

● Chemical Kinetics

It is a branch of chemistry in which rate of reaction and factors affecting it are studied.

Kinetics : Greek word 'Kinesis' $\equiv$ Movement

Types Of Reactions Based On Rate Of Reaction :

- (1) **Very fast reactions** : Ionic reactions (10^{-9} sec)
- (2) **Very slow reactions** : Corrosion of iron, decay of uranium
- (3) **Slow reactions** : Reaction between N_2 and H_2 under specific conditions

Factors Affecting Rate Of Reactions :

- (1) State of substance and surface area (2) Concentration of solution (3) Temperature of system
- (4) Pressure of system (5) Effect of catalyst (6) Presence of light

If there is any impurity in a catalyst which decreases the rate of reaction, then it is called catalytic poison.

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1. Which reaction possessing following units of time will be the fastest ?
(A) pico seconds (B) micro seconds (C) femto seconds (D) nano seconds
 2. Under which of the following conditions a match stick will lit faster ?
(A) in air (21 % O_2) (B) in vacuum
(C) in atmosphere of He (D) in a jar containing 100% O_2
 3. does not affect rate of reaction ?
(A) ΔH of reaction (B) Volume of reaction vessel
(C) Amount of reactants (D) Physical state of reactants
 4. Which of the following reactant will react fastest under identical conditions ?
(A) $PCl_{5(s)}$ (B) $PCl_{5(g)}$ (C) $PCl_{5(aq)}$ (D) $PCl_{5(l)}$
 5. Which statement is wrong ?
(A) More time is required to cook rice in Massoorie than that required in KanyaKumari.
(B) Compared to piece of sugar its powder dissolves earlier in water.
(C) The time taken to boil potatoes in closed pressure cooker is same at both sea level and top of mountain.
(D) Reaction of sodium is faster than sodium-amalgam with ethanol.
 6. What is rate of reaction ?
(A) decrease in concentration of reactants.
(B) increase in concentration of products.
(C) Change in concentration of reactants or products in unit time.
(D) All three given above are true.

7. Which of the following reaction will be comparatively slower ?
 (A) reverse reaction in presence of catalyst.
 (B) Combination of N_2 and O_2 in sky during lightening.
 (C) Corrosion of iron in presence of inhibitors
 (D) hydrolysis of urea in presence of enzyme urease.
8. The rate of reaction of spontaneous reaction is generally slow because
 (A) equilibrium constant of reactions is < 1 (B) Energy of activation of reactions is high
 (C) reactions are endothermic (D) reactions are exothermic
9. Rate of reaction increases with increase in temperature usually because,
 (A) energy barrier decreases (B) activation energy increases
 (C) effective collisions increases (D) threshold energy increases
10. For reaction A : $10 \text{ g CaCO}_{3(s)} + 20 \text{ ml } 2 \text{ M HCl}$ if rate of reaction is r_a and for reaction B : $10 \text{ g CaCO}_{3(s)} + 2 \text{ ml } 4 \text{ M HCl}$ rate of reaction is r_B then which of the following relation is true ?
 (A) $r_a > r_B$ (B) $r_B = 1 - r_a$ (C) $r_a = r_B$ (D) $r_a < r_B$

Answers : 1. (C), 2. (D), 3. (A), 4. (B), 5. (C), 6. (D), 7. (C), 8. (B), 9. (C), 10. (A).

● Rate of reaction and its determination

The change in concentration of reactants or products in unit time is called rate of reaction.

Average rate of reaction : $r_{av} = -\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$

Instantaneous rate of reaction $r_{inst} = -\frac{d[R]}{dt} = +\frac{d[P]}{dt}$

$\Delta t \rightarrow 0$ for small change

Rate of reaction is always positive. Negative sign is used to indicate the decrease in concentration of reactants.

Rate determination : In chemical kinetics following convention is accepted.

$$\text{Rate of reaction} = -\frac{1}{\nu_R} \left[\frac{d[R]}{dt} \right] = +\frac{1}{\nu_P} \left[\frac{d[P]}{dt} \right]$$

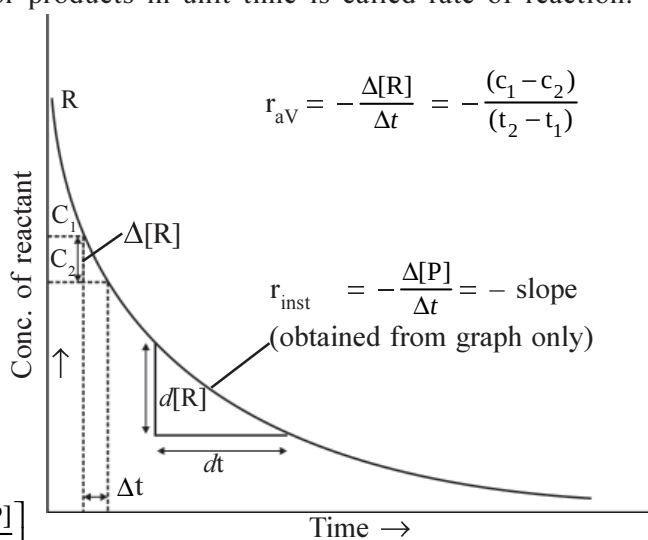
For any reaction : $n_1 A + n_2 B \rightarrow n_3 C + n_4 D$,

$$\text{Rate of reaction} = -\frac{1}{n_1} \frac{d[A]}{dt} = -\frac{1}{n_2} \frac{d[B]}{dt} = +\frac{1}{n_3} \frac{d[C]}{dt} = +\frac{1}{n_4} \frac{d[D]}{dt}$$

For a reaction, $5\text{Br}^-_{(aq)} + \text{BrO}_3^-_{(aq)} + 6\text{H}^+_{(aq)} \rightleftharpoons 3\text{Br}_{2(aq)} + 3\text{H}_2\text{O}_{(l)}$

$$\text{Rate of reaction} = -\frac{1}{5} \frac{d[\text{Br}^-]}{dt} = -\frac{d[\text{BrO}_3^-]}{dt} = -\frac{1}{6} \frac{d[\text{H}^+]}{dt} = +\frac{1}{3} \frac{d[\text{Br}_2]}{dt}$$

Note : In aqueous solution, there is negligible change in concentration of water and so the change in its concentration is not expressed.



11. Which expression of rate of reaction is correct for a reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$?

- (A) $-\frac{2d[\text{H}_2]}{dt} = -\frac{2d[\text{I}_2]}{dt} = +\frac{d[\text{HI}]}{dt}$ (B) $-\frac{d[\text{H}_2]}{2dt} = -\frac{d[\text{I}_2]}{2dt} = +\frac{d[\text{HI}]}{4dt}$
 (C) $-\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{I}_2]}{dt} = +\frac{d[\text{HI}]}{dt}$ (D) $-\frac{d[\text{H}_2]}{2dt} = -\frac{d[\text{I}_2]}{2dt} = +\frac{d[\text{HI}]}{dt}$

12. The balanced equation for a reaction having rate of reaction

$$+\frac{1}{3} \frac{d[\text{Br}_2]}{dt} = -\frac{d[\text{BrO}_3^-]}{dt} = -\frac{1}{5} \frac{d[\text{Br}^-]}{dt} = -\frac{1}{6} \frac{d[\text{H}^+]}{dt} \text{ is}$$

- (A) $\text{Br}_{2(\text{aq})} + \text{BrO}_{3(\text{aq})}^- \rightarrow 5\text{Br}_{(\text{aq})}^- + 6\text{H}_{(\text{aq})}^+$
 (B) $\text{BrO}_{3(\text{aq})}^- + 5\text{Br}_{(\text{aq})}^- + 6\text{H}_{(\text{aq})}^+ \rightarrow 3\text{Br}_{2(\text{aq})} + 3\text{H}_2\text{O}_{(\text{l})}$
 (C) $3\text{Br}_{2(\text{aq})} \rightarrow \text{BrO}_{3(\text{aq})}^- + 5\text{Br}_{(\text{aq})}^- + 6\text{H}_{(\text{aq})}^+$
 (D) $\text{BrO}_{3(\text{aq})}^- + 5\text{Br}_{(\text{aq})}^- + 6\text{H}_{(\text{aq})}^+ \rightarrow 3\text{Br}_{2(\text{aq})}$

13. Which of the following statement is wrong for $4\text{A} + \text{B} \rightarrow 2\text{C} + 2\text{D}$?

- (A) rate of production of C and D is same.
 (B) rate of production of C is half than rate of consumption of A.
 (C) rate of production of C is half than rate of consumption of B.
 (D) The rate of consumption of B is one-fourth the rate of consumption of A.

