

CHAPTER

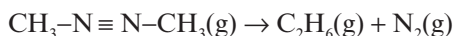
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Chemical Kinetics

EXERCISE I (JEE MAIN)

Rate of Reaction, Rate Law, Order and Molecularity of a Reaction

1. Azomethane, CH_3NNCH_3 , decomposes according to the following equation:



The initial concentration of azomethane was 1.50×10^{-2} M. After 10 min, the concentration decreased to 1.29×10^{-2} M. The average rate of reaction during this time interval is

- $3.5 \times 10^{-6} \text{ Ms}^{-1}$
 - $2.1 \times 10^{-4} \text{ Ms}^{-1}$
 - $3.5 \times 10^{-6} \text{ M h}^{-1}$
 - $2.1 \times 10^{-3} \text{ Mmin}^{-1}$
2. For the reaction: $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$, the expression, $-\frac{1}{2} \frac{d[\text{HI}]}{dt}$ represents
- the rate of formation of HI
 - the rate of disappearance of HI
 - the instantaneous rate of the reaction
 - the average rate of the reaction
3. For reaction: $4\text{A} + \text{B} \rightarrow 2\text{C} + 2\text{D}$, the only incorrect statement is
- The rate of disappearance of B is one-fourth the rate of disappearance of A
 - The rate of appearance of C is half the rate of disappearance of B

- The rate of formation of D is half the rate of consumption of A
- The rates of formation of C and D are equal

4. For the reaction: $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$, the concentration of NO_2 increases by 2.4×10^{-2} M in 6 s. What will be the average rate of appearance of NO_2 and the average rate of disappearance of N_2O_5 ?
- $2 \times 10^{-3} \text{ Ms}^{-1}$, $4 \times 10^{-3} \text{ Ms}^{-1}$
 - $2 \times 10^{-3} \text{ Ms}^{-1}$, $1 \times 10^{-3} \text{ Ms}^{-1}$
 - $2 \times 10 \text{ Ms}^{-1}$, $2 \times 10^{-3} \text{ Ms}^{-1}$
 - $4 \times 10^{-3} \text{ Ms}^{-1}$, $2 \times 10^{-3} \text{ Ms}^{-1}$
5. Which is wrong about the rate of a reaction among the following?
- Rate of a reaction cannot be negative.
 - Rate of a reaction is change in concentration of the reactant per unit time per unit stoichiometric coefficient of that component.
 - Average rate and instantaneous rate are always different.
 - Rate may depend upon surface area of the reactants.
6. For a reaction $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$, it is observed that

$$-\frac{d[\text{NH}_3]}{dt} = K_1[\text{NH}_3]; +\frac{d[\text{N}_2]}{dt} = K_2[\text{NH}_3]$$

$$\text{and } +\frac{d[\text{H}_2]}{dt} = K_3[\text{NH}_3]$$

The correct relation between K_1 , K_2 and K_3 is

- (a) $K_1 = K_2 = K_3$
- (b) $2K_1 = 3K_2 = 6K_3$
- (c) $3K_1 = 6K_2 = 2K_3$
- (d) $6K_1 = 3K_2 = 2K_3$

7. Rate constant of a reaction depends upon

- (a) Concentration
- (b) Pressure
- (c) Temperature
- (d) All

8. Sometimes, reaction rates can be estimated by knowing

- (a) the atmospheric pressure
- (b) the number of bond changes
- (c) the number of apparatus used in the experiment
- (d) the net ionic equation

9. The rate expression for the reaction: $\text{A(g)} + \text{B(g)} \rightarrow \text{C(g)}$ is $\text{rate} = K \cdot C_A^2 \cdot C_B^{1/2}$. What changes in the initial concentration of A and B will cause the rate of reaction increase by a factor of eight?

- (a) $C_A \times 2$; $C_B \times 2$
- (b) $C_A \times 2$; $C_B \times 4$
- (c) $C_A \times 1$, $C_B \times 4$
- (d) $C_A \times 4$, $C_B \times 1$

10. The rate constant of a second-order reaction is $10^{-2} \text{ lit mole}^{-1} \text{ s}^{-1}$. The rate constant, when expressed in $\text{ml molecule}^{-1} \text{ min}^{-1}$, is ($N_A = 6 \times 10^{23}$)

- (a) 0.01
- (b) 1.0×10^{-21}
- (c) 1.0×10^{21}
- (d) 3.6×10^{20}

11. Rate of a reaction: $\text{A} + 2\text{B} \rightarrow \text{P}$ is $2 \times 10^{-2} \text{ M/min}$, when concentrations of each A and B are 1.0 M. If the rate of

reaction, $r = K[\text{A}]^2[\text{B}]$, the rate of reaction when half of the B has reacted should be

- (a) $5.625 \times 10^{-3} \text{ M/min}$
- (b) $3.75 \times 10^{-3} \text{ M/min}$
- (c) 9.375 M/min
- (d) $2.5 \times 10^{-3} \text{ M/min}$

12. For the reaction: $\text{A}_2(\text{g}) \rightarrow \text{B(g)} + \frac{1}{2} \text{C(g)}$, pressure of the system increases from 100 to 120 mm in 5 min. The average rate of disappearance of A_2 (in mm/min) in this time interval is

- (a) 4
- (b) 8
- (c) 2
- (d) 16

13. The condition at which average rate can be equal to instantaneous rate of the reaction is

- (a) $\Delta n = 0$
- (b) $\Delta t \rightarrow 0$
- (c) reaction is elementary
- (d) reaction is complex

14. The rate constant for the reaction, $\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, is $3.0 \times 10^{-5} \text{ s}^{-1}$. If the rate of reaction is $2.4 \times 10^{-5} \text{ mol litre}^{-1} \text{ s}^{-1}$, then the concentration of N_2O_5 (in mole litre⁻¹) is

- (a) 1.4
- (b) 1.2
- (c) 0.04
- (d) 0.8

15. Consider the chemical reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$. The rate of this reaction can be expressed in terms of time derivative of concentration of $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$ or $\text{NH}_3(\text{g})$. Identify the correct relationship amongst the rate expressions

$$\begin{aligned} \text{(a) rate} &= -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} \\ &= +\frac{1}{2} \frac{d[\text{NH}_3]}{dt} \end{aligned}$$

$$\begin{aligned} \text{(b) rate} &= -\frac{d[\text{N}_2]}{dt} = -3 \frac{d[\text{H}_2]}{dt} \\ &= +2 \frac{d[\text{NH}_3]}{dt} \end{aligned}$$

$$\begin{aligned} \text{(c) rate} &= -\frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} \\ &= +\frac{1}{2} \frac{d[\text{NH}_3]}{dt} \end{aligned}$$

$$\begin{aligned} \text{(d) rate} &= -\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} \\ &= +\frac{d[\text{NH}_3]}{dt} \end{aligned}$$

16. For the reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is $10^{-3} \text{ kg h}^{-1}$. The rate of consumption of H_2 under same condition is
- $1.5 \times 10^{-3} \text{ kg h}^{-1}$
 - $1.76 \times 10^{-4} \text{ kg h}^{-1}$
 - $6.67 \times 10^{-4} \text{ kg h}^{-1}$
 - $3 \times 10^{-3} \text{ kg h}^{-1}$
17. The reaction: $2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow 2\text{FeCl}_2 + \text{SnCl}_4$ is a reaction of
- zero order
 - first order
 - second order
 - third order
18. Which one of the following statement is wrong regarding molecularity of a reaction?
- It may be 1, 2 or 3.
 - It may be either a whole number or fraction.
 - It is the number of molecules of the reactants taking part in a single-step chemical reaction.
 - It depends on the rate determining step reaction in the reaction.
19. The incorrect statement is
- Rate law is an experimental fact whereas law of mass action is a theoretical proposal.
 - Rate law is always different from the expression of law of mass action.
 - Rate law is more informative than law of mass action for the development of mechanism.
 - Order of a reaction is equal to the sum of powers of concentration terms in the rate law.
20. The rate constant is numerically the same for first-, second- and third-order reactions, respectively. Which one is true for rate of three reactions, if concentration of reactant is lesser than 1 M?
- $r_1 = r_2 = r_3$
 - $r_1 > r_2 > r_3$
 - $r_1 < r_2 < r_3$
 - none
21. For the elementary reaction: $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, the volume of a container is tripled. The rate becomes
- 3 times
 - 27 times
 - $\frac{1}{27}$ times
 - as initial
22. A zero-order reaction is one
- in which reactants do not react.
 - in which one of the reactants is in large excess.
 - whose rate does not change with time.
 - whose rate increases with time.
23. Which of the following is incorrect statement?
- Stoichiometry of a reaction tells about the order of the elementary reactions.
 - For a zero-order reaction, rate and the rate constant are identical.
 - A zero-order reaction is controlled by factors other than concentration of reactants.
 - A zero-order reaction is always elementary reaction.
24. If the rate of a gaseous reaction is independent of partial pressure of reactant, the order of reaction is
- 0
 - 1
 - 2
 - 3

25. When the concentration of reactant in the reaction: $A \rightarrow B$ is increased by 8 times, the rate increases only by 2 times. The order of reaction is

(a) 3 (b) $\frac{1}{3}$
(c) 2 (d) $\frac{1}{2}$

26. The rate constant (K) for the reaction: $2A + B \rightarrow \text{Products}$, was found to be $2.58 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$ after 15 s, $2.59 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$ after 30 s and $2.57 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$ after 50 s. The overall order of the reaction is

(a) 0 (b) 1
(c) 2 (d) 3

27. Which of the following statements is incorrect?

- (a) The order of reaction is the sum of powers of all the concentration terms in the rate equation.
(b) The order of reaction with respect to one reactant is the ratio of the change of logarithm of the rate of the reaction to the change in the logarithm of the concentration of the particular reactant, keeping the concentrations of all other reactants constant.
(c) Orders of reactions can be whole numbers or fractional numbers.
(d) The order of a reaction can only be determined from the stoichiometric equation for the reaction.

28. For a chemical reaction: $X \rightarrow Y$, the rate of reaction increases by a factor of 1.837 when the concentration of X is increased by 1.5 times. The order of the reaction with respect to X is

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

29. The order of a reaction is zero. It will be definitely

- (a) exothermic
(b) endothermic
(c) elementary
(d) complex

30. Which one of the following statements for order of a reaction is not correct?

- (a) Order can be determined experimentally.
(b) Order of reaction is equal to sum of the powers of concentration terms in differential rate law.
(c) It is not affected with the stoichiometric coefficient of the reactants.
(d) Order cannot be fractional.

31. Select the rate law that corresponds to the data shown for the following reaction:

Exp. no.	$[A_0]$ (M)	$[B_0]$ (M)	Initial rate (M s ⁻¹)
1	0.012	0.035	0.1
2	0.024	0.070	0.8
3	0.024	0.035	0.1
4	0.012	0.070	0.8

- (a) $r = K[B]^3$
(b) $r = K[B]^4$
(c) $r = K[A][B]^3$
(d) $r = K[A]^2[B]^3$

32. The rate law for a reaction between the substances A and B is given by rate = $K[A]^n[B]^m$. On doubling the concentration of A and halving the concentration of B , the ratio of the new rate to the earlier rate of the reaction will be as

- (a) $1/2^{m+n}$
(b) $(m+n)$
(c) $(n-m)$
(d) $2^{(n-m)}$

33. Which of the following reactions is of fractional order?

- (a) Decomposition of N_2O_5
(b) Isomerization: $CH_3-NC \rightarrow CH_3-CN$

- (c) Thermal decomposition of $\text{CH}_3 - \text{CHO}$
 (d) Isomerization: $\triangle \rightarrow \text{CH}_3 - \text{CH} = \text{CH}_2$

34. For a reaction $2\text{A} + \text{B} + 3\text{C} \rightarrow \text{D} + 3\text{E}$, the following data is obtained:

Reaction	Concentration in mole per litre			Initial rate of formation of D (torr s ⁻¹)
	A	B	C	
1	0.01	0.01	0.01	2.5×10^{-4}
2	0.02	0.01	0.01	1.0×10^{-3}
3	0.01	0.02	0.01	2.5×10^{-4}
4	0.01	0.02	0.02	5.0×10^{-4}

The order with respect to A, B and C are, respectively,

- (a) 0, 1, 2
 (b) 2, 0, 1
 (c) 1, 0, 2
 (d) 2, 1, 1
35. In the gas phase, two butadiene molecules can dimerize to give larger molecules according to the reaction: $2\text{C}_4\text{H}_6(\text{g}) \rightarrow \text{C}_8\text{H}_{12}(\text{g})$. The rate law for this reaction is, $r = K[\text{C}_4\text{H}_6]^2$ with $K = 6.1 \times 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$ at the temperature of reaction. The rate of formation of C_8H_{12} , when the concentration of C_4H_6 is 0.02 M, is
- (a) $2.44 \times 10^{-5} \text{ Ms}^{-1}$
 (b) $1.22 \times 10^{-5} \text{ Ms}^{-1}$
 (c) $1.22 \times 10^{-3} \text{ Ms}^{-1}$
 (d) $2.44 \times 10^{-6} \text{ Ms}^{-1}$
36. For the reactions of first, second and third orders, $K_1 = K_2 = K_3$, where concentrations are expressed in 'M'. The correct relation in K_1 , K_2 and K_3 , if concentrations are expressed in mol ml^{-1} , is
- (a) $K_1 = K_2 = K_3$
 (b) $K_1 \times 10^{-3} = K_2 = K_3 \times 10^3$
 (c) $K_1 = K_2 \times 10^{-3} = K_3 \times 10^{-6}$
 (d) $K_1 \times 10^3 = K_2 \times 10^{-3} = K_3$

37. The rate of the reaction $3\text{A} + 2\text{B} \rightarrow \text{Products}$ is given by the rate expression: rate $= K[\text{A}][\text{B}]^2$. If A is taken in large excess, the reaction starts obeying

- (a) third-order kinetics
 (b) second-order kinetics
 (c) first-order kinetics
 (d) zero-order kinetics
38. The hydrolysis of an ester was carried out separately with 0.05 M HCl and 0.05 M H_2SO_4 . Which of the following is true for the first-order rate constant of the reaction?
- (a) $K_{\text{HCl}} > K_{\text{H}_2\text{SO}_4}$
 (b) $K_{\text{HCl}} < K_{\text{H}_2\text{SO}_4}$
 (c) $K_{\text{HCl}} = K_{\text{H}_2\text{SO}_4}$
 (d) $K_{\text{H}_2\text{SO}_4} = (K_{\text{HCl}})^2$
39. The hydrolysis of methyl formate in acid solution has rate expression: rate $= K[\text{HCOOCH}_3][\text{H}^+]$. The balanced equation is $\text{HCOOCH}_3 + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{CH}_3\text{OH}$. The rate law contains $[\text{H}^+]$ though the balanced equation does not contain H^+ , because
- (a) more for convenience to express the rate law.
 (b) H^+ ion is a catalyst of the reaction.
 (c) H^+ ion is an important constituent of any reaction.
 (d) all acids contain H^+ ions.
40. In the acid hydrolysis reaction: $\text{A} + \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{Products}$, where $[\text{H}^+] = 0.1 \text{ M}$ and H_2O is present in large excess, the apparent rate constant is $1.5 \times 10^{-5} \text{ s}^{-1}$.

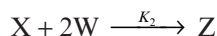
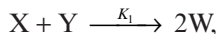
$$r = K[\text{A}][\text{H}_2\text{O}][\text{H}^+] = K_{\text{app}}[\text{A}]$$

The true rate constant (third-order rate constant) of reaction is

- (a) $2.7 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$
 (b) $1.5 \times 10^{-4} \text{ M}^{-2} \text{ s}^{-1}$
 (c) $2.7 \times 10^{-6} \text{ M}^{-2} \text{ s}^{-1}$
 (d) $2.7 \times 10^{-6} \text{ M}^2 \text{ s}^{-1}$

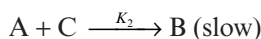
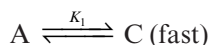
Mechanism of Reaction

41. A complex reaction: $2X + Y \rightarrow Z$, takes place in two steps



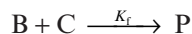
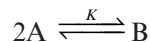
If $K_1 \ll K_2$, order of reaction will be

- (a) 1 (b) 2
(c) 3 (d) 0
42. For the reaction: $A \xrightarrow{K_1} B \xrightarrow{K_2} C \xrightarrow{K_3} D$, where $K_3 > K_2 > K_1$; the rate of formation of D is determined by
- (a) the rate of reaction: $A \rightarrow B$
(b) the rate of reaction: $B \rightarrow C$
(c) the rate reaction: $C \rightarrow D$
(d) the rate of reaction: $A \rightarrow B$ with rate constant K_1 , K_2 , K_3
43. For hypothetical reaction: $A \rightarrow B$ takes place according to



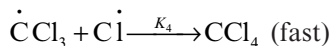
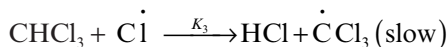
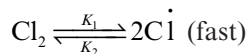
the rate of reaction is (K_1 is equilibrium constant)

- (a) $K_2[B][C]$ (b) $K_1K_2[A]$
(c) $K_1K_2[A]^2$ (d) $K_1[B][C]$
44. The overall rate, $+\frac{d[P]}{dt}$, for the reaction: $2A + C \rightarrow P$, from the mechanism



where, K = equilibrium constant and K_f = forward rate constant, is given by

- (a) $\frac{d[P]}{dt} = K K_f [A]^2 [C]$
(b) $\frac{d[P]}{dt} = K [A][B]$
(c) $\frac{d[P]}{dt} = K_f [B][C]$
(d) $\frac{d[P]}{dt} = K K_f [A]^2 [B][C]$
45. The suggested mechanism for the reaction: $CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$, is



The experimental rate law consistent with the mechanism is

- (a) $\text{rate} = K_3 [CHCl_3][Cl_2]$
(b) $\text{rate} = K_4 [CCl_3][Cl]$
(c) $\text{rate} = K_{eq} [CHCl_3][Cl_2]$
(d) $\text{rate} = K_3 K_{eq}^{1/2} [CHCl_3][Cl_2]^{1/2}$

Integrated Rate Law

46. For a zero-order reaction,
- (a) the reaction rate is doubled when the initial concentration is doubled.
(b) the time for half change is half the time taken for completion of the reaction.
(c) the time for half change is independent of the initial concentration.
(d) the time for completion of the reaction is independent of the initial concentration.
47. The time taken in 75% completion of a zero-order reaction is 10 h. In what time, the reaction will be 90% completed?
- (a) 12.0 h (b) 16.6 h
(c) 10.0 h (d) 20.0 h
48. A zero-order reaction $A \rightarrow B$. At the end of 1 h, A is 75% reacted. How much of it will be left unreacted at the end of 2 h.
- (a) 12.5% (b) 6.25%
(c) 3.12% (d) 0%

49. Which of the following represents the expression for $3/4^{\text{th}}$ the life of a first-order reaction?

(a) $\frac{k}{2.303} \log \frac{4}{3}$
 (b) $\frac{2.303}{k} \log \frac{4}{3}$
 (c) $\frac{2.303}{k} \log 4$
 (d) $\frac{2.303}{k} \log 3$

50. The decomposition of H_2O_2 can be followed by titration with KMnO_4 and is found to be a first-order reaction. The rate constant is 4.5×10^{-2} . In an experiment, the initial titre value was 25 ml. The titre will be 5 ml after

(a) $4.5 \times 10^{-2} \times 5 \text{ min}$
 (b) $\frac{\ln 5}{4.5 \times 10^{-2}} \text{ min}$
 (c) $\frac{\ln(5/4)}{4.5 \times 10^{-2}} \text{ min}$
 (d) $4.5 \times 1.25 \text{ min}$

51. For the first-order reaction $t_{99\%} = x \times t_{90\%}$. The value of 'x' will be

(a) 10
 (b) 6
 (c) 3
 (d) 2

52. The half-life of a first-order reaction is 10 min. In what time, the rate of reaction will decrease from $6.0 \times 10^{21} \text{ molecules ml}^{-1} \text{ s}^{-1}$ to $4.5 \times 10^{25} \text{ molecules litre}^{-1} \text{ min}^{-1}$? ($N_A = 6.0 \times 10^{23}$)

(a) 10 min
 (b) 20 min
 (c) 30 min
 (d) 40 min

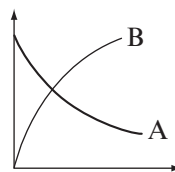
53. For the second-order reaction: $2\text{A} \rightarrow \text{B}$, time taken for the $[\text{A}]$ to fall to one-fourth value is how many times the time it takes for $[\text{A}]$ to fall to half of its initial value?

