is doubled when the concentration of B is doubled and rate increases by a factor of 8, when the concentrations of both the reactants (A and B) are doubled. Rate law for the reaction can be written as (CBSE AIPMT 2012)

- (a) rate = $k[A][B]^2$
- (b) rate = $k[A]^2[B]^2$
- (c) rate = $k[A][B]$
- (d) rate = $k[A]^2[B]$

21. On mixing 1 dm^3 of 3 M ethanol with 1 dm^3 of 2 M ethanoic acid, an ester is formed.



If each solution is diluted with an equal volume of water, the decrease in the initial rate would be

- (a) 0.5 times
- (b) 4 times
- (c) 0.25 times
- (d) 2 times

22. The rate law for a reaction between the substances P and Q is given by rate = $k[P]^a[Q]^b$. On doubling the concentration of P and reducing the concentration of Q to one-half, the ratio of the new rate to the earlier rate of the reaction will be

- (a) $\frac{1}{2^{(a+b)}}$
- (b) $2^{(a-b)}$
- (c) $(a-b)$
- (d) $(a+b)$

23. The incorrect statement among the following is

- (a) order of reaction is the sum of powers of concentration of the reactants in the rate law expression
- (b) elementary reactions are only one step reactions
- (c) rate of elementary reactions depends upon the slowest step, i.e. rate determining step of reaction
- (d) All of the above

24. Which one of the following statements for the order of a reaction is incorrect? (CBSE AIPMT 2011)

- (a) Order is not influenced by stoichiometric coefficient of the reactants
- (b) Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction
- (c) Order of reaction is always whole number
- (d) Order can be determined only experimentally

25. For the given rate expression = $k[A]^{3/2}[B]^{-1}$, the overall order of a reaction is

- (a) zero
- (b) half
- (c) one
- (d) two

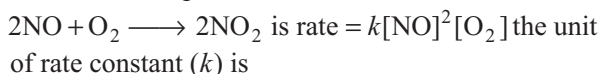
26. The unit of the rate constant of n th order is

- (a) $\text{mol}^{1-n} \text{ L}^{n-1} \text{ s}^{-1}$
- (b) $\text{mol}^{n-1} \text{ L}^{1-n} \text{ s}^{-1}$
- (c) $\text{mol}^{n-1} \text{ L}^{n-1} \text{ s}$
- (d) $\text{mol}^n \text{ L}^{1-n} \text{ s}^{-1}$

27. Reaction of chloroform with chlorine is an example of fraction order reaction. Its rate law expression is rate = $k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$. If both are assumed in gaseous state and pressure is measured in bar then units of rate and rate constant respectively are

- (a) bar min^{-1} , $\text{bar}^2 \text{ min}^{-1}$
- (b) bar min^{-1} , $\text{bar}^{-1/2}$, min^{-1}
- (c) $\text{bar}^{-1/2}$, min^{-1} , $\text{bar}^2 \text{ min}^{-1}$
- (d) bar min^{-1} , $\text{bar}^{-1/2} \text{ min}^{-1}$

28. The rate law expression for the reaction,



- (a) $\text{mol L}^{-1} \text{ s}^{-1}$
- (b) s^{-1}
- (c) $\text{mol}^{-2} \text{ L}^2 \text{ s}^{-1}$
- (d) mol L^{-1}

29. Find the order of the reaction whose rate constant is $2.5 \times 10^{-2} \text{ min}^{-1}$.
 (a) zero (b) three (c) two (d) one
30. For which of the following, the units of rate constant and rate of the reaction are same?
 (a) Zero order reaction (b) First order reaction
 (c) Second order reaction (d) Third order reaction
31. Consider the data given below for a hypothetical reactions, $M \rightarrow N$

Time(s)	Rate of reaction ($\text{mol L}^{-1} \text{ s}^{-1}$)
0	4.20×10^{-4}
10	4.20×10^{-4}
20	4.20×10^{-4}
30	4.20×10^{-4}
40	4.18×10^{-4}

For the above data, the order of reaction is

- (a) one (b) two (c) three (d) zero
32. Following data is given for the reaction, $X + Y \rightarrow P$

Experiment	$[X] \text{ mol L}^{-1}$	$[Y] \text{ mol L}^{-1}$	Initial rate ($\text{mol L}^{-1} \text{ s}^{-1}$)
I	2.5×10^{-4}	6×10^{-5}	5×10^{-4}
II	5×10^{-4}	12×10^{-5}	4×10^{-3}
III	1×10^{-3}	12×10^{-5}	1.6×10^{-2}

The order of reaction with respect to X and Y respectively are

- (a) 1 and 2 (b) 2 and 1
 (c) 1 and 1 (d) 2 and 2
33. For the non-stoichiometric reaction $2A + B \longrightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

(JEE Main 2014)

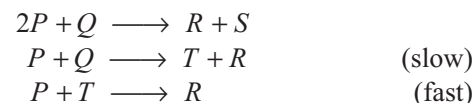
Initial concentration $[A]$	Initial concentration $[B]$	Initial rate of formation of C ($\text{mol L}^{-1} \text{ s}^{-1}$)
0.1 M	0.1 M	1.2×10^{-3}
0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is

- (a) $\frac{dC}{dt} = k[A][B]$ (b) $\frac{dC}{dt} = k[A]^2[B]$
 (c) $\frac{dC}{dt} = k[A][B]^2$ (d) $\frac{dC}{dt} = k[A]$
34. When $\text{CH}_3\text{COOC}_2\text{H}_5$ was hydrolysed in presence of 0.1 M HCl, the rate constant obtained as $5.40 \times 10^{-5} \text{ s}^{-1}$. But when 0.1 M H_2SO_4 was fused for hydrolysis, the rate constant obtained as $6.20 \times 10^{-5} \text{ s}^{-1}$.

From these it can be said that

- (a) H_2SO_4 is stronger than HCl
 (b) H_2SO_4 is weaker than HCl
 (c) Both HCl and H_2SO_4 are of same strength
 (d) insufficient data to compare the strength of H_2SO_4 and HCl
35. The inversion of cane sugar proceeds with half-life of 500 min at pH= 5 for any concentration of sugar. However, if pH= 6, the half-life changes to 50 min. Expression for the rate law for sugar inversion is
 (a) $r = k [\text{sugar}]^1 [\text{H}^+]^0$ (b) $r = k [\text{sugar}]^0 [\text{H}^+]^1$
 (c) $r = k [\text{sugar}]^2 [\text{H}^+]^0$ (d) $r = k [\text{sugar}]^1 [\text{H}^+]^1$
36. The following mechanism has been proposed for a reaction,



The rate law expression for the reaction is

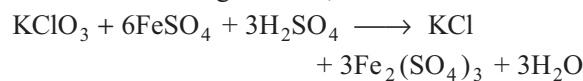
- (a) $r = k[P][Q]$ (b) $r = k[P]^2$
 (c) $r = k[P][T]$ (d) $r = k[P]^2[Q]$
37. Consider the following reactions,
- $$\begin{aligned} \text{O}_3 &\rightleftharpoons \text{O}_2 + \text{O} \quad (\text{fast}) \quad \dots(\text{i}) \\ \text{O} + \text{O}_3 &\longrightarrow 2\text{O}_2 \quad (\text{slow}) \quad \dots(\text{ii}) \end{aligned}$$

The rate law expression should be

- (a) $r = k[\text{O}_3]^2 [\text{O}_2]^{-1}$ (b) $r = k[\text{O}_3][\text{O}_2]$
 (c) $r = k[\text{O}_3]^2$ (d) $r = k[\text{O}_2]^{-1}$
38. The reaction,
- $$2\text{N}_2\text{O}_5 \rightleftharpoons 2\text{N}_2\text{O}_4 + \text{O}_2$$

- (a) bimolecular and first order
 (b) unimolecular and second order
 (c) bimolecular and second order
 (d) unimolecular and first order

39. Consider the following reaction,



Which of the following statements regarding the equation (mentioned above) is incorrect?

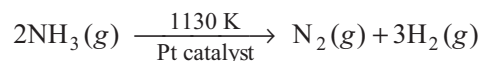
- (a) It is a complex reaction
 (b) It is a tenth order reaction
 (c) It is a completed in several steps
 (d) It is a second order reaction
40. The rate constant is numerically equal for three reactions of first, second and third order respectively. Which of the following is true?
 (a) If $[A] > 1$; $r_3 > r_2 > r_1$ (b) If $[A] = 1$; $r_1 = r_2 = r_3$
 (c) If $[A] < 1$; $r_1 > r_2 > r_3$ (d) All of these are true

Topic 3

Integrated Rate Law

41. When the rate of reaction is independent of the concentration of reactants, then the order of that chemical reaction is
(a) one (b) two (c) three (d) zero
42. Four reactions are given below. Which one of them is of zero order?
(a) $\text{PCl}_5 \longrightarrow \text{PCl}_3 + \text{Cl}_2$
(b) $2\text{FeCl}_3 + \text{SnCl}_2 \longrightarrow 2\text{FeCl}_2 + \text{SnCl}_4$
(c) $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$
(d) $\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$

43. At high pressure the following reaction is zero order



Choose the correct option which is not true with respect to the reaction, from the choices given below.

- (a) Rate of the reaction depends on concentration of NH_3
(b) Rate constant = Rate of reaction
(c) Further any increase in pressure will change the rate of reaction
(d) Rate of decomposition of ammonia will remain constant
44. Expression for the half-life of zero order reaction is given as
(a) $t_{1/2} = \frac{[R]}{2k}$ (b) $t_{1/2} = \frac{[R]_0}{2k}$
(c) $t_{1/2} = \frac{0.693}{k}$ (d) $t_{1/2} = \frac{0.301}{k}$
45. For a zero order reaction a graph of concentration (along y -axis) and time (along x -axis) is linear with
(a) a zero intercept and a +ve slope
(b) a zero intercept and a -ve slope
(c) a non-zero intercept and a -ve slope
(d) a non-zero intercept and a +ve slope
46. The reaction, $2A \longrightarrow B + C$ would be of zero order if
(a) rate of the reaction remains the same at all the concentrations of B and C
(b) rate of reaction doubles on doubling the concentration of B
(c) rate of reaction remains the same for all the concentration of A
(d) rate of the reaction is directly proportional to square of concentration of A

47. The rate constant of the reaction, $A \rightarrow B$ is 0.6×10^{-3} mole per second. If the concentration of A is 5 M then concentration of B after 20 min is (JEE Main 2015)

- (a) 1.08 M
(b) 3.60 M
(c) 0.36 M
(d) 0.72 M

48. In a first order reaction, reactant concentration ' C ' varies with time ' t ' as

- (a) C decreases with $\frac{1}{t}$
(b) $\log C$ decreases with $\frac{1}{t}$
(c) $\frac{1}{C}$ increases linearly with t
(d) $\log C$ decrease linearly with t

49. For a hypothetical reaction,



the rate constant is 0.12 s^{-1} . Which of the following statements is/are correct, if $[R]_0$ is the initial concentration?

- (a) $t_{1/2} = \frac{[R]_0}{0.12 \times 12}$
(b) $t_{1/2} = \frac{3}{2(0.12)[R]_0^2}$
(c) $t_{1/2} = \frac{0.693}{0.12}$
(d) $t_{1/2} = \frac{0.693}{0.12 \times 3}$

50. N_2 is obtained by the decomposition of benzene diazonium chloride at constant temperature. It is a first-order reaction the various volumes obtained at different time intervals are as

Time (min)	0	20	50	70	∞
N_2 (mL)	0	10	25	32	162

The rate constant of the reaction is

- (a) $3.54 \times 10^{-2} \text{ min}^{-1}$
(b) $3.2 \times 10^{-3} \text{ min}^{-1}$
(c) $3.89 \times 10^{-3} \text{ min}^{-1}$
(d) $3.1 \times 10^{-5} \text{ min}^{-1}$

51. For the decomposition of azoisopropane into hexane and nitrogen at 543 K, the following data is obtained.



Experiment	Time (s)	Total pressure (mm Hg)
I	0	35.0
II	360	54.0

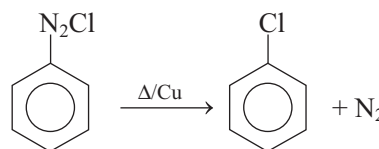
The rate constant at 360 is

- (a) $2.17 \times 10^{-3} \text{ s}^{-1}$ (b) $3.25 \times 10^{-3} \text{ s}^{-1}$
 (c) $3.25 \times 10^{-3} \text{ min}^{-1}$ (d) $1.98 \times 10^{-3} \text{ s}^{-1}$
52. A first order reaction is found to have a rate constant, $k = 4.2 \times 10^{-12} \text{ s}^{-1}$. Find the half-life of the reaction
 (a) $1.26 \times 10^{13} \text{ s}$ (b) $1.65 \times 10^{11} \text{ s}$
 (c) $1.65 \times 10^{-11} \text{ s}$ (d) $1.26 \times 10^{-13} \text{ s}$
53. 10 g of a radioactive isotope is reduced to 1.25 g in 12 yr. Calculate the half-life period of the isotope.
 (a) 4 yr (b) 3 yr (c) 8 yr (d) 24 yr
54. Half-life period of a first order reaction is 1386 s. The specific rate constant of the reaction is
 (a) $0.5 \times 10^{-3} \text{ s}^{-1}$ (b) $0.5 \times 10^{-2} \text{ s}^{-1}$
 (c) $5.0 \times 10^{-3} \text{ s}^{-1}$ (d) $5.0 \times 10^{-2} \text{ s}^{-1}$
55. Which of the following represent the expression for 5/6 life of a first order reaction?
 (a) $\frac{k}{2.303} \log \frac{6}{5}$ (b) $\frac{2.303}{k} \log \frac{5}{6}$
 (c) $\frac{2.303}{k} \log 6$ (d) $\frac{2.303}{k} \log 5$
56. A first order reaction takes $1.26 \times 10^{14} \text{ s}$ for its 50% completion. How much time would it take for 100% completion?
 (a) $2.52 \times 10^{28} \text{ s}^{-1}$ (b) $1.26 \times 10^{28} \text{ s}^{-1}$
 (c) $3.78 \times 10^{28} \text{ s}^{-1}$ (d) Infinite

