CHAPTER

11

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.

$$CH_3{-}N \equiv N{-}CH_3(g) \rightarrow C_2H_6(g) + N_2(g)$$

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

(a) 3.5×10^{-6} Ms^{-1} (b) 2.1×10^{-4} Ms^{-1}

(c) 3.5×10^{-6} M h^{-1} (d) 2.1×10^{-3} Mmin^{-1}

2. For the reaction 2HI $\rightarrow$ H_2 + I_2, the expression $-\frac{1}{2}\frac{d[HI]}{dt}$ represents

(a) the rate of formation of HI.

(b) the rate of disappearance of HI.

(c) the instantaneous rate of the reaction.

(d) the average rate of the reaction.

3. For the reaction 4A + B $\rightarrow$ 2C + 2D, the only incorrect statement is

(a) the rate of disappearance of B is one-fourth the rate of disappearance of A.

(b) the rate of appearance of C is half the rate of disappearance of B.

(c) the rate of formation of D is half the rate of consumption of A.

(d) the rates of formation of C and D are equal.

4. For the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$, 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?

(a) 2×10^{-3} Ms^{-1}, 4×10^{-3} Ms^{-1}

(b) 2×10^{-3} Ms^{-1}, 1×10^{-3} Ms^{-1}

(c) 2×10 Ms^{-1}, 2×10^{-3} Ms^{-1}

(d) 4×10^{-3} Ms^{-1}, 2×10^{-3} Ms^{-1}

5. Which of the following statement is wrong about the rate of reaction?

(a) Rate of a reaction cannot be negative.

(b) Rate of a reaction is the change in concentration of the reactant per unit time per unit stoichiometric coefficient of that component.

(c) Average rate and instantaneous rate are always different.

(d) Rate may depend upon the surface area of the reactants.

6. For a reaction $2NH_3 \rightarrow N_2 + 3H_2$, it is observed that

$$-\frac{d[NH_3]}{dt} = K_1[NH_3]; \; +\frac{d[N_2]}{dt} = K_2[NH_3] \text{ and } +\frac{d[H_2]}{dt} = K_3[NH_3]$$

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. The rate constant of a reaction depends upon

(a) concentration (b) pressure
(c) temperature (d) All of these

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 A(g) + B(g) → C(g) is 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} lit mole^{-1} s^{-1}. The rate constant when expressed in ml molecule^{-1} 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. The rate of a reaction A + 2B → P is 2×10^{-2} M/min, when concentrations of each A and B are 1.0 M. If the rate of reaction $r = K[A]^2[B]$, the rate of reaction when half of the B has reacted should be

(a) 5.625×10^{-3} M/min (b) 3.75×10^{-3} M/min
(c) 9.375 M/min (d) 2.5×10^{-3} M/min

12. For the reaction $A_2(g) \rightarrow B(g) + \frac{1}{2}C(g)$, pressure of the system increases from 100 to 120 mm in 5 minutes. 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 $N_2O_5 \rightarrow 4NO_2 + O_2$ is 3.0×10^{-5} s^{-1}. If the rate of reaction is 2.4×10^{-5} mol litre^{-1} 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 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions.

(a) $$\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

(b) $$\text{Rate} = -\frac{d[N_2]}{dt} = -3\frac{d[H_2]}{dt} = +2\frac{d[NH_3]}{dt}$$

(c) $$\text{Rate} = -\frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

(d) $$\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{d[H_2]}{dt} = +\frac{d[NH_3]}{dt}$$

16. For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is 10^{-3} kg h^{-1}. The rate of consumption of H_2 under same condition is

(a) 1.5×10^{-3} kg h^{-1} (b) 1.76×10^{-4} kg h^{-1}
(c) 6.67×10^{-4} kg h^{-1} (d) 3×10^{-3} kg h^{-1}

17. The reaction $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$ is a reaction of

(a) zero-order (b) first-order
(c) second-order (d) third-order

18. Which one of the following statement is wrong regarding molecularity of a reaction?

(a) It may be 1, 2 or 3.
(b) It may be either a whole number or fraction.
(c) It is the number of molecules of the reactants taking part in a single-step chemical reaction.
(d) It depends on the rate determining step reaction in the reaction.

19. Which of the following statement is incorrect?

(a) Rate law is an experimental fact, whereas law of mass action is a theoretical proposal.

(b) Rate law is always different from the expression of law of mass action.

(c) Rate law is more informative than law of mass action for the development of mechanism.

(d) 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?

(a) $r_1 = r_2 = r_3$ (b) $r_1 > r_2 > r_3$

(c) $r_1 < r_2 < r_3$ (d) None of these

21. For the elementary reaction $2NO + O_2 \rightarrow 2NO_2$, the volume of a container is tripled. The rate becomes

(a) 3 times (b) 27 times

(c) $\frac{1}{27}$ times (d) as initial

22. A zero-order reaction is one

(a) in which reactants do not react.

(b) in which one of the reactants is in large excess.

(c) whose rate does not change with time.

(d) whose rate increases with time.

23. Which of the following statement is incorrect

(a) Stoichiometry of a reaction tells about the order of the elementary reactions.

(b) For a zero-order reaction, rate and the rate constant are identical.

(c) A zero-order reaction is controlled by factors other than concentration of reactants.

(d) A zero-order reaction is always an elementary reaction.

24. If the rate of a gaseous reaction is independent of partial pressure of reactant, then the order of reaction is

(a) 0 (b) 1

(c) 2 (d) 3

25. When the concentration of reactant in the reaction A → 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 $2A + B \rightarrow$ Products was found to be 2.58×10^{-5} L mol^{-1} s^{-1} after 15 s, 2.59×10^{-5} L mol^{-1} s^{-1} after 30 s and 2.57×10^{-1} L mol^{-1} 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 → 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

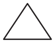
Exp. no.	$[A_0]$ (M)	$[B_0]$ (M)	Initial rate ($\mathrm{M\ s^{-1}}$)
1	0.012	0.035	0.1
2	0.024	0.070	0.8
3	0.024	0.035	0.1
4	0.012	0.070	0.8

(a) $r = K[\mathrm{B}]^3$ (b) $r = K[\mathrm{B}]^4$
(c) $r = K[\mathrm{A}][\mathrm{B}]^3$ (d) $r = K[\mathrm{A}]^2[\mathrm{B}]^3$

32. The rate law for a reaction between the substances A and B is given by rate $= K[\mathrm{A}]^n\ [\mathrm{B}]^m$. 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 CH_3-CHO
(d) Isomerization:  $\rightarrow CH_3-CH=CH_2$

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

Exp. No.	Concentration in mole per litre			Initial rate of formation of D ($\mathrm{torr\ s^{-1}}$)
	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 $2C_4H_6(g) \rightarrow C_8H_{12}(g)$. The rate law for this reaction is $r = K[C_4H_6]^2$ with $K = 6.1 \times 10^{-2}$ $\mathrm{L\ mol^{-1}\ s^{-1}}$ 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) $2.44 \times 10^{-5}\ \mathrm{Ms^{-1}}$ (b) $1.22 \times 10^{-5}\ \mathrm{Ms^{-1}}$
(c) $1.22 \times 10^{-3}\ \mathrm{Ms^{-1}}$ (d) $2.44 \times 10^{-6}\ \mathrm{Ms^{-1}}$

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 is mol $\mathrm{ml^{-1}}$ 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 $3A + 2B \rightarrow$ Products is given by the rate expression rate $= K[\mathrm{A}][\mathrm{B}]^2$. If A is taken in large excess, then the reaction start 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) $K_{\mathrm{HCI}} > K_{\mathrm{H_2SO_4}}$ (b) $K_{\mathrm{HCI}} < K_{\mathrm{H_2SO_4}}$
(c) $K_{\mathrm{HCI}} = K_{\mathrm{H_2SO_4}}$ (d) $K_{\mathrm{H_2SO_4}} = \left(K_{\mathrm{HCI}}\right)^2$

39. The hydrolysis of methyl formate in acid solution has the rate expression rate $= K\,[\mathrm{HCOOCH_3}][\mathrm{H^+}]$. The balanced equation is $HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH$. The rate law contains $[\mathrm{H^+}]$ 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 $A + H_2O + H^+ \rightarrow$ Products, where $[\mathrm{H^+}] = 0.1$ M and H_2O is present in large excess, the apparent rate constant is $1.5 \times 10^{-5}\ \mathrm{s^{-1}}$.

$$r = K[\mathrm{A}][\mathrm{H_2O}][\mathrm{H^+}] = K_{\mathrm{app}}[\mathrm{A}]$$

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

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

Mechanism of Reaction

41. A complex reaction $2\mathrm{X} + \mathrm{Y} \rightarrow \mathrm{Z}$, takes place in the following two steps.

$$\mathrm{X} + \mathrm{Y} \xrightarrow{K_1} 2\mathrm{W},$$

$$\mathrm{X} + 2\mathrm{W} \xrightarrow{K_2} \mathrm{Z}$$

If $K_1 << K_2$, then the order of reaction will be

(a) 1 (b) 2

(c) 3 (d) 0

42. For the reaction $\mathrm{A} \xrightarrow{K_1} \mathrm{B} \xrightarrow{K_2} \mathrm{C} \xrightarrow{K_3} \mathrm{D}$, where $K_3 > K_2 > K_1$; the rate of formation of D is determined by

(a) the rate of reaction: $\mathrm{A} \rightarrow \mathrm{B}$

(b) the rate of reaction: $\mathrm{B} \rightarrow \mathrm{C}$

(c) the rate of reaction: $\mathrm{C} \rightarrow \mathrm{D}$

(d) the rate of reaction: $\mathrm{A} \rightarrow \mathrm{B}$ with rate constant $K_1 . K_2 . K_3$

43. For hypothetical reaction $\mathrm{A} \rightarrow \mathrm{B}$ takes place according to

$$\mathrm{A} \overset{K_1}{\rightleftharpoons} \mathrm{C} \text{ (fast)}$$

$$\mathrm{A} + \mathrm{C} \xrightarrow{K_2} \mathrm{B} \text{ (slow)}$$

the rate of reaction is (K_1 is equilibrium constant)

(a) $K_2[\mathrm{B}][\mathrm{C}]$ (b) $K_1K_2[\mathrm{A}]$

(c) $K_1K_2[\mathrm{A}]^2$ (d) $K_1[\mathrm{B}][\mathrm{C}]$

44. The overall rate $+\dfrac{\mathrm{d}[P]}{\mathrm{d}t}$ for the reaction $2\mathrm{A} + \mathrm{C} \rightarrow \mathrm{P}$ from the mechanism

$$2\mathrm{A} \overset{K}{\rightleftharpoons} \mathrm{B} \text{ (fast)}$$

$$\mathrm{B} + \mathrm{C} \xrightarrow{K_\mathrm{f}} \mathrm{P} \text{ (slow)}$$

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

(a) $\dfrac{\mathrm{d}[P]}{\mathrm{d}t} = K\,K_\mathrm{f}\,[\mathrm{A}]^2[\mathrm{C}]$

(b) $\dfrac{\mathrm{d}[P]}{\mathrm{d}t} = K\,[\mathrm{A}][\mathrm{B}]$

(c) $\dfrac{\mathrm{d}[P]}{\mathrm{d}t} = K_\mathrm{f}\,[\mathrm{B}][\mathrm{C}]$

(d) $\dfrac{\mathrm{d}[P]}{\mathrm{d}t} = K\,K_\mathrm{f}\,[\mathrm{A}]^2[\mathrm{B}][\mathrm{C}]$

45. The suggested mechanism for the reaction $\mathrm{CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)}$ is

$$\mathrm{Cl}_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2\mathrm{C}\dot{\mathrm{l}} \text{ (fast)}$$

$$\mathrm{CHCl}_3 + \mathrm{C}\dot{\mathrm{l}} \xrightarrow{K_3} \mathrm{HCl} + \dot{\mathrm{C}}\mathrm{Cl}_3 \text{ (slow)}$$

$$\dot{\mathrm{C}}\mathrm{Cl}_3 + \mathrm{C}\dot{\mathrm{l}} \xrightarrow{K_4} \mathrm{CCl}_4 \text{ (fast)}$$

The experimental rate law consistent with the mechanism is

(a) rate $= K_3[\mathrm{CHCl_3}][\mathrm{Cl_2}]$

(b) rate $= K_4[\mathrm{CCl_3}][\mathrm{Cl}]$

(c) rate $= K_\mathrm{eq}[\mathrm{CHCl_3}][\mathrm{Cl_2}]$

(d) rate $= K_3 K_\mathrm{eq}^{1/2}[\mathrm{CHCl_3}][\mathrm{Cl_2}]^{1/2}$

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 $\mathrm{A} \rightarrow \mathrm{B}$. 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 th the life of a first-order reaction?

(a) $\dfrac{k}{2.303}\log\dfrac{4}{3}$ (b) $\dfrac{2.303}{k}\log\dfrac{4}{3}$

(c) $\dfrac{2.303}{k}\log 4$ (d) $\dfrac{2.303}{k}\log 3$

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) $4.5 \times 10^{-2} \times 5$ min (b) $\dfrac{\ln 5}{4.5 \times 10^{-2}}$ min

(c) $\dfrac{\ln(5/4)}{4.5 \times 10^{-2}}$ min (d) 4.5×1.25 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 minutes. In what time, the rate of reaction will decrease from 6.0×10^{21} molecules ml^{-1} s^{-1} to 4.5×10^{25} molecules $litre^{-1}$ 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 $2A \rightarrow B$, time taken for the [A] to fall to one-fourth value is how many times the time it takes for [A] to fall to half of its initial value?

(a) Two (b) Three

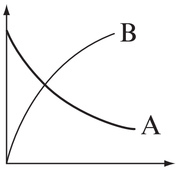
(c) Four (d) Seven

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 ($A \rightarrow nB$)

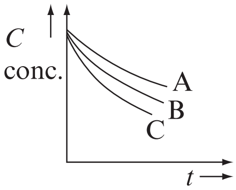


(a) $\dfrac{A_0}{n}$ (b) $\dfrac{A_0}{n-1}$

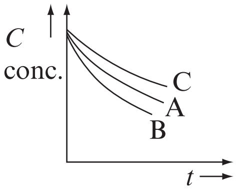
(c) $\dfrac{nA_0}{n+1}$ (d) $\dfrac{n-1}{n+1}A_0$

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

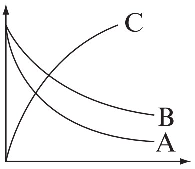
(a)



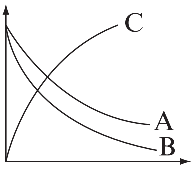
(b)



(c)



(d)



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 $t_{1/2} = \dfrac{\left[2-\sqrt{2}\right]}{k} \times C_0^{1/2}$, 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 $H_3C–CH_2–NO_2 + OH^- \rightarrow H_3C–CH^-–NO_2 + H_2O$ obeys the rate law for pseudo first-order kinetics in the presence of a large excess of hydroxide ion. If 1% of nitroethane undergoes reaction in half a minute when the reactant concentration is 0.002 M, what is the pseudo first-order rate constant?

(a) 2×10^{-2} min^{-1} (b) 6×10^{-3} min^{-1}

(c) 4×10^{-2} min^{-1} (d) 1×10^{-2} 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 the initial concentration of the reactant.

62. For the first-order reaction $A(g) \rightarrow 2B(g) + C(g)$, 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 of the following is correct about first-order reaction?

(a) $t_{0.5} = 50$ s, $t_{0.75} = 100$ s

(b) $t_{0.5} = 50$ s, $t_{0.75} = 75$ s

(c) $t_{0.5} = 50$ s, $t_{0.75} = 50$ s

(d) $t_{0.5} = 50$ s, $t_{0.25} = 25$ s

65. $t_{1/2}$ of a reaction: A → Products $\left(\text{order} = \frac{3}{2}\right)$ is represented by $t_{1/2} \ \alpha \ \frac{1}{[A_0]^m}$. 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 2×10^4 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 $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is a first-order reaction. After 30 minutes, 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) 6.0×10^{-3} min^{-1} (b) 0.18 min^{-1}

(c) 6.0×10^{-2} min^{-1} (d) 3.0×10^{-3} 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 A + B → 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 $b >> a$, the reaction reduces to

(a) first-order with respect to 'A'.