14. The rate of production of D in $2\text{A} + \text{B} \rightarrow 2\text{C} + 4\text{D}$ is $1.6 \times 10^{-3} \text{ Ms}^{-1}$. Which of the following statement is true for this reaction ?

- (A) $-\frac{d[\text{B}]}{dt} = 3.2 \times 10^{-3} \text{ Ms}^{-1}$ (B) $-\frac{d[\text{A}]}{dt} = 6.4 \times 10^{-3} \text{ Ms}^{-1}$
 (C) $\frac{d[\text{C}]}{dt} = 8.0 \times 10^{-4} \text{ Ms}^{-1}$ (D) $-\frac{1}{2} \frac{d[\text{A}]}{dt} = 1.6 \times 10^{-3} \text{ Ms}^{-1}$

15. For a reaction : $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ the rate law can be presented in three different ways as follows, then which relation between K and K' and K and K'' holds ?

$$\frac{-d[\text{N}_2\text{O}_5]}{dt} = K[\text{N}_2\text{O}_5] \quad \frac{d[\text{NO}_2]}{dt} = K'[\text{N}_2\text{O}_5] \quad \frac{d[\text{O}_2]}{dt} = K''[\text{N}_2\text{O}_5]$$

- (A) $K' = 2K, K'' = \frac{K}{2}$ (B) $K' = 2K, K'' = K$
 (C) $K' = K, K'' = K$ (D) $K' = 2K, K'' = 2K$

16. In a reaction : $\text{BrO}_{3(\text{aq})}^- + 5\text{Br}_{(\text{aq})}^- + 6\text{H}_{(\text{aq})}^+ \rightarrow 3\text{Br}_{2(\text{l})} + 3\text{H}_2\text{O}_{(\text{l})}$ the rate of consumption of Br^- is $1.5 \times 10^{-2} \text{ Ms}^{-1}$. The rate of consumption of H^+ and rate of production of Br_2 will be respectively

- (A) $(5 \times 6) 1.5 \times 10^{-2}, (3 \times 6) 1.5 \times 10^{-2}$ (B) $\left(\frac{6}{5}\right) 1.5 \times 10^{-2}, \left(\frac{3}{5}\right) 1.5 \times 10^{-2}$
 (C) $\left(\frac{5}{6}\right) 1.5 \times 10^{-2}, \left(\frac{5}{3}\right) \times 1.5 \times 10^{-2}$ (D) $(5 + 6) 1.5 \times 10^{-2}, (3 + 6) 1.5 \times 10^{-2}$

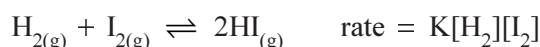
17. The change in concentration of hydrogen in a reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ is $-0.3 \times 10^{-4} \text{ Ms}^{-1}$. The change in concentration of ammonia at that time is
- (A) 0.2×10^{-4} (B) -0.2×10^{-4} (C) 0.1×10^{-4} (D) 0.3×10^{-4}
18. The pressure of N_2O_4 in a reaction $\text{N}_2\text{O}_{4(\text{g})} \rightarrow 2\text{NO}_{2(\text{g})}$ reduces from 0.5 atm to 0.32 atm in 30 minutes. Find rate of production of NO_2 .
- (A) $0.012 \text{ atm min}^{-1}$ (B) $0.024 \text{ atm min}^{-1}$ (C) $0.006 \text{ atm min}^{-1}$ (D) $0.003 \text{ atm min}^{-1}$
19. In a reaction : $\text{A} + 2\text{B} \rightarrow \text{C}$, at a time t_1 , $-\frac{d[\text{A}]}{dt} = 2.6 \times 10^{-2} \text{ M sec}^{-1}$, then at a time t_1 , $-\frac{d[\text{B}]}{dt} =$?
- (A) 2.6×10^{-2} (B) 5.2×10^{-2} (C) 1.0×10^{-1} (D) 6.5×10^{-3}
20. In a reaction $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$, the time required for a decrease of 0.02 M in concentration of H^+ ions is 2 nano second. What will be the average rate of reaction ?
- (A) 2 Ms^{-1} (B) $1 \times 10^7 \text{ Ms}^{-1}$ (C) 0.02 Ms^{-1} (D) $0.02 \times 10^9 \text{ Ms}^{-1}$

Answers : 11. (B), 12. (B), 13. (C), 14. (C), 15. (A), 16. (B), 17. (A), 18. (A), 19. (B), 20. (B)

● Rate law, rate constant and order of reaction

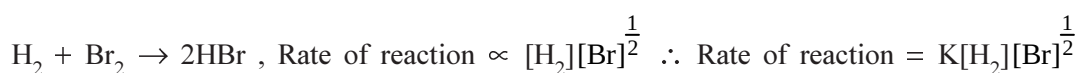
The presentation of rate of reaction with reference to concentration of reactants is called rate law.

This rate law in the wide range of concentrations of reactant or product is studied and the law that is established is called differential rate equation or rate expression. For eg.,



● Rate constant and order of reaction :

In most of the reactions the simple rate equation can be obtained in which rate is proportional to exponent of the concentration of reactant. This exponent is called **order of reaction**.

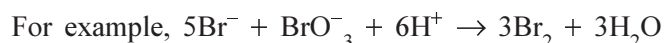


$2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, Rate of reaction $\propto [\text{N}_2\text{O}_5]$ $\therefore$ Rate of reaction = $K[\text{N}_2\text{O}_5]$ where K is rate constant and it is called specific rate constant when concentration of reactant is 1M. At that time, rate of reaction = rate constant.



$$\text{Rate of reaction} = K[\text{A}]^x[\text{B}]^y$$

Here, order of reaction with respect to A is x and that with respect to B is y. Hence total order of reaction = x + y. Thus, total order of reaction is equal to the sum of exponent of concentration of all reactants.



$$\text{Rate of reaction} = K[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2$$

$$\therefore \text{Overall order of reaction} = 1 + 1 + 2 = 4$$

The order of reaction can be positive integer, zero or even a fraction.