57. 99% completion of a first order reaction takes place in 32 min. The time taken in 99.9% completion of the reaction will be

- (a) 48 min (b) 52 min
 (c) 56 min (d) 44 min

58. For the reaction,



Half-life does not depend on the concentration of the reactant. After 10 min, volume of N_2 gas is 20 L and after the completion of reaction, it is 100 L. Hence, rate constant is

- (a) $\frac{2.303}{10} \log 5 \text{ min}^{-1}$ (b) $\frac{2.303}{10} \log 10 \text{ min}^{-1}$
 (c) $\frac{2.303}{10} \log 10 \text{ min}^{-1}$ (d) $\frac{2.303}{10} \log 20 \text{ min}^{-1}$
59. When one reactant is present in large excess in a chemical reaction between two substances, then the reaction is known as
 (a) first order reaction
 (b) second order reaction
 (c) zero order reaction
 (d) pseudo first order reaction
60. The rate constant 'k' for pseudo first order reaction is
 (a) $\frac{2.303}{t} \log C_0 - C$
 (b) $\frac{2.303}{t} \log \frac{C}{C_0}$
 (c) $\frac{2.303}{t} \log C_0 + C$
 (d) $\frac{2.303}{t} \log \frac{C_0}{C}$

Topic 4

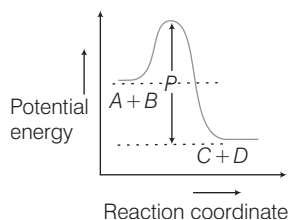
Effect of Temperature and Catalyst on Rate of Reaction

61. The temperature coefficient of a reaction is
 (a) the ratio of rate constant at two temperatures
 (b) the ratio of rate constant differing by 10° preferably 25°C and 35°C
 (c) the rate constant at a fixed temperature
 (d) None of the above
62. In a zero order reaction for every 10°C rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C , the rate of the reaction will become (CBSE AIPMT 2012)
 (a) 256 times (b) 512 times (c) 64 times (d) 128 times
63. The correct increasing order of the time taken for half of the decomposition of N_2O_5 at the temperature 50°C , 0°C and 25°C will be
 (a) $50^\circ\text{C} < 0^\circ\text{C} < 25^\circ\text{C}$ (b) $50^\circ\text{C} < 25^\circ\text{C} < 0^\circ\text{C}$
 (c) $0^\circ\text{C} < 25^\circ\text{C} < 50^\circ\text{C}$ (d) $0^\circ\text{C} < 50^\circ\text{C} < 25^\circ\text{C}$
64. Arrhenius equation may not be represented as
 (a) $\ln \frac{A}{k} = \frac{E_a}{RT}$ (b) $k = Ae^{-E_a/RT}$
 (c) $\log A = \log k + \frac{E_a}{2.303RT}$ (d) $\log k - \left(\frac{E_a}{RT}\right) = A$

65. In the Arrhenius equation, $k = Ae^{-E_a/RT}$, the factor $e^{-E_a/RT}$ corresponds to the

- (a) fraction of molecules that have kinetic energy = E_a
- (b) fraction of molecules that have kinetic energy $> E_a$
- (c) fraction of molecules that have kinetic energy $< E_a$
- (d) None of the above

66. Consider the following graph,

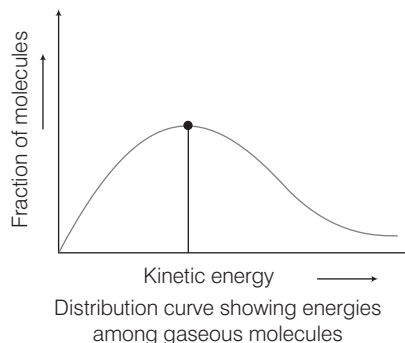


The above graph represents the change in energy for the reaction, $A + B \longrightarrow C + D$.

Here P is the

- (a) energy change for the reaction, $C + D \longrightarrow A + B$
- (b) energy change for the reaction, $A + B \longrightarrow C + D$
- (c) activation energy for the reaction, $A + B \longrightarrow C + D$
- (d) activation energy for the reaction, $C + D \longrightarrow A + B$

67.



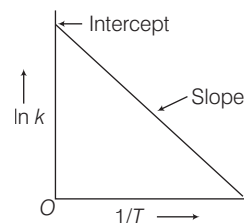
The peak of the above shown curve corresponds to

- (a) most probable kinetic energy
- (b) activation energy of forward reaction
- (c) activation energy of backward reaction
- (d) cannot be predicted

68. In the figure (shown in Q. 67), fraction of molecules represents

- (a) $\frac{N_E}{N_T}$
- (b) $\frac{N_T}{N_E}$
- (c) $\frac{E}{N_E}$
- (d) $\frac{E}{N_T}$

69. Consider the following plot between $\ln k$ and $1/T$,



In this plot, the intercept and slope respectively are

- (a) $-\frac{E_a}{R}$; $\ln A$
- (b) $\ln A$; $-\frac{E_a}{R}$
- (c) $\frac{E_a}{R}$; $-\ln A$
- (d) $\frac{E_a}{R}$; A

70. If a biochemical reaction is carried out in laboratory (outside the human body in absence of enzyme), then the rate of reaction is found to be 10^{-6} times. The activation energy of reaction in presence of enzyme is

- (a) p is needed
- (b) $\frac{6}{RT}$
- (c) different from E_a obtained in laboratory
- (d) cannot be determined

71. Relationship between threshold energy, activation energy and energy possessed by reacting species is

- (a) threshold energy = activation energy + energy possessed by reacting species
- (b) threshold energy = activation energy – energy possessed by reacting species
- (c) activation energy = threshold energy – energy possessed by reacting species
- (d) activation energy = threshold energy + energy possessed by reacting species

72. What is the activation energy for a reaction, if its rate doubles when the temperature is raised from 20°C to 35°C ? ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) (NEET 2013)

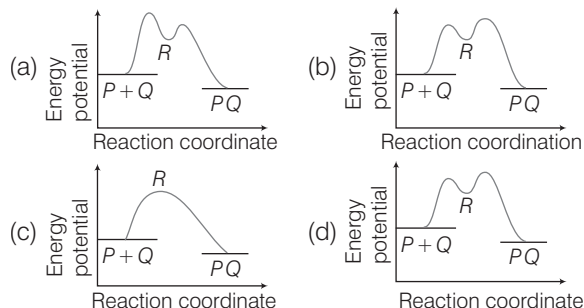
- (a) 342 kJ mol^{-1}
- (b) 269 kJ mol^{-1}
- (c) 34.7 kJ mol^{-1}
- (d) 15.1 kJ mol^{-1}

73. The rate of a reaction doubles, when its temperature changes from 300 K to 310 K . Activation energy of such a reaction will be ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\log 2 = 0.301$) (JEE Main 2013)

- (a) 53.6 kJ mol^{-1}
- (b) 48.6 kJ mol^{-1}
- (c) 58.5 kJ mol^{-1}
- (d) 60.5 kJ mol^{-1}

74. For an exothermic chemical process occurring in two steps as I. $P + Q \longrightarrow R$ (slow) II. $R \longrightarrow PQ$ (fast)

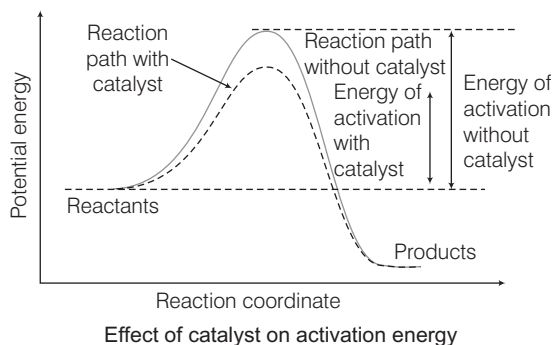
The progress of the reaction can be best described by



75. Which of the following statements explained the role of catalyst in increasing the rate of a reaction?

- Catalyst provides an alternative path of lower activation energy to the reactants
- It decreases the rate of backward reaction
- It increases the number of collisions between the reacting molecules
- It provides extra energy to the reacting molecules

76.



On the basis of the curve shown above, identify the incorrect statement.

- Catalyst provides an alternate pathway or reaction mechanism
- It increases the activation energy between reactants and products
- It lowers the potential energy barrier
- Catalyst reduces the activation energy between reactants and products

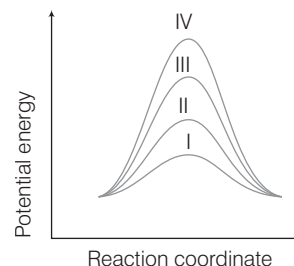
77. A catalyst has no effect on

- rate of reaction
- equilibrium constant of reaction
- Gibbs energy
- activation energy

The correct option is

- I, II and III
- II and III
- Only II
- II, III and IV

78. If a homogeneous catalytic reaction can take place through four alternative paths as shown below.



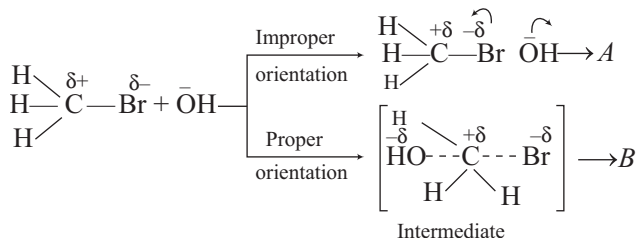
The catalytic efficiency of I, II, III, IV representing the relative case would be

- $I > II > III > IV$
- $I < II < III < IV$
- $I = II = III = IV$
- $IV > II > III > I$

Topic 5

Collision Theory

79.



What will come in place of A and B in the above reaction?

- No products = A; $\text{HO}-\text{C}(\text{H})_3 = \text{B}$

- No products = A; $\text{HO}-\text{C}(\text{H})_3 + \text{Br}^- = \text{B}$

- $\text{HO}-\text{C}(\text{H})_3 = \text{A}$, No products = B

- $\text{HO}-\text{C}(\text{H})_3 + \text{Br} = \text{A}$; No products = B

80. Select the incorrect statement.
- Collision theory is based on kinetic theory of gases
 - Reaction is a result of collision between the molecules
 - Collision frequency is the number of collision per second per unit length
 - Rate of reaction for a bimolecular elementary reaction is $\text{rate} = Z_{AB} e^{-E_a/RT}$
81. After introducing the factor P , expression for the rate of a reaction, becomes
- $\text{Rate} = \frac{Z_{AB} e^{-E_a/RT}}{P}$
 - $\text{Rate} = PZ_{AB} e^{-E_a/RT}$
 - $\text{Rate} = \frac{Z_{AB} \cdot P}{e^{E_a/RT}}$
 - $\text{Rate} = \frac{e^{E_a/RT}}{PZ_{AB}}$
82. The modified Arrhenius equation (according to collision theory) is
- $k = PZ_{AB} e^{-E_a/RT}$
 - $k = Z_{AB} \cdot e^{-E_a/RT}$
 - $k = Ae^{-E_a/RT}$
 - None of these
83. In order to produce the effective collisions, the colliding molecules must have
- a certain minimum amount of energy
 - proper orientation
 - Both threshold energy and proper orientation
 - energy equal to or greater than threshold energy
84. The rate constant is given by the equation, $k = P \cdot Z e^{-E_a/RT}$. To increase the rate of reaction, which of the factor should decrease?
- Z
 - T
 - P
 - E_a
85. Higher order (>3) reactions are rare due to
- (JEE Main 2015)
- low probability of simultaneous collision of all the reacting species
 - increase in entropy and activation energy as more molecules are involved
 - shifting of equilibrium towards reactants due to elastic collisions
 - loss of active species on collision

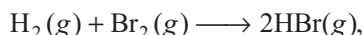
[Special Format Questions]