(a) two
 (b) three
 (c) four
 (d) seven

54. The half-life for a given reaction is doubled if the initial concentration of the reactant is doubled. The order of the reaction is

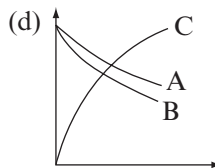
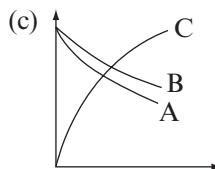
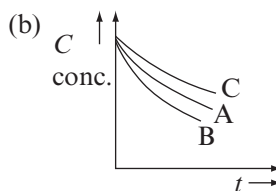
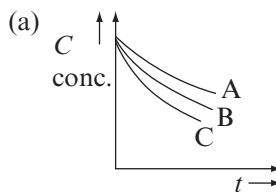
(a) 0
 (b) 1
 (c) 2
 (d) 3

55. At the point of intersection of the two curves shown, the concentration of B is given as ($\text{A} \rightarrow n\text{B}$)



(a) $\frac{A_0}{n}$
 (b) $\frac{A_0}{n-1}$
 (c) $\frac{nA_0}{n+1}$
 (d) $\frac{n-1}{n+1} A_0$

56. Which of the following graphs is correct representation for the reaction of type: $\text{A} + 2\text{B} \rightarrow \text{C}$?



57. For a given reaction, the concentration of the reactant plotted against time gave a straight line with negative slope. The order of the reaction is

- (a) 3 (b) 2
(c) 1 (d) 0
58. For a certain reaction involving a single reactant, it is found that $C_0\sqrt{T}$ is constant, where C_0 is the initial concentration of the reactant and T is the half-life. What is the order of the reaction?
(a) 1 (b) 1.5
(c) 2 (d) 3
59. For a certain reaction of order ' n ', the time for half change, $t_{1/2}$, is given by $t_{1/2} = \frac{[2 - \sqrt{2}]}{k} \times C_0^{1/2}$, where k is the rate constant and C_0 is the initial concentration. The value of n is
(a) 1 (b) 2
(c) 1.5 (d) 0.5
60. The reaction: $\text{H}_3\text{C}-\text{CH}_2-\text{NO}_2 + \text{OH}^- \rightarrow \text{H}_3\text{C}-\text{CH}^--\text{NO}_2 + \text{H}_2\text{O}$ obeys the rate law for pseudo first-order kinetics in the presence of a large excess of hydroxide ion. If 1% of nitro ethane undergoes reaction in half a minute when the reactant concentration is 0.002 M, what is the pseudo first-order rate constant?
(a) $2 \times 10^{-2} \text{ min}^{-1}$
(b) $6 \times 10^{-3} \text{ min}^{-1}$
(c) $4 \times 10^{-2} \text{ min}^{-1}$
(d) $1 \times 10^{-2} \text{ min}^{-1}$
61. Which of the following is an incorrect statement about first-order reaction?
(a) The time for 93.75% completion of reaction is two times the time for 75% completion of reaction.
(b) Half-life is the half of the time of complete reaction.
(c) About 63% reaction completes in time, equal to $1/K$.
(d) The time for 90% reaction will be equal to $2.303/K$, irrespective of initial concentration of the reactant.
62. For the first-order reaction: $\text{A}(\text{g}) \rightarrow 2\text{B}(\text{g}) + \text{C}(\text{g})$, the total pressure, after time t from the start of reaction with A, is P and after infinite time, it is, P_∞ . Then the rate constant of the reaction is
(a) $\frac{1}{t} \ln \frac{P_\infty}{P}$
(b) $\frac{1}{t} \cdot \ln \frac{2P_\infty}{3(P_\infty - P)}$
(c) $\frac{1}{t} \cdot \ln \frac{2P_\infty}{3P_\infty - P}$
(d) $\frac{1}{t} \ln \frac{2P_\infty}{P_\infty - 3P}$
63. As the initial concentration increases from 0.75 to 1.55 M in a reaction, $t_{1/2}$ decreases from 60 to 29 s. The order of the reaction is
(a) zero (b) first
(c) second (d) third
64. Which is correct about first-order reaction?
(a) $t_{0.5} = 50 \text{ s}$, $t_{0.75} = 100 \text{ s}$
(b) $t_{0.5} = 50 \text{ s}$, $t_{0.75} = 75 \text{ s}$
(c) $t_{0.5} = 50 \text{ s}$, $t_{0.75} = 50 \text{ s}$
(d) $t_{0.5} = 50 \text{ s}$, $t_{0.25} = 25 \text{ s}$
65. $t_{1/2}$ of a reaction: $\text{A} \rightarrow \text{Products}$ (order = $\frac{3}{2}$) is represented by $t_{1/2} \propto \frac{1}{[A_0]^m}$. The value of m is
(a) 0.5 (b) -0.5
(c) 1.5 (d) -1.5
66. If $t_{1/2}$ of a second-order reaction is 1.0 h. After what time, the amount will be 25% of the initial amount?
(a) 1.5 h (b) 2 h
(c) 2.5 h (d) 3 h
67. In a first-order reaction, the activity of reactant drops from 800 mol/dm^3 to 50 mol/dm^3 in $2 \times 10^4 \text{ s}$. The rate constant of the reaction, in s^{-1} , is

- (a) 1.386×10^{-4}
 (b) 1.386×10^{-3}
 (c) 1.386×10^{-5}
 (d) 5.0×10^3
68. The decomposition of N_2O_5 according to the equation: $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ is a first-order reaction. After 30 min, from the start of the decomposition in a closed vessel, the total pressure developed is found to be 300 mm of Hg and on complete decomposition, the total pressure is 600 mm of Hg. The rate constant of the reaction is ($\ln 1.2 = 0.18$)
- (a) $6.0 \times 10^{-3} \text{ min}^{-1}$
 (b) 0.18 min^{-1}
 (c) $6.0 \times 10^{-2} \text{ min}^{-1}$
 (d) $2.5 \times 10^{-3} \text{ min}^{-1}$
69. For a first-order reaction, the ratio of time for 99.9% of the reaction to complete and half of the reaction to complete is
- (a) 1 (b) 2
 (c) 4 (d) 10
70. For the second-order reaction: $\text{A} + \text{B} \rightarrow \text{Products}$, the rate constant, k , is given as
- $$k = \frac{2.303}{(a-b)t} \log \frac{b(a-x)}{a(b-x)},$$
- where, a and b are the initial concentrations of 'A' and 'B' and x is the change in concentration after time, t . If $b \gg a$, the reaction reduces to
- (a) first order w.r.t. 'A'
 (b) zero order w.r.t. 'A'
 (c) first order w.r.t. 'B'
 (d) overall zero order
71. For a first-order reaction, $t_{0.75} = 1386 \text{ s}$. Its specific reaction rate is
- (a) 10^{-3} s^{-1} (b) 10^{-2} s^{-1}
 (c) 10^{-4} s^{-1} (d) 10^{-5} s^{-1}
72. It takes 40 min for the completion of 50% of the reaction: $\text{A} \rightarrow \text{Products}$. For the completion of next 50% of the reaction, time taken is 80 min. The order of the reaction is
- (a) 2 (b) 0
 (c) 3 (d) 1
73. At 325°C , 1, 3-butadiene dimerizes according to the equation: $2\text{C}_4\text{H}_6(\text{g}) \rightarrow \text{C}_8\text{H}_{12}(\text{g})$. It is found that the partial pressure, P , of the reactant obeys the law: $\frac{1}{P} = kt + \frac{1}{P_0}$. Order of the reaction is
- (a) 1 (b) 0.5
 (c) 2 (d) 1.5
74. The half-life for the first-order reaction: $\text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g})$ is 30 min. If the volume of $\text{O}_2(\text{g})$ collected is 100 ml after a long time, then the volume of $\text{O}_2(\text{g})$ collected (at the same pressure and temperature) after 60 min from the start of reaction is
- (a) 25 ml (b) 12.5 ml
 (c) 75 ml (d) 50 ml
75. The decomposition of hydrogen peroxide in aqueous solution is a first-order reaction:
- | | | |
|-----------------------|------|------|
| Time in min | 0 | 10 |
| Volume (V , in ml) | 25.0 | 20.0 |
- where V is the number of ml of potassium permanganate required to decompose a definite volume of hydrogen peroxide solution, at the given time. From the following data, the rate constant (min^{-1}) of reaction is ($\ln 5 = 1.6$, $\ln 2 = 0.7$)
- (a) 0.09 (b) 0.02
 (c) 0.2 (d) 0.16

Parallel, Sequential and Reversible Reactions

76. For irreversible elementary reactions in parallel: $A \xrightarrow{K_1} R$ and $A \xrightarrow{K_2} S$, the rate of disappearance of reactant 'A' is

- (a) $(k_1 - k_2) C_A$
 (b) $(k_1 + k_2) C_A$
 (c) $1/2 (k_1 + k_2) C_A$
 (d) $k_1 C_A$

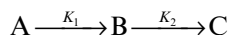
77. For the consecutive unimolecular-type first-order reaction: $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, the concentration of component 'R', C_R , at any time, 't' is given by

$$C_R = C_{AO} \cdot K_1 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)} \right]$$

If $C_A = C_{AO}$, $C_R = C_S = 0$ at $t = 0$, the time at which the maximum concentration of 'R' occurs is

- (a) $t_{\max} = \frac{k_2 - k_1}{\ln(k_2 / k_1)}$
 (b) $t_{\max} = \frac{\ln(k_2 / k_1)}{k_2 - k_1}$
 (c) $t_{\max} = \frac{e^{k_2 / k_1}}{k_2 - k_1}$
 (d) $t_{\max} = \frac{e^{k_2 - k_1}}{k_2 - k_1}$

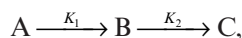
78. Consider the following consecutive first-order reaction:



If $K_1 = 0.01 \text{ min}^{-1}$ and $K_1:K_2 = 1:2$, after what time from the start of reaction, the concentration of 'B' will be maximum? ($\ln 2 = 0.7$)

- (a) 70 min (b) 140 min
 (c) 35 min (d) 700 min

79. For the consecutive first-order reactions:



in what condition, $[C] = [A_0] \cdot (1 - e^{-K_1 t})$?

- (a) $K_1 < K_2$ (b) $K_1 < < K_2$
 (c) $K_2 < K_1$ (d) $K_2 < < K_1$

80. When excess toluene- α -d ($C_6H_5CH_2D$) was photochemically monochlorinated at 80°C with 0.1 mole of chlorine, there was obtained 0.0212 mole DCl and 0.0848 mole HCl. What is the value of the isotope effect, K^H/K^D ?

- (a) $\frac{1}{4}$ (b) $\frac{4}{1}$
 (c) $\frac{5}{1}$ (d) $\frac{1}{5}$

Dependence of Reaction Rate on Temperature and Catalyst

81. The activation energy for a chemical reaction is primarily dependent on

- (a) temperature
 (b) nature of the reacting species
 (c) collision frequency
 (d) concentration of reactants

82. The activation energy of a reaction is zero. The rate constant of the reaction

- (a) increases with increase of temperature
 (b) decreases with increase of temperature

- (c) decreases with decrease of temperature
 (d) is nearly independent of temperature

83. The activation energy of a reaction can be lowered by

- (a) increasing temperature
 (b) lowering temperature
 (c) adding a catalyst
 (d) removing one or more products.

84. At a certain temperature, the reaction between NO and O_2 to form NO_2 is fast,

while that between CO and O₂ is slow. It may be concluded that

- (a) NO is more reactive than CO.
 - (b) CO is smaller in size than NO.
 - (c) activation energy for the reaction: $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ is less.
 - (d) activation energy for the reaction: $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ is high.
- 85.** Rate of which type of elementary reaction increases with increase in temperature?
- (a) Thermal
 - (b) Exothermic
 - (c) Endothermic
 - (d) All
- 86.** In gaseous reactions important for the understanding of the upper atmosphere, H₂O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and E_a is 77 kJ/mol, then E_a for the bimolecular recombination of two OH radicals to form H₂O and O is
- (a) 149 kJ/mol
 - (b) 72 kJ/mol
 - (c) 5 kJ/mol
 - (d) 7 kJ/mol
- 87.** The rate constant is given by the equation: $K = P \cdot A \cdot e^{-E_a/RT}$. Which factor should register a decrease for the reaction to proceed more rapidly?
- (a) T
 - (b) A
 - (c) E_a
 - (d) P
- 88.** According to the collisions theory, the rate of reaction increases with temperature due to
- (a) increase in number of collisions between reactant molecules.
 - (b) increase in speed of reacting molecules.
 - (c) increase in number of molecules having sufficient energy for reaction.
 - (d) decrease in activation energy of reaction.
- 89.** Select the incorrect statement among the following.
- (a) It is possible to change the rate constant for a reaction by changing the temperature.
 - (b) The rate constant for a reaction is independent of reactant concentrations.
 - (c) The rate of a catalysed reaction is always independent from the concentration of the catalyst.
 - (d) In multistep reactions, the rate determining step is the slowest one.
- 90.** On increasing the temperature, half-life of reactions
- (a) remains unchanged
 - (b) increases
 - (c) decreases
 - (d) increases or decreases
- 91.** According to the Arrhenius equation, straight line is to be obtained by plotting the logarithm of the rate constant of a chemical reaction ($\log K$) against
- (a) T
 - (b) $\log T$
 - (c) $\frac{1}{T}$
 - (d) e^T
- 92.** The rate of a reaction is approximately doubled for every 10°C rise in temperature. If the temperature is raised by 50°C, the reaction rate increases by about
- (a) 10 times
 - (b) 16 times
 - (c) 32 times
 - (d) 64 times
- 93.** In general, the rate of a reaction can be increased by all the factors except
- (a) increasing the temperature
 - (b) increasing the concentration of reactants
 - (c) increasing the activation energy
 - (d) using a catalyst
- 94.** The rate of chemical reactions is independent of
- (a) molecularity
 - (b) nature of reactants
 - (c) concentration of reactants
 - (d) temperature of reaction

95. The activation energies of two reactions are E_1 and E_2 with $E_1 > E_2$. If the temperature of the reacting system is increased from T_1 (rate constants are K_1 and K_2) to T_2 (rate constants are K'_1 and K'_2), predict which of the following alternative is correct?
- (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) $K'_1 < K'_2$
96. Which of the following statements is not correct?
- (a) The efficiency of a solid catalyst depends upon its surface area.
 (b) Catalyst operates by providing alternate path for the reaction that involves lower activation energy.
 (c) Catalyst lowers the energy of activation of the forwards direction without affecting the energy of activation of the backward direction.
 (d) Catalyst does not affect the overall enthalpy change of the reaction.
97. Collision theory of chemical reactions explains
- (a) rate of reactions
 (b) order of reactions
 (c) molecularity of reactions
 (d) all of these
98. The values of enthalpies of reactants and products are x and y J/mol, respectively. If the activation energy for the backward reaction is z J/mol, then the activation energy for forward reaction will be (in J/mol)
- (a) $x - y - z$ (b) $x - y + z$
 (c) $y - x - z$ (d) $y - x + z$
99. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, 104.4 kJ/mol and $6.0 \times 10^{14} \text{ s}^{-1}$, respectively. The value of the rate constant as $T \rightarrow \infty$, is
- (a) $2.0 \times 10^{18} \text{ s}^{-1}$ (b) $6.0 \times 10^{14} \text{ s}^{-1}$
 (c) infinity (d) $3.0 \times 10^{-4} \text{ s}^{-1}$
100. If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process: $\text{AB} + h\nu \rightarrow \text{AB}^*$, the rate of formation of AB^* is directly proportional to
- (a) C (b) I
 (c) I^2 (d) $C \cdot I$

Answer Keys – Exercise I

Rate of Reaction, Rate Law, Order and Molecularity of a Reaction

1. (a) 2. (c) 3. (b) 4. (d) 5. (c) 6. (c) 7. (c) 8. (b) 9. (b) 10. (b)
 11. (a) 12. (b) 13. (b) 14. (d) 15. (a) 16. (b) 17. (d) 18. (b) 19. (b) 20. (b)
 21. (c) 22. (c) 23. (d) 24. (a) 25. (b) 26. (c) 27. (d) 28. (b) 29. (d) 30. (d)
 31. (a) 32. (d) 33. (c) 34. (b) 35. (a) 36. (c) 37. (b) 38. (b) 39. (b) 40. (c)

Mechanism of Reaction

41. (b) 42. (a) 43. (c) 44. (a) 45. (d)

Integrated Rate Law

46. (b) 47. (a) 48. (d) 49. (c) 50. (b) 51. (d) 52. (c) 53. (b) 54. (a) 55. (c)
56. (d) 57. (d) 58. (d) 59. (d) 60. (a) 61. (b) 62. (b) 63. (c) 64. (a) 65. (a)
66. (a) 67. (a) 68. (a) 69. (d) 70. (a) 71. (a) 72. (a) 73. (c) 74. (c) 75. (b)

Parallel, Sequential and Reversible Reactions

76. (b) 77. (b) 78. (a) 79. (b) 80. (b)