Reaction	Rate law	order of reaction
(1) $2\text{NH}_{3(g)} \xrightarrow{\text{Mo}} \text{N}_{2(g)} + 3\text{H}_{2(g)}$	rate = $K[\text{NH}_3]^0$	0
(2) $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$	rate = $K[\text{H}_2\text{O}]$	1
(3) $2\text{NO}_2 \rightarrow \text{F}_2 + 2\text{NO}_2\text{F}$	rate = $K[\text{NO}_2] [\text{F}]$	2
(4) $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	rate = $K[\text{NO}]^2 [\text{O}_2]$	3
(5) $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$	rate = $K[\text{CH}_3\text{CHO}]^{1.5}$	1.5
(6) $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$	rate = $K[\text{CO}]^2 [\text{Cl}_2]^{1.5}$	3.5

21. If for a reaction : $p\text{A} + q\text{B} \rightarrow \text{products}$, rate of reaction = $K[\text{A}]^m[\text{B}]^n$ then ...
 (A) $(p + q) = (m + n)$ (B) $p + q \neq m + n$
 (C) $(p + q) > (m + n)$ (D) $(p + q) = (m + n)$ OR $(p + q) \neq (m + n)$
22. Which reaction has its order in fraction ?
 (A) $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ (B) $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$
 (C) $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ (D) $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$
23. A reaction $2\text{A} + 2\text{B} \rightarrow \text{D} + \text{E}$ takes place in two steps
 (i) $\text{A} + 2\text{B} \rightarrow 2\text{C} + \text{D}$ (slow) (ii) $\text{A} + 2\text{C} \rightarrow \text{E}$ (fast)
 The rate law of the reaction is
 (A) rate = $K[\text{A}]^2[\text{B}]^2$ (B) rate = $[\text{A}]^2[\text{B}]^2[\text{C}]$
 (C) rate = $K[\text{A}][\text{B}]$ (D) rate = $K[\text{A}][\text{B}]^2$
24. The decay of $^{238}_{100}\text{Fm}$ is order reaction.
 (A) zero (B) first (C) 100 (D) 138
25. The rate of reaction doubles on increasing concentration of reactant by 8 times, then what will be the order of reaction ?
 (A) 1 (B) $\frac{1}{2}$ (C) $\frac{1}{3}$ (D) $\frac{1}{4}$
26. In a reaction having rate determining step $\text{A} + 2\text{B} \rightarrow \text{C}$, if concentration of B is doubled, then rate
 (A) will be double (B) will remain constant (C) will be $\frac{1}{2}$ times (D) will be four times
27. In a reaction having rate law, rate = $K[\text{A}]^2[\text{B}]$. On doubling the concentrations of A and B the rate of reaction x will be
 (A) 8x (B) 9x (C) x^3 (D) $4x^2$
28. The rate of reaction doubles by increasing concentration of reactant 16 times. What will be the order of reaction ?
 (A) 2 (B) 4 (C) $\frac{1}{2}$ (D) $\frac{1}{4}$

29. The rate of reaction becomes 100 times on changing concentration of reactant A from 0.1M to 1M. What will be the order of reaction with respect to A ? (Reaction : $A \rightarrow B$)
 (A) 10 (B) 1 (C) 2 (D) 3
30. $\text{rate} = K[A][B]^2$ for a reaction $2A + B \rightarrow \text{products}$. By doubling the concentration of A and decreasing the concentration of B to half in this reaction, rate of reaction will be...
 (A) double. (B) half. (C) constant. (D) four times.
31. Experimental data for reaction $A + 2B \rightarrow C + D$ is as follows. Give the rate law of reaction.

Experiment	Initial concentration (M)		rate in term of D M Min ⁻¹
	[A]	[B]	
(1)	0.1	0.1	6.0×10^{-3}
(2)	0.3	0.2	7.2×10^{-2}
(3).	0.3	0.4	2.88×10^{-1}
(4)	0.4	0.1	2.4×10^{-2}

- (A) $\text{rate} = K[A]^2 [B]$ (B) $\text{rate} = K[A]^2 [B]^2$
 (C) $\text{rate} = K[A] [B]^2$ (D) $\text{rate} = K[A] [B]$
32. The rate of reaction increases by 4 times on doubling the concentration of reactant A in a reaction $A + B \rightarrow \text{products}$. There is no effect on rate when concentration of reactant B is doubled. What will be the rate equation ?
 (A) $\text{rate} = K[A]^2$ (B) $\text{rate} = K[A]$ (C) $\text{rate} = K[A]^2[B]^2$ (D) $\text{rate} = K[A][B]$
33. For a reaction containing only gaseous components, $\text{rate} = K[A][B]$. What will be the rate if volume of container is made $\frac{1}{4}$ of original volume. (Reaction : $2A + B \rightarrow C + D$)
 (A) $\frac{1}{16}$ times (B) 4 times (C) $\frac{1}{8}$ times (D) 16 times
34. The volume is made half of the original volume in a reaction $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{2(g)}$. If order of reaction with respect to O_2 is one and that with respect to NO is two, then initial rate is how many times more than the rate ?
 (A) 8 (B) $\frac{1}{4}$ (C) $\frac{1}{2}$ (D) 2
35. In a reaction two reactants take part. Rate of reaction is directly proportional to concentration of one reactant and inversely proportional to concentration of second reactant. What will be the order of reaction ?
 (A) 0 (B) 1 (C) 2.0 (D) 0.5
36. The rate determining step for the reaction $Y_2 + 2Z \rightarrow \text{products}$ is $Y + \frac{1}{2}Z \rightarrow Q$. If concentration of Z is double then rate of reaction will
 (A) constant. (B) increase by 4 times. (C) increase by 1.414 times. (D) double.

37. The rate of reaction becomes 8 times on doubling the concentration of reactant. What will be the order of reaction ?

(A) 2.5 (B) 2 (C) 1.5 (D) 0.5

Answers : 21. (D), 22. (C), 23. (D), 24. (B), 25. (C), 26. (D), 27. (A), 28. (D), 29. (C), 30. (B), 31. (C), 32. (A), 33. (D), 34. (A), 35. (A), 36. (C), 37. (C)

● **Units of rate constant :**

$$\text{rate} = \frac{dx}{dt} = K(\text{concentration})^n$$

$$\therefore K = \frac{dx}{dt} \times \frac{1}{(\text{conc.})^n} = \frac{\text{conc.}}{\text{time}} \times \frac{1}{(\text{conc.})^n}$$

$$\therefore K = (\text{concentration})^{1-n} \text{ time}^{-1}$$

order of reaction	Units of rate constant K	
0	M s ⁻¹	mol L ⁻¹ time ⁻¹
1	s ⁻¹	time ⁻¹
2	M ⁻¹ s ⁻¹	L mol ⁻¹ time ⁻¹
n	M ¹⁻ⁿ s ⁻¹	L ¹⁻ⁿ mol ⁿ⁻¹ time ⁻¹

38. What is the unit of rate constant for zero order reaction ?

(A) litre sec⁻¹ (B) litre mol sec⁻¹ (C) mol litre⁻¹ sec⁻¹ (D) mol sec⁻¹

39. What will be the order of reaction if units of rate of reaction and rate constant are same ?

(A) 3 (B) 2 (C) 1 (D) 0

40. The rate constant of a reaction is $3 \times 10^{-3} \text{ bar}^{-1} \text{ sec}^{-1}$ then state the order of reaction.

(A) 1 (B) 2 (C) 3 (D) 0

41. Which dimensions are included in the unit of a third order reaction ?

(A) only time (B) time and concentration
(C) time, concentration and temperature (D) only concentration

42. The rate constant of a reaction is $5 \times 10^{-2} \text{ L}^3 \text{ mol}^{-3} \text{ min}^{-1}$ then state the order of reaction.

(A) 1 (B) 2 (C) 3 (D) 4

43. The rate equation of a reaction $\text{Cl}_3\text{C}\cdot\text{CHO} + \text{NO} \rightarrow \text{CHCl}_3 + \text{NO} + \text{CO}$, is $\text{rate} = K[\text{Cl}_3\text{C}\cdot\text{CHO}][\text{NO}]$. If concentrations of reactants are in molar units, then state the units of rate constant K.

(A) L² mol⁻² s⁻¹ (B) mol L⁻¹ s⁻¹ (C) L mol⁻¹ s⁻¹ (D) s⁻¹

44. On what does the unit of rate constant depend ?

(A) on rate of reaction. (B) on molecularity of reaction.
(C) on order of reaction. (D) All three given.

45. The rate constant of a reaction containing gaseous components is $5.0 \times 10^{-4} \text{ bar}^{-2} \text{ min}^{-1}$. State the order of reaction.
- (A) 0 (B) 1 (C) 2 (D) 3

Answers : 38. (C), 39. (D), 40. (B), 41. (B), 42. (D), 43. (C), 44. (C), 45. (D)

● **Molecularity and order of reaction**

Molecularity :

The number of atoms, ions, or molecules that participate in an elementary reaction and collide simultaneously as a result of which reaction takes place is called molecularity of reaction.