I. More Than One Correct Option

86. Consider the following reaction, $4A + B \longrightarrow 2C + 2D$
- The true statements about this reaction are
- the rate of appearance of C is one-half of the rate of disappearance of B
 - the rate of formation of D is one-half of the rate of consumption of A
 - the rate of disappearance of B is one-fourth of the rate of disappearance of A
 - the rates of formation of C and D are equal
87. The rate of a reaction can be increased by
- increasing temperature
 - using a suitable catalyst
 - increasing the concentration of reactants
 - increasing activation energy
88. At high pressure the following reaction is zero order.
- $$2\text{NH}_3(g) \xrightarrow[\text{Platinum catalyst}]{1130\text{ K}} \text{N}_2(g) + 3\text{H}_2(g)$$
- Which of the following options are correct for this reaction?
- Rate of reaction = Rate constant
 - Rate of the reaction depends on concentration of ammonia
 - Rate of decomposition of ammonia will remain constant until ammonia disappears completely
 - Further increase in pressure will change the rate of reaction
89. The rate constant of a reaction depends upon
- temperature
 - activation energy
 - catalyst
 - concentration of reactants and products
90. Rate law cannot be determined from balanced chemical equation if
- reverse reaction is involved
 - it is an elementary reaction
 - it is a sequence of elementary reactions
 - any of the reactants is in excess
91. Which of the following statements are correct about order of reaction?
- Order can be determined experimentally
 - Order cannot be fractional
 - Order of reaction is equal to sum of powers of concentration terms in differential rate law
 - It is not affected by the stoichiometric coefficient of the reactants
92. For the reaction, $X \rightarrow Y$ the rate law is, $\text{rate} = k[X]$. The correct statement about it are
- the reaction follows first order kinetics
 - half-life of the reaction depends upon initial concentration
 - at constant temperature, k is constant
 - the rate law provides a simple way of predicting the concentration of reactants at any time after the start of the reaction

93. The correct statement about molecularity are
 (a) it depends upon the slowest step
 (b) it may be either whole number or fractional
 (c) it is obtained from mechanism of reaction
 (d) it shows the number of reactant molecules involving in elementary step of a chemical reaction

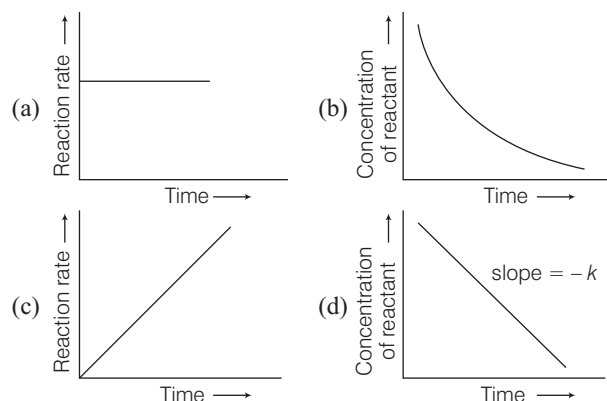
94. For the reaction,



the rate of a reaction is $k[\text{H}_2][\text{Br}_2]^{1/2}$. The false

statements about this reaction are

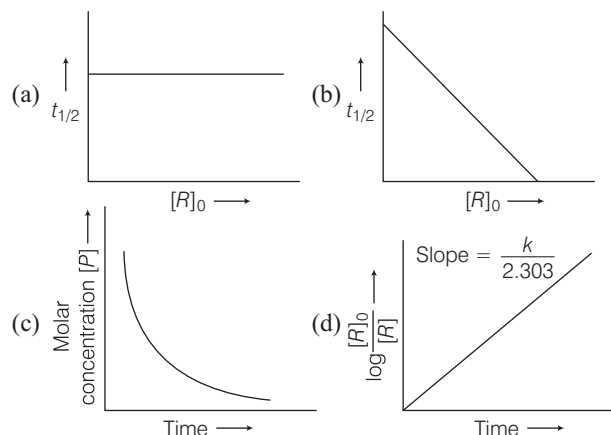
- (a) the order of the reaction is 1.5
 (b) the unit of rate constant is s^{-1}
 (c) the molecularity of the reaction is 3/2
 (d) the unit of rate is $\text{mol L}^{-1}\text{s}^{-1}$
95. Which of the following graphs are correct for a zero order reaction?



96. The examples of first order reaction are

- (a) $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$
 (b) $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
 (c) $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \longrightarrow \text{CH}_3\text{COO}^-\text{Na}^+ + \text{C}_2\text{H}_5\text{OH}$
 (d) $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$

97. Which of the following graphs are correct for a first order reaction?



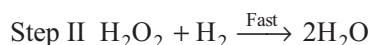
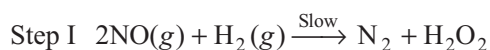
98. The incorrect statements among the following are

- (a) molecularity of a reaction can be fractional
 (b) first order reaction never go to the completion
 (c) first order reaction must be homogeneous
 (d) the frequency factor A in the Arrhenius equation increases with rise in temperature

99. Consider the following reaction,



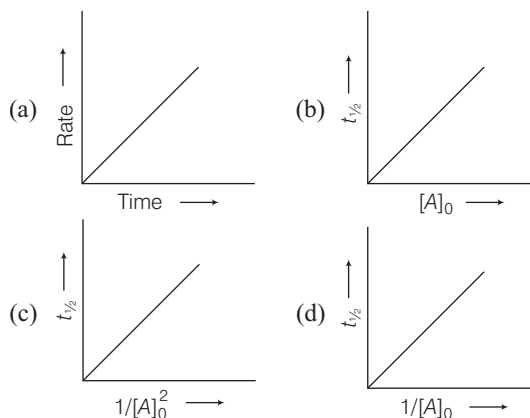
It involves following steps:



The correct statements about this reaction are

- (a) $\text{rate} = k[\text{NO}]^2[\text{H}_2]$
 (b) $\text{rate} = k[\text{H}_2\text{O}_2][\text{H}_2]$
 (c) on doubling the concentration of hydrogen, keeping the concentration of NO constant, the rate will become double
 (d) if initial concentration of H_2 and NO is CO and after time t , the concentration of N_2 is x , then
 $\text{Rate} = k(\text{CO}) - 2x^x$

100. Which of the following graphs are correct?



101. For a first order reactions,

- (a) $t_{1/2} = \frac{k}{a}$
 (b) $t_{3/4} = 2t_{1/2}$
 (c) $t_{1/2} = \frac{0.693}{k}$
 (d) $t_{1/2} = k \times 0.693$

102. Which of the following statements are correct accordance with the Arrhenius equation?

- (a) Rate of a reaction increases with increase in temperature
 (b) Rate of a reaction increases with decrease in activation energy
 (c) Rate constant decreases exponentially with increase in temperature
 (d) Rate of reaction decreases with decrease in activation energy

103. Correct statements for Arrhenius equation,

$$k = Ae^{-E_a/RT} \text{ is/are}$$

- (a) a may be termed as rate constant at very high temperature
- (b) a may be termed as the rate constant at zero activation energy
- (c) E_a is the activation energy of the reaction
- (d) k is the rate of reaction at zero concentration

104. During decomposition of an activated complex

- (a) energy is always released
- (b) energy is always absorbed
- (c) energy does not change
- (d) reactants may be formed

105. According to Maxwell Boltzmann distribution of energy,.....

- (a) the fraction of molecules with most probable kinetic energy decreases at higher temperatures
- (b) the fraction of molecules with most probable kinetic energy increases at higher temperatures
- (c) most probable kinetic energy increases at higher temperatures
- (d) most probable kinetic energy decreases at higher temperatures

II. Statement Based Questions Type I

■ **Directions** (Q. Nos. 106-114) *In the following questions, a Statement I is followed by a corresponding Statement II. Of the following statements, choose the correct one.*

- (a) Both Statement I and II are correct and Statement II is the correct explanation of Statement I.
- (b) Both Statement I and II are correct and Statement II is not the correct explanation of Statement I.
- (c) Statement I is correct, Statement II is incorrect.
- (d) Statement II is correct, but Statement I is incorrect.

106. Statement I At the macroscopic level, the reaction mechanisms involving orientation and energy of molecules undergoing collisions are discussed.

Statement II At the molecular level the amounts of substances reacted or formed and the rates of their consumption or formation are discussed.

107. Statement I Concentration of reactant has direct dependence on the partial pressure of it, in a gaseous reaction.

Statement II Rate can be expressed as rate of change in partial pressure of the reactant/product.

108. Statement I The rate law may not depend on the concentration of every reactant.

Statement II With increase in temperature, the rate of reaction increases.

109. Statement I For a complex reaction, order is given by the slowest step of the reaction.

Statement II Molecularity of the slowest step is same as the order of the overall reaction.

110. Statement I Zero order reactions are relatively uncommon but these occur under special conditions.

Statement II Thermal decomposition of HI on gold surface is a zero order reactions.

111. Statement I The rate of zero order reaction is independent of concentration of reactants.

Statement II The $t_{1/2}$ of zero order reaction depends on concentration of reactants.

112. Statement I The rate of a first order reaction depends on the concentration of the reactant raised to the first power.

Statement II Decomposition of H_2O_2 follows zero order reaction.

113. Statement I Collision theory provides a greater insight into the energetic and mechanistic aspects of reactions.

Statement II Collision theory has no link with kinetic theory of gases.

114. Statement I To account for effective collisions another factor P is introduced.

Statement II In a collision, molecules must be properly oriented.

III. Statement Based Questions Type II

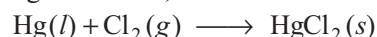
115. Rate of a reaction can be expressed as

- I. the rate of decrease in concentration of any one of the reactant.
- II. the rate of increase in concentration of any one of the product.

Which of the above mentioned statements is/are correct? Choose the correct option.

- (a) Only I
- (b) Only II
- (c) Both I and II
- (d) Neither I nor II

116. Consider the following statements regarding the equation given below,



- I. Stoichiometric coefficients of the reactants and products are same in the above reaction.

$$\text{II. Rate of reaction} = -\frac{\Delta[\text{Hg}]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = \frac{\Delta[\text{HgCl}_2]}{\Delta t}$$

- III. Rate of disappearance of any of the reactant = Rate of appearance of product.

The correct statements are

- (a) I and II
- (b) I and III
- (c) II and III
- (d) I, II and III

117. Factors affecting the rate of a reaction are

- I. ΔH of reaction.
- II. size of the vessel.
- III. amount of the reactants taken.
- IV. physical state of the reactants.

The option with all correct factors is

- (a) I, II and III
- (b) II, III and IV
- (c) I, III and IV
- (d) I, II and IV

118. For the reaction,



which of the following statements are true?

- I. Rate of appearance of S is doubled the rate of the disappearance of Q .
- II. Rate of disappearance of Q is one fourth the rate of disappearance of P .
- III. Rate of formation of R is equal to the rate of formation of S .

Choose the correct option.

- (a) I and II
- (b) II and III
- (c) I and III
- (d) All of these

119. Which of the following statements are true?

- I. Rate law is an experimental fact while law of mass action is a theoretical proposal.
- II. Rate law is more informative than law of mass action for the development of mechanism.
- III. Rate law is always different from the expression of law of mass action.

Choose the correct option.

- (a) I and III
- (b) III and II
- (c) I and II
- (d) All of these

120. Consider a general reaction,



In the given reaction,

- I. Rate = $k[A]^x[B]^y$ (rate equation).
- II. $\frac{d[R]}{dt} = k[A]^x[B]^y$ (differential rate equation).
- III. k = rate constant.

Which of the following facts mentioned above are correct?

- (a) I and III
- (b) I and II
- (c) II and III
- (d) I, II and III

121. I. Order of a reaction can be 0, 1, 2, 3, ...

II. Order of a reaction can never be a fraction.

Which of the above statements is/are true? Choose the correct option.

- (a) Only I
- (b) Only II
- (c) Both I and II
- (d) Neither I nor II

122. Consider some facts about decomposition of H_2O_2 .

- I. It is catalysed by iodide ion in acidic or alkaline medium.
- II. It is second order reaction with respect to both H_2O_2 and I^- .
- III. Rate equation of this particular reaction will be

$$\text{Rate} = \frac{-d[H_2O_2]}{dt} = k[H_2O_2]^2 [I^-]$$

- IV. It completes in two steps and both steps are unimolecular elementary reactions.

Which of the above written facts are correct, regarding decomposition of H_2O_2 ? Choose the correct option.

- (a) I, II and III
- (b) I, II, III and IV
- (c) I, III and IV
- (d) None of these

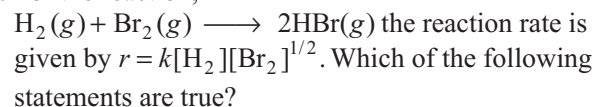
123. Which of the following statements are correct about order of a reaction?

- 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.

Choose the correct option.

- (a) I, II and III
- (b) I, II and IV
- (c) II, III and IV
- (d) I, II, III and IV
- (e) I and II

124. For the reaction,



- I. Molecularity of reaction is 1.5.
- II. Order of reaction is 2.
- III. Molecularity of reaction is 2.
- IV. Order of reaction is 1.5.

Choose the correct option.

- (a) I and III
- (b) I and II
- (c) II and III
- (d) III and IV

125. Consider the following statements.

- I. For first order reactions, the rate of reaction is proportional to the first power of the concentration of the reactant R .
- II. The first order rate equation can be represented as

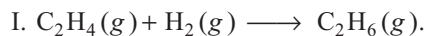
$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

- III. All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

Which of the above mentioned statements are true?
Choose the correct option.

- (a) I and II (b) II and III
(c) I, II and III (d) All of these

126. Consider the following.



This reaction is an example of first order kinetics.

II. Rate of this reaction will be given as

$$\text{Rate} = k [\text{C}_2\text{H}_4].$$

Which of the above statements is/are correct?

- (a) Only I (b) Only II
(c) Both I and II (d) Neither I nor II

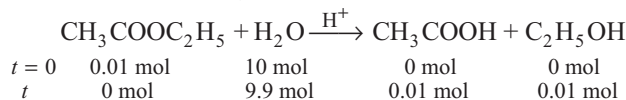
127. Which among the following is/are true statement(s)?

- I. For a first order reaction, $t_{1/2} = \frac{0.693}{k}$.
II. Molecularity of a reaction may be a fraction or zero.
III. Rate of zero order reaction is independent of initial concentration of reaction.