Dependence of Reaction Rate on Temperature and Catalyst

81. (b) 82. (d) 83. (c) 84. (c) 85. (d) 86. (c) 87. (c) 88. (c) 89. (c) 90. (c)
91. (c) 92. (c) 93. (c) 94. (a) 95. (b) 96. (c) 97. (a) 98. (d) 99. (b) 100. (b)
-

EXERCISE II (JEE ADVANCED)

Section A (Only one Correct)

1. The rate of a reaction may be expressed as: $+\frac{1}{2} \frac{d[C]}{dt} = -\frac{1}{3} \frac{d[D]}{dt} = +\frac{1}{4} \frac{d[A]}{dt} = -\frac{d[B]}{dt}$. The reaction is

- (a) $4A + B \rightarrow 2C + 3D$
 (b) $B + 3D \rightarrow 4A + 2C$
 (c) $4A + 2C \rightarrow B + 3D$
 (d) $2A + 3B \rightarrow 4C + D$

2. For a reversible reaction: $2NO_2 \xrightleftharpoons[K_2]{K_1} N_2O_4$, the rate of disappearance of NO_2 is equal to

- (a) $\frac{2k_1}{k_2} [NO_2]^2$
 (b) $2K_1[NO_2]^2 - 2K_2[N_2O_4]$
 (c) $2K_1[NO_2]^2 - K_2[N_2O_4]$
 (d) $(2K_1 - K_2) [NO_2]$

3. For a gaseous reaction: $A(g) \rightarrow \text{Products}$ (order = n), the rate may be expressed as:

- (i) $-\frac{dP_A}{dt} = K_1 \cdot P_A^n$
 (ii) $-\frac{1}{V} \frac{dn_A}{dt} = K_2 \cdot C_A^n$

The rate constants, K_1 and K_2 are related as (P_A and C_A are the partial pressure and molar concentration of A at time ' t ', respectively)

- (a) $K_1 = K_2$
 (b) $K_2 = K_1 \cdot (RT)^n$
 (c) $K_2 = K_1 \cdot (RT)^{1-n}$
 (d) $K_2 = K_1 \cdot (RT)^{n-1}$

4. For the reaction: $H_2 + I_2 \xrightleftharpoons[K_2]{K_1} 2HI$. The rate law expression is

- (a) $-\frac{1}{2} \frac{d[HI]}{dt} = K_1[H_2][I_2]$
 (b) $-\frac{1}{2} \frac{d[HI]}{dt} = \frac{K_1[HI]^2}{K_2[H_2][I_2]}$

- (c) $-\frac{1}{2} \frac{d[HI]}{dt} = K_1[H_2][I_2] - K_2[HI]^2$
 (d) $-\frac{1}{2} \frac{d[HI]}{dt} = K_2[HI]^2$

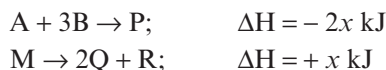
5. For the reaction: $aA + bB \rightarrow P$, $r = K[A]^a[B]^b$. If concentration of A is doubled, the rate is doubled. If concentration of B is doubled, the rate becomes four times. The correct relation is

- (a) $-\frac{d[A]}{dt} = -\frac{d[B]}{dt}$
 (b) $-\frac{d[A]}{dt} = +2 \cdot \frac{d[B]}{dt}$
 (c) $-2 \cdot \frac{d[A]}{dt} = +\frac{d[B]}{dt}$
 (d) $-\frac{d[A]}{dt} = +\frac{d[B]}{dt}$

6. The reaction: $A(g) + 2B(g) \rightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A and B are $P_A = 0.60$ atm and $P_B = 0.80$ atm. When $P_B = 0.20$ atm, the rate of reaction, relative to the initial rate is

- (a) $\frac{1}{16}$ (b) $\frac{1}{24}$
 (c) $\frac{1}{32}$ (d) $\frac{1}{48}$

7. The following reactions are occurring simultaneously in a vessel such that the temperature of the system is not changing:



If the rate of disappearance of 'B' is $y \text{ M s}^{-1}$, the rate of appearance of 'Q' (in M s^{-1}) is

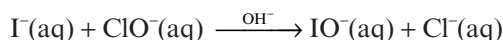
- (a) $y \text{ M s}^{-1}$ (b) $1.33 y \text{ M s}^{-1}$
 (c) $0.75 y \text{ M s}^{-1}$ (d) $2y \text{ M s}^{-1}$

8. What is the order of a chemical reaction: $A + 2B \rightarrow C$, if the rate formation of C increases by a factor of 2.82 on doubling the concentration of A and increases by a factor of 9 on tripling the concentration of B?
- (a) $\frac{7}{2}$ (b) $\frac{7}{4}$
(c) $\frac{5}{2}$ (d) $\frac{5}{4}$
9. For the chemical reaction between mercuric chloride and potassium oxalate, the mass of Hg_2Cl_2 precipitated in different time intervals, at $100^\circ C$, is given below:

Exp. no.	$[HgCl_2]_0$ (M)	$[K_2C_2O_4]_0$ (M)	Time (min)	Hg_2Cl_2 formed (g)
1	0.0836	0.404	65	0.0068
2	0.0836	0.202	120	0.0031
3	0.0418	0.404	60	0.0032

What is the rate law expression of this reaction?

- (a) $r = K[HgCl_2][K_2C_2O_4]$ (b) $r = K[HgCl_2]^2[K_2C_2O_4]$
(c) $r = K[HgCl_2]^2[K_2C_2O_4]^2$ (d) $r = K[HgCl_2][K_2C_2O_4]^2$
10. Iodide ion is oxidized to hypoiodite ion, IO^- , by hypochlorite ion, ClO^- , in basic solution as:



The following initial-rate experiments were run and, for each, the initial rate of formation of IO^- was determined.

Exp. no.	Initial concentration (mol/L)			Initial rate (mol L ⁻¹ s ⁻¹)
	I^-	ClO^-	OH^-	
1	0.010	0.020	0.010	12.2×10^{-2}
2	0.020	0.010	0.010	12.2×10^{-2}
3	0.010	0.010	0.010	6.1×10^{-2}
4	0.010	0.010	0.020	3.0×10^{-2}

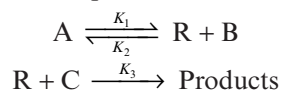
The correct rate law for the reaction is

- (a) $r = K[I^-][ClO^-][OH^-]^0$ (b) $r = K[I^-]^2[ClO^-]^2[OH^-]^0$
(c) $r = K[I^-][ClO^-][OH^-]$ (d) $r = K[I^-][ClO^-][OH^-]^{-1}$
11. For the chemical reaction: $A \rightarrow \text{products}$, the rate of disappearance of A is a given by

$$r_A = -\frac{dC_A}{dt} = \frac{K_1 \cdot C_A}{1 + K_2 \cdot C_A}$$

At low concentration of A, C_A , the reaction is of the first order with the rate constant

12. For a two-step reaction:



- (a) $\frac{K_1}{K_2}$ (b) K_1
(c) $\frac{K_2}{K_1}$ (d) $\frac{K_1}{K_1 + K_2}$

(where R is a reactive intermediate whose concentration is maintained at some low steady-state throughout the reaction), the rate law expression will be

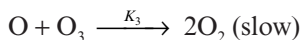
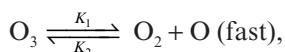
$$(a) \frac{dx}{dt} = \frac{k_1[A]}{1 + \frac{k_2[B]}{k_3[C]}}$$

$$(b) \frac{dx}{dt} = k_1[A]$$

$$(c) \frac{dx}{dt} = k_1[A]^2$$

$$(d) \frac{dx}{dt} = k_1[A][B][R]$$

13. The chemical reaction: $2O_3 \rightarrow 3O_2$ proceeds as



The rate law expression will be

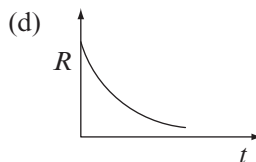
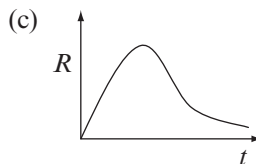
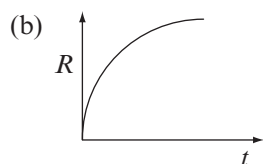
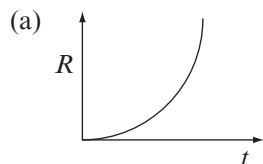
$$(a) \text{ rate} = K_1[O][O_3]$$

$$(b) \text{ rate} = K_1[O_3]$$

$$(c) \text{ rate} = \frac{K_1 \cdot K_3}{K_2} \frac{[O_3]^2}{[O_2]}$$

$$(d) \text{ rate} = K_3 \frac{[O_3]^2}{[O_2]}$$

14. The reaction: $X(g) \rightarrow Y(g)$ follows first-order kinetics. The correct graph representing the rate of formation (R) of Y(g) with time (t) is



15. The initial rate of a zero-order reaction: $A(g) \rightarrow 2B(g)$ is 0.01 M min^{-1} . If the initial concentration of 'A' is 0.1 M , the concentration of 'B' after 60 s is

(a) 0.09 M

(b) 0.01 M

(c) 0.02 M

(d) 1.2 M

16. For a zero-order reaction: $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$, the rate of reaction is 0.1 atm/s . Initially only $NH_3(g)$ was present at 3 atm and the reaction is performed at constant volume and temperature. The total pressure of gases after 10 s from the start of reaction will be

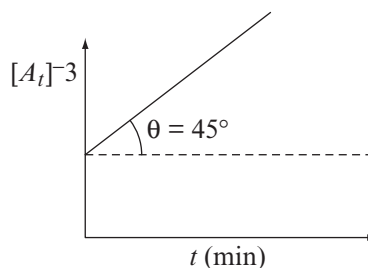
(a) 4 atm

(b) 5 atm

(c) 3.5 atm

(d) 4.5 atm

17. For the reaction: $3A \rightarrow 2B$, the following graph is obtained experimentally. The rate of reaction when $[A] = 0.2 \text{ M}$, is



(a) $4 \times 10^{-4} \text{ M min}^{-1}$

(b) $\frac{16}{9} \times 10^{-4} \text{ M min}^{-1}$

(c) $1.6 \times 10^{-3} \text{ M min}^{-1}$

(d) $\frac{16}{3} \times 10^{-3} \text{ M min}^{-1}$

18. A substance 'A' decomposes in solution following first-order kinetics. Flask 1 contains 1 l of 1 M solution of 'A' and flask 2 contains 100 ml of 0.6 M solution of 'A'. After 8.0 h, the concentration of 'A' in flask 1 becomes 0.25 M. In what time, the concentration of 'A' in flask 2 becomes 0.3 M?
- (a) 8.0 h (b) 3.2 h
(c) 4.0 h (d) 9.6 h
19. A kinetic study of the reaction: $A \rightarrow \text{products}$ provides the data: $t = 0$ s, $[A] = 2.00$ M; 500 s, 1.00 M; 1500 s, 0.50 M; 3500 s, 0.25 M. In the simplest possible way determine, whether this reaction is of
- (a) zero order (b) first order
(c) second order (d) third order
20. After 20% completion, the rate of reaction: $A \rightarrow \text{products}$, is 10 unit and after 80% completion, the rate is 0.625 unit. The order of the reaction is
- (a) zero (b) first
(c) second (d) third
21. At a certain temperature and fixed volume, the rate constant for the decomposition of $C_2H_6(g)$ into $C_2H_4(g)$ and $H_2(g)$ is $0.0015 \text{ Pa}^{-1} \text{ h}^{-1}$. If the initial pressure of $C_2H_6(g)$ is 3 bar, the time for the pressure of system (reaction mixture) to become 5 bar is
- (a) 0.01 s (b) 0.01 min
(c) 0.06 min (d) 36 s
22. For the irreversible reaction: $A \rightarrow \text{products}$ in a batch reactor, 80% reactant ($[A_0] = 1$ M) is converted in a 8 min run and conversion is 90% after 18 min. The order of this reaction is
- (a) 1 (b) 2
(c) 1/2 (d) 3/2
23. 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. The rate law expression for the sugar inversion can be written as
- (a) $r = K [\text{sugar}]^2 [H^+]^0$
(b) $r = K [\text{sugar}] [H^+]^2$
(c) $r = K [\text{sugar}] [H^+]$
(d) $r = K [\text{sugar}]^0 [H^+]^0$
24. Hydrolysis of ethyl acetate is catalysed by HCl. The rate is proportional to the concentration of both the ester and HCl. The rate constant is $0.1 \text{ M}^{-1} \text{ h}^{-1}$. What is the half-life, if the initial concentrations are 0.02 M for the ester and 0.01 M for the catalysing acid?
- (a) 347 h (b) 519 h
(c) 836 h (d) 693 h
25. The order of the reaction: $A \rightarrow \text{products}$ is 0.5. The time for complete reaction, T and time for 50% reaction, $t_{1/2}$ will be related as
- (a) $T = 2 \times t_{1/2}$
(b) $T = 4 \times t_{1/2}$
(c) $t_{1/2} = 0.3T$
(d) $t_{1/2} = 0.7T$
26. Two substances, 'A' and 'B' are initially present as $[A_0] = 8[B_0]$ and $t_{1/2}$ for the first-order decomposition of 'A' and 'B' are 10 and 20 min, respectively. If they start decomposing at the same time, after how much time, the concentration of both of them would be same?
- (a) 20 min (b) 40 min
(c) 60 min (d) 200 min
27. For a first-order reaction: $A \rightarrow \text{Product}$, the initial concentration of A is 0.1 M and after time 40 min, it becomes 0.025 M. What is the rate of reaction at reactant concentration 0.01 M?
- (a) $3.465 \times 10^{-4} \text{ mol lit}^{-1} \text{ min}^{-1}$
(b) $3.465 \times 10^{-5} \text{ mol lit}^{-1} \text{ min}^{-1}$
(c) $6.93 \times 10^{-4} \text{ mol lit}^{-1} \text{ min}^{-1}$
(d) $1.7325 \times 10^{-4} \text{ mol lit}^{-1} \text{ min}^{-1}$
28. The rate of change of concentration of 'B' for reaction: $A \rightarrow B$, is given as:

+ $\frac{d[B]}{dt} = K[A]^{1/3}$. The half-life period of the reaction will be

- (a) $\frac{3[A_0]^{2/3}(2^{2/3} - 1)}{2^{5/3} \cdot K}$
 (b) $\frac{3[A_0]^{2/3}(2^{2/3} - 1)}{2^{2/3} \cdot K}$
 (c) $\frac{3[A_0]^{2/3}(2^{2/3} - 1)^2}{2^{5/3} \cdot K}$
 (d) $\frac{2[A_0]^{2/3}(2^{2/3} - 1)}{3 \times 2^{2/3} \times K}$

29. A solution of N_2O_5 in CCl_4 yields by decomposition at $45^\circ C$, 4.8 ml of O_2 , 20 min after the start of the experiment and 9.6 ml of O_2 after a very long time. The decomposition obeys first-order kinetics. What volume of O_2 would have evolved, 40 min after the start?

- (a) 7.2 ml (b) 2.4 ml
 (c) 9.6 ml (d) 6.0 ml

30. The decomposition of NH_3 on tungsten surface follows zero-order kinetics. The half-life is 315 s for an initial pressure of 70 mm of NH_3 . If the initial pressure had been 150 mm, what would be the half-life?

- (a) 315 s (b) 472.5 s
 (c) 675 s (d) 630 s

31. A first-order reaction: $A(g) \rightarrow nB(g)$ is started with 'A'. The reaction takes place at constant temperature and pressure. If the initial pressure was P_0 and the rate constant of reaction is ' K ', then at any time, t , the total pressure of the reaction system will be

- (a) $P_0[n + (1 - n)e^{-kt}]$
 (b) $P_0(1 - n)e^{-kt}$
 (c) $P_0 \cdot n \cdot e^{-kt}$
 (d) $P_0[n - (1 - n)e^{-kt}]$

32. For a reaction of order n , the integrated form of the rate equation is: $(n - 1) \cdot K \cdot t = (C_0)^{1-n} - (C)^{1-n}$, where C_0 and C are the

values of the reactant concentration at the start and after time ' t '. What is the relationship between $t_{3/4}$ and $t_{1/2}$, where $t_{3/4}$ is the time required for C to become $C_0/4$.