(b) zero-order with respect to 'A'.

(c) first-order with respect to 'B'.

(d) overall zero-order.

71. For a first-order reaction, $t_{0.75} = 1386$ 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 minutes for the completion of 50% of the reaction A → Products. For the completion of next 50% of the reaction, the time taken is 80 minutes. 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: $2C_4H_6(g) \rightarrow C_8H_{12}(g)$. It is found that the partial pressure P, of the reactant obeys the law: $\frac{1}{P} = kt + \frac{1}{P_0}$. The order of the reaction is

(a) 1 (b) 0.5
(c) 2 (d) 1.5

74. The half-life for the first-order reaction $H_2O_2(aq) \rightarrow H_2O(l) + \frac{1}{2}O_2(g)$ is 30 minutes. If the volume of $O_2(g)$ collected is 100 ml after a long time, then the volume of $O_2(g)$ collected (at the same pressure and temperature) after 60 minutes 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 minutes	0	10
Volume (V, in ml)	25.0	20.0

Here, 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 (in 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

$$C_R = C_A^o \,.\, K_1 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)} \right]$$

If $C_A = C_A^o$, $C_R = C_S = 0$ 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.

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

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:

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C,$$

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

(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 in temperature.
(b) decreases with increase in temperature.
(c) increases with decrease in temperature.
(d) is nearly independent in 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 O_2 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 $2NO + O_2 \rightarrow 2NO_2$ is less.
(d) activation energy for the reaction $2NO + O_2 \rightarrow 2NO_2$ is high.

85. Rate of which type of elementary reaction increases with increase in temperature?

(a) Thermal (b) Exothermic
(c) Endothermic (d) All of these

86. In gaseous reactions important for the understanding of the upper atmosphere, H_2O 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 H_2O 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 the number of molecules having sufficient energy for reaction.
(d) decrease in activation energy of reaction.

89. Select the incorrect statement from 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, the half-life of reactions

(a) remain 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, then 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'), then 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 forward 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) $C \cdot I$

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 $2NO_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} N_2O_4$, 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) → 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 pressures 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 $H_2 + I_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2HI$, 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) $-\frac{1}{2}\frac{d[HI]}{dt} = K_2[HI]^2 - K_1[H_2][I_2]$

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

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

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

6. The reaction: A(g) + 2B(g) → 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.

$A + 3B \rightarrow P$: $\Delta H = -2x$ kJ
$M \rightarrow 2Q + R$: $\Delta H = +x$ kJ

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

(a) y M s^{-1} (b) $1.33y$ M s^{-1}

(c) $0.75y$ M s^{-1} (d) $2y$ M s^{-1}

8. What is the order of a chemical reaction A + 2B → 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°C is given below.

Exp. no.	**$[HgCl_2]_0$ (M)**	**$[K_2C_2O_4]_0$ (M)**	**Time (minutes)**	**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:

$$I^-(aq) + ClO^-(aq) \xrightarrow{OH^-} IO^-(aq) + Cl^-(aq)$$

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 → products, the rate of disappearance of A is a given by

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

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

(a) $\dfrac{K_1}{K_2}$　　(b) K_1

(c) $\dfrac{K_2}{K_1}$　　(d) $\dfrac{K_1}{K_1 + K_2}$

12. For a two-step reaction:

$$A \xrightleftharpoons[K_2]{K_1} R + B$$

$$R + C \xrightarrow{K_3} \text{Products}$$

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

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

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

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

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

$$O_3 \xrightleftharpoons[K_2]{K_1} O_2 + O \text{ (fast)},$$

$$O + O_3 \xrightarrow{K_3} 2O_2 \text{ (slow)}$$

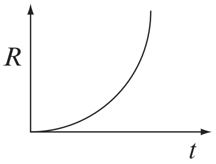
The rate law expression will be

(a) rate = $K_1[O][O_3]$　　(b) rate = $K_1[O_3]$

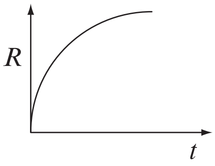
(c) rate = $\dfrac{K_1.K_3}{K_2}\dfrac{[O_3]^2}{[O_2]}$　　(d) rate = $K_3\dfrac{[O_3]^2}{[O_2]}$

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

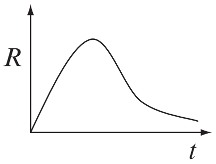
(a)



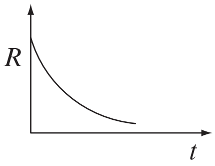
(b)



(c)



(d)



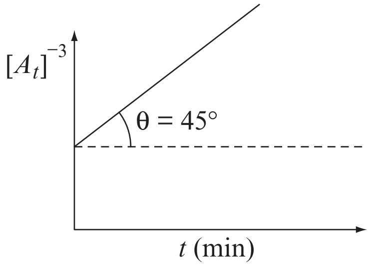
15. The initial rate of a zero-order reaction A(g) → 2B(g) is 0.01 M min^{-1}. If the initial concentration of 'A' is 0.1 M, then the concentration of 'B' after 60 s is

(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 → 2B, the following graph is obtained experimentally. The rate of reaction when [A] = 0.2 M, is



(a) 4×10^{-4} M min^{-1} (b) $\frac{16}{9} \times 10^{-4}$ M min^{-1}
(c) 1.6×10^{-3} M min^{-1} (d) $\frac{16}{3} \times 10^{-3}$ 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 → 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 → 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 Pa^{-1} 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) 16 s (b) 0.01 min
(c) 0.06 min (d) 36 s

22. For the irreversible reaction A → products in a batch reactor, 80% reactant ($[A_0]$ = 1 M) is converted in a 8 minute run and conversion is 90% after 18 minute. 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 minute at pH = 5 for any concentration of sugar. However, if pH = 6, the half-life changes to 50 minute. 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) $r = K\,[\text{sugar}][H^+]^{-1}$

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 M^{-1}h^{-1}. What is the half-life, if the initial concentrations are 0.02 M for 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 → 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 minutes, 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 → Product, the initial concentration of A is 0.1 M and after 40 minutes of time, it becomes 0.025 M. What is the rate of reaction at reactant concentration 0.01 M?

(a) 3.465×10^{-4} mol lit^{-1} min^{-1}
(b) 3.465×10^{-5} mol lit^{-1} min^{-1}
(c) 6.93×10^{-4} mol lit^{-1} min^{-1}
(d) 1.7325×10^{-4} mol lit^{-1} min^{-1}

28. The rate of change of concentration of ‘B’ for the reaction A → B is given as $+\dfrac{d[B]}{dt} = K[A]^{1/3}$. The half-life period of the reaction will be

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

29. A solution of N_2O_5 in CCl_4 yields by decomposition at 45°C, 4.8 ml of O_2, 20 minutes 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 minutes 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, then 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) → nB(g) is started with ‘A’. The reaction takes place at constant temperature and volume. 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) $t_{3/4} = t_{1/2}.[2^{n-1} - 1]$
(c) $t_{3/4} = t_{1/2}\cdot[2^{n+1} - 1]$
(d) $t_{3/4} = t_{1/2}.[2^{n+1} + 1]$

33. Rate of the chemical reaction A → products, is doubled, when the concentration of ‘A’ is increased four times. If the half-life of the reaction is 16 minutes, 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°C. The percentage of SO_2Cl_2 decomposed on heating for 100 minutes 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 $6.93 \times 10^{-2}\ \text{min}^{-1}$. The reactant ‘A’ in the presence of catalyst gives ‘Y’ by a second-order mechanism with the rate constant of $0.2\ \text{min}^{-1}\ M^{-1}$. 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 minute, 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 minutes. The population relative to the initial value at 60 minutes is (ln 2 = 0.7)

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

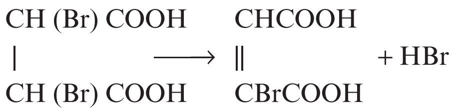
39. A study of the conversion of ammonium cyanate to urea in the solution $NH_4CNO \rightarrow CO(NH_2)_2$ gave the following results.

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

The value of $t_{1/2}$ 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.



$$\begin{array}{l}\text{CH (Br) COOH}\\ |\\ \text{CH (Br) COOH}\end{array} \longrightarrow \begin{array}{l}\text{CHCOOH}\\ \|\\ \text{CBrCOOH}\end{array} + \text{HBr}$$

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 $B^{(n+4)+}$ 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 $B^{(n+4)+}$. In the process, it converts B^{n+} to $B^{(n-2)+}$ and $B^{(n+4)+}$ to $B^{(n-1)+}$. At $t = 0$, the volume of reagent consumed is 25 ml and at t = 10 minute, the volume used is 32.5 ml. The rate constant for the conversion of B^{n+} of $B^{(n+4)+}$ 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 $A(g) \rightarrow 2B(g) + C(g)$ 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 A + B → products, the rate law is $r = K[A]^2[B]$, where $K = 0.5\ M^{-2}\,\text{min}^{-1}$. 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 1/100th 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 → C + D follows the rate law: $r = (2.31 \times 10^{-3}\ s^{-1})[A]^{1/2}[B]^{1/2}$. The reaction is started with 1.0 mole each of 'A' and 'B'. In what time, the moles of 'A' becomes 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:

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$$

follows the rate law $-\dfrac{d[CH_3COOH]}{dt} = K[H^+][CH_3COOH]\,[C_2H_5OH] = K'\,[CH_3COOH][C_2H_5OH]$. When $[CH_3COOH]_0 = [C_2H_5OH]_0 = 0.2$ M and pH = 3, the half-life for the reaction is 50 minutes. 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) $13.86\ \text{min}^{-1}$

48. The reaction A + B → C + D, has been studied under the following initial conditions.

Case I	Case II
$[A]_0 = 2.0$ M	$[A]_0 = 0.02$ M
$[B]_0 = 0.01$ M	$[B]_0 = 1.0$ M

The variation of concentration with time was noted as follows.

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

The rate constant of the reaction is (ln 3 = 1.1, ln 5 = 1.6, ln 10 = 2.3)

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

(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 $k_{\text{app}} = \dfrac{k_1 C}{1+\alpha C}$, 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} mole/litre (b) 10^{-4} mole/litre

(c) 10^{-5} mole/litre (d) 5×10^{-5} 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 follows:

$$A \rightarrow 2B + C$$

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

$$A + R \xrightarrow{k} R + R \text{ is } r_A = -\frac{dC_A}{dt} = kC_A C_R$$

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, $\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{k[C_0 - y]}{1+by}$, where C_0 = initial concentration and k and b are constants. The half-life of reaction is

(a) $[(1 + C_0b)\ \ln 2 - \frac{C_0b}{2}]\frac{1}{K}$

(b) $[(1 - C_0b)\ \ln 2 + \frac{C_0b}{2}]\frac{1}{K}$

(c) $[(1 - C_0b)\ \ln 2 - \frac{C_0b}{2}]\frac{1}{K}$

(d) $[(1 + C_0b)\ \ln 2 + \frac{C_0b}{2}]\frac{1}{K}$

54. For the following first-order competing reaction,

$$\mathrm{A + Reagent \rightarrow Product}$$
$$\mathrm{B + Reagent \rightarrow Product}$$

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.

$$-\frac{\mathrm{d[RX]}}{\mathrm{d}t} = (4.8 \times 10^{-5}\ \mathrm{M^{-1}\ s^{-1}})$$
$$\mathrm{[RX]\ [OH^-]} + 2.4 \times 10^{-6}\ \mathrm{s^{-1}\ [RX]}$$

What percentage of isopropyl bromide reacts by the S_{N_2} mechanism when $[\mathrm{OH^-}] = 0.01$ M?

(a) 16.67% (b) 83.33%
(c) 66.67% (d) 33.33%

56. For the series of competitive reactions.

$$\mathrm{H + HO_2 \xrightarrow{K_1} H_2 + O_2}$$
$$\mathrm{H + HO_2 \xrightarrow{K_2} 2\ OH}$$
$$\mathrm{H + HO_2 \xrightarrow{K_3} H_2O + O}$$

It has been found that K_1:K_2:K_3 = 0.60:0.30:0.10. The molar ratio of the products, $\mathrm{H_2}$, $\mathrm{O_2}$, OH, $\mathrm{H_2O}$ and O, at time 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 $\xrightarrow{K_1 = \ln 3\ \mathrm{min^{-1}}}$ B and A $\xrightarrow{K_2 = \ln 3\ \mathrm{min^{-1}}}$ 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 $\xrightarrow{K_1 = 0.02\ \mathrm{min^{-1}}}$ B $\xrightarrow{K_2 = 0.02\ \mathrm{min^{-1}}}$ 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 given first-order sequential reactions 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 the following two parallel first-order reactions A $\xrightarrow{K_1}$ B and A $\xrightarrow{K_2}$ C. If K_1 is 1.25×10^{-5} $\mathrm{s^{-1}}$ and $\frac{K_1}{K_2} = \frac{1}{9}$, then the value of $\frac{[\mathrm{C}]}{[\mathrm{A}]}$ 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 2.5×10^{-4} $\mathrm{min^{-1}}$, then what is the value of K_2?

(a) $5.0 \times 10^{-3}\ \mathrm{min^{-1}}$ (b) $2.5 \times 10^{-4}\ \mathrm{min^{-1}}$
(c) $1.25 \times 10^{-5}\ \mathrm{min^{-1}}$ (d) $5.0 \times 10^{-4}\ \mathrm{min^{-1}}$

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, $[\mathrm{A}] = [\mathrm{A}]_0$ and [B] = [C] = 0.

(a) 0 (b) $[\mathrm{A}]_0$
(c) $[\mathrm{A}]_0.(1 - e^{-K_1t})$ (d) $[\mathrm{A}]_0.\ e^{-K_1t}$

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 $t = 10$ minute and the pressure is 1.5 atm after a very long time. The only correct information about the reactions is (ln 2 = 0.7, ln 10 = 2.3)

(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 → Products, the average speed of reactant molecules is 2×10^4 cm/s, the molecular diameter is 4 Å 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 $\ln K = \alpha + \beta \ln T - \dfrac{\gamma}{T}$, 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.

$$\text{A} \xrightarrow{\text{Ea = 20 kcal/mol}} \text{B} \quad \text{A} \xrightarrow{\text{Ea = 40 kcal/mol}} \text{C}$$

(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, then find the temperature at which B and C will be obtained in 2 : 1 mole ratio. (ln 2 = 0.7)

(a) 400 K (b) 385.5 K
(c) 379.75 K (d) 412.25 K

69. The two reactions (I) A → Products, and (II) B → 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 minutes. 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) $0.0233\ \text{min}^{-1}$ (b) $0.0327\ \text{min}^{-1}$
(c) $0.0164\ \text{min}^{-1}$ (d) $0.0654\ \text{min}^{-1}$

70. A first-order reaction A → B, activation energy is 9.6 kcal/mol. When a 20% solution of 'A' was kept at 27°C for 21.6 minutes, 75% decomposition took place. What will be the percent decomposition in 8.0 minutes 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? [Antilog(0.30) = 2.0, Antilog(0.280) = 1.91, Antilog(0.322) = 2.1]

(a) 1.81 (b) 1.71
(c) 1.91 (d) 2.1

73. For the combustion of carbon, $\Delta H = -\text{ve}$ and $\Delta S = +\text{ve}$ and hence, thermodynamically the process is spontaneous at all temperatures. But coal stored in coal depots does not burn automatically due to

(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?

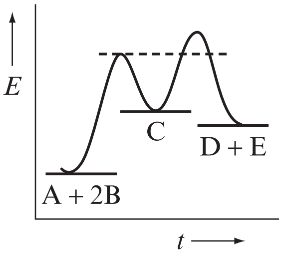
(a) For endothermic reactions, energy of activation is always greater than the heat of reaction.
(b) For exothermic reactions, the energy of activation is always smaller than heat of reaction.
(c) Rate of elementary reaction always increases with increase in temperature.
(d) Temperature coefficient of a reaction is 1.0, when $T \to \infty$.