Choose the most appropriate option regarding the above statements.

- (a) I and II (b) I and III
(c) II and III (d) Only III

128. Consider the following equation,



- I. The concentration of water does not get altered much during the course of the reaction.
II. Rate equation for this reaction is

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

Which of the following statements is/are true about the reaction? Choose the correct option.

- (a) Only I (b) Only II
(c) Both I and II (d) Neither I nor II

129. The rate constant of a reaction is shown as

$$k = 2.1 \times 10^{10} e^{-2700/RT}$$

It means that

- I. $\log k$ vs $1/T$ will be a straight line with intercept $= \log 2.1 \times 10^{10}$.
II. Number of effective collisions are $2.1 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$.
III. Half-life of a reaction increases with increase of temperature.
IV. $\log k$ vs $1/T$ will be a straight line with slope $= -\frac{2700}{2.303R}$.

Which of the above statements are true? Choose the correct option.

- (a) I and II (b) II and III (c) III and IV (d) I and IV

130. The theory which are related to chemical kinetics are

- I. transition theory
II. Ostwald's theory
III. absolute reaction rate theory
IV. Maxwell's theory

The most appropriate option with all correct theories is

- (a) I and II (b) II and III
(c) III and IV (d) I and IV

131. Which of the following statements are true about the collision theory of chemical reaction?

- I. Number of effective collisions determine the rate of reaction.
II. Collision of atoms/molecules possessing sufficient threshold energy results into the formation of products.
III. It helps in considering reacting atoms/molecules to be hard spheres and ignore their structural features.
IV. Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective.

Choose the most appropriate option regarding the above statements.

- (a) I, II and III (b) I, III and IV
(c) II, III and IV (d) I, II, III and IV

IV. Assertion-Reason Type Questions

■ **Directions** (Q. Nos. 132-147) *In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.*

- (a) Both A and R are correct and R is the correct explanation of A.
(b) Both A and R are correct, but R is not the correct explanation of A.
(c) A is correct but, R is incorrect.
(d) R is correct but, A is incorrect.

132. Assertion (A) $\Delta[R]$ is multiplied with -1 to make the rate of the reaction a positive quantity.

Reason (R) $\Delta[R]$ is a negative quantity in the expression, rate of disappearance of $R = \frac{-\Delta[R]}{\Delta t}$.

133. Assertion (A) It is not always convenient to determine the instantaneous rate.

Reason (R) Instantaneous rate is measured by the determination of slope of the tangent at point 't' in concentration *versus* time plot.

- 134. Assertion** (A) Order of the following reaction,
 $2\text{NO}(g) + 2\text{H}_2(g) \longrightarrow 2\text{H}_2\text{O}(g) + \text{N}_2(g)$ is 3.

Reason (R) Order of the reaction with respect to given reactant is the power of the reactant's concentration in the rate equation.

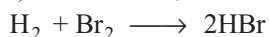
- 135. Assertion** (A) Some zero order reactions may have order in fractions.

Reason (R) Order cannot be determined from balanced chemical equation.

- 136. Assertion** (A) The molecularity can be a fraction.

Reason (R) The molecularity of a reaction is the number of molecules whether of the same or different species that must contact simultaneously in a single step in order to reaction to occur.

- 137. Assertion** (A) The reaction,



has a molecularity of two.

Reason (R) Order of reaction is $\frac{3}{2}$.

- 138. Assertion** (A) The multimolecular reactions are quite rare in comparison with bimolecular reactions.

Reason (R) At normal pressure, triple collisions are much less frequent than double ones.

- 139. Assertion** (A) Decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.

Reason (R) At high pressure, the metal surface gets saturated with gas molecules.

- 140. Assertion** (A) In a mixture of $\text{H}_2\text{C}_2\text{O}_4$ and KMnO_4 the later decolourises faster at a higher temperature than that at a lower temperature.

Reason (R) No effect of temperature on decolourisation.

- 141. Assertion** (A) E_{act} of the forward reaction is higher than that of the backward reaction in a reversible endothermic reaction.

Reason (R) Threshold energy of the forward reaction is more than that of backward reaction.

- 142. Assertion** (A) A catalyst increases the rate of reaction.

Reason (R) Catalyst also changes the equilibrium constant.

- 143. Assertion** (A) In Arrhenius equation, frequency factor, $A = PZ$.

Reason (R) With increasing E_a , the rate constant increases too.

- 144. Assertion** (A) A bimolecular reaction takes place when two properly oriented reactant molecules come together in a sufficiently energetic collision.

Reason (R) When the temperature is increased by 10°C , the reaction rate tends to be doubled.

- 145. Assertion** (A) Catalyst changes the individual energies of the reactants and products.

Reason (R) A Catalyst allows more number of molecules are able to cross the barrier per unit time.

- 146. Assertion** (A) A positive catalyst increases the rate of reaction.

Reason (R) A catalyst increases the rate of reaction by making available a new and more efficient mechanism.

- 147. Assertion** (A) All collisions of reactant molecules lead to formation of product.

Reason (R) Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to formation of compound.

V. Matching Type Questions

- 148.** Match the following columns and choose the correct option from the codes given below.

Column I (Reaction)	Column II (Units of rate constant)
A. Zero order reaction	1. $\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1} \text{s}^{-1}$
B. First order reaction	2. $\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$
C. Second order reaction	3. $\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1} \text{L s}^{-1}$

Codes

A	B	C	A	B	C
(a) 2	1	3	(b) 3	2	1
(c) 1	2	3	(d) 3	1	2

- 149.** Match the following columns and choose the correct option from the codes given below.

Column I (Type of reaction)	Column II (Example)
A. Unimolecular	1. $2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$
B. Bimolecular	2. $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$
C. Trimolecular	3. $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$

Codes

A	B	C	A	B	C
(a) 2	1	3	(b) 2	3	1
(c) 3	1	2	(d) 3	2	1

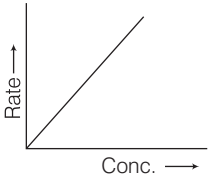
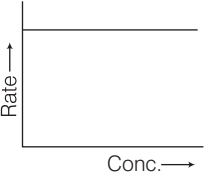
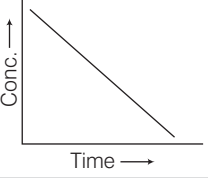
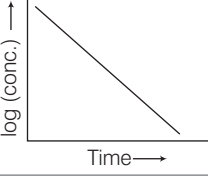
150. Match the terms of Column I with Column II and choose the correct option from the codes given below.

Column I	Column II
A. Inversion of cane sugar.	1. Zero order reaction
B. Decomposition of N_2O .	2. First order reaction
C. Thermal decomposition of HI on gold surface.	3. Pseudo order reaction

Codes

A	B	C	A	B	C
(a) 1	2	3	(b) 2	3	1
(c) 3	2	1	(d) 2	1	3

151. 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
A. 	1. First order
B. 	2. Zero order
C. 	
D. 	

Codes

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

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

Column I	Column II
A. Catalyst alters the rate of reaction.	1. Cannot be fraction or zero.
B. Molecularity	2. Proper orientation is not there.
C. Second half-life of first order reaction.	3. By lowering the activation energy.

D. $e^{-E_a/RT}$	4. Is same as the first.
E. Energetically favourable reactions are sometimes slow.	5. Total probability is one.
F. Area under the Maxwell, Boltzmann curve is constant.	6. Refers to the fraction of molecules with energy equal to or greater than activation energy.

A	B	C	D	E	F
(a) 3	1	4	6	2	5
(b) 4	3	1	6	2	5
(c) 1	3	4	2	6	5
(d) 6	2	5	4	3	1

VI. Passage Based Questions

■ **Directions** (Q.Nos. 153-154) *These questions are based on the following situation. Choose the correct options from those given below.*

Order of a reaction is an experimentally determined quantity. It may be zero, positive, negative and fractional. It is obtained by several methods. One such method is by varying concentration of only one reactant, keeping the concentration of others constant.

153. In the chemical reaction, $A \rightarrow B$, the rate of a reaction doubles on increasing the concentration of A four times. The order of reaction with respect to A is
(a) 0 (b) 0.5 (c) 1 (d) 2

154. For the reaction,

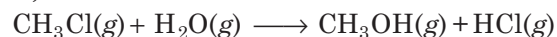


in aqueous medium, the rate of a reaction is given by

$$\frac{d[IO^-]}{dt} = k \frac{[I^-][OCl^-]}{[OH^-]}$$

- the overall of the reaction is
(a) -1 (b) 1 (c) 0 (d) 2

■ **Directions** (Q.Nos. 155-157) *Consider the following reaction,*



following kinetic data were obtained for this reaction.

Initial concentration [CH ₃ Cl]	Initial concentration [H ₂ O]	Initial rate of disappearance of CH ₃ Cl M s ⁻¹
0.2	0.2	1
0.4	0.2	2
0.4	0.4	8

Answer the following questions on the basis of above data.

155. Order of reaction with respect to CH_3Cl is
(a) 0 (b) 1 (c) 2 (d) 3

156. The rate law for the reaction is

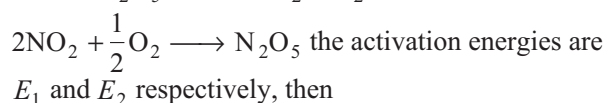
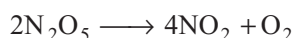
- (a) $r = k[CH_3Cl]^2[H_2O]^1$ (b) $r = k[CH_3Cl]^2[H_2O]^2$
(c) $r = k[CH_3Cl][H_2O]^2$ (d) $r = k[CH_3Cl]^2[H_2O]^4$

157. The units of rate constant for the given reaction is
 (a) s^{-2} (b) $\text{L}^2\text{mol}^{-2}\text{s}^{-1}$ (c) $\text{L}^2\text{mol}^{-1}\text{s}^{-1}$ (d) $\text{molL}^{-1}\text{s}^{-1}$

■ **Directions** (Q.Nos. 158-159) *These questions are based on the following situation. Choose the correct options from those given below.*

A collision between reactant molecules must occur with a certain minimum energy before it is effective in yielding product. This minimum energy is called activation energy (E_a). Its value varies inversely with rate constant. Moreover, larger the value of activation energy, more is the effect of increase in temperature on rate constant (k).

158. For the following reactions at a particular temperature,

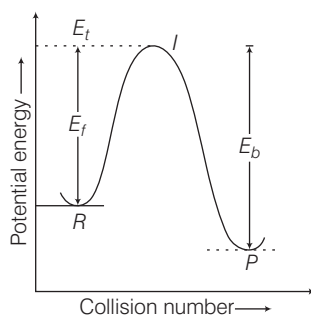


- (a) $E_1 > E_2$ (b) $E_1 < E_2$ (c) $E_1 = 2E_2$ (d) $\sqrt{E_1 > E_2^2} = 1$

159. The rate constant for a reaction is given by $k = Ae^{-E_a/RT}$. Which factor should be lowered so that the rate of reaction may increase?

- (a) T (b) Z (c) A (d) E_a

■ **Directions** (Q.Nos. 160-161) *Consider the following diagram.*

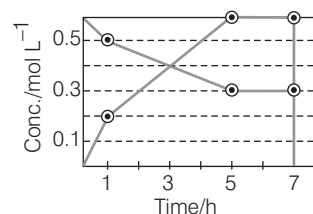


E_f = activation energy of forward reaction
 E_b = activation energy of backward reaction
 E_t = threshold energy

160. In a reaction, $A + B \rightarrow C$ is exothermic to the extent of 30 kJ/mol and the activation energy of the forward reaction is 249 kJ/mol, then the activation energy of reverse reaction (in kJ/mol) is
 (a) 324 (b) 279 (c) 40 (d) 100
161. The activation energies for forward and backward reactions of a chemical reaction are 30.5 and 45.4 kJmol^{-1} respectively. The reaction is
 (a) exothermic
 (b) endothermic
 (c) neither exothermic nor endothermic
 (d) independent of temperature

■ **Directions** (Q. Nos. 162-164) *Study the following passage and answer the questions on the basis of the passage.*

The progress of the reaction, $P \rightarrow nQ$ with time is represented in the graph shown below.



162. The equilibrium constant (K) will be

- (a) 1.2 (b) 6.67
 (c) 2 (d) 0.5

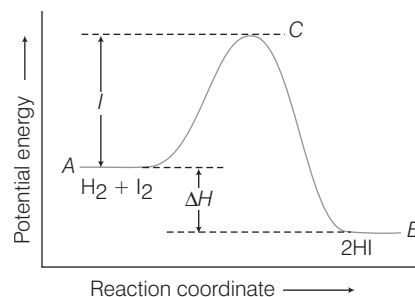
163. Value of n is

- (a) 2 (b) 1
 (c) 1.5 (d) 3

164. The initial rate of conversion of P will be

- (a) $0.2 \text{ mol L}^{-1}\text{h}^{-1}$
 (b) $0.4 \text{ mol L}^{-1}\text{h}^{-1}$
 (c) $0.8 \text{ mol L}^{-1}\text{h}^{-1}$
 (d) $0.1 \text{ mol L}^{-1}\text{h}^{-1}$

■ **Directions** (Q. Nos. 165-166) *On the basis of graph shown below answer the following questions.*



165. In the graph shown above, I means

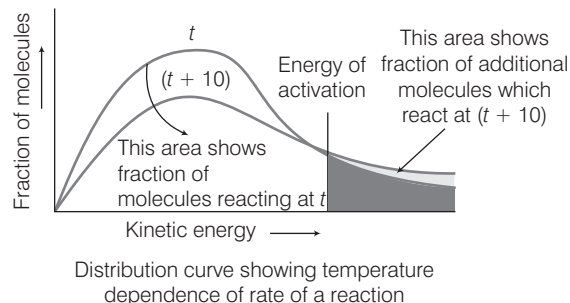
- (a) activated complex
 (b) activation energy
 (c) E_a in joules
 (d) None of the above

166. **Assertion** (A) Final enthalpy of the reaction depends upon the nature of reactants and products.