- (a) $t_{3/4} = t_{1/2} \cdot [2^{n-1} + 1]$
 (b) $t_{3/4} = t_{1/2} \cdot [2^{n-1} - 1]$
 (c) $t_{3/4} = t_{1/2} \cdot [2^{n+1} - 1]$
 (d) $t_{3/4} = t_{1/2} \cdot [2^{n+1} + 1]$

33. Rate of the chemical reaction: $A \rightarrow$ products, is doubled, when the concentration of 'A' is increased four times. If the half-life of the reaction is 16 min, at a given concentration, then the time required for 75% of the reaction to complete is

- (a) 24.0 min (b) 27.3 min
 (c) 48 min (d) 49.4 min

34. $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ is a first-order gaseous reaction with $K = 2.5 \times 10^{-5} s^{-1}$ at $320^\circ C$. The percentage of SO_2Cl_2 decomposed on heating for 100 min is ($\ln 1.16 = 0.15$)

- (a) 86.2 (b) 15.0
 (c) 85.0 (d) 13.8

35. When the concentration of 'A' is 0.1 M, it decomposes to give 'X' by a first-order process with a rate constant of $6.93 \times 10^{-2} min^{-1}$. The reactant 'A', in the presence of catalyst, gives 'Y' by a second-order mechanism with the rate constant of $0.2 min^{-1} M^{-1}$. In order to make half-life of both the processes, same, one should start the second-order reaction with an initial concentration of 'A' equal to

- (a) 0.01 M (b) 2.0 M
 (c) 1.0 M (d) 0.5 M

36. The half-life periods of two first-order reactions are in the ratio 3:2. If t_1 is the time required for 25% completion of the first reaction and t_2 is the time required for 75% completion of the second reaction, then the ratio, $t_1:t_2$, is ($\log 3 = 0.48$, $\log 2 = 0.3$)

- (a) 3:10 (b) 12:25
 (c) 3:5 (d) 3:2

37. If 1% of a substance undergoing decomposition is consumed in 1 min, when the concentration is 0.02 M and in 15 s, when the concentration is 0.04 M, the order of the reaction is

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

38. In the biological processes, the time taken by certain virus or bacteria to double its population, is called generation time. In milk, at 37°C, *Lactobacillus acidophilus* has a generation time of about 75 min. The population relative to the initial value at 60 min is ($\ln 2 = 0.7$)

(a) 0.8 (b) $e^{0.56}$
(c) $e^{0.8}$ (d) $e^{0.875}$

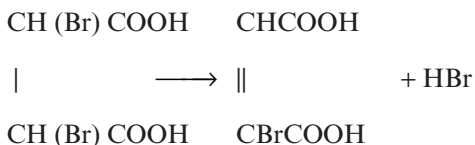
39. A study of the conversion of ammonium cyanate to urea in solution, $\text{NH}_4\text{CNO} \rightarrow \text{CO}(\text{NH}_2)_2$ gave the following results:

Initial concentration (moles/litre)	0.05	0.10	0.20
Time for half conversion (h)	37.82	18.95	9.45

$t_{1/2}$ of reaction for an initial concentration of 0.15 M, is

(a) ≈ 56.77 h (b) ≈ 12.6 h
(c) ≈ 14.2 h (d) ≈ 13.7 h

40. Thermal decomposition of dibromosuccinic acid (DBSA) taking place according to the following equation, obeys first-order kinetics



The progress of reaction may be followed by means of alkali titration of the solution (definite volume of reaction mixture) at various time intervals. If T_0 and T_t be the ml of alkali solution at zero time and at any time t , respectively and a and

$(a - x)$ be the concentrations of DBSA at zero time and at any time t , respectively, then the value of $\frac{a}{a - x}$ is

(a) $\frac{T_0}{3T_0 - 2T_t}$ (b) $\frac{T_0}{T_t}$
(c) $\frac{T_0}{T_0 - T_t}$ (d) $\frac{T_0}{2T_0 - T_t}$

41. In a certain first-order reaction, B^{n+} is getting converted to $\text{B}^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing agent which reacts only with B^{n+} and $\text{B}^{(n+4)+}$. In the process, it converts B^{n+} to $\text{B}^{(n-2)+}$ and $\text{B}^{(n+4)+}$ to $\text{B}^{(n-1)+}$. At $t = 0$, the volume of reagent consumed is 25 ml and at $t = 10$ min, the volume used is 32.5 ml. The rate constant for the conversion of B^{n+} of $\text{B}^{(n+4)+}$ is ($\ln 2 = 0.7$, $\ln 5 = 1.6$)

(a) 0.2 min^{-1}
(b) 0.8 min^{-1}
(c) 0.02 min^{-1}
(d) 0.08 min^{-1}

42. The reaction: $\text{A(g)} \rightarrow 2\text{B(g)} + \text{C(g)}$ follows first-order kinetics. The reaction is started with pure 'A' in a rigid closed vessel maintained at constant temperature. After 10 s, a pin hole is developed in the vessel. If the molar ratio of gases 'A' and 'B' coming out initially is 1 : 2, the rate constant of reaction is (Molar masses of A, B and C are 16, 4 and 8 g/mol, respectively, $\ln 2 = 0.7$, $\ln 3 = 1.1$)

(a) 0.04 s^{-1} (b) 0.4 s^{-1}
(c) 0.11 s^{-1} (d) 0.07 s^{-1}

43. For the reaction: $\text{A} + \text{B} \rightarrow \text{products}$, rate law is $r = K[\text{A}]^2[\text{B}]$, where $K = 0.5 \text{ M}^{-2}\text{min}^{-1}$. The time in which the concentration of 'A' becomes half of its initial concentration if the initial concentrations of 'A' and 'B' are 0.002 M and 2.0 M, respectively, is

(a) 50 min (b) 500 min
(c) 1.0 min (d) 100 min

44. The initial rate of hydrolysis of methyl acetate (1.0 M) by a weak acid (HA, 1.0 M) is $1/100^{\text{th}}$ of that of a strong acid (HX, 1.0 M), at 25°C . The K_a of HA is

- (a) 1×10^{-4}
 (b) 1×10^{-5}
 (c) 1×10^{-6}
 (d) 1×10^{-3}

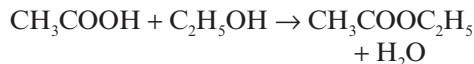
45. Reaction: $A + B \rightarrow C + D$, follows the rate law: $r = (2.31 \times 10^{-3} \text{ s}^{-1})[A]^{1/2}[B]^{1/2}$. The reaction is started with 1.0 mole each of 'A' and 'B'. In what time, the moles of 'A' become 0.25?

- (a) 150 s (b) 300 s
 (c) 450 s (d) 600 s

46. The rate expression for a reaction is $\frac{-dC}{dt} = \frac{\alpha C}{1 + \beta C}$, where α, β are constants and C is the concentration of reactant at time, t . The half-life for this reaction is

- (a) $\frac{1}{\alpha} \ln 2 + \frac{\beta C_0}{2\alpha}$ (b) $\frac{1}{\beta} \ln 2 + \frac{\beta C_0}{2\alpha}$
 (c) $\frac{\beta \ln 2}{\alpha}$ (d) $\frac{\alpha}{\beta}$

47. The acid catalysed reaction of acetic acid with ethanol:



follows the rate law: $-\frac{d[\text{CH}_3\text{COOH}]}{dt}$

$= K[\text{H}^+][\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]$
 $= K'[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]$. When $[\text{CH}_3\text{COOH}]_0 = [\text{C}_2\text{H}_5\text{OH}]_0 = 0.2 \text{ M}$ and $\text{pH} = 3$, the half-life for the reaction is 50 min. The value of true rate constant, K , of the reaction is

- (a) $1.386 \times 10^{-2} \text{ min}^{-1}$ (b) $0.1 \text{ M}^{-1} \text{ min}^{-1}$
 (c) $100 \text{ M}^{-2} \text{ min}^{-1}$ (d) 13.86 min^{-1}

48. The reaction: $A + B \rightarrow C + D$, has been studied under the following initial conditions:

Case I	Case II
$[A]_0 = 2.0 \text{ M}$	$[A]_0 = 0.02 \text{ M}$
$[B]_0 = 0.01 \text{ M}$	$[B]_0 = 2.0 \text{ M}$

The variation of concentration with time was noted as:

Case I	time (min)	0	10	20	30
	[B]	0.0100 M	0.0080 M	0.0064 M	0.00512 M
Case II	time (min)	0	10	20	30
	[A]	0.0200 M	0.0180 M	0.0162 M	0.0146 M

The rate constant of reaction is

- (a) 0.02 min^{-1} (b) 0.01 min^{-1}
 (c) $0.01 \text{ M}^{-1} \text{ min}^{-1}$ (d) $0.02 \text{ M}^{-1} \text{ min}^{-1}$

49. In Lindemann theory of unimolecular reactions, it is shown that the apparent rate constant for such a reaction is $k_{\text{app}} = \frac{k_1 C}{1 + \alpha C}$, where C is the concentration of the reactant, k_1 and α are constants. The value of C for which k_{app} has 90% of its

limiting value at C tending to infinitely large is ($\alpha = 9 \times 10^5$)

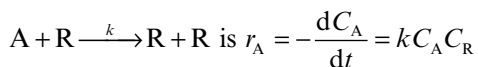
- (a) $10^{-6} \text{ mole/litre}$
 (b) $10^{-4} \text{ mole/litre}$
 (c) $10^{-5} \text{ mole/litre}$
 (d) $5 \times 10^{-5} \text{ mole/litre}$

50. Decomposition of a non-volatile solute 'A' into another non-volatile solute 'B' and 'C', in aqueous solution follows first-order kinetics as:



When one mole of 'A' is dissolved in 180 g water and left for decomposition, the vapour pressure of solution was found to be 20 mm Hg after 12 h. What is the vapour pressure of solution after 24 h? Assume constant temperature of 25°C, throughout. The vapour pressure of water at 25°C is 24 mm Hg.

- (a) 18 mm Hg
(b) 19.2 mm Hg
(c) 10 mm Hg
(d) 16 mm Hg
51. A substance undergoes first-order decomposition. The decomposition follows two parallel first-order reaction with $K_1 = 1.26 \times 10^{-4} \text{ s}^{-1}$ for the formation of 'B' and $K_2 = 3.15 \times 10^{-5} \text{ s}^{-1}$ for the formation of 'C'. The percentage distribution of 'B' and 'C' are
- (a) 80% B, 20% C
(b) 75% B, 25% C
(c) 90% B, 10% C
(d) 60% B, 40% C
52. The rate equation for an autocatalytic reaction



The rate of disappearance of reactant A is maximum when

- (a) $C_A = 2C_R$
(b) $C_A = C_R$
(c) $C_A = C_R/2$
(d) $C_A = (C_R)^{1/2}$
53. Surface-catalysed reactions that are incorporated by the product, obey the differential rate expression, $\frac{dy}{dt} = \frac{k[C_0 - y]}{1 + by}$, where C_0 = initial concentration and k and b are constants. The half-life of reaction is

- (a) $(1 + C_0 b) \ln 2 - \frac{C_0 b}{2}$
(b) $(1 - C_0 b) \ln 2 + \frac{C_0 b}{2}$
(c) $(1 - C_0 b) \ln 2 - \frac{C_0 b}{2}$
(d) $(1 + C_0 b) \ln 2 + \frac{C_0 b}{2}$

54. For the following first-order competing reaction:



the ratio of K_1/K_2 , if only 50% of 'B' will have been reacted when 94% of 'A' has been reacted is ($\log 2 = 0.3$, $\log 3 = 0.48$)

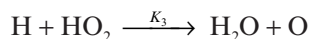
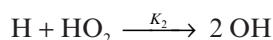
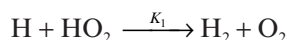
- (a) 4.06
(b) 0.246
(c) 8.33
(d) 0.12
55. In 80% ethanol at 55°C, isopropyl bromide reacts with hydroxide ion according to the following kinetics:

$$-\frac{d[\text{RX}]}{dt} = (4.8 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1})$$

$$[\text{RX}][\text{OH}^-] + 2.4 \times 10^{-6} \text{ s}^{-1} [\text{RX}]$$

What percentage of isopropyl bromide reacts by the S_N2 mechanism when $[\text{OH}^-] = 0.01 \text{ M}$?

- (a) 16.67%
(b) 83.33%
(c) 66.67%
(d) 33.33%
56. For the series of competitive reactions:



It has been found that $K_1:K_2:K_3 = 0.60:0.30:0.10$. The molar ratio of the products, H_2 , O_2 , OH , H_2O and O , at time, t , is

- (a) 6:6:6:1:1
(b) 6:6:3:1:1
(c) 3:3:6:0.5:0.5
(d) 3:3:3:1:1

57. In the parallel reactions: $A \xrightarrow{K_1 = \ln 3 \text{ min}^{-1}}$
 B and $A \xrightarrow{K_2 = \ln 3 \text{ min}^{-1}} C$, the time when
the concentrations of A, B and C becomes
equal is
(a) 0.5 s (b) 30 s
(c) 45 s (d) 60 s
58. For the sequential reactions:
 $A \xrightarrow{K_1 = 0.02 \text{ min}^{-1}} B \xrightarrow{K_2 = 0.02 \text{ min}^{-1}} C$,
the initial concentration of 'A' was 0.2 M
and initially 'B' and 'C' were absent. The
time at which the concentration of 'B'
becomes maximum and the maximum
concentration of 'B' are, respectively,
(a) 50 min, $\left(\frac{0.2}{e}\right)$ M
(b) 50 min, 0.2 M
(c) infinite, 0.2 M
(d) 25 min, $\left(\frac{0.2}{e}\right)$ M
59. In the give first-order sequential reac-
tions: $A \xrightarrow{K_1} B \xrightarrow{K_2} C \xrightarrow{K_3} D$,
what is the ratio of number of atoms
of A to the number of atoms of B after
long time interval starting with pure A?
 $\left(K_1 = \frac{\ln 2}{1200} \text{ and } K_2 = \frac{\ln 2}{30}\right)$
(a) 0.67 (b) 10
(c) 20 (d) 40
60. An organic compound A decomposes
following two parallel first-order reac-
tions: $A \xrightarrow{K_1} B$ and $A \xrightarrow{K_2} C$. If K_1 is
 $1.25 \times 10^{-5} \text{ s}^{-1}$ and $\frac{K_1}{K_2} = \frac{1}{9}$, the value of
 $\frac{[C]}{[A]}$ after one hour of start of reaction
by taking only A, is ($\ln 1.568 = 0.45$)
(a) $\frac{1}{9}$ (b) 0.5112
(c) 1.4112 (d) $\frac{9}{20}$
61. For the consecutive first-order reactions:
 $A \xrightarrow{K_1} B \xrightarrow{K_2} C$, the concentrations
of A and B are 0.2 M and 0.01 M,
respectively, at steady state. If K_1 is
 $2.5 \times 10^{-4} \text{ min}^{-1}$, what is the value of K_2 ?
(a) $5.0 \times 10^{-3} \text{ min}^{-1}$
(b) $2.5 \times 10^{-4} \text{ min}^{-1}$
(c) $1.25 \times 10^{-5} \text{ min}^{-1}$
(d) $5.0 \times 10^{-4} \text{ min}^{-1}$
62. For the consecutive first-order reactions:
 $A \xrightarrow{K_1} B \xrightarrow{K_2} C$, B is in steady state.
What will be the concentration of C at
this stage? At $t = 0$, $[A] = [A]_0$ and $[B]$
 $= [C] = 0$.
(a) 0 (b) $[A]_0$
(c) $[A]_0 \cdot (1 - e^{-K_1 t})$ (d) $[A]_0 \cdot e^{-K_1 t}$
63. For the first-order gaseous reaction:
 $A(g) \xrightarrow{K_1} 2B(g)$, $A(g) \xrightarrow{K_2} C(g)$,
the initial pressure in a container of fixed
volume, V litre, is 1 atm. Pressure of the
system is 1.4 atm at $t = 10$ min and the
pressure is 1.5 atm after a very long
time. The only correct information about
the reactions is
(a) $2K_1 = K_2 = 0.08 \text{ min}^{-1}$
(b) $K_1 = K_2 = 0.08 \text{ min}^{-1}$
(c) $K_1 = 2K_2 = 0.08 \text{ min}^{-1}$
(d) $K_1 = K_2 = 0.16 \text{ min}^{-1}$
64. For a bimolecular gaseous reaction of
type: $2A \rightarrow \text{Products}$, the average speed
of reactant molecules is $2 \times 10^4 \text{ cm/s}$, the
molecular diameter is 4 \AA and the number
of reactant molecules per cm^3 is 2×10^{19} .
The maximum rate of reaction should be
(a) $4.72 \times 10^7 \text{ mol l}^{-1} \text{ s}^{-1}$
(b) $1.18 \times 10^7 \text{ mol l}^{-1} \text{ s}^{-1}$
(c) $9.44 \times 10^7 \text{ mol l}^{-1} \text{ s}^{-1}$
(d) $2.36 \times 10^7 \text{ mol l}^{-1} \text{ s}^{-1}$
65. For certain reaction it is observed that
 $\ln K = \alpha + \beta \ln T - \frac{\gamma}{T}$, where K is the rate
constant, T is the temperature (Kelvin)
and α , β and γ are constants. What is the
Arrhenius activation energy?

- (a) $\beta RT + \gamma R$ (b) γR
 (c) $\beta + \gamma R$ (d) $\beta RT + \gamma R$
66. For two parallel first-order reactions, what is the overall activation energy of reaction? The yields of B and C in products are 40% and 60%, respectively.
- $$A \xrightarrow{E_a = 20 \text{ kcal/mol}} B \quad A \xrightarrow{E_a = 40 \text{ kcal/mol}} C$$
- (a) 60 kcal/mol
 (b) 32 kcal/mol
 (c) 28 kcal/mol
 (d) 20 kcal/mol
67. Rate of an uncatalysed first-order reaction at T K is half of the rate of catalysed reaction at ' $0.5T$ ' K. If the catalyst lowers the threshold energy by 20 kcal, what is the activation energy of uncatalysed reaction? ($T = 300$ K, $\ln 2 = 0.7$)
- (a) 39.58 kcal/mol
 (b) 19.58 kcal/mol
 (c) 40.42 kcal/mol
 (d) 20.42 kcal/mol
68. For the first-order parallel reactions: $A \xrightarrow{K_1} B$ and $A \xrightarrow{K_2} C$, $K_1 = 8 \text{ min}^{-1}$ and $K_2 = 2 \text{ min}^{-1}$ at 300 K. If the activation energies for the formation of B and C are 20 and 28.314 kJ/mol, respectively, find the temperature at which B and C will be obtained in 2:1 mole ratio.
- (a) 400 K
 (b) 385.5 K
 (c) 379.75 K
 (d) 412.25 K
69. Two reactions: (I) $A \rightarrow \text{Products}$, and (II) $B \rightarrow \text{Products}$, follow first-order kinetics. The rate of reaction-I is doubled when temperature is raised from 300 to 310 K. The half-life for this reaction at 310 K is 30 min. At the same temperature, B decomposes twice as fast as A. If the energy of activation for the reaction-II is half that of reaction-I, the rate constant of reaction-II at 300 K is
- (a) 0.0233 min^{-1}
 (b) 0.0327 min^{-1}
- (c) 0.0164 min^{-1}
 (d) 0.0654 min^{-1}
70. A first-order reaction: $A \rightarrow B$, activation energy is 4.8 kcal/mol. When a 20% solution of 'A' was kept at 27°C for 21.6 min, 75% decomposition took place. What will be the per cent decomposition in 8.0 min in a 30% solution maintained at 47°C ? Assume that activation energy remains constant in this range of temperature. ($e = 2.7$)
- (a) 25% (b) 50%
 (c) 75% (d) 87.5%
71. Arrhenius equation gives the change in rate constant (and hence rate of reaction) with temperature. If the activation energy of the reaction is found to be equal to RT , then
- (a) The rate of reaction does not depend upon initial concentration.
 (b) The rate constant becomes about 37% of the Arrhenius constant A .
 (c) The rate constant becomes equal to 73% of the Arrhenius constant A .
 (d) The rate of the reaction becomes infinite or zero.
72. The rate of the reaction gets doubled when the temperature changes from 7°C to 17°C . By what factor will it change for the temperature change from 17°C to 27°C ? [$\text{Antilog}(0.30) = 2.0$, $\text{Antilog}(0.280) = 1.91$, $\text{Antilog}(0.322) = 2.1$]
- (a) 1.81 (b) 1.71
 (c) 1.91 (d) 2.1
73. For the combustion of carbon, $\Delta H = -ve$ and $\Delta S = +ve$ and hence, thermodynamically the process is spontaneous at all temperatures. But coal stored in coal depots does not burn automatically because of
- (a) very high threshold energy barrier
 (b) thermodynamic stability of coal
 (c) lower energy of activation needed for burning
 (d) low temperature in coal depots

74. Which of the following statements is incorrect?

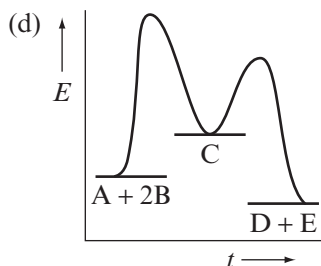
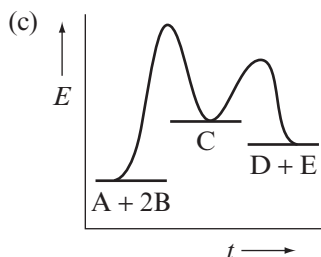
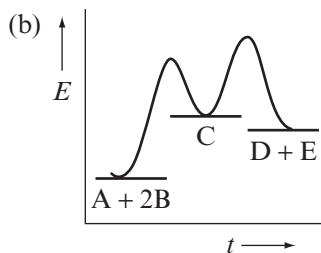
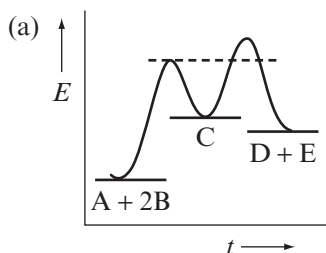
- For endothermic reactions, energy of activation is always greater than heat of reaction.
- For exothermic reactions, energy of activation is always smaller than heat of reaction.
- Rate of elementary reaction always increases with increase in temperature.
- Temperature coefficient of a reaction is 1.0, when $T \rightarrow \infty$.