75. The mechanism of the reaction $A + 2B \to D + E$; $\Delta H = -\text{ve}$ is

Step I: $A + 2B \to C$ (slow)
Step II: $C \to D + E$ (fast)

The energy profile of the reaction should be

(a)



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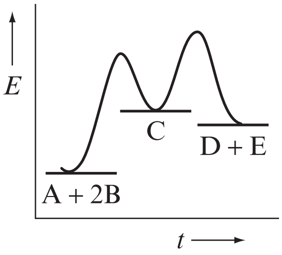

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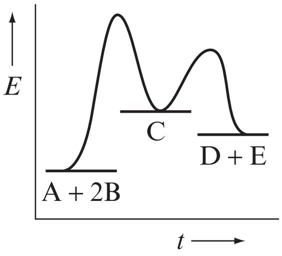
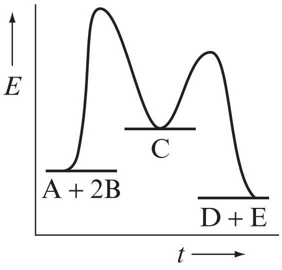


(d)



Section B (One or More than one Correct)

1. For a complex (multistep) reaction,

(a) the overall rate of reaction is the rate of slowest step.
(b) the overall molecularity has no significance.
(c) molecularity and order may or may not be same.
(d) the number of rate determining steps may be more than one.

2. Which of the following statements is true?

(a) 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 → Products, may be given by which of the following expression(s)?

(a) $\dfrac{\ln r_2 - \ln r_1}{\ln[A]_2 - \ln[A]_1}$

(b) $\dfrac{\ln[A_0]_2 - \ln[A_0]_1}{\ln[t_{1/2}]_2 - \ln[t_{1/2}]_1}$

(c) $1 + \dfrac{\ln[A_0]_2 - \ln[A_0]_1}{\ln[t_{1/2}]_2 - \ln[t_{1/2}]_1}$

(d) $\dfrac{\ln(r/K)}{\ln[A]}$

5. For a first-order reaction,

(a) the degree of dissociation is equal to $(1 - e^{-kt})$.

(b) a plot of reciprocal concentration of the reactant vs time gives a straight line.

(c) the time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction.

(d) 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)

(a) If f is the fraction of the reactant concentration consumed over time interval 't', then $\log\left(\dfrac{f}{t}\right)$ is linearly related to (log C), when f << 1.

(b) A plot of $C^{(n-1)}$ vs t is linear with slope proportional to $(n - 1)$.

(c) If $t_{1/2}$ and $t_{3/4}$ are the time intervals for 50% and 75% consumption of the reactant, then $t_{3/4} : t_{1/2} = 2^{n-1} + 1$

(d) A plot of log C vs log t is linear with slope = 1.

7. Initial concentration of reactant for nth order reaction is C_0. Which of the following relation is/are not correct about $t_{1/2}$ of the reaction?

(a) $\ln t_{1/2} = \text{Constant} - (n - 1) \ln C_0$

(b) $\ln t_{1/2} = \ln n + \text{Constant} - \ln C_0$

(c) $t_{1/2} \cdot \ln n = \text{Constant} + \ln C_0$

(d) $\ln t_{1/2} = n \ln C_0$

8. Consider the following statements. The law for the acid-catalysed hydrolysis of an ester being given as rate = $K[H^+]$[ester] = K'[ester]. If the acid (strong) concentration is doubled at constant ester concentration,

1. the second-order rate constant, K, is doubled.
2. the pseudo first-order rate constant, K' is doubled.
3. the rate of reaction is doubled.

Which of the above statement is correct?

(a) 1 and 2
(b) 2 and 3
(c) 1 and 3
(d) 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[RCl]. The rate of the reaction will be

1. doubled on doubling the concentration of NaOH.
2. halved on reducing the concentration of alkyl halide to one half.
3. increased on increasing the temperature of the reaction.
4. unaffected by increasing the temperature of the reaction.

The correct answer is

(a) 1, 2, 3
(b) 3, 4
(c) 1, 3
(d) 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.

(a) Concentration of SO_3 in Kota is 1.25×10^{-5} M (assume SO_3 present in air reaches steady state).

(b) If 10^3 L of air is passed through 1 L pure water (assuming all SO_3 is dissolved in it) and the resulting solution is titrated against 1 N NaOH solution, 15 ml of NaOH solution is required to reach the end point.

(c) An industry is manufacturing H_2SO_4 at the rate of 980 kg per day with the use of SO_3 in air and it should use 8×10^5 L air per day.

(d) If SO_3 emission is stopped, then after 1000 days, its concentration will reduce to 1.22×10^{-8} M.

11. The decomposition reaction $3A(g) \rightarrow 2B(g) + 2C(s)$ follows first-order kinetics. Starting with pure 'A' (at 6 atm), the pressures of system after 20 minutes and after a very long time are 5.05 atm and 4.05 atm, respectively. Identify the correct statement(s) related with the reaction.

(a) Time for 75% completion of reaction is slightly more than 40 minutes.
(b) Time for 87.5% completion of reaction is slightly less than 60 minutes.
(c) Time for 93.75% completion of reaction is exactly 80 minutes.
(d) The pressure of system after 40 minutes 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 [$\ln 2 = 0.7$, $\ln(323/25) = 2.6$]

(a) the time taken for that body to go from 323°C to 25°C is 17.5 s.
(b) the time taken for that body to go from 1192 K to 298 K is 35 s.
(c) the time taken for that body to go from 323°C to 25°C is 65 s.
(d) the time taken for that body to go from 1192 K to 298 K is 130 s.

13. For a gaseous reaction $A + B \rightarrow 2C$, the rate law is $r = k[A]^{-1}[B]^2$. Which of the following statement is incorrect?

(a) If the initial concentration of 'A' is double of 'B', then the half-life of reaction will remain same throughout the reaction.
(b) If initially 'A' is taken in very large amount, then the half-life of reaction will keep on increasing as reaction proceeds.
(c) If initially 'B' is taken in very large amount, then the half-life of reaction will remain same throughout the reaction.
(d) If 'A' and 'B' are taken in equal concentration, then both will be reduced to half of the original amount in the same time.

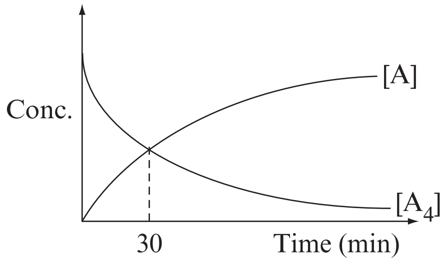
14. For two reactions $A \xrightarrow{K_1} P$ and $B \xrightarrow{K_2} Q$ of first and second order, respectively, if the initial concentrations of A and B are same (1 M), then the time taken by A and B to reach at 0.5 M concentration is same. Which of the following is/are correct statement(s) regarding the reactions?

(a) The initial rate of reaction of A is greater.
(b) The initial rate of reaction of B is greater.
(c) The magnitude of K_1 is greater than that of K_2.
(d) The magnitude of K_2 is greater than that of K_1.

15. Consider the following first-order decomposition reaction.

$$A_4(g) \rightarrow 4A(g)$$

Which of the following statement(s) is/are correct regarding the reaction? (log 2 = 0.3)



(a) At 30 min, only 20% reaction is complete.
(b) $t_{1/2}$ of reaction is 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 follows.

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow 2C_6H_{12}O_6(aq)$$

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

$$\Delta_f H^\circ_{C_{12}H_{22}O_{11}(aq)} = -2238 \text{ kJ/mol},$$
$$\Delta_f H^\circ_{C_6H_{12}O_6(aq)} = -1263 \text{ kJ/mol},$$
$$\Delta_f H^\circ_{H_2O(l)} = -285 \text{ kJ/mol}$$

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

(a) The hydrolysis of α-maltose is an exothermic process.
(b) Heat liberated in the combustion of 1.0 mole of α-maltose must be 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 → Products (order = n), the theoretical time of completion of reaction is

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

18. Consider the following reactions.

$$\mathrm{A} \xrightarrow{K_1 = 6.93\times10^{-2}\ \mathrm{min}^{-1}} \mathrm{B} \text{ and}$$

$$\mathrm{A} \xrightarrow{K_2 = 13.86\times10^{-2}\ \mathrm{min}^{-1}} \mathrm{C}$$

Here, 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 minutes.

(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?

$$\mathrm{A} \xrightarrow{3K} \mathrm{B}$$

$$\mathrm{A} \xrightarrow{2K} 2\mathrm{C}$$

$$\mathrm{A} \xrightarrow{K} 3\mathrm{D}$$

(a) $[\mathrm{B}]_t : [\mathrm{C}]_t : [\mathrm{D}]_t$ is independent of time.

(b) $[\mathrm{C}]_t > [\mathrm{B}]_t = [\mathrm{D}]_t$

(c) $[C]_\infty = 0.67$ M

(d) If $K = 0.5\ \mathrm{min}^{-1}$, then [B] = 1 M after 1.386 min.

20. When secondary alkyl halide undergoes $\mathrm{S_N}$ reaction, it follows $\mathrm{S_{N_1}}$ (first-order) and $\mathrm{S_{N_2}}$ (second-order) pathway simultaneously. The dominant pathway depends on large number of factors. An alkyl halide undergoes both pathway with rate constants $3\times10^{-4}\ \mathrm{s}^{-1}$ and $5\times10^{-4}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, respectively. Which of the following is/are correct information for the reaction?

(a) If the concentration of nucleophile is 0.1 M, then the dominant pathway of reaction is $\mathrm{S_{N_1}}$.

(b) If the concentration of nucleophile is 1.0 M, then the dominant pathway of reaction is $\mathrm{S_{N_2}}$.

(c) The percentage of $\mathrm{S_{N_1}}$ product will be 50, when the nucleophile concentration is 0.6 M.

(d) The percentage of $\mathrm{S_{N_1}}$ product will be 40, when the nucleophile concentration is 0.9 M.

21. For the reversible reaction $\mathrm{A} \rightleftharpoons \mathrm{B}$, 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) $t =$ infinite

22. For the parallel reactions $\mathrm{A} \xrightarrow{K_1} \mathrm{B}$ and $\mathrm{A} \xrightarrow{K_2} \mathrm{C}$, the initial concentration of 'A' is C_{A_o} 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) $C_\mathrm{A} + C_\mathrm{B} + C_\mathrm{C} = C_{A_o}$

(b) $\dfrac{\mathrm{d}C_\mathrm{A}}{\mathrm{d}t} + \dfrac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}t} + \dfrac{\mathrm{d}C_\mathrm{C}}{\mathrm{d}t} = 0$

(c) $\dfrac{C_B}{C_C} = \dfrac{K_1}{K_2}$

(d) $\dfrac{C_B}{C_{A_o} - C_A} = \dfrac{K_1}{K_1 + K_2}$

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 $B_3(g)$ follows first-order kinetics as follows.

$$A_2(g) \rightarrow 2A(g);\ K_1\ (/h^{-1}) = e^{-\frac{14000(/J)}{RT}+5}$$

$$B_3(g) \rightarrow 3B(g);\ K_2\ (/h^{-1}) = e^{-\frac{20000(/J)}{RT}+10}$$

Here, 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 $\frac{1.25\times10^6}{T^3}$ 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 which of the following statement is correct about the reaction?

(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 $2N_2O_5 \rightarrow 4NO_2 + O_2$. Experimental studies suggest that the 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.

1. The correct mechanism for the decomposition of N_2O_5 may be

   (a) Step-I: $N_2O_5 \xrightarrow{\text{slow}} NO_2 + NO_3$

   Step-II: $N_2O_5 + NO_3 \xrightarrow{\text{fast}} 3NO_2 + O_2$

   (b) Step-I: $N_2O_5 \xrightarrow{\text{fast}} NO_2 + NO_3$

   Step-II: $N_2O_5 + NO_3 \xrightarrow{\text{slow}} 3NO_2 + O_2$

   (c) $N_2O_5 \xrightarrow{\text{fast}} 2NO_2 + \frac{1}{2}O_2$

   (d) Step-I: $N_2O_5 \xrightarrow{\text{fast}} NO + NO_2 + O_2$

   Step-II: $N_2O_5 + NO_2 \xrightarrow{\text{slow}} 3NO_2 + \frac{1}{2}O_2$

2. If the 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

   (a) $K_1 = K_2 = K_3$ (b) $2K_1 = K_2 = 4K_3$

   (c) $K_1 = 2K_2 = K_3$ (d) $2K_1 = 4K_2 = K_3$

3. If the rate of formation of O_2 is 16 g/h, then the rate of decomposition of N_2O_5 and the rate of formation of NO_2 are

   (a) 108 g/h, 92 g/h (b) 54 g/h, 46 g/h

   (c) 32 g/h, 64 g/hr (d) 16 g/h, 16 g/h

Comprehension II

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

(1) $Cl_2 \longrightarrow 2Cl$ $[K_1 = A_1 \cdot e^{-E_{a_1}/RT}]$
(2) $2Cl \longrightarrow Cl_2$ $[K_2 = A_2 \cdot e^{-E_{a_2}/RT}]$
(3) $Cl + CO \longrightarrow COCl$ $[K_3 = A_3 \cdot e^{-E_{a_3}/RT}]$
(4) $COCl \longrightarrow Cl + CO$ $[K_4 = A_4 \cdot e^{-E_{a_4}/RT}]$
(5) $COCl + Cl_2 \longrightarrow COCl_2 + Cl$ $[K_5 = A_5 \cdot e^{-E_{a_5}/RT}]$

4. Assuming steady-state approximation for [Cl] and [COCl], the rate law for the formation of $COCl_2$ is

   (a) $\dfrac{K_5K_2K_1^{1/2}[Cl_2]^{3/2}[CO]}{K_3^{1/2}(K_4 + K_5[Cl_2])}$

   (b) $\dfrac{K_5K_3K_1^{1/2}[Cl_2][CO]^{3/2}}{K_2^{1/2}(K_4 + K_5[Cl_2])}$

   (c) $\dfrac{K_5K_3K_1^{1/2}[Cl_2]^{3/2}[CO]}{K_2^{1/2}(K_4 + K_5[Cl_2])}$

   (d) $\dfrac{K_5K_2K_1^{1/2}[Cl_2][CO]^{3/2}}{K_3^{1/2}(K_4 + K_5[Cl_2])}$

5. 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)

   (a) $\dfrac{K_4K_3K_2^{1/2}[Cl_2]^{3/2}[CO]}{K_4K_2}$

   (b) $\dfrac{K_4K_3K_2^{1/2}[Cl_2][CO]^{3/2}}{K_2K_3^{1/2}}$

   (c) $\dfrac{K_5K_3K_1^{1/2}[Cl_2][CO]^{3/2}}{K_4^{1/2}K_2}$

   (d) $\dfrac{K_5K_3K_1^{1/2}[Cl_2]^{3/2}[CO]}{K_4K_2^{1/2}}$

6. What is the overall pre-exponential factor of reaction, if steps (1) to (4) are much faster than (5)?

   (a) $\dfrac{A_5A_3A_1^{1/2}}{A_4A_2^{1/2}}$ (b) $\dfrac{A_5A_3^{1/2}A_1}{A_2A_4^{1/2}}$

   (c) $\dfrac{A_5A_4A_1^{1/2}}{A_4A_2^{1/2}}$ (d) $\dfrac{A_4A_3A_2^{1/2}}{A_2A_4^{1/2}}$

7. What is the overall activation energy of reaction, if steps (1) to (4) are much faster than (5)?

(a) $\dfrac{Ea_5.Ea_3.Ea_1^{1/2}}{Ea_4.Ea_2^{1/2}}$

(b) $Ea_5 + Ea_3 + \dfrac{1}{2}Ea_1 - \dfrac{1}{2}Ea_2 - Ea_4$

(c) $Ea_1 + Ea_3 + Ea_5 - Ea_2 - Ea_4$

(d) $-Ea_5 - Ea_3 - \dfrac{1}{2}Ea_1 + Ea_2 + \dfrac{1}{2}Ea_4$

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.