The order of reaction and molecularity of bimolecular, trimolecular elementary reactions are the same.

The probability of collision between more than three molecules is very less. Therefore, molecularity more than three is not found.

Molecularity	Order of reaction
It is a sum of number of molecules participating in one step reaction.	It is a sum of exponents of molar concentration of reactants expressed in rate equation derived experimentally.
It is always an integer.	It may be a fraction.
It can never be zero.	It can be zero.
Molecularity is applicable for one step reaction or any of the step of a reaction occurring in more than one step. It has no meaning for reactions involving more than one step.	The order of reaction can be applied to all steps indicating its completion
It can be obtained from simple balanced equation for one step reaction.	It can be obtained only from experimentally derived rate law.
It is not helpful in explaining mechanism of reaction.	It is helpful in explaining mechanism of reaction.

46. A reaction containing two different reactants is never
(A) bimolecular. (B) unimolecular. (C) of first order. (D) of second order.
47. What will be the order of reaction $3A \rightarrow \text{products}$?
(A) 3 (B) 1, 2, or 3 (C) 0 (D) any one from 1 to 3
48. Reactions having very high order are very rarely seen. Because
(A) more activation energy is required for the active collision of more molecules.
(B) the possibility of active collision between more molecules is very less.
(C) with reference to energy active collision of more molecules is not supported.
(D) Active collision of more molecules is possible in gas phase only.

49. The molecularity of a single step reaction $A + 2B \rightarrow \text{products}$ is.....
 (A) 0 (B) 1 (C) 2 (D) 3
50. Which of the following is unimolecular reaction ?
 (A) $HI \rightarrow \frac{1}{2}H_2 + \frac{1}{2}I_2$ (B) $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$
 (C) $H_2 + Cl_2 \rightarrow 2HCl$ (D) $PCl_3 + Cl_2 \rightarrow PCl_5$
51. From the experimental results for a reaction $H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$, if rate = $K[H_2][Br_2]^{\frac{1}{2}}$, then its molecularity and overall order are respectively
 (A) 2, 2 (B) 2, $1\frac{1}{2}$ (C) $1\frac{1}{2}$, 2 (D) $1\frac{1}{2}$, $1\frac{1}{2}$
52. The order and molecularity of a hydrolysis reaction between ethyl acetate and ethanol in basic medium are respectively.
 (A) 1, 1 (B) 1, 2 (C) 2, 1 (D) 2, 2
53. Hydrolysis of organic chloride in presence of excess of water occurs as
 $R - Cl + H_2O \rightarrow R-OH + HCl$. The molecularity and order of reaction are respectively.
 (A) 1, 1 (B) 2, 1 (C) 2, 2 (D) 1, 2

Answers : 46. (B), 47. (D), 48. (B), 49. (D), 50. (B), 51. (B), 52. (D), 53. (B)

● Reactions of various order and half reaction time

Zero order reaction :

Rate of reaction is directly proportional to the zeroth power of concentration of reactant.

$$-\frac{d[R]}{dt} = K[R]^0 \quad \therefore [R] = -Kt + [R]_0$$

So, the graph of $[R] \rightarrow t$ is a straight line with the slope = $-K$ and intercept = $[R]_0$

$$t_{\frac{1}{2}} \propto \frac{[R]_0}{2} \text{ i.e. } t_{\frac{1}{2}} = \frac{[R]_0}{2K}$$

First order reaction :

Rate of reaction is directly proportional to the first power of concentration of reactant.

$$-\frac{d[R]}{dt} = K[R] \quad \therefore Kt = \ln \frac{[R]_0}{[R]_t} \text{ and } [R]_t = [R]_0 e^{-Kt}$$

and $\log[R]_t = -\frac{K}{2.303} \times t \times \log[R]_0$, hence graph of $\log[R]_t \rightarrow t$ is straight line.

Slope = $-\frac{K}{2.303}$ and intercept = $\log[R]_0$

$$t_{\frac{1}{2}} = \frac{0.693}{K}$$

● Pseudo first order reaction

Several reactions are not of first order but under certain conditions they become first order reactions. Such reactions are

(1) Hydrolysis of ethyl acetate (2) Hydrolysis of cane sugar

Determination of order of reaction

Methods : (1) Initial rate method

(2) Integrate rate equation method or graphical method

(3) Half reaction time method : Time required for half completion of reaction =

Half reaction time = $t_{\frac{1}{2}}$ It is very simple method.

For zero order reaction $t_{\frac{1}{2}} \propto [R]_0$

For first order reaction $t_{\frac{1}{2}}$ is independent of concentration of reactant

For n^{th} order reaction $t_{\frac{1}{2}} \propto [R]_0^{1-n}$ or $t_{\frac{1}{2}} \propto \frac{1}{[R]_0^{n-1}}$

-
54. The rate of a zero order reaction is always independent of
- (A) volume of reaction vessel. (B) temperature.
(C) presence of light. (D) concentration of reactant.
55. $\text{CH}_3\text{COCH}_3 + \text{I}_2 \xrightarrow{\text{H}^+} \text{products}$. If rate = $K[\text{CH}_3\text{COCH}_3][\text{H}^+]$, then what will be order of reaction with respect to I_2 ?
- (A) 0 (B) 1 (C) 2 (D) 3
56. Zeroth order reaction means....
- (A) rate is independent of concentration.
(B) rate independent of concentration of active reactants.
(C) rate of formation of activated complex is zero.
(D) rate of decomposition of activated complex is zero.
57. Which of the following statement is wrong ?
- (A) The rate of zeroth order reaction varies with temperature.
(B) Order and molecularity of a reaction are always same.
(C) If 128 gram HI is in 2 L container then its active mass = 0.5
(D) The rate of reaction is halved on decreasing concentration of reactant to half in first order reaction.
58. How much time would require for completion of a reaction if in a zeroth order reaction the initial concentration of reactant is 'a' and rate constant is 'K'.
- (A) $\frac{a}{K}$ (B) $\frac{K}{2a}$ (C) $\frac{a}{2K}$ (D) $\frac{K}{a}$
59. For a zero order reaction,

(A) $K = \frac{[A]_0}{t}$ (B) $Kt = [A]_t - [A]_0$ (C) $Kt = 2.303 \ln \frac{[A]_0}{[A]_t}$ (D) $Kt = [A]_0 - [A]_t$

60. The half reaction time becomes double on doubling the initial concentration of reactant, then state the order of reaction is
 (A) 1 (B) 2 (C) 3 (D) 0
61. For a zero order reaction
 (A) $t_{\frac{1}{2}} \propto C_0$ (B) $t_{\frac{1}{2}} \propto C_0^2$ (C) $t_{\frac{1}{2}} \propto \sqrt{C_0}$ (D) $t_{\frac{1}{2}} \propto C_0^{-1}$
62. The initial concentration of reactant of n^{th} order reaction is 'a', the half reaction time will be directly proportional to
 (A) a^{n+1} (B) a^{1-n} (C) a^{n-1} (D) a^n
63. If concentration of reactant is made 'x' times, then its rate constant =
 (A) $\ln \frac{K}{x}$ (B) $\frac{K}{x}$ (C) $K \cdot x$ (D) K
64. The half reaction time of a zero order reaction is 1 hr. The initial concentration of reactant A is 2M. How much time will be required for the concentration of reactant to become 0.25 M from 0.5 M ?
 (A) 1 hr (B) 4 hr (C) 0.5 hr (D) 0.25 hr
65. For a first order reaction, ...
 (A) $t = K \times 2.303 \log \frac{[A]}{[A]_0}$ (B) $K = \frac{2.303}{t} \log \frac{[A]}{[A]_0}$
 (C) $[A] = [A]_0 e^{-Kt}$ (D) $t = \frac{2.303}{K} \log \frac{a}{a+x}$
66. For a first order reaction
 (A) $t_{\frac{1}{2}} = \frac{0.693}{K}$ (B) $t_{\frac{1}{2}} = \frac{0.693}{C_0}$ (C) $t_{\frac{1}{2}} \propto \frac{0.693}{K}$ (D) $t_{\frac{1}{2}} \propto \frac{0.693}{C_0}$
67. Which of the following indicates $\frac{3}{4}$ th reaction time for first order reaction ?
 (A) $\frac{K}{2.303} \log 4$ (B) $\frac{2.303}{K} \log \frac{3}{4}$ (C) $\frac{2.303}{K} \log 4$ (D) $\frac{2.303}{K} \log 3$
68. The half reaction time of a first order reaction is 14 second. How much time will be required to reduce initial concentration to $\frac{1}{8}$ th of its original concentration ?
 (A) 28 s (B) 42 s (C) $(14)^2$ s (D) $(14)^3$ s
69. The time required to reduce original concentration of reactant to its 25 % is 1 hour for first order reaction. State half reaction time.
 (A) 120 min (B) 4 hr (C) 30 min (D) 15 min
70. How much approximate time would be required to decrease original concentration of a reactant from $\frac{M}{10}$ to $\frac{M}{100}$ in a first order reaction ? The half life period of reaction is 150 seconds.
 (A) 600 s (B) 900 s (C) 500 s (D) 1500 s