Reason (R) Some energy is released when the complex intermediate decomposes to form products.

- (a) Both A and R are correct and R is the correct explanation of A
 (b) Both A and R are correct and R is not the correct explanation of A
 (c) A is correct and R is incorrect
 (d) R is correct and A is incorrect

■ **Directions** (Q. Nos. 167-168) Analyse the figure given below and answer the following questions.



167. The curve shown in the above figure is known as

- (a) Ludwig-Clark curve
- (b) Arrhenius-van't Hoff curve
- (c) Maxwell-Boltzmann distribution
- (d) None of the above

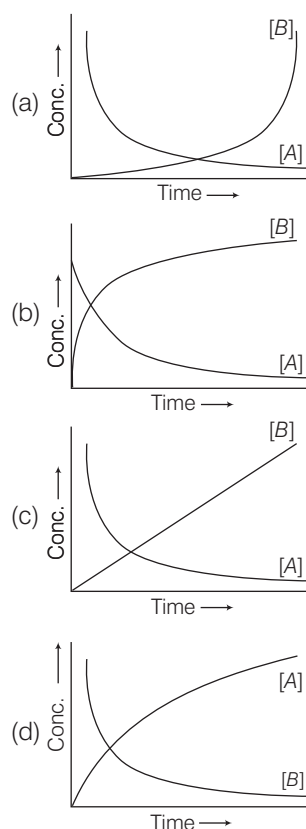
168. Which of the following statements is not correct regarding the given graph?

- (a) When the temperature is risen, the maximum of the curve moves to the higher energy value
- (b) At higher temperature curve broadens out
- (c) Area under the curve changes with change in temperature
- (d) Increasing the temperature, is increases action of molecules

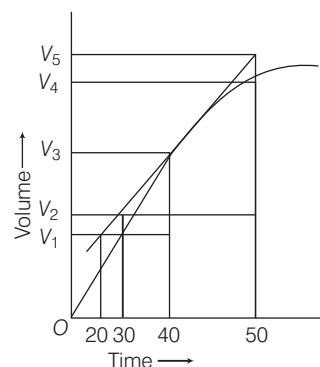
[NCERT & NCERT Exemplar Questions]

NCERT

169. Consider the reaction, $A \longrightarrow B$. 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?



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



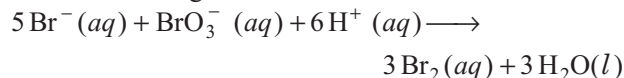
- (a) Average rate upto 40 s is $\frac{V_3 - V_2}{40}$
- (b) Average rate upto 40 s is $\frac{V_3 - V_2}{40 - 30}$
- (c) Average rate upto 40 s is $\frac{V_3}{40}$
- (d) Average rate upto 40 s is $\frac{V_3 - V_1}{40 - 20}$

171. Consider the graph given in Q.170. Which of the following options does not show instantaneous rate of reaction at 40 s ?

- (a) $\frac{V_5 - V_2}{50 - 30}$
- (b) $\frac{V_4 - V_2}{50 - 30}$
- (c) $\frac{V_3 - V_2}{40 - 30}$
- (d) $\frac{V_3 - V_1}{40 - 20}$

NCERT Exemplar

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



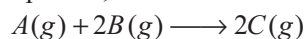
- (a) $\frac{\Delta[\text{Br}^-]}{\Delta t} = 5 \frac{\Delta[\text{H}^+]}{\Delta t}$ (b) $\frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{6}{5} \frac{\Delta[\text{H}^+]}{\Delta t}$
 (c) $\frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$ (d) $\frac{\Delta[\text{Br}^-]}{\Delta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

173. Rate law for the reaction, $A + 2B \longrightarrow C$ is found to be
 Rate = $k[A][B]$

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

- (a) the same (b) doubled (c) quadrupled (d) halved

174. 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 of this reaction.

Exp.	Initial concentration of $[A]/\text{mol L}^{-1}$	Initial concentration of $[B]/\text{mol L}^{-1}$	Initial concentration of $[C]/\text{mol L}^{-1}\text{s}^{-1}$
1.	0.30	0.30	0.10
2.	0.30	0.60	0.40
3.	0.60	0.30	0.20

- (a) Rate = $k[A]^2[B]$ (b) Rate = $k[A][B]^2$
 (c) Rate = $k[A][B]$ (d) Rate = $k[A]^2[B]^0$

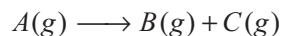
175. Which of the following statements is correct?

- (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

176. Which of the following statements is not correct about order of a reaction?

- (a) The order of a reaction can be a fractional number
 (b) Order of a reaction is experimentally determined quantity
 (c) 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
 (d) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression

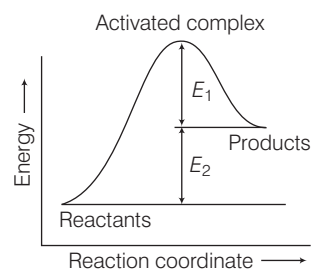
177. Consider a first order gas phase decomposition reaction given below.



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

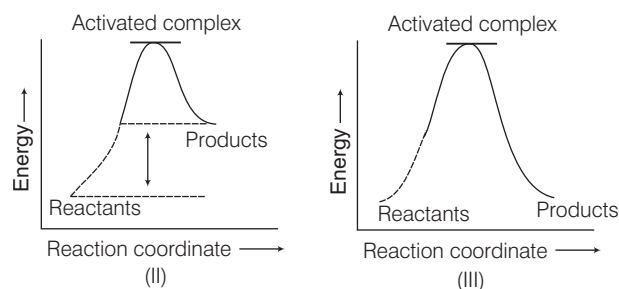
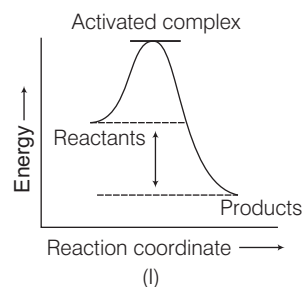
- (a) $k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$ (b) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$
 (c) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i + p_t}$ (d) $k = \frac{2.303}{t} \log \frac{p_i}{p_i + x}$

178. Consider the figure and mark the correct option.



- (a) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant
 (b) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant
 (c) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product
 (d) Activation energy of backward reaction is E_1 and product is more stable than reactant

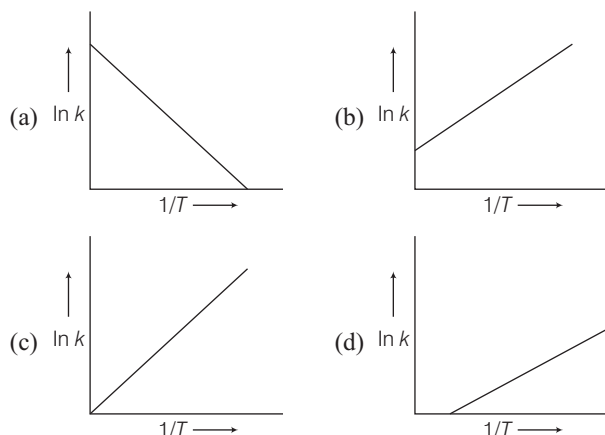
179. Which of the following graphs represents exothermic reaction?



- (a) Only I (b) Only II
 (c) Only III (d) I and II

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

- 181.** According to Arrhenius equation rate constant (k) is equal to $Ae^{-E_a/RT}$. Which of the following options represent the graph of $\ln k$ vs $\frac{1}{T}$?



- (a) determining the rate constant at standard temperature
- (b) determining the rate constant at two temperatures
- (c) determining probability of collision
- (d) using catalyst

(a) increases (b) decreases
(c) remains unchanged (d) may increase or decrease

- (a) It catalyses the forward and backward reactions 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

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

Answers

[illegible]

Hints & Explanations

- (b) Rate of only those chemical reactions can be determined easily which occurs at moderate speed, e.g. hydrolysis of starch, inversion of cane sugar etc.
- (a) Rate of reaction = Decrease in the concentration of reactant per unit time
= Increase in the concentration of any one of the product per unit time.
- (a) The curve *P* tells the gradual increase in concentration with the passage of time and concentration of product increases in the course of reaction.
- (b) Square bracket in the expression $\Delta[R]$ shows molar concentration. Unit of rate are concentration time⁻¹ or mol L⁻¹ s⁻¹, atm s⁻¹. Rate at any instant of time is called instantaneous rate.
- (d) Rate of reaction = $-\frac{\Delta[\text{Hg}]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = \frac{\Delta[\text{HgCl}_2]}{\Delta t}$
- (d) All the statements are true.
- (a) $-\frac{d[X]}{2dt} = -\frac{d[Y]}{dt} = +\frac{d[X_2Y]}{dt}$
- (a) $-\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{3dt} = +\frac{d[\text{NH}_3]}{2dt}$
or $\frac{d[\text{NH}_3]}{dt} = -\frac{2}{3} \frac{d[\text{H}_2]}{dt}$
- (a) Rate of reaction = $-\frac{1}{2} \frac{d[x]}{dt} = -\frac{1}{2} \frac{[1.5 - 3.0]}{4} = \frac{1.5}{8} = 0.1875 \text{ M min}^{-1}$
- (a) For the reaction,
 $2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$
Rate = $-\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{NO}]}{2dt} = \frac{d[\text{O}_2]}{dt}$
 $\therefore -\frac{d[\text{NO}_2]}{dt} = 6 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$
 $\therefore \frac{d[\text{O}_2]}{dt} = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \times 6 \times 10^{-12} = 3 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$
- (a) For the reaction,
 $5\text{Br}^- + \text{BrO}_3^- + 6\text{H}^+ \longrightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$
 $\frac{-1}{5} \frac{d[\text{Br}^-]}{dt} = -\frac{d[\text{BrO}_3^-]}{dt} = \frac{1}{3} \frac{d[\text{Br}_2]}{dt}$
 $\frac{1}{5} k_1 [\text{Br}^-] = k_2 [\text{Br}^-] = \frac{1}{3} k_3 [\text{Br}^-]$
or $3k_1 = 15k_2 = 5k_3$
 $k_1 = 5k_2 = 1.66k_3$
- (a) $\frac{-\Delta[\text{SO}_2]}{\Delta t} = 2 \left(-\frac{\Delta[\text{O}_2]}{\Delta t} \right)$
 $\therefore \frac{-\Delta[\text{SO}_2]}{\Delta t} = 2 \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 $= 5.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 $= 50.0 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$
- (d) The factors affecting the rate of a reaction are temperature, pressure, concentration of reactant or product and catalyst.
- (b) Rate of reaction $\propto$ concentration of reactant so rate of reaction decreases with decrease in concentration of reactants.
Units of rate constant depend upon the order of reaction.
Rate law expression shows the rate of reaction is terms of concentration.
i.e. $r = [A]^x [B]^y$
Here, *x* and *y* may or may not be equal to stoichiometric coefficients.
- (c) Since, the rate law contains $[\text{H}^+]$ term. This means that rate changes with variation in the value of pH.
- (b) For elementary reaction, $M \rightarrow N$
Rate law can be written as rate $\propto [M]^n$
Rate = $k[M]^n$... (i)
When we double the concentration of $[M]$, rate becomes 8 times, hence, new rate law can be written as
 $8 \times \text{rate} = k[2M]^n \Rightarrow \frac{\text{Rate}}{8 \times \text{rate}} = \frac{k[M]^n}{k[2M]^n}$
 $\therefore \frac{1}{8} = \frac{1}{[2]^n} \Rightarrow 2^n = 8 = 2^3 \Rightarrow n = 3$
- (b,c) $r = k[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]$ or $r = k \left[\frac{n}{V} \right] \left[\frac{n}{V} \right]$
Increasing volume (*V*) by twice (due to dilution) will reduce the rate by 4 times.
i.e. $r = 0.25 k [\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]$
- (b) Rate = $k[P]^a [Q]^b$
New rate = $k[2P]^a \left[\frac{Q}{2} \right]^b = k \cdot 2^a [P]^a \cdot \frac{[Q]^b}{2^b}$
 $= 2^{(a-b)} \cdot k[P]^a [Q]^b = 2^{(a-b)} \cdot \text{rate}$
 $\therefore \frac{\text{New rate}}{\text{Rate}} = 2^{(a-b)}$
- (c) Elementary reactions are single step reactions so no slowest step is involved.
- (c) Order of reaction may be zero, whole number or fraction number.
- (b) Rate = $k[A]^x [B]^y$
order = *x* + *y*
 $\therefore$ Order is $\left(\frac{3}{2} \right) + (-1) = 1/2$ i.e. half-order.

26. (a) The units of rate constant of n th order is $\text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$.

27. (b,d) Given, rate = $k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$

$$\text{Order} = 1 + \frac{1}{2} = \frac{3}{2}$$

$$\text{So, units of rate constant} = \frac{\text{Units of rate}}{[\text{CHCl}_3][\text{Cl}_2]^{1/2}} = \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}}$$

$$= \text{bar}^{-1/2} \text{min}^{-1}$$

Units of rate is bar min^{-1} .