Step I: $Br_2 \xrightarrow{K_1} 2Br$ **(Chain initiation)**
Step II: $Br + H_2 \xrightarrow{K_2} HBr + H$ **(Chain propagation)**
Step III: $H + Br_2 \xrightarrow{K_3} HBr + Br$ **(Chain propagation)**
Step IV: $H + HBr \xrightarrow{K_4} H_2 + Br$ **(Chain retardation)**
Step V: $2Br \xrightarrow{K_5} Br_2$ **(Chain termination)**

8. The concentration of bromine radical is

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

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

9. The concentration of hydrogen radical is

(a) $\dfrac{K_2K_1[Br_2][H_2]}{K_5(K_3[Br_2]+K_4[HBr])}$

(b) $\dfrac{K_2K_1[Br_2]^{1/2}[H_2]}{K_5(K_3[Br_2]+K_4[HBr])}$

(c) $\dfrac{K_2K_1^{1/2}[Br_2]^{1/2}[H_2]}{K_5^{1/2}(K_3[Br_2]+K_4[HBr])}$

(d) $\dfrac{K_2K_1^{1/2}[Br_2]^{1/2}[H_2]^2}{K_5^{1/2}(K_3[Br_2]^{1/2}+K_4[HBr])}$

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

(a) $\dfrac{2K_3K_2K_1^{1/2}[Br_2]^{3/2}[H_2]}{K_5^{1/2}(K_3[Br_2]+K_4[HBr])}$

(b) $\dfrac{2K_2K_1^{1/2}[Br_2]^{3/2}[H_2]}{K_5^{1/2}(K_3[Br_2]+K_4[HBr])}$

(c) $\dfrac{K_2K_1^{1/2}[Br_2]^{1/2}[H_2]}{K_5^{1/2}(K_3[Br_2]+K_4[HBr])}$

(d) $\dfrac{2K_2K_1^{1/2}[Br_2]^{1/2}[H_2]}{K_5^{1/2}}$

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

(a) $\dfrac{2K_2K_1^{1/2}[Br_2]^{1/2}[H_2]}{K_5^{1/2}}$

(b) $\dfrac{2K_2K_1^{1/2}[Br_2]^{1/2}[H_2]}{K_5^{1/2}K_3}$

(c) $\dfrac{K_2K_1^{2}[Br_2]^{1/2}[H_2]}{K_5^{2}K_3}$

(d) Zero

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 minutes, the volumes of permanganate required were 16.0 and 10.0 ml, respectively ($\log 2 = 0.3$, $(1.6)^5 = (3.2)^2$).

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 minutes is

(a) $\frac{5}{16}$ (b) 0.6

(c) $\frac{1}{3.2}$ (d) $\frac{11}{16}$

15. The reaction $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ 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-butyl peroxide (DTBP) to acetone is given by the following equation.

$$C_8H_{18}O_2(g) \rightarrow 2CH_3COCH_3(g) + C_2H_6(g)$$

The reaction has a half-life of 80 minutes 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: $4OH(g) + H_2S(g) \rightarrow SO_2(g) + 2H_2O(g)$ was studied at a particular temperature.

[OH] mol/litre	[H_2S] mol/litre	Rate of disappearaces of H_2S 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) $r = K[OH]^2[H_2S]$ (b) $r = K[OH][H_2S]^2$

(c) $r = K[OH]^{-1}[H_2S]$ (d) $r = K[OH][H_2S]$

20. What is the rate constant of the reaction at the given temperature?

(a) 5.1×10^9 $M^{-1}s^{-1}$ (b) 2.8×10^{15} $M^{-1}s^{-1}$

(c) 1.5×10^{10} $M^{-1}s^{-1}$ (d) 3.9×10^{17} $M^{-2}s^{-1}$

21. What is the rate, mol $l^{-1}s^{-1}$, at the instant when [OH] = 1.7×10^{-8} M and [H_2S] = 1.0×10^{-8} 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 [OH] = 1.7×10^{-8} M and [H_2S] = 1.0×10^{-8} 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 $2X(g) \rightarrow 3Y(g) + 2Z(g)$. 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) 6.93×10^{-3} min^{-1}

(b) 1.386×10^{-2} min^{-1}

(c) 2×10^{-4} M^{-1}min^{-1}

(d) 3.465×10^{-3} 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.

$$\begin{array}{lccccccccc} & A(g) & + & 2B(g) & \rightarrow & C(g) & + & D(g) \\ t=0 & a\,M & & b\,M & & 0 & & 0 \end{array}$$

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. The concentration of 'A' at time 't' is

(a) $C_A = a - kt$

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

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

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

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

(a) $\dfrac{a}{2k}$ (b) $\dfrac{a}{k}$

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

29. The 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) → 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) $a\left(1-e^{-n_1kt}\right)$

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

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

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

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

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

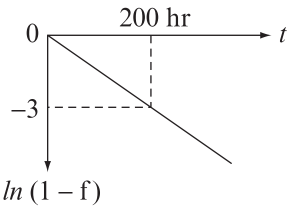
32. What will be the concentration of 'A' at time *t*, if $n_1 = 1$ and $n_2 = 2$?

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

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

Comprehension X

The 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: $\dfrac{df}{dt} = K(1-f)$,

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

(a) 23.1 h (b) 46.2 h

(c) 100 h (d) 92.4 h

34. The exponential variation of *f* with *t* (h) is

(a) $f = 1 - e^{-3t/200}$ (b) $f = e^{-3t/200} - 1$

(c) $f = e^{-3t/200}$ (d) $f = e^{3t/200}$

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 1.5×10^{-4} 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). The compound '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?

(a) 0 (b) 0.5

(c) 1 (d) 2

36. The rate constant for the formation of 'B' is

(a) 1.5×10^{-4} s^{-1} (b) 1.35×10^{-5} s^{-1}

(c) 1.5×10^{-5} s^{-1} (d) 1.5×10^{-3} 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 minutes?

(a) 0.5 M (b) 0.368 M
(c) 0.135 M (d) 0.223 M

38. What is the concentration of ‘B’ after 25 minutes?

(a) 0.223 M (b) 0.29 M
(c) 0.27 M (d) 0.145 M

39. What is the concentration of ‘C’ after 25 minutes?

(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 minutes (b) 20 minutes
(c) 25 minutes (d) 40 minutes

41. What is the maximum concentration of ‘B’?

(a) 0.290 M (b) 0.296 M
(c) 0.50 M (d) 0.3 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 $-\dfrac{d[A]}{dt} = +\dfrac{d[C]}{dt}$?

(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) 1.8×10^{-2} M/min

Comprehension XIII

For the first-order reaction opposed by first-order reaction A $\underset{K_b}{\overset{K_f}{\rightleftharpoons}}$ B, $[A]_0 = 0.15$ M, $[A]_{eq} = 0.10$ M, $[A]_{10} = 0.125$, where times are given in minutes.

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 minutes (b) 15 minutes
(c) 5 minutes (d) 20 minutes

Comprehension XIV

A substance ‘X’ dissociates simultaneously into ‘Y’ and ‘Z’ as

$$\text{X(g)} \xrightarrow{A_1 = 2\times10^{14}\ \text{s}^{-1},\ Ea_1 = 12\ \text{kcal/mol}} \text{Y(g)}$$

$$\text{X(g)} \xrightarrow{A_1 = 2\times10^{14}\times e^{-2}\ \text{s}^{-1},\ Ea_1 = 9\ \text{kcal/mol}} \text{Z(g)}$$

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 $A \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} B \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} C \underset{K_{-3}}{\overset{K_3}{\rightleftharpoons}} D$, 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 of the following 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 of the following 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 of the following 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 of the following is therate-determining step in forward direction?

(a) A $\longrightarrow$ B
(b) B $\longrightarrow$ C
(c) C $\longrightarrow$ D
(d) Cannot be predicted

56. Which of the following is the 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 the answer as follows.

(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 → 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 increase in concentration of that reactant.

4. **Statement I:** The overall rate of a reversible reaction may decrease with 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, the 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 $L^2\ mol^{-2}\ s^{-1}$.

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 the density and molecular mass.

Section E (Column Match)

1. Match the columns.

Column I (Reactions)	Column II (Unit of rate constant, K)
(A) $SO_2Cl_2 \rightarrow SO_2 + Cl_2$	(P) s^{-1}
(B) $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$	(Q) min^{-1}
(C) $2H_2O_2 \rightarrow 2H_2O + O_2$	(R) $L\ mol^{-1}\ min^{-1}$
(D) $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$	(S) $L\ mol^{-1}\ s^{-1}$

2. Match the columns.

Column I (Reactions)	Column II (Increase in rate when concentration of reactant is doubled)
(A) $CH_3CHO \rightarrow CH_4 + CO$	(P) 2 times
(B) $SO_2Cl_2 \rightarrow SO_2 + Cl_2$	(Q) $2^{1.5}$ times
(C) $2\ H_2O_2 \rightarrow 2H_2O + O_2$	(R) 2 times in acid medium
(D) $CH_3COOC_2H_5 \xrightarrow{HOH} CH_3COOH + C_2H_5OH$	(S) 2^2 times in basic medium

3. Match the columns.

Column I	Column II
(A) Rate = $k \times$ Intensity of light	(P) Second-order
(B) Rate = $k[A]^1[B]^1$	(Q) Zero-order
(C) Rate = $k[A]^{3/2}[B]^{1/2}$	(R) First-order when A is excess.
(D) Rate = $k[A]^2[B]^1$	(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) $L\ mol^{-1}\ s^{-1}$
(C) $k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$	(R) $mol\ L^{-1}\ s^{-1}$
(D) $k = \frac{2.303}{t(a-b)}\log\left[\frac{b(a-x)}{a(b-x)}\right]$	(S) $atm^{-1}\ s^{-1}$

5. Match the half-life in Column I with the order in Column II for the reaction: A → 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

Here, a = Initial concentration of the reactant.

6. Match Column I with Column II and Column III for the reaction A → Products.

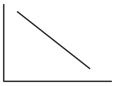
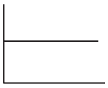
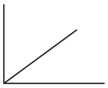
Column I	Column II	Column III
(A) x is plotted against t in zero-order reaction.	(P) Slope = $-k/2.303$	(U) Intercept = a
(B) $\log (a - x)$ is plotted against 't' in first-order reaction.	(Q) Slope = $2k$	(V) Intercept = $1/a$
(C) $(a - x)^{-1}$ is plotted against 't' in second order reaction.	(R) Slope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

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

7. Match Column I with Column II for the reaction A → 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 columns.

Column I (Graphs for reaction: A → Products)	Column II (Coordinates, 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)
(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 → Products, $t_{x/y}$ represents the time in which x/y fraction of reactant is converted 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) $t = \frac{1}{K_2 - K_1}.\ln\left(\frac{K_2}{K_1}\right)$
(C) $[A]_t = [B]_t$	(R) t = time at which the rate of formation of 'B' is maximum.
	(S) $t = \frac{1}{K_1 - K_2} \cdot \ln\left(\frac{2K_1 - K_2}{K_1}\right)$

Section F (Subjective)

Single Digit Integer Type

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

(i) $Cl_2 + CO \rightarrow COCl_2$; $r = K[Cl_2]^{3/2}[CO]$
(ii) $PCl_3 + Cl_2 \rightarrow PCl_5$; $r = K[PCl_3][Cl_2]$
(iii) $2NO + H_2 \rightarrow N_2O + H_2O$; $r = K[NO][H_2]$
(iv) $2NO + O_2 \rightarrow 2NO_2$; $r = K[NO]^2[O_2]$
(v) $NO + O_3 \rightarrow NO_2 + O_2$; $r = K[NO][O_3]$

2. The following mechanisms are proposed for the reaction $CO + NO_2 \rightarrow CO_2 + NO$, at low temperature.

Mechanism 1:
$2NO_2 \rightleftharpoons N_2O_4$ (fast)
$N_2O_4 + 2CO \rightarrow 2CO_2 + 3NO$ (slow)

Mechanism 2:
$2NO_2 \rightarrow NO_3 + NO$ (slow)
$NO_3 + CO \rightarrow NO_2 + CO_2$ (fast)

Which of the above mechanism is consistent with the observed rate law: $+\frac{d[CO_2]}{dt} = K[NO_2]^2$?

3. For the reaction $3BrO^- \rightarrow BrO_3^- + 2Br^-$ in alkaline aqueous solution, the value of the second-order rate constant (in BrO^-) in rate law for $-\frac{d[BrO^-]}{dt}$ was found to be 0.06 $M^{-1}s^{-1}$. The rate constant (in $M^{-1}s^{-1}$), when the rate law is written as $+\frac{d[BrO_3^-]}{dt}$ is a $M^{-1}s^{-1}$ and as $+\frac{d[Br^-]}{dt}$ is b $M^{-1}s^{-1}$, then the value of $(a + b) \times 100$ is

4. In a certain polluted atmosphere containing O_3 at a steady-state concentration of 2×10^{-8} M, the hourly production of O_3 by all sources was estimated as 7.2×10^{-15} M. If only mechanism for the destruction of O_3 is second-order reaction, then the rate constant (in ml mol^{-1} s^{-1}) for the destruction reaction is

5. For the reaction $2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$, 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 NO, the pressure of H_2 being constant. If pressure of NO was kept constant, the value of $-\frac{dP}{dt}$ was found to be 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 A + B → Products, the order is one with respect to each A and B. The sum of x and y from the following data is as follows.

Rate (mol $l^{-1}s^{-1}$)	**[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 $9.0 \times 10^{-5}\ s^{-1}$.

$$Cr^{3+}(aq) + SCN^-(aq) \rightarrow Cr(SCN)^{2+}(aq)$$

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

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

$$CH_3C(S)NH_2(aq) + H_2O \rightarrow H_2S(aq) + CH_3C(O)NH_2(aq)$$

The rate of reaction is given by the rate law Rate = $k[H_3O^+][CH_3C(S)NH_2]$. Consider 1 L of solution that is 0.20 M in $CH_3C(S)NH_2$ 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

(i) a 4.0 g sample of NaOH is added to the solution.
(ii) 500 ml of water is added to the solution.
(iii) the 0.15 M HCl solution is replaced by 0.15 M acetic acid solution.
(iv) 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 $C_4H_8 \rightarrow 2C_2H_4$. The rate constant is $\frac{25}{18} \times 10^{-5}\ s^{-1}$. 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 = 0.7, ln 3 = 1.10)

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 $K\ min^{-1}$, 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 $7.50 \times 10^{-4}\ s^{-1}$. What quantity of heat (in J) is initially liberated per second from 2.0 L of solution that is 0.02 M of H_2O_2? Given $\Delta_f H$ of $H_2O_2(l) = -187.0$ kJ/mol and $\Delta_f H\ H_2O(l) = -287.0$ 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 the original. It was found that mutarotation of this drug was first-order reaction with rate constant $\frac{4.5}{3.1536} \times 10^{-8}\ s^{-1}$. 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 $A(g) \rightarrow nB(g)$, the rate constant is $6.93 \times 10^{-4}\ s^{-1}$. 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 ($\times 10^{-3}\ s^{-1}$)	1.0	10	100

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

16. The complex $[Co(NH_3)_5F]^{2+}$ reacts with water as

$$[Co(NH_3)_5F]^{2+} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + F^-.$$

The rate of reaction may be given as $r = K[\text{complex}]^a [H^+]^b$. The reaction is acid catalysed and hence, $[H^+]$ does not change during the reaction. Thus, the rate may be given as $r = K'[\text{complex}]^a$ where $K' = K[H^+]^b$. The value of $(a + b)$ is

[Complex]	**[H^+]**	**$t_{1/2}$ (h)**	**$t_{3/4}$ (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 → products, the concentration of A are C_o, $a \cdot C_o$, $a^2 \cdot C_o$, $a^3 \cdot C_o$, ... after time interval 0, t, $2t$, $3t$ ...., where a is a 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 = osmotic pressure of solution (in Pascal) at $t = 20$ minutes and $y = t_{3/4}$ of the dissociation reaction (in min) [Given: Density of final solution in each case = 1.0 g/ml, $g = 10$ 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 10^{-5} M s^{-1}) at the concentration, [A] = 0.2 M is

20. In order to determine the order of reaction $A(g) \rightarrow 2B(g)$, the 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 as follows.