71. How much amount of reactant would be left after one hour in a first order reaction having half life period of 15 min ?
 (A) $\frac{1}{2}$ (B) $\frac{1}{4}$ (C) $\frac{1}{8}$ (D) $\frac{1}{16}$
72. The $t_{\frac{1}{2}} = 24$ hours for a reaction : $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$. What amount of N_2O_5 will be left on decomposing 10 gram N_2O_5 after 96 hours ?
 (A) 0.63 g (B) 0.5 g (C) 1.77 g (D) 1.25 g
73. The decomposition of 75 % reactant takes place in 1.386 hours in a first order reaction. Give the value of rate constant.
 (A) $3.6 \times 10^{-3} \text{ s}^{-1}$ (B) $2.8 \times 10^{-4} \text{ s}^{-1}$ (C) $17.2 \times 10^{-3} \text{ s}^{-1}$ (D) $1.8 \times 10^{-3} \text{ s}^{-1}$
74. The half life period of a first order reaction is 6.93 minutes. How much time would require for 99 % completion of this reaction ?
 (A) 460.6 min (B) 23.03 min (C) 46.06 min (D) 230.5 min
75. The time required to reduce to $\frac{1}{4}$ th of its original concentration of a first order reaction is 20 minutes. What will be the time to decrease initial concentration to its $\frac{1}{16}$ th.
 (A) 20 min (B) 10 min (C) 80 min (D) 40 min
76. What will be the half life period if a radio active substance decay to its $\frac{3}{4}$ th in 2 hours ?
 (A) 60 min (B) 30 min (C) 45 min (D) 15 min
77. A molecule decompose to 50 % in 120 minutes. How much time would require for 90 % of this first order thermal decomposition ?
 (A) 360 min (B) 398.8 min (C) 300 min (D) 400 min
78. The time required to decrease concentration of reactant R from 0.1 M to 0.025 M in a first order reaction $\text{R} \rightarrow \text{P}$ is 40 minutes. State the rate of reaction when concentration of reactant R in this reaction is 0.01M.
 (A) $1.733 \times 10^{-4} \text{ M min}^{-1}$ (B) $3.466 \times 10^{-4} \text{ M min}^{-1}$
 (C) $3.466 \times 10^{-5} \text{ M min}^{-1}$ (D) $3.466 \times 10^{-3} \text{ M min}^{-1}$
79. If the time required for 25 % completion of first order reaction is expressed by $\frac{t_1}{4}$ and its rate constant is K, then its $t_{\frac{1}{4}}$ is equal to what ?
 (A) $\frac{1.38}{K}$ (B) $\frac{0.25}{K}$ (C) $\frac{0.346}{K}$ (D) $\frac{0.29}{K}$

Answers : 54. (D), 55. (A), 56. (B), 57. (B), 58. (A), 59. (D), 60. (D), 61. (A), 62. (B), 63. (D), 64. (D), 65. (C), 66. (A), 67. (C), 68. (B), 69. (C), 70. (C), 71. (D), 72. (A), 73. (B), 74. (C), 75. (D), 76. (A), 77. (B), 78. (B), 79. (D).

- **Arrhenius equation and collision theory**

Arrhenius equation : $K = A e^{-E_a/RT}$ $\therefore \ln K = \ln A - \frac{E_a}{RT}$

$$\therefore \log K = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$

the graph of $\log K \rightarrow \frac{1}{T}$ is straight line.

$$\text{slope} = -\frac{E_a}{2.303R}$$

$$\text{Also, } \log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] = \frac{E_a \Delta T}{2.303R T_1 \times T_2}$$

- **Threshold energy :**

Arrhenius equation indicates that rate constant increases exponentially with temperature.

By increasing temperature from 300 K to 310 K, the kinetic energy increases only by 3 % because it is proportional to temperature.

For most of the reactions the rates almost double by increase in temperature by 10 K.

The explanation for this can be given that there must be some pushing energy or threshold energy required for the reaction of molecules.

- **Arrhenius Parameters**

$E_a = N_A E^*$ where, E_a = activation energy, N_A = Avogadro number E^* = Kinetic energy

$K = A e^{-E_a/RT}$ where, A = pre exponential or frequency factor

Here, A and E_a are called Arrhenius parameters.

- **Theory of collision**

Developed by Max Trauz and Willium Lewis (1916-18).

In chemical reaction, the number of collision per second per unit volume is called collision frequency (Z).

For a bimolecular reaction, $A + B \rightarrow \text{products}$

$$\text{Rate} = Z_{AB} e^{-E_a/RT} \text{ and } \text{Rate} = P Z_{AB} e^{-E_a/RT}$$

where, Z_{AB} = collision frequency of reactants A and B whose energy is equal to or more than activation energy

P = Steric factor or probability parameters

Those collisions in which molecules possess sufficient kinetic energy (threshold energy) and molecules collide in proper directions are called fruitful collisions or effective collisions. Such collisions results into a chemical reaction.

80. The minimum energy that must be required by reactants for a reaction to occurs is
- (A) potential energy (B) internal energy (C) activation energy (D) threshold energy
81. Which of the following is correct Arrhenius equation ?
- (A) $\ln \frac{K_2}{K_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ (B) $K = A e^{-E_a/RT}$
- (C) $\ln K = \ln A - \frac{E_a}{RT}$ (D) given all three
82. What is changed by increasing concentration of reactants ?
- (A) Collision frequency (B) Heat of reaction (C) Threshold energy (D) Activation energy
83. For exothermic reactions, activation energy
- (A) is zero. (B) is negative. (C) is positive. (D) cannot be predicted.
84. Reactions which require high activation energy are mostly
- (A) slow. (B) fast. (C) very fast. (D) spontaneous.
85. Activation energy of reaction =
- (A) threshold energy + energy of products (B) threshold energy – energy of reactants
- (B) threshold energy + energy of reactants (D) threshold energy – energy of products
86. Theory of collision is more satisfactory for reactions.
- (A) first order (B) second order (C) bi-molecular (D) None
87. The rate constant of a reaction at 290 K is 3.2×10^{-3} . What will be its rate constant at 300 K ?
- (A) 1.6×10^{-3} (B) 6.4×10^{-3} (C) 3.2×10^{-4} (D) 3.2×10^{-2}
88. How many times rate of reaction will be on increase of temperature from 10 K to 100 K ?
- (A) 512 (B) 614 (C) 400 (D) 112
89. The rate constants of a reaction at 300 K and 320 K are 0.0231 min^{-1} and 0.0693 min^{-1} respectively. What will be the activation energy of reaction ?
- (A) 84 KJ mole^{-1} (B) 34.84 KJ mole^{-1} (C) 43.84 KJ mole^{-1} (D) 30 KJ mole^{-1}
90. If $E_a = 0$, for a reaction then its rate constant
- (A) increase with increase in temperature (B) increase with decrease in temperature
- (C) decrease with decrease in temperature (D) is independent of temperature
91. Decrease of which term in the equation, $K = P Z e^{-E_a/RT}$ would result into a faster reaction ?
- (A) E (B) T (C) Z (D) P
92. The rate of reaction doubles by increase of 10°C temperature. If there is an increase of 50°C in temperature, how many times rate of reaction would increase ?
- (A) 64 times (B) 32 times (C) 10 times (D) 24 times