28. (c) Order of reaction = $2 + 1 = 3$

$$\text{so, units of rate constant} = \text{mol}^{n-1} \text{L}^{n-1} \text{s}^{-1} = \text{mol}^{1-3} \text{L}^{1-3} \text{s}^{-1}$$

$$= \text{mol}^{-2} \text{L}^2 \text{s}^{-1}$$

29. (d) The value of $k = 2.5 \times 10^{-2} \text{ min}^{-1}$ carries the unit of time alone and therefore it is a first order reaction.

30. (a) The units of rate constant and rate of a reaction are same for zero order reaction.

31. (d) As the rate of the reaction remains constant with time, therefore, reaction is of zero order.

32. (b) Let the order of reaction with respect to X and Y be a and b , the rate law expression

$$r = k[X]^a [Y]^b$$

Similarly,

$$\text{Exp. I. } 5 \times 10^{-4} = k [2.5 \times 10^{-4}]^a [6 \times 10^{-5}]^b \quad \dots(i)$$

$$\text{Exp. II. } 4 \times 10^{-3} = k [5 \times 10^{-4}]^a [12 \times 10^{-5}]^b \quad \dots(ii)$$

$$\text{Exp. III. } 1.6 \times 10^{-2} = k [1 \times 10^{-3}]^a [12 \times 10^{-5}]^b \quad \dots(iii)$$

From Eqs. (i) and (ii),

$$\left(\frac{4 \times 10^{-3}}{5 \times 10^{-4}} \right) = \left(\frac{5 \times 10^{-4}}{2.5 \times 10^{-4}} \right)^a \left(\frac{12 \times 10^{-5}}{6 \times 10^{-5}} \right)^b$$

$$8 = (2)^a (2)^b \quad \dots(iv)$$

From Eq. (ii) and (iii),

$$\left(\frac{1.6 \times 10^{-2}}{4 \times 10^{-3}} \right) = \left(\frac{1 \times 10^{-3}}{5 \times 10^{-4}} \right)^a \left(\frac{12 \times 10^{-5}}{12 \times 10^{-5}} \right)^b$$

$$4 = (2)^a$$

$$(2)^2 = (2)^a$$

$$\therefore a = 2$$

On substituting value of a in Eq. (iv), we get

$$8 = (2)^2 (2)^b$$

$$(2) = (2)^b \text{ or } b = 1$$

Thus, order of reaction with respect to X is 2 and with respect to Y is 1.

33. (d) This problem can be solved by determining the order of reaction with respect to each reactant and then writing rate law equation of the given equation accordingly as,

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

where, x = order of reaction w.r.t A

y = order of reaction w.r.t B

$$1.2 \times 10^{-3} = k(0.1)^x (0.1)^y$$

$$1.2 \times 10^{-3} = k(0.1)^x (0.2)^y$$

$$2.4 \times 10^{-3} = k(0.2)^x (0.1)^y$$

$$\text{or } R = k[A]^1 [B]^0$$

34. (d) The strengths of two acids can be compared only by knowing their dissociation constants.

35. (a) At, $\text{pH} = 5$, the half-life is 500 min for all concentration of sugar, i.e. $t_{1/2} \propto [\text{sugar}]^m$. Thus, the reaction is of first order with respect to sugar.

$$\text{Now, rate} = k[\text{sugar}]^1 [\text{H}^+]^m$$

$$\text{Also for } [\text{H}^+] t_{1/2} \propto [\text{H}^+]^{1-m}$$

$$\therefore 500 \propto [10^{-5}]^{1-m} \quad \dots(i)$$

$$50 \propto [10^{-6}]^{1-m} \quad \dots(ii)$$

$$\therefore 10 = (10)^{(1-m)} \text{ or } (1-m) = 1$$

$$m = 1 - 1 = 0$$

$$\text{rate} = k[\text{sugar}]^1 [\text{H}^+]^0$$

$$37. (a) \text{ From Eq. (i) } K_{\text{eq}} = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]}$$

$$\text{or } [\text{O}] = \frac{K_{\text{eq}}[\text{O}_3]}{[\text{O}_2]}$$

$$\text{From Eq. (ii) rate law} = k[\text{O}_3][\text{O}]$$

$$\text{or } r = \frac{k[\text{O}_3][\text{O}_3]}{[\text{O}_2]} K_{\text{eq}}$$

$$\text{or } r = k'[\text{O}_3]^2 [\text{O}_2]^{-1} [k' = k \times K_{\text{eq}}]$$

39. (b) It appears to be a 10th order reaction but in actual it is of second order.

40. (d) Consider a reaction $A \rightarrow \text{Products}$

$$\therefore r_1 = k[A]^1 \text{ for 1st order} \quad \dots(i)$$

$$r_2 = k[A]^2 \text{ for 2nd order} \quad \dots(ii)$$

$$r_3 = k[A]^3 \text{ for 3rd order} \quad \dots(iii)$$

$\therefore k$ is same in all the three cases.

$$\text{If } [A] = 1, \quad r_1 = r_2 = r_3$$

$$\text{If } [A] < 1, \quad r_1 > r_2 > r_3$$

$$\text{If } [A] > 1, \quad r_3 > r_2 > r_1$$

41. (d) When the rate of a reaction is independent of the concentration of reactants then the order of the chemical reaction is zero.

42. (c) $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$

The rate of reaction for this reaction is zero.

43. (a) Rate of the reaction does not depend on concentration of ammonia as it is a zero order reaction.

$$44. (b) t_{1/2} = \frac{[R]_0}{2k}, \text{ for a zero order reaction.}$$

45. (c) For a zero order reaction, a graph of concentration and time is linear with a non-zero intercept, $[R_0]$ and a $(-)$ ve slope, $-k$.

47. (d) **Key concept** For a zero order reaction unit of rate constant is ($\text{mol L}^{-1} \text{s}^{-1}$). Hence, we can easily calculate concentration of B after 20 min by the following formula,

$$X = kt = 0.6 \times 10^{-3} \times 20 \times 60 = 0.72 \text{ M}$$

48. (d) For first order reaction,

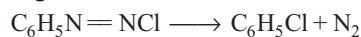
$$\frac{k \cdot t}{2.303} = \log [C_0] - \log [C]$$

$$\text{or, } \log [C] = \log [C_0] - \frac{k \cdot t}{2.303}$$

$\therefore$ Plot of $\log [C]$ vs t is a straight line with negative slope.

49. (c) Since, the unit of rate constant is s^{-1} . Thus, the order of the reaction is 1. Hence, $t_{1/2} = \frac{0.693}{0.12}$.

50. (b) Decomposition of benzene diazonium chloride occur the following manner.



The volume of nitrogen obtained shows the extent of decomposition of benzene diazonium chloride so

$$a \propto V_\infty = 162 \text{ mL}$$

$$(a - x) \propto (V_\infty - V_t) \text{ mL}$$

For first order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty - V_0}{V_\infty - V_t}$$

$$\text{or } k = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t} \quad (\because V_0 = 0)$$

At 20 min

$$\begin{aligned} k &= \frac{2.303}{20} \log_{10} \frac{162}{162 - 10} \\ &= \frac{2.303}{20} \log_{10} \frac{162}{152} \\ &= 3.18 \times 10^{-3} \text{ min}^{-1} \\ &\approx 3.2 \times 10^{-3} \text{ min}^{-1} \end{aligned}$$

51. (a) Let the initial pressure of azoisopropane is p_0 and after (t) time, its pressure reduces by x .



$$\text{At } t = 0 \quad p_0 \quad 0 \quad 0$$

$$\text{After 360 s} \quad p_0 - x \quad x \quad x$$

Total pressure after 360s (p_t) = $p_0 - x + x + x = 35 + x = 54$

$$x = 54 - 35 = 19 \text{ mm Hg}$$

$$x = 19 \text{ mm Hg}$$

$$\text{as, } p_0 = 35 \text{ mm Hg}$$

$$p_0 - x = 35 - 19 = 16 \text{ mm Hg}$$

For first order reaction,

$$\begin{aligned} \text{rate constant, } (k) &= \frac{2.303}{t} \log \frac{p_0}{p_0 - x} \\ &= \frac{2.303}{360} \log \frac{35}{16} = \frac{2.303}{360} \log 2.187 \\ &= \frac{2.303}{360} \times 0.34 = 2.17 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

52. (b) For first order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.2 \times 10^{-12} \text{ s}^{-1}} = 1.65 \times 10^{11} \text{ s}$$

$$53. (a) 10 \text{ g} \xrightarrow{t_{1/2}} 5 \text{ g} \xrightarrow{t_{1/2}} 2.5 \text{ g} \xrightarrow{t_{1/2}} 1.25 \text{ g}$$

$$3 \times t_{1/2} = 12 \text{ yr}$$

$$\therefore t_{1/2} = \frac{12}{3} = 4 \text{ yr}$$

$$54. (a) k = \frac{0.693}{1386} = 0.0005 = 0.5 \times 10^{-3} \text{ s}^{-1}$$

$$55. (c) t_{5/6} = \frac{2.303}{k} \log \frac{[R_0]}{[R_0]/6}$$

$$\therefore t = \frac{2.303}{k} \log 6$$

56. (d) Infinite time will be taken for the 100% completion.

$$57. (a) k = \frac{2.303}{32 \text{ min}} \log \frac{a}{a - 0.99a} = 0.1439 \text{ min}^{-1}$$

$$t = \frac{2.303}{0.1439} \log \frac{a}{a - 0.999a} = 48 \text{ min}$$

$$58. (a) \text{ Here, } \frac{[R]_0}{[R]} = \frac{100}{20} = 5$$

$$t = 10 \text{ min} \quad \text{or } k = \frac{2.303}{10 \text{ min}} \log 5$$

59. (d) When one reactant is present in large excess in a chemical reaction between two substances, then reaction is known as pseudo first order reaction.

60. (d) The rate constant ' k ' for pseudo first order reaction is $\frac{2.303}{t} \log \frac{C_0}{C}$.

61. (b) The temperature coefficient of a reaction is the ratio of rate constant differing by 10° preferably 25°C and 35°C .

62. (b) For 10° rise in temperature $n = 1$

$$\text{So, rate} = 2^n = 2^1 = 2$$

when temperature is increased from 10°C

$$\text{to } 100^\circ\text{C} \text{ change in temperature} = 100 - 10 = 90^\circ\text{C}$$

$$n = 9$$

$$\text{So, rate} = 2^9 = 512 \text{ times}$$

63. (b) The correct increasing order of the time taken for half of the decomposition of N_2O_5 at the temperatures 50°C , 0°C and 25°C will be $50^\circ\text{C} < 25^\circ\text{C} < 0^\circ\text{C}$.

64. (d) Arrhenius equation is

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

On taking $\ln$

$$\ln k = \ln A + \left(-\frac{E_a}{RT} \right)$$

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

$$\text{Or } \log A - \log k = \frac{E_a}{2.303RT} \quad \text{or } \log A = \log k + \frac{E_a}{2.303RT}$$

65. (b) In Arrhenius equation, $k = Ae^{-E_a/RT}$, factor $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy $> E_a$.

66. (d) P = activation energy for the reaction,



67. (a) The peak of the curve corresponds to the most probable kinetic energy.

68. (a) Fraction of molecules represents $\frac{N_E}{N_T}$, where N_E is the number of molecules with energy E and N_T is the total number of molecules.

69. (b) Intercept = $\ln A$.

$$\text{Slope} = -\frac{E_a}{R}$$

70. (c) Different, from E_a obtained in laboratory.

71. (a) Threshold energy = activation energy + energy possessed by reacting species.

72. (c) Given, initial temperature

$$T_1 = 20 + 273 = 293 \text{ K}$$

$$\text{Final temperature, } T_2 = 35 + 273 = 308 \text{ K}$$

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

Since, rate becomes double on raising temperature

$$r_2 = 2r_1 \Rightarrow \frac{r_2}{r_1} = 2$$

$$\text{As rate constant, } k \propto r \Rightarrow \frac{k_2}{k_1} = 2$$

From Arrhenius equation, we know that

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

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \left[\frac{308 - 293}{293 \times 308} \right]$$

$$0.3010 = \frac{E_a}{2.303 \times 8.314} \left[\frac{15}{293 \times 308} \right]$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 293 \times 308}{15} \\ = 34673.48 \text{ J mol}^{-1} = 34.7 \text{ kJ mol}^{-1}$$

73. (a) From Arrhenius equation, $\log \frac{k_2}{k_1} = \frac{-E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

$$\text{Given, } \frac{k_2}{k_1} = 2, T_2 = 310 \text{ K and } T_1 = 300 \text{ K}$$

On putting values,

$$\Rightarrow \log 2 = \frac{-E_a}{2.303 \times 8.314} \left(\frac{1}{310} - \frac{1}{300} \right)$$

$$\Rightarrow E_a = 53598.6 \text{ J/mol} \approx 53.6 \text{ kJ/mol}$$

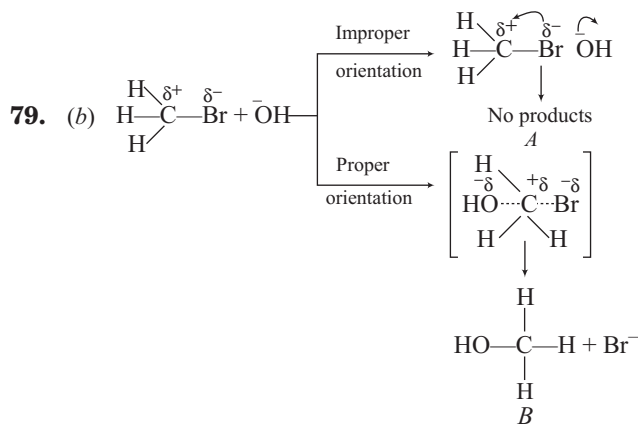
74. (a) As conversion of $P + Q$ to R is slow which suggests that the process has a very high activation energy while conversion of R to PQ is fast. It suggests that the process has a very low activation energy.