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

21. In the reaction A → Products, the rate is doubled when the concentration of 'A' is quadrupled. If 50% of the reaction occurs in $8\sqrt{2}$ h, then 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 2×10^{-3} s^{-1}, 3×10^{-3} s^{-1} and 1.93×10^{-3} 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, then the value of x is

24. If the 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 for milk to sour at 57°C? (ln 2 = 0.7, ln 3 = 1.1)

Four Digit Integer Type

1. The rate constant for the decomposition of ozone following second-order kinetics is 5×10^{-4} L mol^{-1} 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 2×10^{-8} M, is ($N_A = 6 \times 10^{23}$)

2. In thermal decomposition of C_2H_5Br(g) to C_2H_4(g) and HBr(g), the initial pressure changes from 200 to 390 mm of Hg at the end of reaction. Percentage of C_2H_5Br(g) undecomposed, when the pressure of mixture was 342.5 mm of Hg, is

3. 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, then what is the generation time (in h) for it? (log 2 = 0.3, log 3 = 0.48)

4. Nitric oxide reacts with oxygen to give nitrogen dioxide.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The rate law is $-\Delta[NO]/\Delta t = k[NO]^2[O_2]$, where the rate constant is 1.6×10^5 M^{-2} 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 ($R = 0.08$ L-atm/K-mol)

5. A drop (0.05 ml) of solution contains 3×10^{-7} moles of H^+. If the rate constant of disappearance of H^+ is 1.0×10^{-7} mol $l^{-1}s^{-1}$, then how long (in min) would it take for H^+ in drop to disappear?

6. 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

7. 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, ln 3 = 1.1)

8. The decomposition of benzene diazonium chloride in aqueous solution is a reaction of first order which proceeds as $C_6H_5N_2Cl \rightarrow C_6H_5Cl + N_2(g)$. 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 minutes. How long (in min) after the start of the decomposition, will 70 cm^3 of nitrogen have been evolved?

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

$$2P(g) \rightarrow 4Q(g) + R(g) + S(l)$$

is a first-order reaction. After 30 minutes, 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, the total pressure is 625 mm. The vapour pressure of S(*l*) at this temperature is 25 mm. The total pressure after 60 minutes is

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

$$NH_4NO_2(aq) \rightarrow N_2O(g) + H_2O(l)$$

is 123 minutes at 27°C. If 200 ml of 0.02 M NH_4NO_2 solution is allowed to decompose, then how long (in min) must the reaction proceed to produce 49.26 ml of 'wet' $N_2O(g)$ measured at 27°C and 785 mm Hg? The vapour pressure of water at 27°C is 25 mm Hg.

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

Set	$[A_0] \times 10^6$ M	$[B_0] \times 10^6$ M	Half-life (s)
1	300	4	62.5
2	300	6	*x*
3	5	300	625
4	10	300	*y*

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

$$CH_3–O–CH_3 \rightarrow CH_4(g) + H_2(g) + CO(g)$$

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 minutes? Assume ideal gas behaviour.

13. The rate of a first-order reaction is 0.04 mol $litre^{-1}s^{-1}$ at 10 minutes and 0.03 mol $litre^{-1}s^{-1}$ at 22 minutes 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 minutes)

cd = molar concentration of HCl used in the experiment.

15. For the reaction A(g) → 2B(g) + C(g), the rate constant is 1.386×10^{-3} 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 decomposes into optically active substances 'B' and 'C' as follows.

$$A \xrightarrow{K = 0.001\ \text{min}^{-1}} 2B + C$$

The specific rotations of A, B and C are +40°, +10° 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	$[A_0] \times 10^{-2}$ M	$[B_0] \times 10^{-2}$ M	$T_{1/2}$ (min)	$T_{7/8}$ (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.

$$CH_3COOH \longrightarrow CH_4 + CO_2,\ K_1 = 3.2\ s^{-1}$$

$$CH_3COOH \longrightarrow H_2C = C = O + H_2O,\ K_2 = 4.8\ s^{-1}$$

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 follows.

$$r\ (\text{M/min}) = 2 \times 10^{-6}\,[A]^2 - \frac{1.4 \times 10^{-6}\,[D]^2}{[B]\,[C]}$$

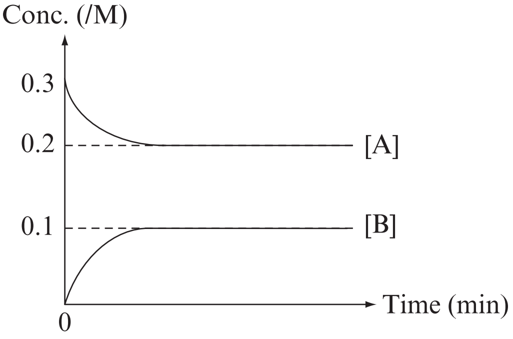
If initially each of the reactant has concentrate 1.0 M, calculate the rate of reaction when the concentration of C becomes 0.7 M assuming no D is present at the start of the reaction. If the rate is 'r' M/min, then the value of $(r \times 10^9)$ is

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

$$A \xrightarrow{T_A} C \text{ and } B \xrightarrow{T_B} C$$

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 minutes and 15 minutes, respectively, the concentration of C (in millimole per litre) after 30 minutes is?

21. For the reversible reaction A(aq) $\rightleftharpoons$ B(aq), which is first-order in both directions, $K_f = \dfrac{1.38}{300}\ \text{min}^{-1}$. 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 °C) must be used to cause the reaction to be completed in 30 minutes? The temperature coefficient of reaction is 2.

23. The rate of decomposition for CH_3NO_2 and $C_2H_5NO_2$ 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 °C) at which rate constant will be same for both decomposition reactions, is ($R = 8.3$ J/K-mol, ln 10 = 2.3)

24. The activation energy of a reaction is 149.4 kJ/mol and its pre-exponential factor is $5 \times 10^{13}\ s^{-1}$. At what temperature (in K) will the reaction have half-life of 1 minute? (ln 2 = 0.7, ln 3 = 1.1, ln 7 = 2.0, ln $10^{-16} = -36.9$, $R = 8.3$ 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 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. (b) 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. (d) 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. (a) 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)

Answer Keys

Exercise II

Section A (Only one Correct)

1. (b) 2. (b) 3. (d) 4. (d) 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. (a) 22. (b) 23. (d) 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)

1. (a), (b), (c), (d) 2. (c) 3. (b), (c) 4. (a), (c), (d)
5. (a), (d) 6. (a), (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), (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. (d) 25. (b) 26. (c)

Comprehension VIII

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

Comprehension IX

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

Comprehension X

33. (b) 34. (a)

Comprehension XI

35. (c) 36. (c)

Comprehension XII

37. (b) 38. (b) 39. (b) 40. (b)
41. (d) 42. (b) 43. (b) 44. (d)

Comprehension XIII

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

Comprehension XIV

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

Comprehension XV

52. (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 → P, Q; B → R, S; C → P, Q; D → R, S
2. A → Q; B → P; C → P; D → R, S
3. A → Q; B → P, R; C → P; D → R, S
4. A → R; B → P; C → Q, S; D → Q, S
5. A → P; B → S; C → R; D → Q
6. A → R, U; B → P, X; C → S, V; D → Q, W
7. A → Q; B → P, R; C → S; D → T
8. A → P; B → Q, S; C → R, T; D → U
9. A → S; B → P; C → R, T; D → Q
10. A → P, Q; B → P, R; C → 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. (1250) 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. (0260) 18. (0060) 19. (1595) 20. (1475)
21. (0100) 22. (0055) 23. (0727) 24. (0500) 25. (0100)

HINTS AND EXPLANATIONS

EXERCISE I (JEE MAIN)

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

1. $$r_{av} = -\frac{\Delta C}{\Delta t} = \frac{-(1.29\times10^{-2} - 1.50\times10^{-2})}{10}$$
$$= 2.1\times10^{-4}\,\text{M min}^{-1}$$
$$= \frac{2.1\times10^{-4}}{60} = 3.5\times10^{-6}\ \text{Ms}^{-1}$$

2. $$r_{\text{inst}} = -\frac{1}{2}\cdot\frac{d[\text{HI}]}{dt}$$

3. $$r = \frac{r_A}{4} = \frac{r_B}{1} = \frac{r_C}{2} = \frac{r_D}{2}$$

4. $$r_{av,\text{NO}_2} = \frac{2.4\times10^{-2}}{6} = 4\times10^{-3}\ \text{Ms}^{-1}$$

And, $$\frac{r_{\text{N}_2\text{O}_5}}{2} = \frac{r_{\text{NO}_2}}{4}$$

$$\Rightarrow r_{\text{N}_2\text{O}_2} = 2\times10^{-3}\ \text{Ms}^{-1}$$

5. r_{av} and r_{inst} may to same.

6. $$r_{rxn} = -\frac{1}{2}\cdot\frac{d[\text{NH}_3]}{dt} = +\frac{d[\text{N}_2]}{dt} = +\frac{1}{3}\cdot\frac{d[\text{H}_2]}{dt}$$

or, $$\frac{1}{2}\cdot K_1[\text{NH}_3] = K_2[\text{NH}_3] = \frac{1}{3}\cdot K_3[\text{NH}_3]$$

$$\therefore\ 3K_1 = 6K_2 = 2K_3$$

7. Rate constant depends on temperature but it is independent from concentration or pressure.

8. Normally, the rate of reaction decreases with increase in number of bonds involved.

9. Check options

10. $$K = 10^{-2}\ \text{L mol}^{-1}\ \text{s}^{-1} = 10^{-2}\times(1000\ \text{ml})$$
$$\times\frac{1}{6\times10^{23}\,\text{molecule}}\times\frac{60}{\text{min}}$$
$$= 1.0\times10^{-21}\ \text{ml molecule}^{-1}\ \text{min}^{-1}$$

11.

	A	+	2B	$\longrightarrow$	P
t_1	1.0 M		1.0 M		
t_2	1.0 – 0.25 = 0.75 M		1.0 – 0.5 = 0.5 M		

Now, $$\frac{r_2}{r_1} = \frac{K[A_2]^2[B_2]}{K[A_1]^2[B_1]} \Rightarrow \frac{r_2}{2\times10^{-2}} = \frac{(0.75)^2\times0.5}{(1.0)^2\times1.0}$$

$$\therefore\ r_2 = 5.625\times10^{-3}\ \text{M/min}$$

12.

	A_2	$\longrightarrow$	B +	$\frac{1}{2}$C
$t = 0$	100 mm		0	0
$t = 5$ min	$(100 - x)$ mm		x mm	$\frac{x}{2}$ mm

Now, $$(100 - x) + x + \frac{x}{2} = 120 \Rightarrow x = 40$$

$$\therefore\ r_{av,A_2} = -\frac{\Delta P}{\Delta t} = \frac{x}{t} = \frac{40}{5} = 8\ \text{mm/ min}$$

13. Theoretical

14. $r = K\,[\text{N}_2\text{O}_5]$

$$\Rightarrow [\text{N}_2\text{O}_5] = \frac{r}{K} = \frac{2.4\times10^{-5}\,\text{M s}^{-1}}{3.0\times10^{-5}\ \text{s}^{-1}} = 0.8\ \text{M}$$

15. $$r = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3}\cdot\frac{d[\text{H}_2]}{dt} = +\frac{1}{2}\cdot\frac{d[\text{NH}_3]}{dt}$$

16. $$\frac{r_{\text{H}_2}}{3} = \frac{r_{\text{NH}_3}}{2}$$

$$\Rightarrow r_{\text{H}_2} = \frac{3}{2}\times\frac{10^{-3}}{17}\times10^3\ \text{mol hr}^{-1}$$

$$= \frac{3}{34}\times\frac{2}{10^3}\ \text{Kg hr}^{-1} = 1.76\times10^{-4}\ \text{Kg hr}^{-1}$$

17. Informative

18. Molecularity can even be fractional.

19. Rate law and law of mass action may be identical.

20. $r_1 = K[A]$, $r_2 = K[A]^2$, $r_3 = K[A]^3$ and $[A] < 1$ M

$\therefore r_1 > r_2 > r_3$

21. $r = K[\text{NO}]^2\,[\text{O}_2]$

On tripling the volume, the concentration becomes $\frac{1}{3}$ and hence, rate becomes $\frac{1}{27}$ times.

22. Theoretical

23. Molecularity can never be zero.

24. $r = K \cdot P^0$

25. $r = K \cdot [A]^n$

$$\therefore \frac{r_2}{r_1} = \left(\frac{[A_2]}{[A_1]}\right)^n$$

$$\Rightarrow 2 = (8)^n \Rightarrow n = \frac{1}{3}$$

26. From the unit of rate constant, order = 2.

27. Order is independent from stoichiometry.

28. $r = K \cdot [A]^n$

$$\therefore \frac{r_2}{r_1} = \left(\frac{[A_2]}{[A_1]}\right)^n \Rightarrow 1.837 = (1.5)^n \Rightarrow n = 1.5$$

29. Order is not related with ΔH.

30. Order may be fractional.

31. $r = K[A]^x\,[B]^y$

$$\text{Exp (1)} \div \text{Exp (3)} : \frac{0.1}{0.1} = \frac{K(0.012)^x(0.035)^y}{K(0.024)^x(0.035)^y}$$

$$\Rightarrow x = 0$$

$$\text{Exp (2)} \div \text{Exp (3)} : \frac{0.8}{0.1} = \frac{K(0.024)^x(0.070)^y}{K(0.024)^x(0.035)y}$$

$$\Rightarrow y = 3$$

32. $$\frac{r_2}{r_1} = \frac{K(2[A])^n \cdot ([B]/2)^m}{K[A]^n \cdot [B]^m} = 2^{n-m}$$

33. Informative

34. $r = K[A]^x\,[B]^y\,[C]^z$

$$\text{Exp (1)} \div \text{Exp (2)} : \frac{2.5\times10^{-4}}{1.0\times10^{-3}} = \frac{K(0.01)^x(0.01)^y(0.01)^z}{K(0.02)^x(0.01)^y(0.01)^z}$$

$$\Rightarrow x = 2$$

$$\text{Exp (1)} \div \text{Exp (3)} : \frac{2.5\times10^{-4}}{2.5\times10^{-4}} = \frac{K(0.01)^x(0.01)^y(0.01)^z}{K(0.01)^x(0.02)^y(0.01)^z}$$

$$\Rightarrow y = 0$$

$$\text{Exp (3)} \div \text{Exp (4)} : \frac{2.5\times10^{-4}}{5.0\times10^{-4}} = \frac{K(0.01)^x(0.02)^y(0.01)^z}{K(0.01)^x(0.02)^y(0.02)^z}$$

$$\Rightarrow z = 1$$

35. $$r = r_{\text{C}_8\text{H}_{12}} = K \cdot [\text{C}_4\text{H}_6]^2$$

$$= (6.1\times10^{-2}\ \text{M}^{-1}\text{s}^{-1})\times(0.02\ \text{M})^2$$

$$= 2.44\times10^{-5}\ \text{M s}^{-1}$$

36. $K_1(\text{Ms}^{-1}) = K_2\,(\text{s}^{-1}) = K_3(\text{M}^{-1}\,\text{s}^{-1})$

or, $K_1 \times 10^{-3}\,(\text{mol ml}^{-1}\ \text{s}^{-1}) = K_2\,(\text{s}^{-1}) = K_3 \times 10^{-3}\,(\text{mol ml}^{-1}\ \text{s}^{-1})$