75. The mechanism of the reaction: $A + 2B \rightarrow D + E$; $\Delta H = -ve$ is

Step I: $A + 2B \rightarrow C$ (slow)

Step II: $C \rightarrow D + E$ (fast)

The energy profile of the reaction should be:



Section B (One or More than one Correct)

1. For a complex (multistep) reaction,

- the overall rate of reaction is the rate of slowest step.
- the overall molecularity has no significance.
- molecularity and order may or may not be same.
- the number of rate determining steps may be more than one.

2. Which of the following statements is true?

- The rate law for a reaction must depend on the concentrations of all reactants that appear in the stoichiometric equation

(b) The rate of a catalysed reaction must be independent of the concentration of catalyst

(c) The rate constant for the reaction is independent of the concentrations of the reacting species

(d) There is a single rate determining step in any reaction mechanism.

3. Which of the following is pseudo first-order reaction?

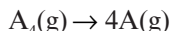
(a) The basic hydrolysis of ethyl acetate

(b) The inversion of sucrose in the presence of an acid

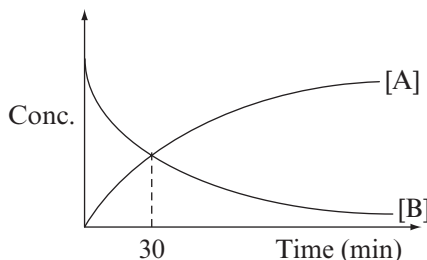
- (c) The acidic hydrolysis of ethyl acetate
 (d) The decomposition of ammonium nitrite in aqueous solution.
4. The order of reaction: $A \rightarrow \text{Products}$, may be given by the expression(s)
- $\frac{\ln r_2 - \ln r_1}{\ln[A]_2 - \ln[A]_1}$
 - $\frac{\ln[A_0]_2 - \ln[A_0]_1}{\ln[t_{1/2}]_2 - \ln[t_{1/2}]_1}$
 - $1 + \frac{\ln[A_0]_2 - \ln[A_0]_1}{\ln[t_{1/2}]_2 - \ln[t_{1/2}]_1}$
 - $\frac{\ln(r/K)}{\ln[A]}$
5. For a first-order reaction,
- The degree of dissociation is equal to $(1 - e^{-kt})$
 - A plot of reciprocal concentration of the reactant vs time gives a straight line
 - The time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction
 - The pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}
6. For a reaction involving a single reactant and order other than one, which of the following statement(s) is/are true? (C = concentration of reactant at time, t)
- If f is the fraction of the reactant concentration consumed over time interval ' t ', then $\log\left(\frac{f}{t}\right)$ is linearly related to $(\log C)$, when $f \ll 1$.
 - A plot of $C^{(n-1)}$ vs t is linear with slope proportional to $(n-1)$.
 - If $t_{1/2}$ and $t_{3/4}$ are the time intervals for 50% and 75% consumption of the reactant, then $t_{3/4} : t_{1/2} = 2^{n-1} + 1$
 - A plot of $\log C$ vs $\log t$ is linear with slope = 1
7. Initial concentration of reactant for n^{th} -order reaction is C_0 . Which of the following relation is/are not correct about $t_{1/2}$ of the reaction?
- $\ln t_{1/2} = \text{constant} - (n-1) \ln C_0$
 - $\ln t_{1/2} = \ln n + \text{constant} - \ln C_0$
 - $t_{1/2} \cdot \ln n = \text{constant} + \ln C_0$
 - $\ln t_{1/2} = n \ln C_0$
8. Consider the following statements: The law for the acid-catalysed hydrolysis of an ester being given as rate = $K[H^+][\text{ester}] = K'[\text{ester}]$. If the acid (strong) concentration is doubled at constant ester concentration,
- The second-order rate constant, K , is doubled.
 - The pseudo first-order rate constant, K' is doubled.
 - The rate of reaction is doubled.
- Which of the above statement is correct?
- 1 and 2
 - 2 and 3
 - 1 and 3
 - 1, 2 and 3
9. The rate law for the reaction:
- $$\text{RCI} + \text{NaOH(aq)} \rightarrow \text{ROH} + \text{NaCl}$$
- is given by, rate = $K_1[\text{RCI}]$. The rate of the reaction will be
- Doubled on doubling the concentration of NaOH
 - Halved on reducing the concentration of alkyl halide to one half
 - Increased on increasing the temperature of the reaction
 - Unaffected by increasing the temperature of the reaction
- Correct answer is
- 1, 2, 3
 - 3, 4
 - 1, 3
 - 2, 3

10. SO_3 gas is entering the environment at a constant rate of 6.93×10^{-6} g/l/day due to emission of polluting gases from thermal power plant at Kota, but at the same time it is decomposing and following first-order kinetics with half-life of 100 days. Based on these details, select the correct statement(s) from the following:
- Concentration of SO_3 in Kota is 1.25×10^{-5} M (assume SO_3 present in air reaches steady state).
 - If 10^3 l of air is passed through 1 l pure water (assuming all SO_3 is dissolved in it) and resulting solution is titrated against 1 N NaOH solution, 15 ml of NaOH solution is required to reach the end point.
 - An industry is manufacturing H_2SO_4 at the rate of 980 kg per day with the use of SO_3 in air; it should use 8×10^5 l air per day.
 - If SO_3 emission is stopped, then after 1000 days, its concentration will reduce to 1.25×10^{-8} M.
11. The decomposition reaction: $3\text{A}(\text{g}) \rightarrow 2\text{B}(\text{g}) + 2\text{C}(\text{s})$ follows first-order kinetics. Starting with pure 'A' (at 6 atm), the pressures of system after 20 min and after a very long time are 5.05 atm and 4.05 atm, respectively. Identify the correct statement(s) related with the reaction.
- Time for 75% completion of reaction is slightly more than 40 min.
 - Time for 87.5% completion of reaction is slightly less than 60 min.
 - Time for 93.75% completion of reaction is exactly 80 min.
 - The pressure of system after 40 min will be 4.55 atm.
12. To very good approximations, the cooling of a hot body to room temperature follows first-order kinetics (in this case, however, the unit that is changing is temperature (in kelvin), not molarity). If the rate constant for a body is 0.04 s^{-1} , then $[\ln 2 = 0.7, \ln(323/25) = 2.6]$
- The time taken for that body to go from 323°C to 25°C is 17.5 s.
 - The time taken for that body to go from 1192 K to 298 K is 35 s.
 - The time taken for that body to go from 323°C to 25°C is 65 s.
 - The time taken for that body to go from 1192 K to 298 K is 130 s.
13. For a gaseous reaction: $\text{A} + \text{B} \rightarrow 2\text{C}$, the rate law is $r = k[\text{A}]^{-1}[\text{B}]^2$. The incorrect information is
- If the initial concentration of 'A' is double of 'B', then the half-life of reaction will remain same throughout the reaction.
 - If initially 'A' is taken in very large amount, then the half-life of reaction will keep on increasing as reaction proceeds.
 - If initially 'B' is taken in very large amount, then the half-life of reaction will remain same throughout the reaction.
 - If 'A' and 'B' are taken in equal concentration, then both will be reduced to half of the original amount in the same time.
14. For two reactions: $\text{A} \xrightarrow{K_1} \text{P}$ and $\text{B} \xrightarrow{K_2} \text{Q}$ of first and second order, respectively, if the initial concentrations of A and B are same (1 M), then the time taken by A and B to reach at 0.5 M concentration is same. Which of the following is/are correct statement(s) regarding the reactions?
- The initial rate of reaction of A is greater.
 - The initial rate of reaction of B is greater.
 - The magnitude of K_1 is greater than that of K_2 .
 - The magnitude of K_2 is greater than that of K_1 .

15. Consider the following first-order decomposition reaction:



Which of the following statement(s) is/are correct regarding the reaction?



- (a) At 30 min, only 20% reaction is complete.
 (b) $t_{1/2}$ of reaction is approximately 90 min.
 (c) Rate of reaction decreases linearly with time.
 (d) The time for intersection of two curves is independent of initial concentration of A_4 .
16. α -maltose ($C_{12}H_{22}O_{11}$) can be hydrolysed to glucose ($C_6H_{12}O_6$) as:



On the basis of following data, identify the correct statement(s) related with the reaction

$$\Delta_f H_{C_{12}H_{22}O_{11}(aq)}^\circ = -2238 \text{ kJ/mol},$$

$$\Delta_f H_{C_6H_{12}O_6(aq)}^\circ = -1263 \text{ kJ/mol},$$

$$\Delta_f H_{H_2O(l)}^\circ = -285 \text{ kJ/mol}$$

Time (min)	0	50	100
Conc. of α -maltose (M)	0.4	0.1	0.025

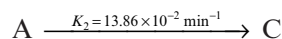
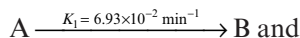
- (a) The hydrolysis of α -maltose is exothermic process.
 (b) Heat liberated in the combustion of 1.0 mole of α -maltose is greater than the heat liberated in combustion of 2.0 moles of glucose.

- (c) On increasing the temperature, the extent of hydrolysis of α -maltose will decrease.
 (d) The hydrolysis of α -maltose follows first-order kinetics.

17. For the reaction: $A \rightarrow \text{Products}$ (order = n), the theoretical time of completion of reaction is

- (a) Infinite for all value of n
 (b) Infinite for $n \geq 1$
 (c) $\frac{[A_0]^{1-n}}{K(1-n)}$ for $n \neq 1$
 (d) $\frac{[A_0]^{1-n}}{K(1-n)}$ for $n < 1$

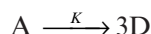
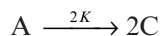
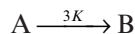
18. Consider the reactions:



A, B and C all are optically active compounds. If the optical rotations of A, B and C per unit concentration are 60° , -72° and 42° , respectively, and the initial concentration of A is 2 M, then

- (a) the solution will be optically active and dextrorotatory after very long time.
 (b) the solution will be optically active and laevorotatory after very long time.
 (c) half-life for overall reaction of A is 15 min.
 (d) after 75% conversion of A into B and C, the optical rotation of solution will be 36° .

19. For the first-order parallel reactions, starting with 1 M of A, which of the following statement(s) is/are correct?



- (a) $[B]_t : [C]_t : [D]_t$ is independent of time
 (b) $[C]_t > [B]_t = [D]_t$
 (c) $[C]_\infty = 0.67 \text{ M}$
 (d) If $K = 0.5 \text{ min}^{-1}$, then $[B] = 1 \text{ M}$ after 1.386 min
20. When secondary alkyl halide undergo S_N reaction, it follow S_{N_1} (first-order) and S_{N_2} (second-order) pathway simultaneously. The dominant pathway depends on large number of factors. An alkyl halide undergoes both pathway with rate constants $3 \times 10^{-4} \text{ s}^{-1}$ and $5 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$, respectively. Which of the following is/are correct information for the reaction?
- (a) If the concentration of nucleophile is 0.1 M, the dominant pathway of reaction is S_{N_1} .
 (b) If the concentration of nucleophile is 1.0 M, the dominant pathway of reaction is S_{N_2} .
 (c) The percentage of S_{N_1} product will be 50, when the nucleophile concentration is 0.6 M.
 (d) The percentage of S_{N_1} product will be 40, when the nucleophile concentration is 0.9 M.
21. For the reversible reaction: $A \rightleftharpoons B$, the time at which the rate of change in concentration of 'A' is equal to the rate of change in concentration of 'B' is/are
- (a) $t = 0$
 (b) $t = t_{1/2}$
 (c) $t = t_{\text{equilibrium}}$
 (d) $t = \text{infinite}$
22. For the parallel reactions: $A \xrightarrow{K_1} B$ and $A \xrightarrow{K_2} C$, the initial concentration of 'A' is C_A and initially 'B' and 'C' are absent. Concentrations of A, B and C at any time 't' is C_A , C_B and C_C , respectively. The correct relation(s) is/are
- (a) $C_A + C_B + C_C = C_{A_0}$
 (b) $\frac{dC_A}{dt} + \frac{dC_B}{dt} + \frac{dC_C}{dt} = 0$
- (c) $\frac{C_B}{C_C} = \frac{K_1}{K_2}$
 (d) $\frac{C_B}{C_{A_0} - C_A} = \frac{K_1}{K_1 + K_2}$
23. Which of the following statement(s) is/are correct for a photochemical reaction?
- (a) Photochemical reactions are complex (multistep) reactions.
 (b) The overall order of such reaction is always zero.
 (c) Only the first step of such reaction follows zero-order kinetics.
 (d) The rate of such reaction depends on the intensity of radiations absorbed.
24. Which of the following statement is/are incorrect?
- (a) When Δt is infinitesimally small, the average rate equals the instantaneous rate.
 (b) Activation energy for the forward reaction equals activation energy for the reverse reaction in a catalysed reaction.
 (c) For a reversible reaction, an increase in temperature, increase the rate for both the forward and backward reaction.
 (d) Larger the initial reactant concentration for a zero-order reaction, shorter is the half-life.
25. In a consecutive reaction system: $A \xrightarrow{E_1} B \xrightarrow{E_2} C$ when E_1 is much greater than E_2 , the yield of B increases with
- (a) increase in temperature
 (b) decreases in temperature
 (c) increase in initial concentration of A
 (d) decrease in initial concentration of A
26. When the temperature of a reaction system is increased by 10°C (from 25°C to 35°C), at constant volume, the reaction rate doubles. It is due to

- (a) The total number of collisions between reacting molecules increases nearly by 100%.
- (b) The number of collisions between the molecules possessing sufficiently high energy increases nearly by 100%.
- (c) The total number of collisions between reacting molecules increases nearly by 1 to 2%.
- (d) The average translational kinetic energy of molecules becomes nearly double.
- 27.** Which of the following quantity/quantities is/are temperature independent?
- (a) A (Pre-exponential factor)
- (b) E_a (Activation energy)
- (c) R (Universal gas constant)
- (d) K (rate constant)
- 28.** Decomposition of $A_2(g)$ and $B_3(g)$ follow first-order kinetics as:
- $$A_2(g) \rightarrow 2A(g); K_1 (/h^{-1}) = e^{-\frac{14000(J)}{RT} + 5}$$
- $$B_3(g) \rightarrow 3B(g); K_2 (/h^{-1}) = e^{-\frac{20000(J)}{RT} + 10}$$
- where K_1 and K_2 are the rate constants with respect to disappearance of A_2 and B_3 , respectively. One mole, each of $A_2(g)$ and $B_3(g)$, is taken in a 100 l evacuated flask and at some temperature at which they start decomposing at the same rate. The incorrect information regarding the reactions is
- (a) The temperature at which the reactions are performed is $\frac{1200}{8.314}$ K.
- (b) At any instant, $\left(\frac{P_{A_2}}{P_{B_3}}\right)$ will be constant and equal to 1.0, where P_{A_2} and P_{B_3} are the partial pressures of gases at that time.
- (c) At some instant, the total pressure of all gases in the flask may be less than 0.2 atm.
- (d) At any instant, $\left(\frac{P_A}{P_B}\right)$ will be constant and equal to 1.0, where P_A and P_B are the partial pressures of gases at that time.
- 29.** In a study of effect of temperature on reaction rate, the value of $\frac{1}{K} \cdot \frac{dK}{dT}$ is found to be $\frac{1.25 \times 10^6}{T^3} K^{-1}$. Identify the correct statement(s).
- (a) The activation energy for the reaction at 250 K is 10 kcal/mol.
- (b) The activation energy for the reaction at 2000 K is 1.25 kcal/mol.
- (c) The rate of increase of rate constant with the increase in temperature is higher at lower temperature than at higher temperature.
- (d) The value of $\frac{d(\ln K)}{dT}$ is 0.625 at 1000 K.
- 30.** For the reversible reaction: $A \rightleftharpoons B$; $\Delta H = -2$ kcal, the pre-exponential factors are same for the forward and backward reactions. If the activation energy of backward reaction is 8 kcal/mol, then the correct information(s) about the reaction is/are
- (a) The activation energy of forward reaction is 6 kcal/mol.
- (b) At 500 K, the fraction of 'A' molecules crossing the energy barrier for forward reaction is e^{-6} .
- (c) At 500 K, the fraction of 'B' molecules crossing the energy barrier for forward reaction is e^{-8} .
- (d) Equilibrium constant for the reaction is e^{-2} at 500 K.

Section C (Comprehensions)

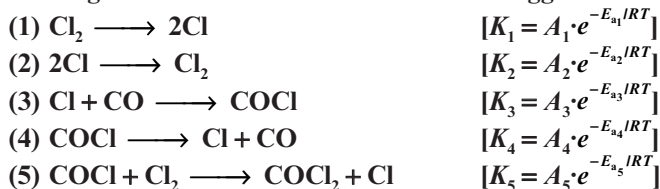
Comprehension I

The thermal decomposition of N_2O_5 occurs as: $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. Experimental studies suggest that rate of decomposition of N_2O_5 , rate of formation of NO_2 or rate of formation of O_2 , all becomes double if concentration of N_2O_5 is doubled.