93. The activation energy of a reaction at definite temperature is $2.303 RT \text{ Jmol}^{-1}$, then the ratio of rate constant and Arrhenius constant will be
 (A) 0.001 (B) 0.01 (C) 0.02 (D) 0.1
94. For a reaction $\text{C}_2\text{H}_5\text{I} + \text{OH}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{I}^-$ at 30°C and 60°C temperature, the values of rate constants are 0.325 and $6.735 \text{ L mol}^{-1} \text{ s}^{-1}$ respectively, what will be the value of activation energy ?
 (A) 20260 K.cal. (B) 84773 cal (C) 361.44 cal (D) 20260 cal
95. The energy of activation of a reaction is 9 K.cal mol^{-1} . How many times the rate constant will increase by increasing temperature of a reaction from 295 K to 300 K ?
 (A) 1.289 times (B) 0.1289 times (C) 12.89 times (D) 25%
96. The reactant A gives two products :
 (i) $\text{A} \xrightarrow{K_1} \text{B}$, activation energy E_1
 (ii) $\text{A} \xrightarrow{K_2} \text{C}$ activation energy E_2 If, $E_2 = 2E_1$, then what is the relation between K_1 and K_2 ?
 (A) $K_2 = K_1 e^{\frac{E_1}{RT}}$ (B) $K_2 = K_1 e^{\frac{E_2}{RT}}$ (C) $K_1 = K_2 A e^{\frac{E_1}{RT}}$ (D) $K_1 = 2K_2 e^{\frac{E_2}{RT}}$
97. The energy of activation of two reactions are E_1 and E_2 . where, $E_1 > E_2$. If temperature is made T_2 from T_1 then rate constant K_1 of the first reaction becomes K_1' and that of second reaction becomes K_2' from K_2 , which of the following reaction is true for this ?
 (A) $\frac{K_1'}{K_1} > \frac{K_2'}{K_2}$ (B) $\frac{K_1'}{K_1} < \frac{K_2'}{K_2}$ (C) $\frac{K_1'}{K_1} = \frac{K_2'}{K_2}$ (D) $\frac{K_1'}{K_1} = \frac{K_2'}{K_2} = 0$
98. Rate constants of two different chemical reactions are $K_1 = 10^{16} e^{-\frac{2000}{T}}$ and $K_2 = 10^{15} e^{-\frac{1000}{T}}$ respectively. At which kelvin temperature $K_1 = K_2$?
 (A) 1000K (B) $\frac{2000}{2.303} \text{ K}$ (C) 2000K (D) $\frac{1000}{2.303} \text{ K}$

Answers : 80. (D), 81. (D), 82. (A), 83. (C), 84. (A), 85. (B), 86. (C), 87. (B), 88. (A), 89. (C), 90. (D), 91. (A), 92. (B), 93. (D), 94. (D), 95. (A), 96. (C), 97. (A), 98. (D)

● Exothermic and Endothermic reactions

A reaction is exothermic if minimum potential energy of products is less than that of reactants.

A reaction is endothermic if minimum potential energy of products is more than that of reactants.

For endothermic reactions : $\Delta H = H_p - H_r = +Ve$

$$\Delta H = E_a - E_a^r = +Ve \text{ where, } E_a > E_a^r$$

For exothermic reactions : $\Delta H = H_p - H_r = -Ve$

$$\Delta H = E_a - E_a^r = -Ve \text{ where, } E_a < E_a^r$$

where, E_a = Activation energy of forward reaction

E_a^r = Activation energy of reverse reaction

99. If activation energies of forward and reverse reaction of an exothermic reaction are E_f and E_r respectively, then
 (A) $E_f < E_r$ (B) $E_f > E_r$ (C) $E_f \gg E_r$ (D) $E_f = E_r$

100. The enthalpy change of a reaction for an endothermic reaction is ΔH . The minimum value of activation energy of reaction will be
 (A) equal to ΔH (B) zero (C) more than ΔH (D) less than ΔH
101. The energy of activation and change in enthalpy of an endothermic reaction $A \rightarrow B$ are 15 and 5 Kcal mol⁻¹ respectively. What will be the energy of activation for a reverse reaction ?
 (A) 10 Kcal mol⁻¹ (B) 20 Kcal mol⁻¹ (C) 15 Kcal mol⁻¹ (D) zero
102. The activation energy and change in enthalpy of an exothermic reaction are 70 and -30 KJmol⁻¹. What will be the energy of activation for a reverse reaction ?
 (A) 70 KJ mol⁻¹ (B) 30 KJ mol⁻¹ (C) 40 KJ mol⁻¹ (D) 100 KJ mol⁻¹
103. The energy of activation for a reaction $A \rightarrow B$ is E_a in forward direction, then activation energy in reverse direction will be
 (A) equal to E_a (B) less than E_a (C) more than E_a (D) less or more than E_a

Answers : 99. (A), 100. (C), 101. (A), 102. (D), 103. (D)

● Effect of catalysts

The main function of catalysts is to decrease the energy of activation of reaction. As a result the height of energy barrier decreases and rate of reaction increases.

By using catalysts the value of equilibrium constant (K) does not change, only the value of rate of reaction increases.

104. A catalyst will increase rate of reaction by
 (A) reacting with reactants. (B) decreasing energy of activation.
 (C) reacting with products. (D) increasing energy of activation.
105. The rate of reaction increases according to the adsorption of catalyst. Because,
 (A) adsorption decreases E_a .
 (B) E_a of molecules increases in adsorption reaction.
 (C) concentration of reactants increases on the active sites of catalyst.
 (D) adsorption energy is produced which increase rate of reaction.
106. The rate of a biochemical reaction out of human body in absence of an enzyme is found to be 10^{-6} times. If this reaction takes place inside the human body then what will be the activation energy of reaction?
 (A) The value of (E_a) for reaction occurring inside the human body is less.
 (B) cannot be said
 (C) $\frac{6}{RT}$ (D) external pressure required
107. Catalyst is a substance, which
 (A) increases concentration of products at equilibrium. (B) vary the equilibrium constant of a reaction.
 (C) provides energy to the reaction. (D) changes the time to acquire equilibrium.
108. Oxidation of acidic KMnO_4 by oxalic acid is an example of auto catalysis. What is responsible for that ?
 (A) SO_4^{2-} (B) MnO_4^{2-} (C) Mn^{2+} (D) K^+

Answers : 104. (B), 105. (A), 106. (A), 107. (D), 108. (C)

● **Mechanism of chemical reaction**

(1) A reaction involving two consecutive steps of first order

Reaction occurs in two steps $R \xrightarrow{K_1} I$ and $I \xrightarrow{K_2} P$

Both steps are first order reactions. In the first step intermediate I is produced and accumulates. When it is maximum it decomposes to product in second step.

(2) A reaction involving slow step

For reactions involving more than one step, the slowest step is rate determining step (r.d.s.).

There may be two reasons for slow step.

- (i) The concentration of one or more species participating in elementary reaction is low.
- (ii) The value of rate constant is low.

e.g., $R \xrightarrow{K_1} I \xrightarrow{K_2} P$

If $K_1 \ll K_2$ then, conversion of I into product will be as soon as I is formed.