37. $r = K[A][B]^2 = K'[B]^2$

38. $r = K[\text{ester}][\text{H}^+]$

39. Informative

40. $$K = \frac{K_{\text{app}}}{[\text{H}_2\text{O}][\text{H}^+]} = \frac{1.5\times10^{-5}\text{s}^{-1}}{\left(\frac{1000}{18}\ \text{M}\right)(0.1\,\text{M})}$$

$$= 2.7\times10^{-6}\ \text{M}^{-2}\text{s}^{-1}$$

Mechanism of Reaction

41. 1st step is RDS and hence, $r = K_1\,[X][Y]$

42. $\text{A} \xrightarrow{K_1} \text{B}$ is RDS

43. $r = K_2\,[A][C]$ and $K_1 = \frac{[C]}{[A]}$

$\therefore r = K_1K_2[A]^2$

44. $r = K_f\,[B][C]$ and $K = \frac{[B]}{[A]^2}$

$\therefore r = K \cdot K_f \cdot [A]^2[C]$

45. $r = K_3\,[\text{CHCl}_3][\dot{\text{C}}\text{l}]\,[\text{Cl}]$ and $\frac{K_1}{K_2} = \frac{[\dot{\text{C}}\text{l}]^2}{[\text{Cl}_2]}$

$$\therefore r = \sqrt{\frac{K_1}{K_2}} \cdot K_3[\text{CHCl}_3][\text{Cl}_2]^{1/2}$$

Integrated Rate Law

46. $t_{1/2} = \frac{[A_0]}{2K}$ and $t_{100\%} = \frac{[A_0]}{K}$

47. $K = \frac{[A_0]-[A]}{t} = \text{Constant}$

or, $\frac{a-0.25a}{10} = \frac{a-0.10a}{t} \Rightarrow t = 12$ hours

48. Reaction will complete before 2 hours

49. when $t = t_{3/4}$, $[A] = [A_0] - \frac{3}{4}[A_0] = \frac{[A_0]}{4}$

Now, $t_{3/4} = \frac{1}{K}\cdot \ln\frac{[A_0]}{\left(\frac{[A_0]}{4}\right)} = \frac{\ln 4}{K} = \frac{2.303}{K}\cdot \log 4$

50. $Kt = \ln\frac{[H_2O_2]_0}{[H_2O_2]_t} = \ln\frac{V_0}{V_t}$

$\therefore\ t = \frac{1}{4.5\times 10^{-2}\ \text{min}}\cdot \ln\frac{25}{5} = \frac{\ln 5}{4.5\times 10^{-2}}\ \text{min}$

51. $t_{99\%} = x \times t_{90\%}$

$\Rightarrow \frac{1}{K}\cdot \ln\frac{100}{1} = x\cdot\frac{1}{K}\cdot \ln\frac{100}{10}$

$\Rightarrow x = 2$

52. $r_0 = 6.0\times 10^{21}$ molecules $\text{ml}^{-1}\ s^{-1}$

$= 6\times 10^{21}\times 10^{3}\times 60$

$= 36\times 10^{25}$ molecules $\text{L}^{-1}\ \text{min}^{-1}$

Now, $t = \frac{t_{1/2}}{\log 2}\cdot \log\frac{r_0}{r} = \frac{10\,\text{min}}{\log 2}\cdot \log\frac{36\times 10^{25}}{4.5\times 10^{25}}$

$= 30$ min

53. For 2nd order reaction, $t_{1/2} = \frac{1}{K\cdot [A_0]}$

Hence, second $t_{1/2}$ is double of first $t_{1/2}$.

$$[A_0] \xrightarrow{x\ \text{min}} \frac{[A_0]}{2} \xrightarrow{2x\ \text{min}} \frac{[A_0]}{4}$$

54. $t_{1/2}\ \alpha\ [A_0]^{1-n}$

55.

$$\begin{array}{lcc} & A & \longrightarrow\ nB \\ t=0 & [A_0] & 0 \\ t=t & [A_0]-x & nx \end{array}$$

At intersection, $[A] = [B] \Rightarrow [A_0] - x = nx$

$\therefore\ [B] = nx = n.\frac{[A_0]}{n+1}$

56. At any instant, $[B] < [A]$ if $[B_0] = [A_0]$

57. For zero order: $[A] = [A_0] - K\cdot t$

58. $t_{1/2}\ \alpha\ [A_0]^{1-n}$

Given: $C_0\cdot\sqrt{T} = \text{constant} \Rightarrow T = \text{constant}\times C_0^{-2}$

As $1-n = -2 \Rightarrow n = 3$

59. $1-n = \frac{1}{2} \Rightarrow n = \frac{1}{2}$

60. $K = \frac{1}{t}\cdot \ln\frac{[A_0]}{[A]} = \frac{1}{0.5\ \text{min}}\cdot \ln\frac{100}{99} = 0.02\ \text{min}^{-1}$

61. The first-order reaction never completes 100%.

62.

$$\begin{array}{lcccc} & A & \longrightarrow\ 2B & + & C \\ t=0 & P_0 & 0 & & 0 \\ t=t & P_0-x & 2x & & x \\ t=\infty & \approx 0 & 2P_0 & & P_0 \end{array}$$

From question: $P_\infty = 2P_0 + P_0$

$\Rightarrow P_0 = \frac{P_\infty}{3}$

and $P = (P_0 - x) + 2x + x$

$\Rightarrow x = \frac{P-P_0}{2} = \frac{3P-P_\infty}{6}$

Now, $K = \frac{1}{t}\cdot \ln\frac{P_A{}^\circ}{P_A} = \frac{1}{t}\cdot \ln\frac{P_0}{P_0-x}$

$= \frac{1}{t}\cdot \ln\frac{P_\infty/3}{\frac{P_\infty}{3} - \frac{3P-P_\infty}{6}}$

$= \frac{1}{t}\cdot \ln\frac{2P_\infty}{3(P_\infty - P)}$

63. $t_{1/2}\alpha[A_0]^{1-n}$

$\Rightarrow \frac{29}{60} = \left(\frac{1.55}{0.75}\right)^{1-n}$

$\Rightarrow n \approx 2$

64. $t_{0.75} = 2 \times t_{0.50}$

65. $t_{1/2}\, \alpha\, [A_0]^{1-n} \qquad \Rightarrow 1 - \frac{3}{2} = -\text{ m} \qquad \Rightarrow m = 0.5$

66. $100 \xrightarrow{1.0\,\text{hr}} 50 \xrightarrow{2.0\,\text{hr}} 25$ as $t_{1/2} = \frac{1}{K[A_0]}$

67. $K = \frac{1}{t} \cdot \ln \frac{[A_0]}{[A]} = \frac{1}{2 \times 10^4\,\text{s}} \cdot \ln \frac{800}{50} = 1.386 \times 10^{-4}\,\text{s}^{-1}$

68.

$$\begin{array}{llll} & 2\text{N}_2\text{O}_5 \longrightarrow & 4\text{NO}_2 \quad + & \text{O}_2 \\ t = 0 & P_0 & 0 & 0 \\ t = 30\text{ min} & P_0 - x & 2x & x/2 \\ t = \infty & \approx 0 & 2P_0 & P_0/2 \end{array}$$

From question: $2P_0 + \frac{P_0}{2} = 600$

$\Rightarrow P_0 = 240$ mm

and $(P_0 - x) + 2x + \frac{x}{2} = 300 \ \Rightarrow x = 40$ mm

Now, $K_{\text{N}_2\text{O}_5} = \frac{1}{t} \cdot \ln \frac{P_{\text{N}_2\text{O}_5}^{\circ}}{P_{\text{N}_2\text{O}_5}} = \frac{1}{30\text{ min}} \cdot \ln \frac{240}{240 - 40}$

$= 6 \times 10^{-3}\text{ min}^{-1}$

$\therefore\ K_{rxn} = \frac{K_{\text{N}_2\text{O}_5}}{2} = 3 \times 10^{-3}\text{ min}^{-1}$

69. $t_{99.9\%} = \frac{t_{1/2}}{\log 2} . \log \frac{100}{0.1} \qquad \Rightarrow \frac{t_{99.9\%}}{t_{1/2}} \approx 10$

70. $(b - a) \simeq b$ and $(b - x) \simeq b$

$\therefore\ Kt = \frac{2.303}{a - b} \cdot \ln \frac{b(a - x)}{a(b - x)} \simeq \frac{2.303}{(-b)} \cdot \ln \frac{b \cdot (a - x)}{a \cdot b}$

or, $(b \cdot K) \cdot t = 2.303 \cdot \ln \frac{a}{a - x}$

$\therefore$ Reaction becomes first-order with respect to A.

71. $t_{0.75} = 2 \times t_{0.50} \qquad \Rightarrow 1386\text{ sec} = 2 \times \frac{0.693}{K}$

$\therefore\ K = 10^{-3}\ \text{s}^{-1}$

72. Next $t_{1/2}$ is double than initial and hence, reaction is second-order.

73. Formula for second-order reaction.

74. $t = \frac{t_{1/2}}{\log 2} \cdot \log \frac{V_\infty}{V_\infty - V_t}$

$\Rightarrow\ 60 = \frac{30}{\log 2} \cdot \log \frac{100}{100 - V_t}$

$\therefore\ V_t = 75$ min

75. $K = \frac{1}{t} \cdot \ln \frac{V_0}{V_t} = \frac{1}{10\text{ min}} \cdot \ln \frac{25}{20} = 0.02\text{ min}^{-1}$

Parallel, Sequential and Reversible Reactions

76. $r_A = \left(-\frac{d[A]}{dt}\right)_1 + \left(-\frac{d[A]}{dt}\right)_2 = K_1\ [A] + K_2\ [A] = (K_1 + K_2) \cdot [A]$

77. For C_R max, $\frac{dC_R}{dt} = 0$

$\Rightarrow\ t_{\max} = \frac{\ln(K_2 / K_1)}{K_2 - K_1}$

78. $t_{\max} = \frac{\ln\left(\frac{K_2}{K_1}\right)}{K_2 - K_1} = \frac{\ln\left(\frac{2}{1}\right)}{0.02 - 0.01} = 70$ min

79. On derivation,

$[C] = [A_0]\left[1 - \frac{K_2 \cdot e^{-K_1 t} - K_1 \cdot e^{-K_2 t}}{K_2 - K_1}\right]$ (when $K_1 \neq K_2$)

If $K_1 << K_2$, $[C]$ becomes $[A_0].(1 - e^{-K_1 t})$

80. $\frac{K^H}{K^D} = \frac{0.0848}{0.0212} = \frac{4}{1}$

Dependence of Reaction Rate on Temperature and Catalyst

81. Theoretical

82. $K = A \cdot e^{-E_a/RT} = A \; \alpha \; \sqrt{T}$ (if $E_a = 0$)

83. Theoretical

84. Lower E_a, faster reaction.

85. The rate of every elementary reaction increases with increase in temperature.

86. $\Delta H = E_{af} - E_{ab}$

$\Rightarrow 72 = 77 - E_{ab} \Rightarrow E_{ab} = 5$ kJ/mol

87. $E_a \downarrow K \uparrow$

88. Theoretical

89. The ratio of catalytic reaction may depend on catalyst concentration.

90. $t_{1/2} \; \alpha \; \frac{1}{K} \quad \Rightarrow T \uparrow \quad K \uparrow \quad t_{1/2} \downarrow$

91. $K = A \cdot e^{-E_a/RT} = \log K = \log A - \frac{E_a}{2.303} \cdot \frac{1}{T}$

92. $\frac{r_2}{r_1} \approx (2)^5 = 32$

93. $E_a \uparrow \quad r \downarrow$

94. Theoretical

95. Reaction with higher E_a are more sensitive towards temperature changes.

96. Catalyst lowers the activation energies of forward as well as backward reactions by the same extent.

97. Theoretical

98. $\Delta H = E_{af} - E_{ab} \Rightarrow y - x = E_{af} - z \Rightarrow E_{af} = y - x + z$

99. $K = A \cdot e^{-E_a/RT} = A$ (when $T \to \infty$)

100. The step of absorption of light depends only on the intensity of absorbed light and follows zero-order kinetics (independent from reactant concentration).

EXERCISE II (JEE ADVANCED)

Section A (Only one Correct)

1. Negative sign is for reactants and positive for products.

2. $r_{rxn} = -\frac{1}{2} \cdot \frac{d[\mathrm{NO_2}]}{dt} = K_1[\mathrm{NO_2}]^2 - K_2[\mathrm{N_2O_4}]$

$\therefore$ Rate of disappearance of $\mathrm{NO_2}$ is given by,

$$-\frac{d[\mathrm{NO_2}]}{dt} = 2K_1[\mathrm{NO_2}]^2 - 2K_2[\mathrm{N_2O_4}]$$

3. $P_A = \frac{n_A RT}{V} \Rightarrow \frac{dP_A}{dt} = \frac{RT}{V} \cdot \frac{dn_A}{dt}$

or, $(-K_1 \cdot P_A^n) = RT(-K_2 \cdot C_A^n)$

$$\therefore \; K_2 = \frac{K_1}{RT} \cdot \left(\frac{P_A}{C_A}\right)^n = \frac{K_1}{RT} \cdot (RT)^n = (RT)^{n-1}$$

4. $-\frac{1}{2} \cdot \frac{d[\mathrm{HI}]}{dt} = K_2[\mathrm{HI}]^2 - K_1[\mathrm{H_2}][\mathrm{I_2}]$

5. Order = 1 $\longleftarrow$ with respect to $A \Rightarrow a = 1$

Order = 2 $\longleftarrow$ with respect to $B \Rightarrow b = 2$

Hence, reaction is A + 2B $\longrightarrow$ P.

$$r = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

6.

$$\begin{array}{llll} & \mathrm{A} \quad + & 2\mathrm{B} \longrightarrow & \mathrm{C} + \mathrm{D} \\ t = 0 & 0.6 \text{ atm} & 0.8 \text{ atm} & \\ t = t & 0.6 - x & 0.8 - 2x & \\ & = 0.3 \text{ atm} & = 0.2 \text{ atm} & \Rightarrow x = 0.3 \end{array}$$

$$\therefore \; \frac{r_t}{r_0} = \frac{K \times 0.3 \times (0.2)^2}{K \times 0.6 \times (0.8)^2} = \frac{1}{32}$$

7. For no change in temperature, $\Delta H_{\text{net}} = 0$ and hence, for 3 moles of *B* reacted, 4 moles of *Q* should form.

8. $2.82 = (2)^x \Rightarrow x = \frac{3}{2}$

$9 = (3)^y \Rightarrow y = 2$

$\therefore$ overall order $= x + y = \frac{7}{2}$

9. $r_1 = 0.0068/65 = 1.046 \times 10^{-4}$ gm/min

$r_2 = 0.0031/120 = 2.583 \times 10^{-5}$ gm/min

$r_3 = 0.0032/60 = 5.333 \times 10^{-5}$ gm/min

From (1) and (2) : order with respect to $K_2C_2O_4 = 2$

From (1) and (3) : order with respect to $HgCl_2 = 1$

10. From (2) and (3) : order with respect to $I^- = 1$

From (1) and (3) : order with respect to $ClO^- = 1$

From (3) and (4) : order with respect to $OH^- = 1$

11. $(1 + K_2 \cdot C_A) \approx 1$

12. For steady state, $+\frac{d[R]}{dt} = 0$

or, $K_1[A] - K_2[R][B] - K_3[R][C] = 0$

$$\therefore\ [R] = \frac{K_1[A]}{K_2[B] + K_3[C]}$$

$$\text{Now, } \frac{dx}{dt} = K_3[R][C] = \frac{K_3K_1[A][C]}{K_2[B] + K_3[C]}$$

13. $r = K_3[O][O_3]$

$$\text{For 1st step, } \frac{K_1}{K_2} = \frac{[O_2][O]}{[O_3]}$$

$$\therefore r = K_3[O][O_3] = \frac{K_3K_1[O_3]^2}{K_2[O_2]}$$

14. $r = -\frac{d[X]}{dt} = +\frac{d[Y]}{dt}$ and rate decreases with time.