- The correct mechanism for the decomposition of N_2O_5 may be
 - Step-I: $\text{N}_2\text{O}_5 \xrightarrow{\text{slow}} \text{NO}_2 + \text{NO}_3$
 Step-II: $\text{N}_2\text{O}_5 + \text{NO}_3 \xrightarrow{\text{fast}} 3\text{NO}_2 + \text{O}_2$
 - Step-I: $\text{N}_2\text{O}_5 \xrightarrow{\text{fast}} \text{NO}_2 + \text{NO}_3$
 Step-II: $\text{N}_2\text{O}_5 + \text{NO}_3 \xrightarrow{\text{slow}} 3\text{NO}_2 + \text{O}_2$
 - $\text{N}_2\text{O}_5 \xrightarrow{\text{fast}} 2\text{NO}_2 + \frac{1}{2}\text{O}_2$
 - Step-I: $\text{N}_2\text{O}_5 \xrightarrow{\text{slow}} \text{NO} + \text{NO}_2 + \text{O}_2$
 Step-II: $\text{N}_2\text{O}_5 + \text{NO}_2 \xrightarrow{\text{fast}} 3\text{NO}_2 + \frac{1}{2}\text{O}_2$
- If rate constants for decomposition of N_2O_5 , formation of NO_2 and formation of O_2 are K_1 , K_2 and K_3 , respectively, then
 - $K_1 = K_2 = K_3$
 - $2K_1 = K_2 = 4K_3$
 - $K_1 = 2K_2 = K_3$
 - $2K_1 = 4K_2 = K_3$
- If rate of formation of O_2 is 16 g/h, then rate of decomposition of N_2O_5 and rate of formation of NO_2 are
 - 108 g/h, 92 g/h
 - 54 g/h, 46 g/h
 - 32 g/h, 64 g/hr
 - 16 g/h, 16 g/h

Comprehension II

The following Rice–Herzfeld mechanism has been suggested for the formation of phosgene COCl_2 :

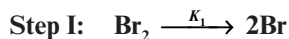


- Assuming steady-state approximation for $[\text{Cl}]$ and $[\text{COCl}]$, the rate law for the formation of COCl_2 is
 - $\frac{K_5 K_2 K_1^{1/2} [\text{Cl}_2]^{3/2} [\text{CO}]}{K_3^{1/2} (K_4 + K_5 [\text{Cl}_2])}$
 - $\frac{K_5 K_3 K_1^{1/2} [\text{Cl}_2] [\text{CO}]^{3/2}}{K_2^{1/2} (K_4 + K_5 [\text{Cl}_2])}$
 - $\frac{K_5 K_3 K_1^{1/2} [\text{Cl}_2]^{3/2} [\text{CO}]}{K_2^{1/2} (K_4 + K_5 [\text{Cl}_2])}$
 - $\frac{K_5 K_2 K_1^{1/2} [\text{Cl}_2] [\text{CO}]^{3/2}}{K_3^{1/2} (K_4 + K_5 [\text{Cl}_2])}$
- The rate law will be if we simplify the rate law obtained in previous question assuming that the reactions (1) – (4) are much faster than reaction (5)
 - $\frac{K_4 K_3 K_2^{1/2} [\text{Cl}_2]^{3/2} [\text{CO}]}{K_4 K_2}$
 - $\frac{K_4 K_3 K_2^{1/2} [\text{Cl}_2] [\text{CO}]^{3/2}}{K_2 K_3^{1/2}}$
 - $\frac{K_5 K_3 K_1^{1/2} [\text{Cl}_2] [\text{CO}]^{3/2}}{K_4^{1/2} K_2}$
 - $\frac{K_5 K_3 K_1^{1/2} [\text{Cl}_2]^{3/2} [\text{CO}]}{K_4 K_2^{1/2}}$

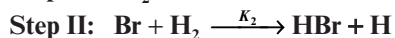
6. What is overall pre-exponential factor of reaction, if steps (1) to (4) are much faster than (5)?
- (a) $\frac{A_5 A_3 A_1^{1/2}}{A_4 A_2^{1/2}}$ (b) $\frac{A_5 A_3^{1/2} A_1}{A_2 A_4^{1/2}}$
- (c) $\frac{A_5 A_4 A_1^{1/2}}{A_4 A_2^{1/2}}$ (d) $\frac{A_4 A_3 A_2^{1/2}}{A_2 A_4^{1/2}}$
7. What is overall activation energy of reaction, if steps (1) to (4) are much faster than (5)?
- (a) $\frac{Ea_5 \cdot Ea_3 \cdot Ea_1^{1/2}}{Ea_4 \cdot Ea_2^{1/2}}$
- (b) $Ea_5 + Ea_3 + \frac{1}{2} Ea_1 - Ea_2 - \frac{1}{2} Ea_4$
- (c) $Ea_1 + Ea_3 + Ea_5 - Ea_2 - Ea_4$
- (d) $-Ea_5 - Ea_3 - \frac{1}{2} Ea_1 + Ea_2 + \frac{1}{2} Ea_4$

Comprehension III

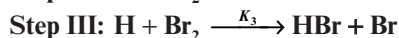
Chain reactions are a specific class of reactions in which highly reactive species are produced as intermediates which carry the reaction at a rapid rate for a long time. These reactions were first studied in 1934 by Frank O. Rice and Karl F. Herzfeld and are referred to as Rice–Herzfeld chain reactions. The steady-state approximation has proved highly useful in accounting for their rate laws. A typical chain reaction is that between H_2 and Br_2 to form HBr : $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, for which a five step mechanism has been proposed:



(Chain initiation)



(Chain propagation)



(Chain propagation)



(Chain retardation)



(Chain termination)

8. The concentration of bromine radical is

(a) $K_1[Br_2]^2$ (b) $\frac{K_1}{K_5} [Br_2]^2$

(c) $\frac{K_1}{K_5} [Br_2]$ (d) $\left(\frac{K_1}{K_5} [Br_2] \right)^{1/2}$

(a) $\frac{2K_2 K_1^{1/2} [Br_2]^{3/2} [H_2]}{K_5^{1/2} (K_3 [Br_2] + K_4 [HBr])}$

(b) $\frac{K_2 K_1^{1/2} [Br_2]^{1/2} [H_2]}{K_5^{1/2} (K_3 [Br_2] + K_4 [HBr])}$

(c) $\frac{K_2 K_1^{1/2} [Br_2]^{1/2} [H_2]}{K_5^{1/2} (K_3 [Br_2] + K_4 [HBr])}$

(d) $\frac{2K_2 K_1^{1/2} [Br_2]^{1/2} [H_2]}{K_5^{1/2}}$

9. The concentration of hydrogen radical is

(a) $\frac{K_2 K_1 [Br_2] [H_2]}{K_5 (K_3 [Br_2] + K_4 [HBr])}$

(b) $\frac{K_2 K_1 [Br_2]^{1/2} [H_2]}{K_5 (K_3 [Br_2] + K_4 [HBr])}$

(c) $\frac{K_2 K_1^{1/2} [Br_2]^{1/2} [H_2]}{K_5^{1/2} (K_3 [Br_2] + K_4 [HBr])}$

(d) $\frac{K_2 K_1^{1/2} [Br_2]^{1/2} [H_2]^2}{K_5^{1/2} (K_3 [Br_2]^{1/2} + K_4 [HBr])}$

11. What is the initial rate of formation of HBr , $+\frac{d[HBr]}{dt}$?

(a) $\frac{2K_2 K_1^{1/2} [Br_2]^{1/2} [H_2]}{K_5^{1/2} K_3}$

(b) $\frac{2K_2 K_1^{1/2} [Br_2]^{3/2} [H_2]}{K_5^{1/2} K_3}$

(c) $\frac{K_2 K_1^2 [Br_2]^{1/2} [H_2]}{K_5^2 K_3}$

(d) zero

10. The rate of formation of HBr , $+\frac{d[HBr]}{dt}$ is

Comprehension IV

A definite volume of H_2O_2 undergoing decomposition required 25.6 ml of standard KMnO_4 solution for titration. After 10 and 20 min, the volumes of permanganate required were 16.0 and 10.0 ml, respectively. ($\log 2 = 0.3$, $\log 3.2 = 0.5$)

12. The order of reaction is
 (a) 1 (b) 2 (c) 3 (d) 0
13. The time (in minutes) required for the decomposition to be half completed is
 (a) 1.5 (b) 7.5 (c) 15.0 (d) 13.3
14. The fraction of H_2O_2 decomposed after 25 min is
 (a) $\frac{5}{16}$ (b) 0.6 (c) $\frac{1}{3.2}$ (d) $\frac{11}{16}$
15. The reaction: $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$, is an example of
 (a) pseudo unimolecular
 (b) pseudo bimolecular
 (c) elementary reaction
 (d) photochemical reaction

Comprehension V

The first-order decomposition of di-tert-butylperoxide (DTBP) to acetone is given by the equation:



The reaction has a half-life of 80 min at 147°C . Starting with pure DTBP in a flask of constant volume at a pressure of 800 torr,

16. In what time (in min), the partial pressure of DTBP is 100 torr?
 (a) 60 (b) 120 (c) 180 (d) 240
17. In what time (in min), the partial pressure of acetone is 1200 torr?
 (a) 80 (b) 160 (c) 120 (d) 240
18. What will be the total gas pressure (in torr), when the partial pressure of DTBP is 700 torr?
 (a) 1000 (b) 700 (c) 900 (d) 1100

Comprehension VI

The reaction of the reactive fragment OH with H_2S : $4\text{OH}(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$, was studied at a particular temperature.

[OH] mol/litre	[H ₂ S] mol/litre	Rate of disappearance of H ₂ S mol l ⁻¹ s ⁻¹
1.3×10^{-8}	2.1×10^{-8}	1.4×10^{-6}
3.9×10^{-8}	2.1×10^{-8}	4.2×10^{-6}
3.9×10^{-8}	4.2×10^{-8}	8.4×10^{-6}

19. What is the rate law expression for the reaction?
 (a) $r = K[\text{OH}]^2[\text{H}_2\text{S}]$
 (b) $r = K[\text{OH}][\text{H}_2\text{S}]^2$
 (c) $r = K[\text{OH}]^{-1}[\text{H}_2\text{S}]$
 (d) $r = K[\text{OH}][\text{H}_2\text{S}]$
20. What is the rate constant of the reaction at the given temperature?
 (a) $5.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
 (b) $2.8 \times 10^{15} \text{ M}^{-1}\text{s}^{-1}$
 (c) $1.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$
 (d) $3.9 \times 10^{17} \text{ M}^{-2}\text{s}^{-1}$
21. What is the rate, $\text{mol l}^{-1}\text{s}^{-1}$, at the instant when $[\text{OH}] = 1.7 \times 10^{-8} \text{ M}$ and $[\text{H}_2\text{S}] = 1.0 \times 10^{-8} \text{ M}$?
 (a) 8.7×10^{-6} (b) 8.7×10^{-8}
 (c) 8.7×10^{-7} (d) 1.15×10^6
22. What is the rate, mol s^{-1} , at the instant when $[\text{OH}] = 1.7 \times 10^{-8} \text{ M}$ and $[\text{H}_2\text{S}] = 1.0 \times 10^{-8} \text{ M}$ and the volume of the reacting system is 0.1 litre?
 (a) 8.7×10^{-6} (b) 8.7×10^{-8}
 (c) 8.7×10^{-7} (d) 1.15×10^6

Comprehension VII

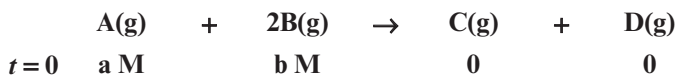
At constant temperature and volume, X decomposes as: $2\text{X}(\text{g}) \rightarrow 3\text{Y}(\text{g}) + 2\text{Z}(\text{g})$. P_x is the partial pressure of X.

Observation no.	Time (min)	P_x (mm Hg)
1	0	800
2	100	400
3	200	200

23. The order of reaction with respect to 'X' is
 (a) 0 (b) 1
 (c) 2 (d) 0.5
24. The rate constant of reaction is
 (a) $6.93 \times 10^{-3} \text{ min}^{-1}$
 (b) $5.0 \times 10^{-3} \text{ M/min}$
 (c) $2 \times 10^{-4} \text{ M}^{-1}\text{min}^{-1}$
 (d) $6.93 \times 10^{-4} \text{ min}^{-1}$
25. The time for 87.5% completion of the reaction is
 (a) 350 min (b) 300 min
 (c) 400 min (d) 600 min
26. The total pressure, when pressure of 'X' is 700 mm of Hg, is
 (a) 1000 mm Hg
 (b) 900 mm Hg
 (c) 950 mm Hg
 (d) 250 mm Hg

Comprehension VIII

Consider the following reaction occurring at constant volume:



The rate of reaction is $r = k \cdot C_B$, where C_B = concentration of 'B' at any time 't' and k = specific reaction rate.

27. Concentration of 'A' at time 't' is

(a) $C_A = a - kt$

(b) $C_A = a \cdot e^{-kt}$

(c) $C_A = a - \frac{b}{2}(1 - e^{-2kt})$

(d) $C_A = a - b(1 - e^{-kt})$

28. Time at which the concentration of 'A' reduces half of its initial value is

(a) $\frac{a}{2k}$

(b) $\frac{a}{k}$

(c) $\frac{1}{2k} \ln \frac{b}{b-a}$

(d) $\frac{\ln 2}{k}$

29. Condition for $(t_{1/2})_A = (t_{1/2})_B$ is

(a) $b = 2a$

(b) $b = a$

(c) $a = 2b$

(d) none of these

Comprehension IX

The gaseous reaction: $n_1A(g) \rightarrow n_2B(g)$, is first order with respect to 'A'. The rate constant of reaction is 'K'. The reaction is studied at a constant pressure and temperature. Initially, the moles of 'A' was 'a' and 'B' was not present.

30. How many moles of 'A' are present at time, t?

(a) $a \cdot e^{-kt}$

(b) $a \cdot e^{-n_1kt}$

(c) $a \cdot e^{-n_2kt}$

(d) $a(1 - e^{-n_1kt})$

(c) $v_0 \left[\frac{n_2}{n_1} + \left(1 - \frac{n_2}{n_1} \right) \cdot e^{-n_1kt} \right]$

(d) $v_0 \left[\frac{n_1}{n_2} - \left(\frac{n_2}{n_1} - 1 \right) \cdot e^{-n_1kt} \right]$

31. If the initial volume of system was V_0 , then the volume of system after time, t, will be

(a) $\frac{n_1 v_0}{n_2}$

(b) $\frac{n_2 v_0}{n_1}$

32. What will be the concentration of 'A' at time t, if $n_1 = 1$ and $n_2 = 2$?

(a) $[A_0] \cdot e^{-kt}$

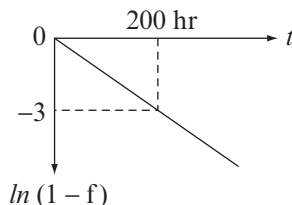
(b) $[A_0] \left(\frac{e^{-kt}}{2 - e^{-kt}} \right)$

(c) $[A_0] \left(\frac{e^{-kt}}{1 - e^{-kt}} \right)$

(d) $[A_0] (1 - 2 \cdot e^{-kt})$

Comprehension X

Oxidation of metals is generally a slow electrochemical reaction involving many steps. These steps involve electron transfer reactions. A particular type of oxidation involve overall first-order kinetics with respect to fraction of unoxidized metal surface thickness $(1 - f)$ relative to the maximum thickness (T) of oxidized surface, when metal surface is exposed to air for a considerable period of time.



Rate law: $\frac{df}{dt} = K(1 - f)$,

where, $f = x/T$,

x = thickness of the oxide film at time ' t '

and, T = thickness of the oxide film at $t = \infty$

For the oxidation of a particular metal, a graph is shown in the figure.

33. The time taken for thickness to grow 50% of T is
- 23.1 h
 - 46.2 h
 - 100 h
 - 92.4 h
34. The exponential variation of f with t (h) is
- $f = 1 - e^{-3t/200}$
 - $f = e^{-3t/200} - 1$
 - $f = e^{-3t/200}$
 - $f = e^{3t/200}$

Comprehension XI

Trans-1,2-dideuterocyclopropane (A) undergoes first-order decomposition. The observed rate constant at a certain temperature, measured in terms of the disappearance of A, was $1.5 \times 10^{-4} \text{ s}^{-1}$. Analysis of the reaction products showed that the reaction follows two parallel paths, one leading to dideuteropropene (B) and the other to *cis*-1,2-dideuterocyclopropane (C). 'B' was found to constitute 10% of the reaction product, independent of the extent of reaction.

35. What is the order of the reaction for each of the paths?
- 0
 - 0.5
 - 1
 - 2
36. The rate constant for the formation of 'B' is
- $1.5 \times 10^{-4} \text{ s}^{-1}$
 - $1.35 \times 10^{-5} \text{ s}^{-1}$
 - $1.5 \times 10^{-5} \text{ s}^{-1}$
 - $1.5 \times 10^{-3} \text{ s}^{-1}$

Comprehension XII

Consider the following first-order consecutive reactions: $A \xrightarrow{K_1} B \xrightarrow{K_2} C$. The initial concentration of A is 1.0 M and $K_1 : K_2 = 2.0 : 3.0$. Given that $K_1 = 0.04 \text{ min}^{-1}$. ($e = 2.72$, $e^{-1} = 0.368$, $e^{1.5} = 4.48$, $e^{-1.5} = 0.223$, $e^{-2} = 0.135$, $e^{0.7} = 2$, $e^{1.1} = 3$, $e^{-0.8} = 0.45$)

37. What is the concentration of 'A' after 25 min?
- 0.5 M
 - 0.368 M
 - 0.135 M
 - 0.223 M
38. What is the concentration of 'B' after 25 min?
- 0.223 M
 - 0.29 M
 - 0.27 M
 - 0.145 M

39. What is the concentration of 'C' after 25 min?
 (a) 0.0 M
 (b) 0.342 M
 (c) 0.29 M
 (d) 0.145 M
40. In what time, the concentration of 'B' will become maximum?
 (a) 10 min
 (b) 20 min
 (c) 25 min
 (d) 40 min
41. What is the maximum concentration of 'B'?
 (a) 0.290 M
 (b) 0.296 M
 (c) 0.50 M
 (d) 0.444 M
42. In what time, the concentrations of A, B and C become equal?
 (a) 20 min
 (b) 27.5 min
 (c) 22.5 min
 (d) never
43. What is the concentration of 'A' when $-\frac{d[A]}{dt} = +\frac{d[C]}{dt}$?
 (a) 0.704 M
 (b) 0.45 M
 (c) 0.33 M
 (d) 0.5 M
44. What is the maximum rate of formation of 'C'?
 (a) 0.342 M/min
 (b) 1.776×10^{-2} M/min
 (c) 2.052×10^{-2} M/min
 (d) 6.0×10^{-2} M/min

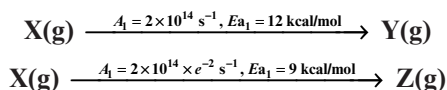
Comprehension XIII

For the first-order reaction opposed by first-order reaction: $A \xrightleftharpoons[K_b]{K_f} B$, $[A]_0 = 0.15$ M, $[A]_e = 0.10$ M, $[A]_{10} = 0.125$, where times are given in min.