75. (a) Catalyst provides an alternative path of lower activation energy to the reactants which helps in the completion of reaction earlier and hence, increases the rate of a reaction.

76. (b) Catalyst reduces the activation energy between reactants and products.

78. (a) $\therefore \text{Rate of reaction} \propto \frac{1}{\text{activation energy}}$

$$\text{I} > \text{II} > \text{III} > \text{IV}$$



81. (b) After introducing the factor P , expression for the rate of reaction becomes $PZ_{AB}e^{-E_a/RT}$.

82. (a) The modified form of Arrhenius equation (according to collision theory) is $k = PZ_{AB}e^{-E_a/RT}$

83. (c) Energy $\geq$ threshold energy and proper orientation both.

84. (d) E_a should be decreased in order to increase the rate of reaction.

85. (a) The main conditions for the occurrence of a reaction are proper orientation and effective collision of the reactants.

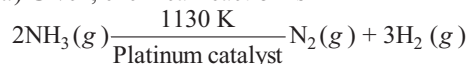
Since, the chances of simultaneous collision with proper orientation between two species in high order reactions are very rare, so reaction with order greater than 3 are rare.

86. (b, c, d) For the reaction, $4A + B \longrightarrow 2C + 2D$,

$$\text{Rate} = -\frac{1}{4} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{2} \frac{d[C]}{dt} = \frac{1}{2} \frac{d[D]}{dt}$$

So, rate of appearance of C is twice of rate of disappearance of B . All other statements are true.

88. (a, c, d) Given, chemical reaction is



At very high pressure reaction become independent of concentration of ammonia, i.e. zero order reaction.

$$\text{Hence, Rate} = k[p_{\text{NH}_3}]^0 \Rightarrow \text{Rate} = k$$

(a) Rate of reaction = Rate constant

(c) Rate of decomposition of ammonia will remain constant until ammonia disappears completely.

(d) Since, formation of ammonia is a reversible process further increase in pressure will change the rate of reaction. According to Le-Chatelier principle increase in pressure will favour in backward reaction.

89. (a, c, b) Rate constant is independent upon the concentration of reactants and products.

90. (a, c) Rate law can be determined from balanced chemical equation if it is an elementary reaction.

91. (a, c) Because order of a reaction can also be fractional.

92. (a, c) Since, it is a first order reaction, so

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

i.e. it does not depend upon initial concentration.

93. (d) Molecularity of reaction is always a whole number because number of molecules can never be in fraction.

94. (a, c) Order of reaction is $1 + \frac{1}{2} = \frac{3}{2} = 1.5$

Molecularity = 2

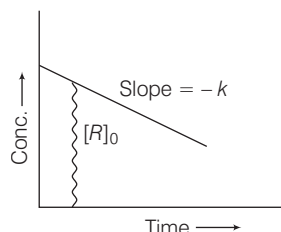
Units of rate = $\text{mol L}^{-1} \text{s}^{-1}$

Rate constant = $\text{mol}^{1-1.5} \text{L}^{-0.5} \text{s}^{-1}$
 $= \text{mol}^{0.5} \text{L}^{-0.5} \text{s}^{-1}$

95. (a, d) For a zero order reaction,

$$[R] = (-k)t + [R]_0 \quad \dots(i)$$

$\uparrow \quad \uparrow \quad \uparrow$
 $y = m \times x + c$



On comparing with equation of straight line

$y = [R]$ concentration

$x = t$ time

Slope (m) = $-k$ rate constant

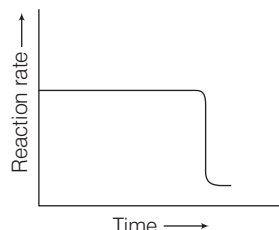
Intercept (c) = $[R]_0$ initial concentration

On rearranging Eq. (i)

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

$$\frac{[R] - [R]_0}{t} = -kt^0$$

Rate $\propto t^0$



96. (b, d) Hydrolysis of ester is a pseudo first order reaction.

97. (a, d) For the first order reaction,

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

$$\log \frac{[R]_0}{[R]} = \left(\frac{k}{2.303} \right) \times t + 0$$

$\uparrow \quad \uparrow \quad \uparrow \quad \uparrow$
 $y = \quad m \quad x + c$

Correct plot of $\log \frac{[R]_0}{[R]}$ can be represented by (d)

where, slope = $\frac{k}{2.303}$

The time taken for any fraction of the reaction to complete is independent of the initial concentration.

Let, us consider it for half of the reaction to complete.

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

For half-life ($t = t_{1/2}$) and $x = \frac{a}{2}$

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a - \frac{a}{2}}$$

$$t_{1/2} = \frac{2.303}{k} \log 2$$

Half-life time ($t_{1/2}$) = $\frac{0.693}{k}$

$t_{1/2}$ is independent of initial concentration. Hence, correct plot of $t_{1/2}$ and $[R]_0$ can be represented by option (a).

99. (a, c) Rate = $k[\text{NO}]^2 [\text{H}_2]$

(Because, rate depends upon slowest step).

Thus, rate $\propto [\text{H}_2]$ if $[\text{NO}] = \text{constant}$

so, on doubling concentration of H_2 , rate become double when $[\text{NO}]$ is constant.

102. (a, b) Arrhenius equation can be written as

$$k = A \cdot e^{-E_a/RT}$$

$k \propto e^{-E_a}$, i.e. rate of reaction increases with decrease in activation energy,

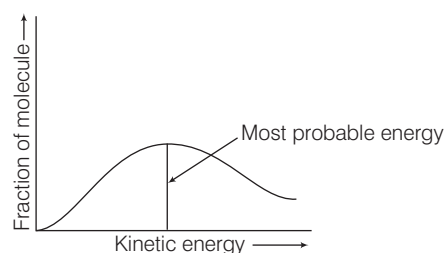
$$k \propto e^{\frac{-1}{T}}$$

$k \propto e^T$, i.e. rate of reaction increases with increase in temperature.

104. (a, d) When the reactant molecules collide each other they lead to formation of an activated complex. It has highest energy among reactants, products and activated complex. When it decomposes to give product, energy is released and stability of product increases.

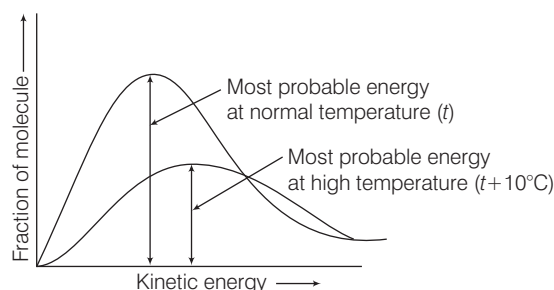
Since, the entire concentration of activated complex do not convert into products while, some activated complex may give reactants also.

105. (a, c) Distribution of kinetic energy may be described by plotting a graph of fraction of molecules versus kinetic energy.



Kinetic energy of maximum fraction of molecule is known as most probable kinetic energy. It is important to note that with increase of temperature, peak shifts forward, then downward. This means that with increase of temperature,

- (i) most probable kinetic energy increases.
- (ii) the fractions of molecules possessing most probable kinetic energy decreases.



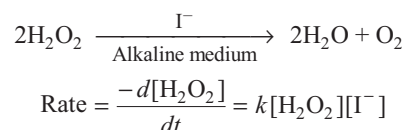
106. (d) At the macroscopic level, the amount of substances reacted or formed and the rates of their consumption or formation is discussed. At the microscopic level, the reaction mechanism involving orientation and energy of molecules undergoing collisions are discussed.
107. (c) Both the statements are true.
108. (b) The rate law may not depend on the concentration of every reactants and rate of reaction increases with increase in temperature.
109. (b) For a complex reaction, order of reaction is given by slowest step of the reaction. Molecularity of slowest step is same as the order of overall reaction.
110. (b) Both the given statements are true. Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions.
111. (c) The rate of zero order reaction is independent of concentration of reactants and $t_{1/2}$ of zero order reaction depends on concentration of reactants.
112. (b) The rate of a first order reaction depends on the concentration of reactant raised to the first power. Decomposition of H_2O_2 follows zero order reaction.
113. (c) Collision theory provides a greater insight into the energetic and mechanistic aspects of reactions as it is based on kinetic theory of gases.
114. (b) According to assumption of collision theory for effective collisions another factor P is introduced and in a collision molecules must be properly oriented.
115. (c) Rate of reaction can be expressed in terms of
 - (i) the rate of decrease in concentration of any one of the reactants.
 - (ii) the rate of increase in concentration of any one of the products.
116. (d) All the statements are correct.
117. (b) Size of the vessel has no role on rate of reaction.
118. (d) All the statements are correct.

119. (c) Rate law expression may come out to be similar to that predicted by law of mass action.

120. (d) All the facts are true.

121. (a) Order of a reaction can be an integer like 1, 2, 3 and also be zero or a fraction.

122. (d) Decomposition of H_2O_2



This reaction is first order with respect to both H_2O_2 and I^- . It takes place in two steps and both are bimolecular elementary reactions.

123. (b) The order of a reaction is not equal to the sum of the stoichiometric coefficients of the reactants in the balanced chemical equation for a reaction.

124. (d) $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \longrightarrow 2\text{HBr}(\text{g})$

$$\text{rate} = k[\text{H}_2][\text{Br}_2]^{1/2}, \text{ molecularity} = 2$$

$$\text{Order} = 1 + \frac{1}{2} = \frac{3}{2}$$

125. (d) According to the given statements,

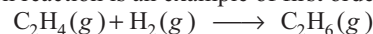
I. Rate of reaction $\propto [\text{concentration}]^1$

II. For first order reaction,

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

III. All the natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

126. (c) I. Given reaction is an example of first order kinetics,



II. $r = k[\text{C}_2\text{H}_4]$

Hence, both the statements are true.

127. (b) Molecularity of a reaction can never be a fraction.

128. (c) According to kinetics of chemical reaction,

$$\text{rate} \propto k'[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$$

Concentration of water does not get altered much during the course of reaction.

129. (d) $k = 2.1 \times 10^{10} e^{-2700/RT}$

$$\log k = \log(2.1 \times 10^{10}) - \log \frac{2700}{2.303RT}$$

Comparing it with respect to straight line equation

$$y = mx + c$$

$$m (\text{slope}) = -\frac{2700}{2.303R}$$

$$c (\text{intercept}) = \log(2.1 \times 10^{10})$$

130. (a) Maxwell's theory is related to gases and Ostwald's theory to dilute solutions that relate the degree of ionisation with concentration.

131. (b) According to collision theory of chemical reaction:

- I. Number of effective collisions determines the rate of reaction.
- II. Collision of atoms/molecules possessing sufficient threshold energy does not result into the formation of product. Only molecule having effective collision lead to the formation of product.
- III. It helps in considering reacting atoms/molecules to be hard spheres and ignores their structural features.
- IV. Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective.

132. (a) Rate of disappearance of $R = -\frac{\Delta[R]}{\Delta t}$

Since, $\Delta[R]$ is a negative quantity, it is multiplied with -1 to make the reaction rate a positive quantity.

133. (a) It is not always convenient to determine the instantaneous rate, as it is measured by determining the slope of the tangent at point 't' in concentration vs time plot. This generally makes it difficult to determine the rate law and hence, the order of the reaction.

134. (a) Order of the following reaction,

$2\text{NO}(g) + 2\text{H}_2(g) \longrightarrow 2\text{H}_2\text{O}(g) + \text{N}_2(g)$ is 3 as we know that order of the reaction with respect to given reactant is the power of the reactants concentration in the rate equation.

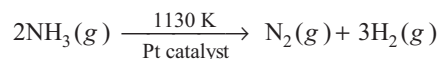
135. (d) Only reactions with zero order do not have the order in fractions.

136. (d) The molecularity cannot be a fraction. As the molecularity of a reaction is the number of molecules whether of the same or different species that must contact simultaneously in a single step in order for a reaction to occur.

137. (b) The molecularity is two and order is $\frac{3}{2}$.

138. (a) The multimolecular reactions are quite rare in comparison with bimolecular reactions because at normal pressure, triple collisions are much less frequent than double ones.

139. (a) It is a zero order reaction at high pressure.



$$\text{Rate} = k [\text{NH}_3]^0 = k$$

In this reaction, Pt acts as a catalyst the metal surface gets saturated with gas molecules at high pressure. Thus, a further change in reaction conditions does not alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration.

140. (c) In a mixture of KMnO_4 and $\text{H}_2\text{C}_2\text{O}_4$, KMnO_4 gets decolourised faster at a higher temperature than that at a lower temperature.

141. (c) Correct reason is threshold frequency for forward reaction is lower than that of backward reaction.