15.

$$\begin{array}{lcc} & A \longrightarrow & 2B \\ t = 0 & 0.1\text{ M} & 0 \\ t = 1\text{ min} & 0.1 - x & 2x \end{array}$$

For zero order reaction: $[A_0] - [A] = Kt$

or, $0.1 - (0.1 - x) = 0.01 \times 1 \Rightarrow x = 0.01$

$\therefore [B] = 2x = 0.02$ M

16. $2NH_3 \longrightarrow N_2 + 3H_2$

$$r_{rxn} = \frac{r_{NH_3}}{2} = \frac{r_{N_2}}{1} = \frac{r_{H_2}}{3} = 0.1\text{ atm/s} = \text{Constant}$$

Hence, after 10 seconds:

$P_{NH_3} = 3 - 2 \times 0.1 \times 10 = 1$ atm

$P_{N_2} = 0.1 \times 10 = 1$ atm

$P_{H_2} = 3 \times 0.1 \times 10 = 3$ atm

$\therefore P_{\text{total}} = 1 + 1 + 3 = 5$ atm

17. For $-\frac{d[A]}{dt} = K[A]^n$ and $n \neq 1$

$[A]^{1-n} = [A_0]^{1-n} - K(1-n) \cdot t$

For given graph, $1 - n = -3 \Rightarrow n = 4$

and $-K(1 - n) = \tan 45° \Rightarrow K(4 - 1) = 1$

$\therefore\ K = \frac{1}{3}\text{ M}^{-3}\text{ min}^{-1}$

$$\text{Now, } r_{rxn} = -\frac{1}{3}\cdot\frac{d[A]}{dt} = \frac{1}{3}\cdot K\cdot[A]^4$$

$$= \frac{1}{3}\times\frac{1}{3}\times(0.2)^4 = \frac{16}{9}\times 10^{-4}\text{ M min}^{-1}$$

18. $1\text{M} \xrightarrow[8.0\text{ hr}]{t=2\times t_{1/2}} 0.25\text{M} \qquad \Rightarrow t_{1/2} = 4.0$ hr

$0.6\text{M} \xrightarrow[4.0\text{ hr}]{t=t_{1/2}} 0.3\text{M}$

19. The successive $t_{1/2}$ are double of previous one and hence, order = 2.

20. $r = K[A]^n$

$10 = K(0.8)^n$ (1)

$0.625 = K(0.2)^n$ (2)

$\therefore n = 2$

21.

$$\begin{array}{llll} & C_2H_6 \longrightarrow & C_2H_4 & + \quad H_2 \\ t = 0 & 3\text{ bar} & 0 & 0 \\ t = ? & (3 - x)\text{ bar} & x\text{ bar} & x\text{ bar} \end{array}$$

From question: $(3 - x) + x + x = 5 \quad \Rightarrow x = 2$

From the unit of rate constant, the order of reaction is 2, hence,

$$t = \frac{1}{K}\left(\frac{1}{P_{C_2H_6}} - \frac{1}{P^{\circ}_{C_2H_6}}\right) = \frac{1}{0.0015}\left(\frac{1}{3-x} - \frac{1}{3}\right)\times\frac{1}{10^5}$$

$= 4.44 \times 10^{-3}$ hr = 16 seconds

22. Let the reaction be first-order.

$$K_1 = \frac{1}{8}\cdot\ln\frac{100}{20} = 0.201$$

$$K_2 = \frac{1}{18}\cdot\ln\frac{100}{10} = 0.128$$

As $K_1 \neq K_2$, the reaction is not first-order. Let the reaction be second-order.

$$K_1 = \frac{1}{8}\left(\frac{1}{0.2} - \frac{1}{1}\right) = 0.5$$

$$K_2 = \frac{1}{18}\left(\frac{1}{0.1} - \frac{1}{1}\right) = 0.5$$

As $K_1 = K_2$, order = 2

23. Here, $t_{1/2}$ is independent from sugar concentration and hence, the order with respect to sugar is 1.

Now, $r = K\,[\text{Sugar}][\text{H}^+]^n = K' \cdot [\text{Sugar}]$

$$t_{1/2} = \frac{\ln 2}{K'} = \frac{\ln 2}{K[\text{H}^+]^n}$$

$$500 = \frac{\ln 2}{K \cdot (10^{-5})^n} \quad \text{and} \quad 50 = \frac{\ln 2}{K \cdot (10^{-6})^n}$$

$\therefore n = -1$

24. $r = K\,[\text{ester}]\,[H^+] = K' \cdot [\text{ester}]$

$$\therefore\ t_{1/2} = \frac{\ln 2}{K'} = \frac{\ln 2}{K[\text{H}^+]} = \frac{0.693}{0.1 \times 0.01} = 693 \text{ hr}$$

25. For nth order reaction ($n \neq 1$)

$$Kt = \frac{[A_0]^{1-n} - [A]^{1-n}}{1-n}$$

For $n = 0.5$, $Kt = \dfrac{[A_0]^{1/2} - [A]^{1/2}}{\frac{1}{2}}$

Now, $t_{100\%} = T = \dfrac{2([A_0]^{1/2} - 0^{1/2})}{K} = \dfrac{2[A_0]^{1/2}}{K}$

and $t_{50\%} = t_{1/2} = \dfrac{2\left([A_0]^{1/2} - \left(\dfrac{[A_0]}{2}\right)^{1/2}\right)}{K}$

$$= \frac{2[A_0]^{1/2}\left(1 - \frac{1}{\sqrt{2}}\right)}{K}$$

$$\therefore\ \frac{T}{t_{1/2}} = \frac{1}{1 - \frac{1}{\sqrt{2}}} = \frac{1}{0.3}$$

26. For A: $t = \dfrac{t_{1/2}}{\log 2} \cdot \log \dfrac{[A_0]}{[A]} = \dfrac{10}{\log 2} \cdot \log \dfrac{8[B_0]}{[A]}$

For B: $t = \dfrac{t_{1/2}}{\log 2} \cdot \log \dfrac{[B_0]}{[B]} = \dfrac{20}{\log 2} \cdot \log \dfrac{[B_0]}{[A]}$

From question, $\dfrac{10}{\log 2} \cdot \log \dfrac{8[B_0]}{[A]} = \dfrac{20}{\log 2} \cdot \log \dfrac{[B_0]}{[A]}$

$$\therefore\ \frac{[B_0]}{[A]} = 8 \Rightarrow t = \frac{20}{\log 2} \cdot \log \frac{[B_0]}{[A]} = 60 \text{ min}$$

Alternate method:

$$A : 8[B_0] \xrightarrow{10} 4[B_0] \xrightarrow{10} 2[B_0] \xrightarrow{10}$$

$$[B_0] \xrightarrow{10} \frac{[B_0]}{2} \xrightarrow{10} \frac{[B_0]}{4} \xrightarrow{10} \frac{[B_0]}{8}$$

$$B : [B_0] \xrightarrow{20} \frac{[B_0]}{2} \xrightarrow{20} \frac{[B_0]}{4} \xrightarrow{20} \frac{[B_0]}{8}$$

27. $0.1\,\text{M} \xrightarrow[40\text{ min}]{t=2t_{1/2}} 0.025\,\text{M}$

$\Rightarrow t_{1/2} = 20$ min

Now, $r = K[A] = \dfrac{\ln 2}{t_{1/2}}[A] = \dfrac{0.693}{20 \text{ min}} \times 0.01\,\text{M}$

$= 3.465 \times 10^{-4}$ M min^{-1}

28. $+\dfrac{d[B]}{dt} = -\dfrac{d[A]}{dt} = K[A]^{1/3}$

or, $-\displaystyle\int_{[A_0]}^{[A_0]/2} \frac{d[A]}{[B]^{1/3}} = K \cdot \int_0^{t_{1/2}} dt$

$$t_{1/2} = \frac{3[A_0]^{2/3}(2^{2/3} - 1)}{2^{5/3} \cdot K}$$

29.

$$\begin{array}{llll} & \text{N}_2\text{O}_5 \longrightarrow & 2\text{NO}_2 + & \frac{1}{2}\ \text{O}_2 \\ t = 0 & a \text{ mole} & & 0 \\ t = t & (a - x) \text{ mole} & & \frac{x}{2} \text{ mole } \alpha\ V_t \\ t = \infty & \simeq 0 & & \frac{a}{2} \text{ mole } \alpha\ V_\infty \end{array}$$

$$K = \frac{1}{t} \cdot \ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]} = \frac{1}{t} \cdot \ln \frac{a}{a - x} = \frac{1}{t} \cdot \ln \frac{V_\infty}{V_\infty - V_t}$$

Now, $\dfrac{1}{20} \cdot \ln \dfrac{9.6}{9.6 - 4.8} = \dfrac{1}{40} \cdot \ln \dfrac{9.6}{9.6 - V_t} \Rightarrow V_t = 7.2$ ml

30. For zero order reaction, $t_{1/2}\ \alpha\ P^{\circ}_{\text{NH}_3}$

$$\therefore\ \frac{315}{t_{1/2}} = \frac{70}{150} \Rightarrow t_{1/2} = 675 \text{ sec}$$

31.

$$\begin{array}{lll} & \text{A} \longrightarrow & n\text{B} \\ t = 0 & P_0 & 0 \\ t = t & P_0 - x & n.x \end{array}$$

Now, $(P_0 - x) = P_0 \cdot e^{-Kt} \Rightarrow x = P_0\,(1 - e^{-Kt})$

$$\text{Now, } P_{\text{total}} = (P_0 - x) + nx$$
$$= P_0 \cdot e^{-Kt} + n \cdot P_0 (1 - e^{-Kt})$$
$$= P_0[n + (1 - n)\, e^{-Kt}]$$

32. $$t_{1/2} = \frac{(C_0)^{1-n} - \left(\frac{C_0}{2}\right)^{1-n}}{K(1-n)} = \frac{(C_0)^{1-n}[1-2^{n-1}]}{K(1-n)}$$

$$\text{and } t_{3/4} = \frac{(C_0)^{1-n} - \left(\frac{C_0}{4}\right)^{1-n}}{K(1-n)} = \frac{(C_0)^{1-n}[1-2^{2(n-1)}]}{K(1-n)}$$

$$\therefore \frac{t_{3/4}}{t_{1/2}} = \frac{1-2^{2(n-1)}}{1-2^{(n-1)}} = 1 + 2^{(n-1)}$$

33. $$\frac{r_2}{r_1} = \left(\frac{[A_2]}{[A_1]}\right)^n \Rightarrow 2 = (4)^n \qquad \Rightarrow n = \frac{1}{2}$$

$$\text{Now, } t_{1/2}\, \alpha\, [A_0]^{1-n} \qquad \Rightarrow t_{1/2}\, \alpha\, [A_0]^{1/2}$$

$$100 \xrightarrow{t=16\text{ min}} 50 \xrightarrow{t=16/\sqrt{2}\text{ min}} 25$$

$$\therefore \text{Time for 75\% reaction} = 16 + \frac{16}{\sqrt{2}} = 27.3 \text{ min}$$

34. $$Kt = \ln\frac{a}{a-x} = \ln\frac{1}{\left(1-\frac{x}{a}\right)}$$

$$\text{or, } 2.5 \times 10^{-5} \times (100 \times 60) = \ln\frac{1}{\left(1-\frac{x}{a}\right)}$$

$$\Rightarrow \qquad \frac{x}{a} = 0.138$$

$$\therefore \text{Percentage decomposition} = \frac{x}{a} \times 100 = 13.8\%$$

35. $$(t_{1/2})_1 = (t_{1/2})_2 \Rightarrow \frac{0.693}{K_1} = \frac{1}{K_2[A_0]}$$

$$\therefore [A_0] = \frac{K_1}{0.693\, K_2} = \frac{6.93 \times 10^{-2}}{0.693 \times 0.2} = 0.5 \text{ M}$$

36. $$\frac{t_1}{t_2} = \frac{\frac{(t_{1/2})_1}{\log 2} \cdot \log\frac{100}{75}}{\frac{(t_{1/2})_2}{\log 2} \cdot \log\frac{100}{25}} = \frac{(t_{1/2})_1}{(t_{1/2})_2} \cdot \frac{\log\left(\frac{4}{3}\right)}{\log 4}$$

$$= \frac{3}{2} \times \frac{0.6 - 0.48}{0.6} = \frac{3}{10}$$

37. $$r = K[A]^n$$

$$\frac{\frac{1}{100} \times 0.02}{60} = K(0.02)^n \qquad (1)$$

$$\frac{\frac{1}{100} \times 0.04}{15} = K(0.04)^n \qquad (2)$$

$$\therefore n = 3$$

38. $$t = \frac{T_{\text{gen}}}{\ln 2} \cdot \ln\frac{[A]}{[A_0]} \Rightarrow 60 = \frac{75}{\ln 2} \cdot \ln\frac{[A]}{[A_0]}$$

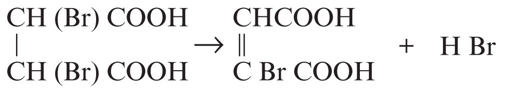
$$\therefore \frac{[A]}{[A_0]} = e^{0.56}$$

39. $$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{[A_0]_1}{[A_0]_2}\right)^{1-n} \Rightarrow \frac{37.82}{18.95} = \left(\frac{0.05}{0.10}\right)^{1-n}$$

$$\Rightarrow n = 2$$

$$\text{Now, } \frac{(t_{1/2})}{37.82} = \left(\frac{0.15}{0.05}\right)^{-1} \Rightarrow t_{1/2} = 12.6 \text{ hr}$$

40.



$$\begin{array}{l} \text{CH (Br) COOH} \\ | \\ \text{CH (Br) COOH} \end{array} \longrightarrow \begin{array}{l} \text{CHCOOH} \\ \| \\ \text{C Br COOH} \end{array} + \text{H Br}$$

$t = 0$	a mole	0	0
$t = t$	$(a - x)$ mole	x mole	x mole

$$\text{Now, } \frac{T_0 \cdot N}{1000} = a \times 2 \qquad (1)$$

$$\text{and } \frac{T_t \cdot N}{1000} = (a-x) \times 2 + x \times 2 + x \times 1 \qquad (2)$$

$$\therefore \frac{a}{a-x} = \frac{T_0}{3T_0 - 2T_t}$$

41.

	$B^{n+} \longrightarrow$	$B^{(n+4)+}$
$t = 0$	a mole	0
$t = 10$ min	$(a - x)$ mol	x mol

$$\text{Now, } \frac{25 \times N}{1000} = a \times 2 \qquad (1)$$

$$\text{and, } \frac{32.5 \times N}{1000} = (a-x) \times 2 + x \times 5 \qquad (2)$$

$$\text{Now, } K = \frac{1}{t} \cdot \ln\frac{a}{a-x} = \frac{1}{10 \text{ min}} \cdot \ln\frac{12.5}{12.5 - 2.5}$$

$$= 0.02 \text{ min}^{-1}$$

42.

$$\begin{array}{lccc} & A & \longrightarrow\ 2B & +\ C \\ t=0 & a\ \text{mol} & 0 & 0 \\ t=10\ \text{sec} & (a-x)\ \text{mol} & 2x\ \text{mol} & x\ \text{mol} \end{array}$$

Now, $\frac{r_A}{r_B}=\frac{P_A}{P_B}\cdot\sqrt{\frac{M_B}{M_A}} \Rightarrow \frac{1}{2}=\frac{a-x}{2x}\cdot\sqrt{\frac{4}{16}}$

$$\Rightarrow x=\frac{a}{3}$$

Now, $K=\frac{1}{t}\cdot\ln\frac{a}{a-x}=\frac{1}{10\ \text{sec}}\cdot\ln\frac{a}{a-\frac{2a}{3}}$

$$=0.04\ \text{sec}^{-1}$$

43. $r=K[A]^2[B]=K'\cdot[A]^2$ as $[B_0]>>[A_0]$

$$\therefore\ t_{1/2}=\frac{1}{K'\cdot[A_0]}=\frac{1}{K[B_0][A_0]}=\frac{1}{0.5\times0.002\times2.0}$$

$$=500\ \text{min}$$

44. $r=K[\text{ester}][\text{H}^+]$

$$\therefore\ \frac{r_{\text{HA}}}{r_{\text{HX}}}=\frac{1}{100}=\frac{[\text{H}^+]_{\text{HA}}}{1.0}\Rightarrow[\text{H}^+]_{\text{HA}}=0.01\ \text{M}$$

Now, $Ka_{(\text{HA})}=\frac{[\text{H}^+][A^-]}{[HA]}=\frac{0.01\times0.01}{(1-0.01)}\approx10^{-4}$

45. As $[A_0]=[B_0]$ and the stoichiometric coefficients of both A and B are 1, at any time $[A]=[B]$. Hence, $r=K[A]^{1/2}[B]^{1/2}=K[A]$.