45. What is the rate constant of forward reaction?
 (a) $2.31 \times 10^{-2} \text{ min}^{-1}$
 (b) $4.62 \times 10^{-2} \text{ min}^{-1}$
 (c) $2.31 \times 10^{-3} \text{ min}^{-1}$
 (d) $1.165 \times 10^{-2} \text{ min}^{-1}$
46. What is the rate constant of backward reaction?
 (a) $2.31 \times 10^{-2} \text{ min}^{-1}$
 (b) $4.62 \times 10^{-2} \text{ min}^{-1}$
 (c) $2.31 \times 10^{-3} \text{ min}^{-1}$
 (d) $1.165 \times 10^{-2} \text{ min}^{-1}$
47. What is the equilibrium constant of the reaction?
 (a) 1.5
 (b) 0.67
 (c) 0.5
 (d) 2.0
48. Half-life of a reversible reaction may be defined as the time in which half of the amount of reactant which should react up to equilibrium, has been reacted. The half-life of the reaction is
 (a) 10 min
 (b) 15 min
 (c) 5 min
 (d) 20 min

Comprehension XIV

A substance 'X' dissociates simultaneously into 'Y' and 'Z' as



49. Temperature at which the net activation energy for the dissociation of 'X' will be 10.5 kcal/mol, is
 (a) 200 K (b) 750 K
 (c) 900 K (d) 625 K
50. Which of the following statement is correct regarding the major product of the reactions?
 (a) 'Y' will be the major product at 300 K.
 (b) 'Y' will be the major product at 700 K.
 (c) 'Y' will be the major product at 900 K.
 (d) 'Z' will be the major product at 900 K.
51. If the temperature is increased, then
 (a) The rate of formation of 'Y' will increase but the rate of formation of 'Z' will decrease.
 (b) The rate of formation of both, 'Y' and 'Z' will increase in such a way that the ratio of rate constants of their formation remains constant.
 (c) The rate of formation of both, 'Y' and 'Z' will increase in such a way that the ratio of rate constants of their formation decreases.
 (d) The rate of formation of both, 'Y' and 'Z' will increase in such a way that the ratio of rate constants of their formation increases.

Comprehension XV

For the reaction sequence: $A \xrightleftharpoons[K_{-1}]{K_1} B \xrightleftharpoons[K_{-2}]{K_2} C \xrightleftharpoons[K_{-3}]{K_3} D$. D is more stable than A by 42.8 kcal/mol, B is more stable than C by 13.2 kcal/mol and A is more stable than C by 20.8 kcal/mol. The transition state going from A to B is more stable than the transition state going from B to C by 10.2 kcal/mol, but it is less stable than the transition state going from C to D by 2.4 kcal/mol. The energy of activation of C for transition state C to D is 4.3 kcal/mol.

52. Which is the faster step in the forward direction?
 (a) $A \longrightarrow B$
 (b) $B \longrightarrow C$
 (c) $C \longrightarrow D$
 (d) Cannot be predicted
53. Which is the faster step in the backward direction?
 (a) $D \longrightarrow C$
 (b) $C \longrightarrow B$
 (c) $B \longrightarrow A$
 (d) Cannot be predicted
54. Which is fastest step among these six steps?
 (a) $C \longrightarrow D$ (b) $C \longrightarrow B$
 (c) $B \longrightarrow A$ (d) $B \longrightarrow C$
55. Which is rate-determining step in forward direction?
 (a) $A \longrightarrow B$
 (b) $B \longrightarrow C$
 (c) $C \longrightarrow D$
 (d) Cannot be predicted
56. Which is rate-determining step in backward direction?
 (a) $D \longrightarrow C$
 (b) $C \longrightarrow B$
 (c) $B \longrightarrow A$
 (d) Cannot be predicted

Section D (Assertion – Reason)

The following questions consist of two statements. Mark

- (a) If both statements are CORRECT, and **Statement II** is the CORRECT explanation of **Statement I**.
- (b) If both statements are CORRECT, and **Statement II** is NOT the CORRECT explanation of **Statement I**.
- (c) If **Statement I** is CORRECT, but **Statement II** is INCORRECT.
- (d) If **Statement I** is INCORRECT, but **Statement II** is CORRECT.

1. **Statement I:** A fractional-order reaction must be a complex reaction.

Statement II: Fractional order of rate-determining step equals to overall order of a complex reaction.

2. **Statement I:** The time of completion of reactions of type: $A \rightarrow \text{products}$ (order < 1) may be determined.

Statement II: Reactions with order ≥ 1 are either too slow or too fast and hence, the time of completion cannot be determined.

3. **Statement I:** The temperature coefficient of a single-step reaction may be negative.

Statement II: The rate of reaction having negative order with respect to a reactant decreases with the increase in concentration of that reactant.

4. **Statement I:** The overall rate of a reversible reaction may decrease with the increase in temperature.

Statement II: When the activation energy of forward reaction is less than that of backward reaction, then the increase in the rate of backward reaction is more than that of forward reaction on increasing the temperature.

5. **Statement I:** In a reversible endothermic reaction, activation energy of forward reaction is higher than that of backward reaction.

Statement II: The threshold energy of forward reaction is more than that of backward reaction.

6. **Statement I:** A catalyst provides an alternative path to the reaction in which conversion of reactants into products takes place quickly.

Statement II: The catalyst forms an activated complex of lower potential energy with the reactants by which more number of molecules are able to cross the barrier per unit time.

7. **Statement I:** In zero-order reactions, half-life is half of the completion time of reaction.

Statement II: Half-life is half of the time for completion of reaction of any order.

8. **Statement I:** $2A + B \rightarrow 2C + D$ must be a third-order reaction.

Statement II: The rate constant for a third-order reaction has unit $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$.

9. **Statement I:** For zero-order reaction ($A \rightarrow B$), successive half-life of reaction decreases with the progress of reaction.

Statement II: Rate of zero-order reaction remains unchanged with the progress of reaction.

10. **Statement I:** The concentration of pure solid and pure liquid is taken as constant at constant temperature.

Statement II: The concentration of pure solid and liquids depends on density and molecular mass.

Section E (Column Match)

1. Match the following

Column I (Reactions)	Column II (Unit of rate constant, K)
(A) $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$	(P) s^{-1}
(B) $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$	(Q) min^{-1}
(C) $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$	(R) $\text{L mol}^{-1} \text{min}^{-1}$
(D) $\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + \text{I}_2$	(S) $\text{L mol}^{-1} \text{s}^{-1}$

2. Match the following

Column I (Reactions)	Column II (Increase in rate when concentration of reactant is doubled)
(A) $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$	(P) 2 times
(B) $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$	(Q) $2^{1.5}$ times
(C) $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$	(R) 2 times in acid medium
(D) $\text{CH}_3\text{COOC}_2\text{H}_5 \xrightarrow{\text{HOH}} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$	(S) 2^2 times in basic medium

3. Match Column I with Column II

Column I	Column II
(A) $\text{Rate} = k \times \text{Intensity of light}$	(P) Second order
(B) $\text{Rate} = k[\text{A}]^1[\text{B}]^1$	(Q) Zero order

Column I	Column II
(C) $\text{Rate} = k[\text{A}]^{3/2}[\text{B}]^{1/2}$	(R) First-order when A is excess
(D) $\text{Rate} = k[\text{A}]^2[\text{B}]^1$	(S) Second order when B is excess

4. Match the kinetic equation of Column I with the unit of its rate constant in Column II

Column I (Kinetic equation)	Column II (Unit of rate constant)
(A) $x = kt$	(P) s^{-1}
(B) $k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$	(Q) $\text{l mol}^{-1} \text{s}^{-1}$
(C) $k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right]$	(R) $\text{mol l}^{-1} \text{s}^{-1}$
(D) $k = \frac{2.303}{t(a-b)} \log \left[\frac{b(a-x)}{a(b-x)} \right]$	(S) $\text{atm}^{-1} \text{s}^{-1}$

5. Match the half-life in Column I with the order in Column II for the reaction:
- $\text{A} \rightarrow \text{Products}$
- .

Column I	Column II
(A) $t_{1/2} = \text{constant}$	(P) First order
(B) $t_{1/2} \propto a$	(Q) Third order
(C) $t_{1/2} \propto 1/a$	(R) Second order
(D) $t_{1/2} \propto 1/a^2$	(S) Zero order

where a = Initial concentration of the reactant

6. Match Column I with Column II and Column III for the reaction:
- $A \rightarrow \text{Products}$
- .

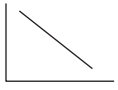
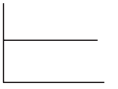
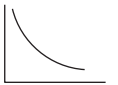
Column I	Column II	Column III
(A) x is plotted against t in zero-order reaction	(P) Slope $= -k/2.303$	(U) Intercept $= a$
(B) $\log(a - x)$ is plotted against ' t ' in first-order reaction	(Q) Slope $= 2k$	(V) Intercept $= 1/a$
(C) $(a - x)^{-1}$ is plotted against ' t ' in second order reaction	(R) Slope $= -k$	(W) Intercept $= 1/a^2$
(D) $(a - x)^{-2}$ is plotted against ' t ' in second order	(S) Slope $= k$	(X) Intercept $= \log a$ reaction

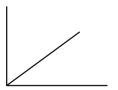
where 'a' = Initial concentration reactant, 'x' = Extent of reaction in time ' t ' s.

7. Match Column I with Column II for the reaction:
- $A \rightarrow \text{Products}$
- , with initial concentration of 'A' equal to 'a' M.

Column I	Column II
(A) $\frac{0.693}{k}$	(P) Half-life of zero-order reaction
(B) $\frac{a}{2k}$	(Q) Half-life of first-order reaction
(C) $\frac{1}{k}$	(R) Average life of zero-order reaction
(D) $\frac{1}{a \cdot k}$	(S) Average life of first-order reaction
	(T) Half-life of second-order reaction

8. Match the following columns

Column I (Graphs for reaction: $A \rightarrow \text{Products}$)	Column II (Co-ordinates, y-axis vs x-axis)
(A) 	(P) $\ln[A]$ vs t (order = 1)
(B) 	(Q) $t_{1/2}$ vs $[A_0]$ (order = 1)
(C) 	(R) r vs t (order > 0)

Column I (Graphs for reaction: $A \rightarrow \text{Products}$)	Column II (Co-ordinates, y-axis vs x-axis)
(D) 	(S) r vs t (order = 0)
	(T) $t_{1/2}$ vs $[A_0]$ (order > 1)
	(U) r vs $[A]$ (order = 1)

9. For the reaction:
- $A \rightarrow \text{Products}$
- ,
- $t_{x/y}$
- represents the time in which
- x/y
- fraction of reactant converts into products.

Column I	Column II
(A) $t_{5/9}$	(P) equal to 54 s, if $t_{1/3}$ is 18 s, in case of first-order reaction.
(B) $t_{19/27}$	(Q) equal to 32 s, if $t_{1/4}$ is 16 s, in case of first-order reaction.
(C) $t_{7/8}$	(R) equal to 56 s, if $t_{1/3}$ is 4 s, in case of second-order reaction.
(D) $t_{7/16}$	(S) equal to 30 s, if $t_{1/3}$ is 18 s, in case of zero-order reaction.
	(T) equal to 28 s, if $t_{1/2}$ is 16 s, in case of zero-order reaction.

10. For the first-order consecutive reactions: $A \xrightarrow{K_1} B \xrightarrow{K_2} C$, the reaction is started with some amount of only 'A'. Match the Column I (observations) with Column II (time) related with reactions.

Column I	Column II
(A) Rate of formation of 'C' is maximum	(P) $t = t_{1/2}$ of A, if $K_2 = 2K_1$
(B) $[B]_t = [C]_t$	(Q) $t = \frac{1}{K_2 - K_1} \cdot \ln \left(\frac{K_2}{K_1} \right)$

Column I	Column II
(C) $[A]_t = [B]_t$	(R) $t =$ time at which the rate of formation of 'B' is maximum
	(S) $t = \frac{1}{K_1 - K_2} \cdot \ln \left(\frac{2K_1 - K_2}{K_1(K_1 - K_2)} \right)$

Section F (Subjective)

Single Digit Integer Type

1. The number of reactions among the following, as written, could describe elementary reaction, is

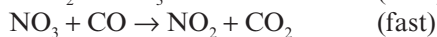
- $\text{Cl}_2 + \text{CO} \rightarrow \text{COCl}_2$; $r = K [\text{Cl}_2]^{3/2} [\text{CO}]$
- $\text{PCl}_3 + \text{Cl}_2 \rightarrow \text{PCl}_5$; $r = K [\text{PCl}_3] [\text{Cl}_2]$
- $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$; $r = K [\text{NO}] [\text{H}_2]$
- $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$; $r = K [\text{NO}]^2 [\text{O}_2]$
- $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$; $r = K [\text{NO}] [\text{O}_3]$

2. The following mechanisms are proposed for the reaction: $\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$, at low temperature:

Mechanism 1



Mechanism 2



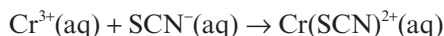
Which of the above mechanism is consistent with the observed rate law: $+\frac{d[\text{CO}_2]}{dt} = K [\text{NO}_2]^2$?

3. For the reaction: $3\text{BrO}^- \rightarrow \text{BrO}_3^- + 2\text{Br}^-$ in alkaline aqueous solution, the value of the second-order rate constant (in BrO^-) in rate law for $-\frac{d[\text{BrO}^-]}{dt}$ was found to be $0.06 \text{ M}^{-1}\text{s}^{-1}$. The rate constant (in $\text{M}^{-1}\text{s}^{-1}$), when the rate law is written as $+\frac{d[\text{BrO}_3^-]}{dt}$ is a and as $+\frac{d[\text{Br}^-]}{dt}$ is b , then the value of $(a + b) \times 100$ is
4. In a certain polluted atmosphere containing O_3 at a steady-state concentration of $2 \times 10^{-8} \text{ M}$, the hourly production of O_3 by all sources was estimated as $7.2 \times 10^{-15} \text{ M}$. If only mechanism for the destruction of O_3 is second-order reaction, the rate constant (in $\text{ml mol}^{-1} \text{ s}^{-1}$) for the destruction reaction is

5. For the reaction: $2\text{NO}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g})$, the value of $-\frac{dP}{dt}$ was found to be 1.5 Pa s^{-1} for a pressure of 372 Pa for NO and 0.25 Pa s^{-1} for a pressure of 152 Pa for H_2 , the pressure of H_2 being constant. If pressure of NO was kept constant, the value of $-\frac{dP}{dt}$ was found 1.60 Pa s^{-1} for a pressure of 289 Pa for H_2 and 0.79 Pa s^{-1} for a pressure of 144 Pa for H_2 . If the order of reaction with respect to NO and H_2 are a and b , respectively, then the value of $(a + b)$ is
6. For a chemical reaction $\text{A} + \text{B} \rightarrow \text{Products}$, the order is one with respect to each A and B. The sum of x and y from the following data is

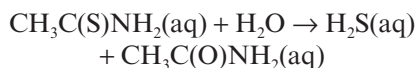
Rate ($\text{mol l}^{-1}\text{s}^{-1}$)	[A] (mol l^{-1})	[B] (mol l^{-1})
0.10	0.20	0.05
0.40	x	0.05
0.80	0.40	Y

7. In the presence of excess thiocyanate ion, SCN^- , the following reaction is first-order in chromium (III) ion, Cr^{3+} ; the rate constant is $9.0 \times 10^{-5} \text{ s}^{-1}$.



If 80.0% reaction is required to obtain a noticeable colour from the formation of the $\text{Cr}(\text{SCN})^{2+}$ ion, how many hours are required? ($\ln 5 = 1.62$)

8. The reaction of thioacetamide with water is shown by the equation below:



The rate of reaction is given by the rate law: $\text{Rate} = k[\text{H}_3\text{O}^+][\text{CH}_3\text{C}(\text{S})\text{NH}_2]$. Consider 1 l of solution that is 0.20 M in $\text{CH}_3\text{C}(\text{S})\text{NH}_2$ and 0.15 M in HCl at 25°C .

For each of the changes listed below, the number of changes that decreases the rate of reaction is

- A 4.0 g sample of NaOH is added to the solution.
 - 500 ml of water is added to the solution.
 - The 0.15 M HCl solution is replaced by 0.15 M acetic acid solution.
 - The reaction is carried out at 35°C instead of 25°C .
9. If 0.01% of a substance undergoing decomposition is consumed in 1 ms when the concentration is 0.02 M and in 0.25 ms when the concentration is 0.04 M. The order of reaction is
10. Ethylene is produced as: $\text{C}_4\text{H}_8 \rightarrow 2\text{C}_2\text{H}_4$. The rate constant is $2.5 \times 10^{-5} \text{ s}^{-1}$. In what time (in hours) will the molar ratio of the ethylene to cyclobutane in the reaction mixture attain the value 1.0? ($\ln 2 = 0.3$, $\ln 3 = 0.48$)
11. A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration and at the beginning of the experiment, 2.0% of the virus was found to be inactivated per minute. If the rate constant for the inactivation process is $K \text{ min}^{-1}$, then the value of $400 K$ is
12. Hydrogen peroxide in aqueous solution decomposes by a first-order reaction to water and oxygen. The rate constant for this decomposition is $7.50 \times 10^{-4} \text{ s}^{-1}$. What quantity of heat (in J) is initially liberated per second from 2.0 l of solution that is 0.02 M H_2O_2 ? Given $\Delta_r H$ of $\text{H}_2\text{O}_2(\text{l}) = -187.0 \text{ kJ/mol}$ and $\Delta_r H$ $\text{H}_2\text{O}(\text{l}) = -287.0 \text{ kJ/mol}$.
13. An optically active drug has one chiral centre and only dextrorotatory isomer is effective. Moreover, it becomes ineffective

when its optical activity is reduced to 40% of original. It was found that mutarotation of this drug was first-order reaction with rate constant $\frac{1}{3.1536} \times 10^{-8} \text{ s}^{-1}$. The expiration time of the drug (in years) is ($\ln 2 = 0.7$, $\ln 3 = 1.1$, $\ln 5 = 1.6$)

14. For the reaction: $A(g) \rightarrow nB(g)$, rate constant is $6.93 \times 10^{-4} \text{ s}^{-1}$. The reaction is performed at constant volume and temperature, starting with pure $A(g)$. If after 1000 s from the start of reaction, the pressure of system becomes 3 times the initial pressure, the value of n is
15. The acidic hydrolysis of ethyl acetate in aqueous solution is first order with respect to ethyl acetate. Upon varying the pH of solution, the first-order rate constant varies as follows:

pH	3	2	1
$K_1 (\times 10^{-3} \text{ s}^{-1})$	1.0	10	100

If the order of reaction with respect to H^+ is x and the value of the rate constant (in $M^{-1} \text{ s}^{-1}$) is y , then the value of $(x + y)$ is

16. The complex $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$ reacts with water as: $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+} + \text{F}^-$. The rate of reaction may be given as, $r = K [\text{complex}]^a [\text{H}^+]^b$. The reaction is acid catalysed and hence $[\text{H}^+]$ does not change during the reaction. Thus, the rate may be given as $r = K' [\text{complex}]^a$ where $K' = K [\text{H}^+]^b$. The value of $(a + b)$ is