(3) Steady state hypothesis

Suppose a chemical reaction occurs in more than one step and certain intermediates are possible.

Here, we assume that intermediates react such that in the short time at beginning (induction time) their concentration increases to some higher value than zero and remains constant during the time period of that reaction. i.e. concentration of such intermediates which can react is zero. Based on this hypothesis the equation for the rates of complex reactions can be derived.

(4) Reactions involving intermediates in equilibrium with reactants : Especially, in the reactions involving H^+ and OH^- ions the rate constants of forward and reverse reactions are very high and equilibrium is established between them.

The intermediate so formed, reacts so slowly that there is negligible change in its concentration.

eg. The $C_2H_5O^-$ ion obtained from o-hydroxy aminoethyl benzoate ($\equiv E$) is catalyzed by OH^- ion.

Its mechanism is as follows,



$$\text{From (ii), rate} = k_3 [I] \quad \text{.....} \quad (iii)$$

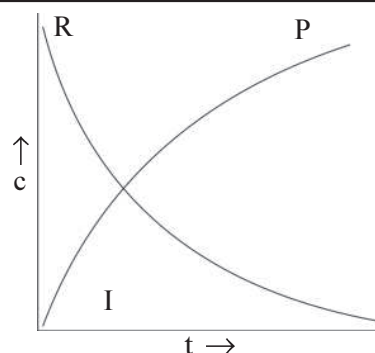
$$\text{From (i), } [I] = \frac{k_1[E][OH^-]}{k_2} \quad \text{.....} \quad (iv)$$

Substituting (iv) into (iii)

$$\text{rate} = K_3 \frac{K_1}{K_2} [E][OH^-] = K_0 [E][OH^-] \quad \text{where, } K_0 = \frac{K_3 K_1}{K_2}$$

109. Which hypothesis of mechanism of reaction a graph given indicates ?

- (A) Hypothesis of a reaction involving two consecutive steps of first order.
- (B) Hypothesis of a reaction involving any one slow step.
- (C) Hypothesis in which steady state is valid
- (D) Hypothesis of a reaction involving intermediate in equilibrium with reactant



110. A reaction $A_2 + B_2 \rightleftharpoons 2AB$ occurs in following steps. Give net order of reaction.
 (1) $A_2 \rightarrow 2A$ (fast) (2) $A + B_2 \rightarrow AB + B$ (slow) (3) $A + B \rightarrow AB$ (fast)
 (A) 1.5 (B) 2 (C) 0 (D) 1
111. A reaction $2O_3 \rightarrow 3O_2$ takes place in following two steps. Give correct rate law of reaction.
 (1) $O_3 \rightleftharpoons O_2 + O$ (fast) (2) $O + O_3 \rightleftharpoons 2O_2$ (slow)
 (A) $r = K[O_3]^2$ (B) $r = K[O_3]^2[O_2]^{-1}$ (C) $r = K[O_3][O_2]$ (D) $r = K[O_3]^2[O_2]$
112. The equilibrium constant of reaction : $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ is K_1 .
 The equilibrium constant of reaction : $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ is K_2 .
 For reaction : $NO_{2(g)} \rightleftharpoons \frac{1}{2}N_{2(g)} + O_{2(g)}$, $K = \dots\dots\dots$
 (A) $\frac{1}{(2K_1K_2)}$ (B) $\frac{1}{(4K_1K_2)}$ (C) $\left[\frac{1}{(K_1K_2)}\right]^{\frac{1}{2}}$ (D) $\frac{1}{(K_1K_2)}$
113. The rate law of a reaction is $\text{rate} = K[A]^n[B]^m$. If concentration of A is doubled and that of B is halved what will the ratio of rate and original rate of reaction ?
 (A) $m + n$ (B) $n - m$ (C) $2^{(n - m)}$ (D) $\frac{1}{2^{(m+n)}}$
114. The half life period of a reaction $A \rightarrow \text{products}$ is 1 hr. The initial concentration is 2 M. How many hours it will take to decrease concentration of reactant from 0.5 M to 0.25 M if reaction is of zero order ?
 (A) 0.25 (B) 1 (C) 4 (D) 0.5
115. The initial pressure and rate constant of a reaction $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$ are 500 atmosphere and $3.38 \times 10^{-5} \text{ s}^{-1}$ respectively. What will be the pressure of N_2O_5 after 10 minutes ?
 (A) 490 atm (B) 250 atm (C) 480 atm (D) 420 atm
116. A reaction $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$ is of first order. Its half-life period is 2.4 hours. If initial amount of reactant is 10.8 gram then how much oxygen would be obtained after 9.6 hours ? (At STP)
 (A) 0.07 L (B) 3.36 L (C) 1.5 L (D) 1.05 L
117. For a first order gaseous state reaction : $A_{(g)} \rightarrow 2B_{(g)} + C_{(g)}$ if initial pressure of 'A' is P_0 atmosphere and at a time 't' total pressure is 'P' atmosphere then its differential rate equation is
 (A) $\frac{2.303}{t} \log \frac{P_0}{P_0 - P_t}$ (B) $\frac{2.303}{t} \log \frac{P_0}{P_0 - P_t}$ (C) $\frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$ (D) $\frac{2.303}{t} \log \frac{2P_0}{2P_0 - P_t}$

Answers : 109. (C), 110. (A), 111. (B), 112. (C), 113. (C), 114. (A), 115. (A), 116. (D), 117. (B)

118. Decide the true (T) and false (F) statements for a reaction : $2N_2O_5 \rightarrow 4NO_2 + O_2$
 (1) concentration of reactants decrease exponentially with time
 (2) Half reaction time of reaction decrease with increase in temperature
 (3) The $t_{1/2}$ of reaction depends on initial concentration of reactants.
 (4) Reaction will be 99.6 % completed after eight half lives.
 (A) TTFT (B) FFTT (C) TTTT (D) TTFF

119. In what condition can nitrogen and oxygen combine ? Decide true (T) or false (F) statements for that.

- (1) Collision must take place between N_2 and O_2 .
- (2) In order to collide molecules must have certain minimum amount of potential energy.
- (3) In order to collide molecules must have certain minimum amount of threshold energy.
- (4) Collision must take place in proper direction

(A) TFFT (B) FFTT (C) TTTF (D) TFTF

120. Which of the following relations are true (T) or false (F) ?

(1) $\text{rate} \propto \frac{1}{\text{energy barrier}} \propto \frac{1}{E_a} \propto \text{effective collisions}$

(2) $\text{rate} \propto \frac{1}{\text{energy barrier}} \propto E_a \propto \frac{1}{\text{effective collisions}}$

(3) Rate of adsorption of gas in heterogeneous system = $\frac{K_1 P_{\text{gas}}}{1 + K_2 P_{\text{gas}}}$

(4) Rusting of iron $\equiv$ first order reaction

(A) TFTF (B) TTTT (C) TTFF (D) FFTT

121. Which statements are true (T) and false (F) for the relations between rate of consumption of A and rate of formation of B for a reaction $\frac{1}{2}A \rightarrow 2B$?

(1) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (2) $-\frac{d[A]}{dt} = 4 \frac{d[B]}{dt}$ (3) $-\frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$ (4) $-\frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$

(A) TTTF (B) FFFT (C) TTFF (D) FFTT

122. Which statements are true (T) and false (F) with reference to reaction $2A + B \rightarrow C$, rate = $K[A][B]$?

(1) Value of K is independent of concentration of A and B.

(2) Unit of K is time^{-1} .

(3) Half reaction time is constant.

(4) rate of formation of C is double than the rate of consumption of A.