142. (c) A small amount of the catalyst can catalyse a large amount of reactants. A catalyst does not alter Gibbs energy,

ΔG of a reaction. It does not change the equilibrium constant rather, it helps in attaining the equilibrium faster, i.e. it catalyses the forward and backward directions both to the same extent so that the equilibrium state remains same and is achieved earlier.

143. (c) With increasing E_a , the rate constant decreases.

144. (b) A bimolecular reaction takes place when two properly oriented reactant molecules come together in a sufficiently energetic collision which is explained by activated complex theory. When the temperature is increased by 10°C , the reaction rate tends to be doubled.

145. (d) Catalyst does not change the individual energies of the reactants and the products. Rather it just alter the pathway of the reaction by lowering the activation energy.

146. (a) A positive catalyst increases rate of reaction by making a new and more efficient mechanism.

147. (d) All collisions of reactant molecules do not lead to product formation.

148. (c) The correct unit of rate constant of
zero order reaction = $\text{mol L}^{-1} \text{s}^{-1}$
first order reaction = s^{-1}
second order reaction = $\text{mol}^{-1} \text{L s}^{-1}$

149. (c) The correct series of options is: $A \rightarrow 3$; $B \rightarrow 1$; $C \rightarrow 2$.

150. (c) The correct matching is: $A \rightarrow 3$; $B \rightarrow 2$; $C \rightarrow 1$

151. (a) $A \rightarrow (1)$ $B \rightarrow (2)$ $C \rightarrow (2)$ $D \rightarrow (1)$

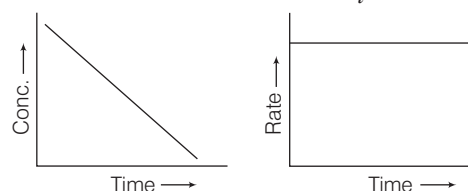
For zero order reaction rate equation may be written as

$$[R] = -kt + [R_0] \quad \dots(i)$$

Which denotes a straight line equation similar to $y = mx + c$

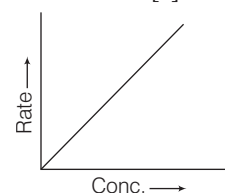
On transforming (i) $\frac{[R] - [R_0]}{t} = -k$

$$k = \frac{[R_0] - [R]}{t}$$



$k = \text{Rate}$

$$\text{Rate} = k \cdot [t]^0 \Rightarrow \text{Rate} \propto [t]^0$$



For a first order reaction $\frac{dx}{dt} \propto [\text{concentration}]$

$\therefore$ Graph between rate and concentration may be drawn as

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

$$\frac{kt}{2.303} = \log \left[\frac{R^\circ}{R} \right] \text{ or } \frac{kt}{2.303} = \log[R]_0 - \log[R]$$

$$\log[R] = \left(\frac{-k}{2.303} \right) t + \log[R]_0$$

Slope Intercept

152. (a) A. → (3) B. → (1) C. → (4) D. → (6) E. → (2) F. → (5)

1. Catalyst alters the rate of reaction by lowering activation energy.
2. Molecularity cannot be fraction or zero. If molecularity is zero, then reaction is not possible.
3. Second half-life of first order reaction is same as first because half-life time is temperature independent.
4. $e^{-E_a/RT}$ refers to the fraction of molecules with kinetic energy equal to or greater than activation energy.
5. Energetically favourable reactions are sometimes slow due to improper orientation of molecule cause some ineffective collision of molecules.
6. Area under the Maxwell, Boltzmann curve is constant because total probability of molecule taking part in a chemical reaction is equal to one.

153. (b) Rate, $r = k[A]^x$... (i)

if $A' = (4A)$ $r' = 2r$

So $r' = k[A]$ or $2r = k[4A]$... (ii)

From Eqs. (i) and (ii)

$$\frac{r}{2r} = \frac{[A]^x}{[4A]} \Rightarrow \frac{1}{2} = \left(\frac{1}{4} \right)^x \Rightarrow x = \frac{1}{2} = 0.5$$

154. (b) Overall order of reaction = $1 + 1 - 1 = 1$

162. (a) At equilibrium, there is no further change in concentration. Hence, concentration at equilibrium are $[P] = 0.3 \text{ mol L}^{-1}$, $[Q] = 0.6 \text{ mol L}^{-1}$.

$$\therefore \text{Equilibrium constant, } (K) = \frac{[Q]^2}{[P]} = \frac{(0.6)^2}{0.3} = 1.2 \text{ mol L}^{-1}$$

163. (a) From time $(t) = 1 \text{ h}$ to time $= 5 \text{ h} \Rightarrow \Delta t = 4 \text{ h}$

Decrease in concentration of $P = 0.5 - 0.3 = 0.2 \text{ mol L}^{-1}$

Decrease in concentration of $Q = 0.6 - 0.2 = 0.4 \text{ mol L}^{-1}$.

$\therefore$ In the same time interval, increase in concentration of Q is double than decrease in concentration of P . Thus, $n = 2$.

164. (d) From $t = 0$ to $t = 1 \text{ h}$ for A .

$$[P] = 0.6 - 0.5 = 0.1 \text{ mol L}^{-1}$$

$$\therefore \text{Initial rate of conversion of } P = \frac{\Delta[A]}{\Delta t} = \frac{0.1 \text{ mol L}^{-1}}{1 \text{ h}} = 0.1 \text{ mol L}^{-1} \text{ h}^{-1}$$

165. (b) It is I means activation energy

166. (a) Final enthalpy of reaction depends upon the nature of reactants and products because some energy is released when complex intermediate decomposes to form products.

167. (c) The curve shown in the above figure is known as Maxwell-Boltzmann distribution curve.

168. (c) The area under the curve must be constant, since total probability must be one at all times.

169. (b) $A \longrightarrow B$

Concentration of reactants and products varies exponentially with respect to time.

(i) Concentration of reactant (here, A) decreases exponentially with respect to time.

(ii) Concentration of product (here, B) increases exponentially with respect to time

170. (c) $\text{Zn} + \text{Dil. HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2 \uparrow$

$$\text{Average rate of reaction} = \frac{\text{Change in concentration of H}_2}{\text{Change in time}}$$

$$= \frac{V_3 - 0}{40 - 0} = \frac{V_3}{40}$$

171. (b) Reaction occurring at smallest time interval is known as instantaneous rate of reaction. e.g. instantaneous rate of reaction at 40 s is rate of reaction during a small interval of time close to 40 s. Volume change during a small time interval is close to 40 s, i.e. $40 - 30 \text{ s}$, $50 - 40 \text{ s}$, $50 - 30 \text{ s}$, $40 - 20 \text{ s}$.

$$\text{Instantaneous rate of reaction} = \frac{\text{Change in volume}}{\text{Time interval close to 40 s}}$$

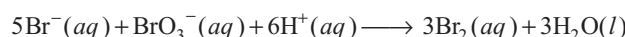
(a) $r_{\text{inst}} (20 \text{ s}) = \frac{V_5 - V_2}{50 - 30}$ correct

(b) $r_{\text{inst}} (20 \text{ s}) = \frac{V_4 - V_2}{50 - 30}$ incorrect, correct is $\frac{V_5 - V_3}{50 - 30}$

(c) $r_{\text{inst}} (10 \text{ s}) = \frac{V_3 - V_2}{40 - 30}$ correct

(d) $r_{\text{inst}} (20 \text{ s}) = \frac{V_3 - V_1}{40 - 20}$ correct

172. (c) Given, chemical reaction is



Rate law expression for the above equation can be written as

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

$$\Rightarrow \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$$

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

173. (b) Rate law can be written as

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

Rate of reaction with respect to B is of first order.

$$R_1 = k[A][B]$$

When concentration of reactant ' B ' is doubled then rate (R_2)

$$R_2 = k[A][2B] = 2k[A][B] = 2R_1$$

Therefore, as concentration of B is doubled keeping the concentration of A constant, rate of reaction doubles.

174. (b) Rate of reaction is changed in concentration of reactant with respect to time.

$$r = k[A]^x[B]^y$$

$$\frac{\text{Rate of exp.1}}{\text{Rate of exp.2}} = \frac{[0.30]^x [0.30]^y}{[0.30]^x [0.60]^y} \Rightarrow \frac{0.10}{0.40} = \frac{[0.30]^y}{[0.60]^y}$$

$$\frac{1}{4} = \left[\frac{1}{2}\right]^y \Rightarrow \left[\frac{1}{2}\right]^2 = \left[\frac{1}{2}\right]^y \Rightarrow y = 2$$

$$\frac{\text{Rate of exp.1}}{\text{Rate of exp.3}} = \frac{[0.30]^x [0.30]^y}{[0.60]^x [0.30]^y}$$

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

$$\frac{1}{2} = \left[\frac{1}{2}\right]^x [1]^y \Rightarrow \frac{1}{2} = \left[\frac{1}{2}\right]^x$$

i.e.

$$x = 1$$

∴

$$\text{Rate} = k[A]^x [B]^y \Rightarrow \text{Rate} = k[A]^1 [B]^2$$

- 175.** (a) Rate of reaction is defined as rate of decrease of concentration of any one of reactant with passage of time.

$$\text{Rate of reaction} = \frac{\text{Rate of disappearance of reactant}}{\text{Time taken}}$$

$$r = \frac{-dx}{dt}$$

Thus, as the concentration of reactant decreases with passage of time, rate of reaction decreases.

- 176.** (c) Out of the given four statements, option (c) is not correct.

Order of a reaction :

Order of a reaction is equal to the sum of powers of concentration of the reactants in rate law expression.

For any chemical reaction, $x A + y B \longrightarrow \text{Product}$

$$\text{Rate} = k[A]^x [B]^y \text{ and Order} = x + y$$

Order of a reaction can be a fraction also. It is not always equal to sum of the stoichiometric coefficients of reactants in the balanced chemical equation. For a reaction, it may or may not be equal to sum of stoichiometric coefficient of reactants.

- 177.** (b) $A(g) \longrightarrow B(g) + C(g)$

$$\begin{array}{ccc} \text{Initially} & p_i & 0 & 0 \\ \text{At time } t & p_i - x & x & x \end{array}$$

$$p_t = p_i - x + x + x = p_i + x$$

For first order reaction $x = p_t - p_i$

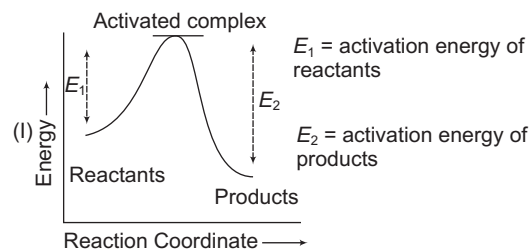
$$\begin{aligned} k &= \frac{2.303}{t} \log \frac{p_i}{p_i - x} = \frac{2.303}{t} \log \frac{p_i}{p_i - (p_t - p_i)} \\ &= \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t} \end{aligned}$$

- 178.** (a) Activation energy is the minimum energy required to convert reactant molecules to product molecules. Here, the energy gap between reactants and activated complex is sum of E_1 and E_2 .

$$\therefore \text{Activation energy} = E_1 + E_2$$

Product is less stable than reactant as energy of product is greater than the reactant.

- 179.** (a) The chemical reaction in which energy is evolved during the reaction is known as exothermic reaction i.e. activation energy of product is greater than activation energy of reactants.



Here, only (I) denotes correct picture of exothermic reaction.

- 180.** (d) According to Arrhenius equation, $k = A e^{-E_a/RT}$

$$k \propto e^{-E_a} \Rightarrow k \propto e^{-1/T} \propto e^T$$

It indicates that as activation energy decreases, rate constant increases and as temperature increases, rate of reaction increases.

- 181.** (a) According to Arrhenius equation, $k = A e^{-E_a/RT}$

$$\text{Taking log on both side } \ln k = \ln (A - e^{-E_a/RT})$$

$$\Rightarrow \ln k = \ln A - \frac{E_a}{RT} \Rightarrow \ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln A$$

$$y = mx + c$$

This equation can be related to equation of straight line as shown above. From the graph, it is very clear that slope of the plot = $-\frac{E_a}{R}$ and intercept = $\ln A$.

- 182.** (b) Activation energy of a chemical reaction is related to rate constant of a reaction at two different temperatures, i.e. k_1

$$\text{and } k_2 \text{ respectively, } \ln \left(\frac{k_1}{k_2} \right) = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

where, E_a = activation energy, T_2 = higher temperature

T_1 = lower temperature, k_1 = rate constant at temperature (T_1)

k_2 = rate constant at temperature T_2

This equation is known as Arrhenius equation.

- 183.** (c) In the presence of catalyst, the heat absorbed or evolved during the reaction remains unchanged as there is no change in stability of reactant and product.

- 184.** (b) Characteristics of catalyst,

- It catalyses the forward and backward reaction to the same extent as it decreases energy of activation hence, increases the rate of both the reactions.
- Since, reaction quotient is the relation between concentration of reactants and products. Hence, catalyst does not alter Gibbs free energy as it is related to reaction quotient. Thus, Gibbs free energy does not change during the reaction when catalyst is added to it, $\Delta G = -RT \ln Q$ where, Q = reaction quotient
- It doesn't alter equilibrium of reaction as equilibrium constant is also concentration dependent term.
- It provides an alternate mechanism by reducing activation energy between reactants and products.

- 185.** (c) According to the postulates of collision theory there are following necessary conditions for any reaction to be occur:

- Molecule should collide with sufficient threshold energy.
- Their orientation must be proper.
- The collision must be effective.