[Complex]	$[\text{H}^+]$	$t_{1/2} \text{ (h)}$	$t_{3/4} \text{ (h)}$
0.1 M	0.01 M	1.0	2.0
0.2 M	0.02 M	0.5	1.0

17. If for a reaction $A \rightarrow \text{products}$, the concentration of A are $C_0, a \cdot C_0, a^2 \cdot C_0, a^3 \cdot C_0, \dots$ after time interval 0, $t, 2t, 3t, \dots$, where a is constant and $0 < a < 1$. The order of reaction is

18. Dissociation of salt $A_2B_3(aq)$ in water follows first-order kinetics: $A_2B_3(aq) \rightarrow 2A^{3+}(aq) + 3B^{2-}(aq)$. Starting from $t = 0$, a definite volume of solution is taken at different instant and its osmotic rise is measured. If the osmotic rise was 2 mm at $t = 0$ and 6 mm at $t = 10$ min, then the value of $\frac{x}{y}$ is, where $x = \text{osmotic pressure of solution (in Pascal) at } t = 20 \text{ min}$ and $y = t_{3/4}$ of the dissociation reaction (in min) [Given: Density of final solution in each case = 1.0 g/ml, $g = 10 \text{ m/s}^2$]

19. A substance, A, undergoes a reaction such that its concentration at any time, t (in seconds), can be represented by the equation: $[A]_t^4 = \frac{1}{(t+1)}$. The rate of disappearance of 'A' (in $M \text{ s}^{-1}$) at the concentration, $[A] = 2.0 \text{ M}$, is

20. In order to determine the order of reaction: $A(g) \rightarrow 2B(g)$, vapour density of the system is determined at different stages of reaction, at constant temperature. The reaction is started with pure $A(g)$. From the following data, the order of reaction is

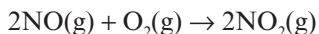
Time (min)	0	10	20
Vapour density	42	35	30

21. In the reaction: $A \rightarrow \text{Products}$, the rate is doubled when the concentration of 'A' is quadrupled. If 50% of the reaction occurs in $8\sqrt{2} \text{ h}$, how long (in hours) would it take for the completion of next 50% reaction?
22. A gaseous compound 'A' decomposes simultaneously into gaseous products 'B', 'C' and 'D' with the rate constants $2 \times 10^{-3} \text{ s}^{-1}$, $3 \times 10^{-3} \text{ s}^{-1}$ and $1.93 \times 10^{-3} \text{ s}^{-1}$, respectively. If only $A(g)$ was present initially at a pressure of 13.86 atm and the reaction is performed at constant volume and temperature, the partial pressure (in atm) of $B(g)$ in the reaction mixture after 100 s from the start of reaction is

23. Consider two first-order reactions I and II. The frequency factor of I is 100 times that of II, the activation energy of I is 4.606 kcal higher than that of II. If the ratio of rate constants for the reactions I and II is $x:1$, at 227°C, the value of x is
24. If activation energy of a reaction is 83.14 kJ/mole, the fraction of molecules at 500 K which have enough energy to form products is $x \times 10^{-y}$. The value of $(y - x)$ is ($\ln 2 \times 10^{-9} = -20$, $\ln 4 \times 10^{-5} = -10$, $\ln 4 \times 10^{-18} = -40$)
25. A given sample of milk turns sour at room temperature (27°C) in 16 h. In a refrigerator at 7°C, milk can be stored three times as long before it sours. How long (in hours) it takes milk to sour at 57°C?

Four Digit Integer Type

- The rate constant for the decomposition of ozone following second-order kinetics is $5 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$ at a certain temperature. The rate of reaction (in terms of number of molecules decomposed per ml per minute, when concentration of ozone is $2 \times 10^{-8} \text{ M}$, is ($N_A = 6 \times 10^{23}$)
- In thermal decomposition of $\text{C}_2\text{H}_5\text{Br(g)}$ to $\text{C}_2\text{H}_4\text{(g)}$ and HBr(g) , the initial pressure changes from 200 to 390 mm of Hg at the end of reaction. Percentage of $\text{C}_2\text{H}_5\text{Br(g)}$ undecomposed, when pressure of mixture was 342.5 mm of Hg, is
- The generation time of any substance is the time in which its concentration doubles. The growth of a certain bacteria follows first-order kinetics. If the population of bacteria triples in 96 h, what is the generation time (in h) for it? ($\log 2 = 0.3$, $\log 3 = 0.48$)
- Nitric oxide reacts with oxygen to give nitrogen dioxide



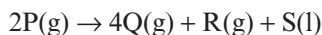
The rate law is $-\Delta[\text{NO}]/\Delta t = k[\text{NO}]^2[\text{O}_2]$, where the rate constant is $1.6 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$ at 327°C. A vessel contains NO and O_2 at 327°C. The initial partial pressures of NO and O_2 are 190 and 288 mm Hg, respectively. The initial rate of decrease

of partial pressure of NO (in mm Hg per second) is ($R = 0.08 \text{ L-atm/K-mol}$)

- A drop (0.05 ml) of solution contains 3×10^{-7} moles of H^+ . If the rate constant of disappearance of H^+ is $1.0 \times 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$, how long (in min) would it take for H^+ in drop to disappear?
- A substance is reduced to one third of its original concentration in 100 minutes, by first-order kinetics. The time (in min) in which it will be reduced to one ninth of its original value is
- A drug is known to be ineffective after it has decomposed 30%. The original concentration of a sample was 500 units/ml. When analysed 20 months later, the concentration was found to be 420 units/ml. Assuming that the decomposition is first order, what will be the expiration time (in month) of the drug? ($\ln 2 = 0.7$, $\ln 5 = 1.6$, $\ln 7 = 1.9$)
- The decomposition of benzene diazonium chloride in aqueous solution is a reaction of first order which proceeds as: $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{N}_2\text{(g)}$. A certain solution of benzene diazonium chloride contains initially an amount of this compound which gives 80 cm^3 of nitrogen on complete decomposition. It is found that at 30°C, 40 cm^3 of nitrogen are evolved

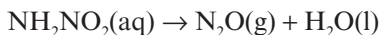
in 40 minute. How long (in min) after the start of the decomposition, will 70 cm³ of nitrogen have been evolved?

9. The decomposition of a compound 'P' at temperature T , according to the equation:



is a first-order reaction. After 30 min, from the start of the decomposition in a closed vessel, the total pressure developed is found to be 445 mm and after a long time, total pressure is 625 mm. The vapour pressure of S(l) at this temperature is 25 mm. The total pressure after 60 min is

10. The half-life for the first-order decomposition of nitramide:

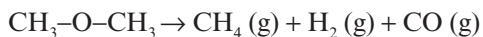


is 123 min at 27°C. If 200 ml of 0.02 M NH_2NO_2 solution is allowed to decompose, how long (in min) must the reaction proceed to produce 49.26 ml of 'wet' $\text{N}_2\text{O(g)}$ measured at 27°C and 785 mm Hg? The vapour pressure of water at 27°C is 25 mm Hg.

11. The reaction $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ goes to completion and follows the rate law $-\frac{d[\text{A}]}{dt} = K[\text{A}]^2[\text{B}]$. The sum of values of x and y in the following data:

Set	$[\text{A}_0] \times 10^6 \text{ M}$	$[\text{B}_0] \times 10^6 \text{ M}$	Half-life (s)
1	300	40	62.5
2	300	60	x
3	5	300	625
4	10	300	y

12. The gas phase decomposition of dimethyl ether follows first-order kinetics:



The reaction is carried out in a constant volume container at 500°C and has a half-life of 14.5 minutes. Initially, only dimethyl ether is present at a pressure of 4.0 atmosphere. What is the total pressure of the system (in atm) after 43.5 min? Assume ideal gas behaviour.

13. The rate of a first-order reaction is 0.04 mol litre⁻¹s⁻¹ at 10 minutes and 0.03 mol litre⁻¹s⁻¹ at 22 minute after initiation. The half-life of the reaction (in seconds) is ($\ln 2 = 0.7$, $\ln 3 = 1.1$)
14. An acid-catalysed hydrolysis of ester is carried out in the presence of HCl. Small but same volume of reaction mixture were taken out at various instant and were titrated with standard NaOH solution. The following data was obtained:

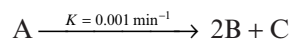
Time (in min)	0	120	∞
Volume (ml) of NaOH solution needed for titration	20	55	60

If the initial concentration of ester was 6.0 M, then calculate the value of $abcd$, where

ab = half-life for the hydrolysis of ester (in min)

cd = molar concentration of HCl used in the experiment.

15. For the reaction: $\text{A(g)} \rightarrow 2\text{B(g)} + \text{C(g)}$, the rate constant is $1.386 \times 10^{-3} \text{ s}^{-1}$. The reaction is performed at constant pressure and temperature, starting with only 'A'. The initial concentration of 'A' was 0.1 M. The concentration of 'A' (in millimole per litre) after 500 s from the start of reaction is
16. An optically active substance, A, decomposes into optically active substances 'B' and 'C' as:



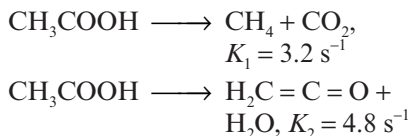
The specific rotations of A, B and C are $+40^\circ$, $+10^\circ$ and -30° per mole, respectively. If initially A and C were present in 4:3 mole ratio, the time (in min), after which the sample becomes optically inactive, is ($\ln 2 = 0.7$, $\ln 5 = 1.6$, $\ln 7 = 2.0$, $\ln 13 = 2.5$)

17. For a reaction: $2A + B \rightarrow C + D$, the following data is collected by experiments:

Set	$[A]_0 \times 10^{-2} \text{ M}$	$[B]_0 \times 10^{-2} \text{ M}$	$T_{1/2} \text{ (min)}$	$T_{7/8} \text{ (min)}$
1	500	2	30	90
2	3	400	10	70
3	6	800	a	b
4	250	1	c	d

The value of $(a + b + c + d)$ is

18. The gas phase decomposition of acetic acid at 1189 K proceeds by way of two parallel reactions:



The maximum percentage yield of the ketene, CH_2CO , obtainable at this temperature, is

19. For overall reaction: $A + 2B + 3C \rightleftharpoons D$, the reaction rate is given as:

$$r \text{ (M/min)} = 2 \times 10^6 [A]^2 - \frac{1.2 \times 10^6 [D]^2}{[B][C]}$$

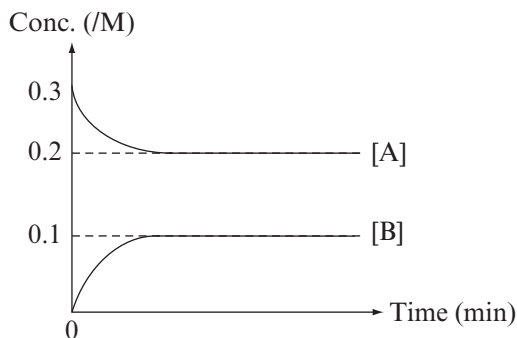
If initially each of the reactant has concentration 1.0 M, calculate the rate of reaction when concentration of C becomes 0.7 M assuming no D is present at the start of the reaction. If the rate is ' r ' M/min, then the value of $(r \times 10^8)$ is

20. A mixture of two substances A and B gives the same product C by two parallel first-order reactions:



If the initial concentrations of A and B are 1.0 and 0.8 M, respectively, and their half-lives, T_A and T_B , are 10 min and 15 min, respectively, the concentration of C (in millimole per litre) after 30 min?

21. For the reversible reaction: $A(\text{aq}) \rightleftharpoons B(\text{aq})$, which is first order in both directions, $K_r = \frac{1.38}{300} \text{ min}^{-1}$. The variation in concentrations with time is shown in the figure:



The time (in min) in which 25% of 'A' would be converted into 'B', is ($\ln 2 = 0.69$)

22. At 25°C , a reaction is complete in 4 h. Approximately what temperature (in $^\circ\text{C}$) must be used to cause the reaction to be completed in 30 min? The temperature coefficient of reaction is 2.
23. The rate of decomposition for CH_3NO_2 and $\text{C}_2\text{H}_5\text{NO}_2$ can be given in terms of rate constant (in s^{-1}) K_1 and K_2 , respectively. The energy of activation for these reactions is 152.30 and 171.39 kJ/mol and the frequency factors are 10^{13} and 10^{14} s^{-1} , respectively. The temperature (in $^\circ\text{C}$) at which rate constant will be same for both decomposition reactions, is ($R = 8.3 \text{ J/K}\cdot\text{mol}$, $\ln 10 = 2.3$)
24. The activation energy of a reaction is 145.25 kJ/mol and pre-exponential factor is $5 \times 10^{13} \text{ s}^{-1}$. At what temperature (in K) will the reaction have half-life of

1 min? ($\ln 2 = 0.7$, $\ln 3 = 1.1$, $\ln 7 = 2.0$, $\ln 10 - 16 = -36.5$, $R = 8.3 \text{ J/K-mol}$)

25. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried

out in the presence of a catalyst at the same rate, the temperature required is 400 K. The activation energy of reaction (in kJ/mol), if the catalyst lowers the activation energy by 20 kJ/mol, is

Answer Keys – Exercise II

Section A (Only one Correct)

- | | | | | | | | | | |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b) | 2. (b) | 3. (d) | 4. (c) | 5. (c) | 6. (c) | 7. (b) | 8. (a) | 9. (d) | 10. (d) |
| 11. (b) | 12. (a) | 13. (c) | 14. (d) | 15. (c) | 16. (b) | 17. (b) | 18. (c) | 19. (c) | 20. (c) |
| 21. (d) | 22. (b) | 23. (b) | 24. (d) | 25. (c) | 26. (c) | 27. (a) | 28. (a) | 29. (a) | 30. (c) |
| 31. (a) | 32. (a) | 33. (b) | 34. (d) | 35. (d) | 36. (a) | 37. (a) | 38. (b) | 39. (b) | 40. (a) |
| 41. (c) | 42. (a) | 43. (b) | 44. (a) | 45. (d) | 46. (a) | 47. (c) | 48. (c) | 49. (c) | 50. (b) |
| 51. (a) | 52. (b) | 53. (a) | 54. (a) | 55. (a) | 56. (a) | 57. (b) | 58. (a) | 59. (d) | 60. (b) |
| 61. (a) | 62. (c) | 63. (b) | 64. (a) | 65. (a) | 66. (b) | 67. (a) | 68. (c) | 69. (b) | 70. (c) |
| 71. (b) | 72. (c) | 73. (a) | 74. (b) | 75. (d) | | | | | |

Section B (One or More than one Correct)

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|------------------------|------------------------|-------------------|------------------------|
| 1. (a), (b), (c), (d) | 2. (c) | 3. (b), (c) | 4. (a), (c), (d) |
| 5. (a), (d) | 6. (a), (b), (c) | 7. (b), (c), (d) | 8. (b) |
| 9. (d) | 10. (a), (d) | 11. (c), (d) | 12. (a), (b) |
| 13. (a), (c) | 14. (b), (d) | 15. (a), (b), (d) | 16. (a), (b), (c), (d) |
| 17. (b), (d) | 18. (a), (d) | 19. (a), (b), (c) | 20. (a), (b), (c), (d) |
| 21. (a), (b), (c), (d) | 22. (a), (b), (c), (d) | 23. (a), (c), (d) | 24. (b), (d) |
| 25. (a), (c) | 26. (b) | 27. (c) | 28. (c), (d) |
| 29. (a), (b), (c) | 30. (a), (b), (c) | | |

Section C

Comprehension I

1. (a) 2. (b) 3. (a)

Comprehension II

4. (c) 5. (d) 6. (a) 7. (b)

Comprehension III

8. (d) 9. (c) 10. (a) 11. (a)

Comprehension IV

12. (a) 13. (c) 14. (d) 15. (a)

Comprehension V

16. (d) 17. (b) 18. (a)

Comprehension VI

19. (d) 20. (a) 21. (c) 22. (b)

Comprehension VII

23. (b) 24. (a) 25. (b) 26. (c)

Comprehension VIII

27. (c) 28. (c) 29. (a)

Comprehension IX

30. (b) 31. (c) 32. (b)

Comprehension X

33. (a) 34. (a)

Comprehension XI

35. (c) 36. (c)

Comprehension XII37. (b) 38. (b) 39. (b) 40. (b)
41. (b) 42. (b) 43. (b) 44. (b)**Comprehension XIII**

45. (a) 46. (b) 47. (c) 48. (a)

Comprehension XIV

49. (b) 50. (c) 51. (d)

Comprehension XV52. (c) 53. (b) 54. (a) 55. (b)
56. (a)**Section D (Assertion – Reason)**

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

Section E (Column Match)

1. $A \rightarrow P, Q; B \rightarrow R, S; C \rightarrow P, Q; D \rightarrow R, S$
2. $A \rightarrow Q; B \rightarrow P; C \rightarrow P; D \rightarrow R, S$
3. $A \rightarrow Q; B \rightarrow P, R; C \rightarrow P; D \rightarrow R, S$
4. $A \rightarrow R; B \rightarrow P; C \rightarrow Q, S; D \rightarrow Q, S$
5. $A \rightarrow P; B \rightarrow S; C \rightarrow R; D \rightarrow Q$
6. $A \rightarrow R, U; B \rightarrow P, X; C \rightarrow S, V; D \rightarrow Q, W$
7. $A \rightarrow Q; B \rightarrow P, R; C \rightarrow S; D \rightarrow T$
8. $A \rightarrow P; B \rightarrow Q, S; C \rightarrow R, T; D \rightarrow U$
9. $A \rightarrow S; B \rightarrow P; C \rightarrow R, T; D \rightarrow Q$
10. $A \rightarrow P, Q; B \rightarrow P, R; C \rightarrow S$

Section F (Subjective)**Single-digit Integer Type**

1. (3) 2. (2) 3. (6) 4. (5) 5. (3) 6. (1) 7. (5) 8. (3) 9. (3) 10. (2)
11. (8) 12. (3) 13. (2) 14. (5) 15. (2) 16. (2) 17. (1) 18. (4) 19. (8) 20. (0)
21. (8) 22. (2) 23. (1) 24. (7) 25. (4)

Four-digit Integer Type

- | | | | | |
|------------|------------|------------|------------|------------|
| 1. (7200) | 2. (0025) | 3. (0060) | 4. (1200) | 5. (1000) |
| 6. (0200) | 7. (0040) | 8. (0120) | 9. (0535) | 10. (0123) |
| 11. (0375) | 12. (0011) | 13. (1680) | 14. (4003) | 15. (0025) |
| 16. (0500) | 17. (0500) | 18. (0060) | 19. (0160) | 20. (1475) |
| 21. (0100) | 22. (0055) | 23. (0727) | 24. (0500) | 25. (0100) |
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