(A) TFFF (B) FFFT (C) TTFF (D) FFTT

Answers : 118. (A), 119. (A), 120. (A), 121. (B), 122. (A)

123. Match the section-I with section-II in true meaning.

section-I	section-II
(a) $2HI \xrightarrow[\Delta]{Au} H_2 + I_2$	(k) 1
(b) $2N_2O_5 \rightarrow 4NO_2 + O_2$	(l) 2
(c) $CH_3COOCH_3 \xrightarrow{OH^-} CH_3COO^- + CH_3OH$	(m) 1.5
(d) $H_2 + Br_2 \rightarrow 2HBr$	(n) 0

(A) (a)-(k), (b)-(n), (c)-(l), (d)-(m)

(B) (a)-(n), (b)-(k), (c)-(l), (d)-(m)

(C) (a)-(m), (b)-(k), (c)-(l), (d)-(n)

(D) (a)-(n), (b)-(k), (c)-(m), (d)-(l)

124. Match the section-I and section-II correctly

section-I	section-II
(a) zeroth order reaction	(k) unit of K is $\text{Lmol}^{-1} \text{s}^{-1}$
(b) first order reaction	(l) half-reaction time is directly proportional to initial concentration of reactant
(c) second order reaction	(m) reaction of acetic anhydride with excess ethanol is example of it.
(d) pseudo first order reaction	(n) % decomposition of reactant at time $t = (1 - e^{-Kt}) \times 100$

(A) (a)-(l), (b)-(n), (c)-(k), (d)-(m)

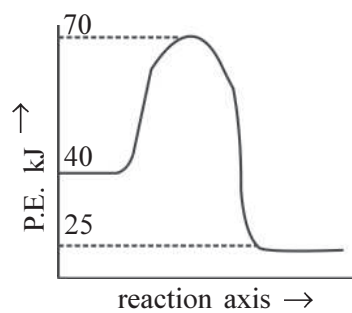
(B) (a)-(k), (b)-(n), (c)-(l), (d)-(m)

(C) (a)-(k), (b)-(l), (c)-(m), (d)-(n)

(D) (a)-(l), (b)-(k), (c)-(n), (d)-(m)

125. Study the graph and match column-I with column-II

column-I	column-II
(a) E_a of forward reaction	(k) 70 KJ mol^{-1}
(b) Threshold energy	(l) 30 KJ mol^{-1}
(c) E_a of reverse reaction	(m) 15 KJ mol^{-1}
(d) Enthalpy change of reaction	(n) 45 KJ mol^{-1}



(A) (a)-(k), (b)-(l), (c)-(n), (d)-(m)

(B) (a)-(l), (b)-(k), (c)-(m), (d)-(n)

(C) (a)-(m), (b)-(k), (c)-(n), (d)-(l)

(D) (a)-(l), (b)-(k), (c)-(n), (d)-(m)

Answers : 123. (B), 124. (A), 125. (D)

• Questions containing one or more than one correct options

126. For a zero order reaction,

(A) half reaction time is inversely proportional to rate constant.

(B) half reaction time is directly proportional to initial concentration of reactant.

(C) time required for completion of reaction, is independent of initial concentration of reactant

(D) there is no effect of doubling concentration of reactant on rate of reaction.

127. The rate of reaction between $[\text{BrO}_3^-]$ and $[\text{Br}^-]$ ions in acidic medium is as follows:

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

that means,

(A) rate constant is dependent of concentration of H^+ ions.

(B) order of reaction is independent of concentration of acid.

(C) change in pH of a reaction mixture will affect order of reaction.

(D) Rate of reaction increases 4 times by doubling the concentration of H^+ ions.

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

(A) $K = \frac{1}{t} \ln \frac{C_0}{C_t}$ (B) $t = \frac{2.303}{K} \log \frac{a}{a-x}$ (C) $[A]_0 = [A] \cdot e^{-Kt}$ (D) $t_{1/2} = \ln \frac{2}{K}$

129. Which of the following statements are incorrect ?

- (A) A catalyst initiates a reaction faster.
- (B) A catalyst decreases activation energy of reaction.
- (C) A catalyst changes the value of reaction enthalpy.
- (D) A catalyst does not affect the rate of a reverse reaction.

130. Which of the following Arrhenius equations are correct ?

(A) $\ln \frac{A}{K} = \frac{E_a}{RT}$ (B) $\frac{\ln K}{\ln A} = -\frac{E}{RT}$

(C) $\log A = \log K + \frac{E_a}{2.303 RT}$ (D) $\log \left(-\frac{E_a}{RT} \right) = \frac{K}{A}$

131. Which of the following reaction is of second order ?



132. A catalyst

- (A) increase average kinetic energy of reactant.
- (B) decreases activation energy of reaction
- (C) alters the mechanism of reaction
- (D) increases number of molecules colliding

133. The activation energies of forward and reverse reactions of a reaction $x \rightarrow y$ are 15 and 9 KJ mol^{-1} . The potential energy of x is 10 KJ mol^{-1} . For this reaction,

- (A) threshold energy of reaction is 25 KJ. (B) potential energy of y is 16 KJ.
- (C) reaction enthalpy is 6 KJ. (D) the reaction is endothermic.

134. For a reaction $R-Cl + NaOH \rightarrow R-OH + NaCl$ the rate law is, rate = $K[R-Cl]$. The rate of this reaction will

- (A) double on doubling concentration of NaOH
- (B) become half on decreasing concentration to R-Cl to half
- (C) increase by increasing temperature
- (D) does not affect by temperature

135. For the given graphs which statement is correct ?

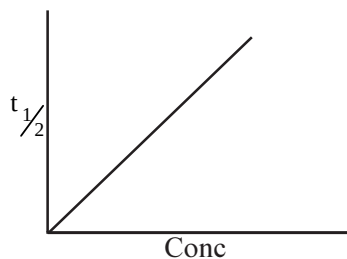
- (A) $\log K_p \rightarrow \frac{1}{T} = \text{straight line}$
- (B) for first order reaction, $\log [x] \rightarrow t = \text{straight line}$
- (C) at constant volume, $\log P \rightarrow \frac{1}{V} = \text{straight line}$
- (D) at constant temperature, $P \rightarrow \frac{1}{V} = \text{straight line}$

136. For a zero order reaction

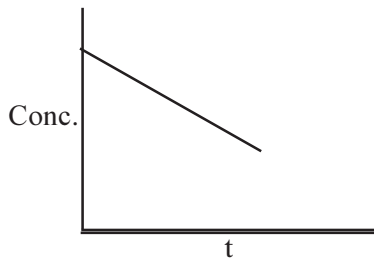
- (A) unit of K is $\text{mol L}^{-1} \text{ time}^{-1}$.
- (B) rate of reaction is independent of concentration of reactant.
- (C) Half reaction time depends on initial concentration of reactant.
- (D) Rate of reaction is independent of temperature.

137. Which of the following graphs are correct ?

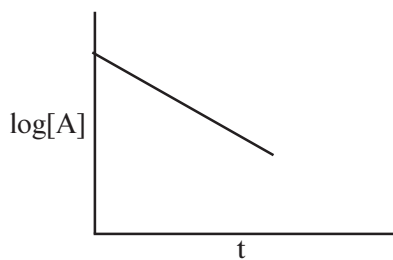
(A) for zero order reaction



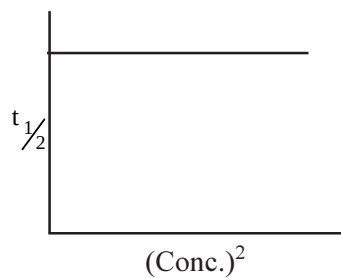
(B) for zero order reaction



(C) For first order reaction



(D) For second order reaction



Answers : 126. (A), (B), (D), 127. (C), (D), 128. (A), (B), (D), 129. (A), (C), (D),
 130. (A), (B) (C), 131. (B), (D), 132. (B), (C), 133. (A), (B), (C), (D),
 134. (B), (C), 135. (A), (B), (D). 136. (A), (B), (C), 137. (A), (B), (C)

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