Required time $=2\times t_{1/2}=2\times\frac{0.693}{2.31\times10^{-3}}=600$ sec

46. $-\frac{dC}{dt}=\frac{\alpha C}{1+\beta C}\Rightarrow-\int_{Co}^{Co/2}\left(\frac{1}{C}+\beta\right)\cdot dC=\alpha\cdot\int_0^{t_{1/2}}dt$

$$\therefore\ t_{1/2}=\frac{1}{\alpha}\left(\ln2+\frac{\beta\cdot C_0}{2}\right)$$

47. $r=K'[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]=K'\cdot[\text{CH}_3\text{COOH}]^2$

$$\therefore\ t_{1/2}=\frac{1}{K'\cdot[\text{CH}_3\text{COOH}]_0}$$

$$\Rightarrow 50=\frac{1}{(K\times10^{-3})\times0.2}$$

$$\therefore\ \text{K}=100\ \text{M}^{-2}\ \text{min}^{-1}$$

48. $r=K[A]^x[B]^y$

For case-I : $r=K[A]^x[B]^y=K'\cdot[B]^y$
where $K'=K[A_0]^x$

In equal time interval, the concentrations of B are in G.P. and hence, $y=1$ and

$$K'=\frac{1}{10}\cdot\ln\frac{0.01}{0.008}=0.02\ \text{min}^{-1}$$

For case-II: $r=K[A]^x[B]^y=K''[A]^x$
where $K''=K[B_0]^y$

In equal time interval, the concentration of A are in G.P. and hence, $x=1$ and

$$K''=\frac{1}{10}\cdot\ln\frac{0.02}{0.018}=0.01\ \text{min}^{-1}$$

Now, $r=K[A][B]$

$$\therefore\ K=\frac{K'}{[A_0]}\ \text{or,}\ \frac{K''}{[B_0]}=\frac{0.02}{2.0}\ \text{or}\ \frac{0.01}{1.0}$$

$$=0.01\ \text{M}^{-1}\ \text{min}^{-1}$$

49. $K_{\text{app}}=\frac{K_1\cdot C}{1+\alpha\cdot C}=\frac{K_1}{\frac{1}{C}+\alpha}$

$$\lim_{C\to\infty}K_{\text{app}}=\frac{K_1}{\alpha}$$

From question, $\frac{K_1\cdot C}{1+\alpha\cdot C}=\frac{90}{100}\times\frac{K_1}{\alpha}$

or, $\frac{C}{1+9\times10^5C}=\frac{90}{100}\times\frac{1}{9\times10^5}\Rightarrow C=10^{-5}$ M

50.

$$\begin{array}{lccc} & A & \longrightarrow\ 2B & +\ C \\ t=0 & 1 & 0 & 0 \\ t=12\ \text{hr} & 1-x & 2x & x \\ t=24\ \text{hr} & 1-y & 2y & y \end{array}$$

V.P. of solution, $P=X_2\cdot P^{\text{o}}$

or, $20=\frac{180/18}{\frac{180}{18}+(1+2x)}\times24\Rightarrow x=0.5$

$\therefore\ t=12\ \text{hr}=t_{1/2}$

Now, $t=24\ \text{hr}=2\times t_{1/2}\Rightarrow y=0.75$

Now, V.P. of solution, $P=X_2\cdot P^\circ$

$$=\frac{10}{10+(1+2y)}\times24$$

$$=19.2\ \text{mm Hg}$$

51. $\frac{[B]}{[C]}=\frac{K_1}{K_2}=\frac{1.26\times10^{-4}}{3.15\times10^{-5}}=\frac{4}{1}$

$\therefore$ Percentage of $B=\frac{4}{5}\times100=80\%$

52.
$$\begin{array}{ccc} & A \longrightarrow & R \\ t=t & a-x & x \end{array}$$

$\therefore\ r = K(a-x)\cdot x$

For maximum rate, $\frac{dr}{dx} = 0 \Rightarrow x = \frac{a}{2} \Rightarrow C_A = C_R$

53. $K\cdot\int_0^{t_{1/2}} dt = \int_0^{\text{Co}/2} \frac{1+by}{\text{Co}-y}\cdot dy$

$\Rightarrow t_{1/2} = \frac{1}{K}\left[(1+\text{Co}\cdot b)\cdot\ln 2 - \frac{\text{Co}\cdot b}{2}\right]$

54. $t_{50\%,\,B} = t_{94\%,\,A}$

or, $\frac{1}{K_2}\cdot\ln\frac{100}{50} = \frac{1}{K_1}\cdot\ln\frac{100}{6} \Rightarrow \frac{K_1}{K_2} = \frac{4.067}{1}$

55. Percentage product by S_{N^2} mechanism

$= \frac{(4.8\times10^{-5})[\text{RX}](0.01)}{(4.8\times10^{-5})[\text{RX}](0.01)+2.4\times10^{-6}[\text{RX}]}\times100$

$= 16.67\%$

56. $[H_2] : [O_2] : [OH] : [H_2O] : [O]$

$= K_1 : K_1 : 2K_2 : K_3 : K_3$

$= 0.60 : 0.60 : 2\times0.30 : 0.10 : 0.10 = 6 : 6 : 6 : 1 : 1$

57. $[A] + [B] + [C] = [A_0]$

when $[A] = [B] = [C]$, $[A] = \frac{[A_0]}{3} = [A_0]\cdot e^{-Kt}$

or, $\frac{1}{3} = e^{-(\ln3+\ln3)\cdot t} \Rightarrow t = 0.5$ min

58. As $K_1 = K_2 = K$ (Say),

$t_{\max} = \frac{1}{K} = \frac{1}{0.02} = 50$ min

and $[B]_{\max} = \frac{[A_0]}{e} = \frac{0.2}{e}$ M

59. After long time, $r_A = r_B \Rightarrow K_1[A] = K_2[B]$

$\therefore\ \frac{[A]}{[B]} = \frac{K_2}{K_1} = 40$

60. $\frac{[C]}{[A]} = \frac{\frac{K_2[A_0]}{K_1+K_2}\left(1-e^{-(K_1+K_2)t}\right)}{[A_0]\cdot e^{-(K_1+K_2)\cdot t}}$

$= \frac{K_2}{K_1+K_2}\left(e^{(K_1+K_2)\cdot t}-1\right)$

$= \frac{9K_1}{10K_1}\left(e^{10K_1\cdot t}-1\right) = \frac{9}{10}\left[e^{10\times1.25\times10^{-5}\times3600}-1\right]$

$= 0.5112$

61. At steady state, $K_1[A] = K_2[B]$

$\therefore\ K_2 = \frac{K_1[A]}{[B]} = \frac{2.5\times10^{-4}\times0.2}{0.01} = 5\times10^{-3}\ \text{min}^{-1}$

62. Reaction may be considered as $A \xrightarrow{K_1} C$

$\therefore\ [C] = [A_0]\ (1-e^{-K_1t})$

63.
$$\begin{array}{lcccc} & A \xrightarrow{K_1} & 2B & A \xrightarrow{K_2} & C \\ t=0 & 1\text{ atm} & 0 & 1\text{ atm} & 0 \\ t=10\text{ min} & (1-x-y) & 2x & 1-x-y & y \\ t=\infty & (1-a-b) & 2a & (1-a-b) & b \\ & \approx 0 & & \approx 0 & \end{array}$$

From question, $a + b = 1$ and $2a + b = 1.5$

$\therefore\ a = b = 0.5$

Now, $\frac{P_B}{P_C} = \frac{2K_1}{K_2} = \frac{2a}{b} = \frac{2x}{y} \Rightarrow \frac{K_1}{K_2} = 1 = \frac{x}{y}$ 0

Now, $P_{10\text{ min}} = (1-x-y)+2x+y = 1.4$

$\Rightarrow x = y = 0.4$

$\therefore\ P_A = 1-x-y = 0.2$ atm at $t = 10$ min

Now, $K_1 + K_2 = \frac{1}{t}\cdot\ln\frac{P_A{}^\circ}{P_A} = \frac{1}{10}\cdot\ln\frac{1}{0.2}$

$= 0.16\ \text{min}^{-1}$

$\therefore\ K_1 = K_2 = 0.08\ \text{min}^{-1}$

64. $r_{\max} = z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2\cdot u_{av}\cdot N^{*2}$

$= \frac{1}{\sqrt{2}}\pi\times(4\times10^{-8}\text{cm})^2\times(2\times10^4\text{cm s}^{-1})$

$\times(2\times10^{19}\ \text{cm}^{-3})^2$

$= 2.842\times10^{28}\ \text{cm}^{-3}\ \text{s}^{-1} = 4.74\times10^7\ \text{mol l}^{-1}\ \text{s}^{-1}$

65. $\frac{d(\ln K)}{dT} = \frac{E_a}{RT^2}$

or, $0+\frac{\beta}{T}+\frac{\gamma}{T^2} = \frac{E_a}{RT^2} \Rightarrow E_a = (\beta T+\gamma)R$

66. $\frac{K_1}{K_2} = \frac{[B]}{[C]} = \frac{40}{60} = \frac{2}{3}$

Now, $E_{a(\text{overall})} = \frac{K_1\cdot E_{a1}+K_2\cdot E_{a2}}{K_1+K_2} = 32$ kcal/mol

67. $r_{\text{uncat}} = \frac{1}{2}\times r_{\text{cat}} \Rightarrow K_{\text{uncat}} = \frac{1}{2}\times K_{\text{cat}}$

or, $A\cdot e^{-E_{a(\text{uncat})}/RT} = \frac{1}{2}\times A\cdot e^{-E_{a(\text{cat})}/RT\times 0.5T}$

or, $\ln 2 - \frac{E_{a(\text{uncat})}}{RT} = -\frac{E_{a(\text{uncat})}-20}{0.5RT}$

$\therefore E_{a(\text{uncat})} = 38.58$ kcal/mol

68. For $A \longrightarrow B$; $K_1 = 8\ \text{min}^{-1}$ at $T = 300\ K$

$K_1' = ?$ at $T = ?$

$$\ln\frac{K_1'}{8} = \frac{20\text{KJ}}{R}\left(\frac{1}{300}-\frac{1}{T}\right) \quad (1)$$

For $A \longrightarrow C$; $K_2 = 2\ \text{min}^{-1}$ at $T = 300\ K$

$K_2' = ?$ at $T = ?$

$$\ln\frac{K_2'}{2} = \frac{28.314\ \text{KJ}}{R}\left(\frac{1}{300}-\frac{1}{T}\right) \quad (2)$$

From (1) and (2), $\ln\frac{K_2'/2}{K_1'/8} = \frac{8.314\times 10^3}{8.314}\left(\frac{1}{300}-\frac{1}{T}\right)$

or, $\ln\left(\frac{1}{2}\times\frac{8}{2}\right) = \left(\frac{1}{300}-\frac{1}{T}\right)\times 10^3 \Rightarrow T = 379.75\ \text{K}$

69. Given: $\frac{K_{1(310)}}{K_{1(300)}} = 2$, $K_{1(310)} = \frac{\ln 2}{30\ \text{min}}$

$\frac{K_{1(310)}}{K_{1(310)}} = 2$ and $E_{a_2} = \frac{1}{2}E_{a_1}$

For reaction 1: $\ln\left[\frac{K_{1(310)}}{K_{1(300)}}\right] = \frac{E_{a_1}}{R}\left(\frac{1}{300}-\frac{1}{310}\right)$ (1)

For reaction 2: $\ln\left[\frac{K_{2(310)}}{K_{2(300)}}\right] = \frac{E_{a_2}}{R}\left(\frac{1}{300}-\frac{1}{310}\right)$ (2)

From (1) ÷ (2) : $\frac{\ln 2}{\ln\left[\frac{K_{2(310)}}{K_{2(300)}}\right]} = 2$

or, $\left[\frac{K_{2(310)}}{K_{2(300)}}\right] = \sqrt{2}$

$\Rightarrow K_{2(300)} = \frac{K_{2(310)}}{\sqrt{2}} = \frac{2\times\frac{\ln 2}{30}}{\sqrt{2}}$

$= 0.0327\ \text{min}^{-1}$

70. At 27°C, $K_1 = \frac{1}{21.6}\cdot\ln\frac{100}{25} = \frac{\ln 2}{10.8}\text{min}^{-1}$

Now, $\ln\frac{K_2}{K_1} = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$

$= \frac{9.6\times 10^3}{2}\left(\frac{1}{300}-\frac{1}{320}\right) = 1.0$

$\therefore \frac{K_2}{K_1} = e = 2.7$

$\Rightarrow K_2 = 2.7\times\frac{\ln 2}{10.8} = \frac{\ln 2}{4}$

$\Rightarrow (t_{1/2})_2 = 4$ min

∴ Percentage decomposition in 8.0 min = 75%

71. $K = A\cdot e^{-E_a/Rt} = A\cdot e^{-RT/RT} = \frac{A}{e} \simeq 0.37\ A$

72. $\ln 2 = \frac{E_a}{R}\left(\frac{1}{280}-\frac{1}{290}\right) \quad (1)$

and $\ln x = \frac{E_a}{R}\left(\frac{1}{290}-\frac{1}{300}\right) \quad (2)$

From (2) ÷ (1), $\frac{\ln x}{\ln 2} = \frac{280}{300} \Rightarrow x = 1.91$

73. Informative

74. Theory based

75. First energy barrier is high as Step-I is slow.

Section B (One or More than one Correct)

1. Theory based

2. Theory based

3. Informative

4. $r = K\cdot[A]^n \quad \Rightarrow n = \frac{\ln(r/K)}{\ln[A]}$

Now, $\frac{r_2}{r_1} = \left(\frac{[A_2]}{[A_1]}\right)^n \Rightarrow n = \frac{\ln r_2 - \ln r_1}{\ln[A_2]-\ln[A_1]}$

And, $t_{1/2} \,\alpha\, [A_0]^{1-n} \Rightarrow \dfrac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\dfrac{[A_0]_2}{[A_0]_1}\right)^{1-n}$

$$\therefore\ n = 1 - \frac{\ln[A_0]_2 - \ln[A_0]_1}{\ln(t_{1/2})_2 - \ln(t_{1/2})_1}$$

5. $[A] = [A_0]\,(1 - \alpha) = [A_0] \cdot e^{-Kt} \Rightarrow \alpha = 1 - e^{-Kt}$

6. (a) $-\dfrac{d[A]}{dt} = K \cdot [A]^n \quad f = \dfrac{[A_1]-[A_2]}{[A_1]} = \dfrac{-d[A]}{[A]}$

From question, $f = \dfrac{-d[A]}{[A]}$

$\therefore\ \dfrac{f[A]}{t} = K[A]^n \Rightarrow \dfrac{f}{t} = K \cdot [A]^{n-1}$

or, $\log\left(\dfrac{f}{t}\right) = \log K + (n-1) \cdot \log[A]$

(b) $\dfrac{[A_0]^{1-n} - [A]^{1-n}}{1-n} = Kt$

$\Rightarrow [A]^{1-n} = [A_0]^{1-n} + (n-1) \cdot Kt$

(c) $\dfrac{t_{3/4}}{t_{1/2}} = \dfrac{[A_0]^{1-n} - \left(\dfrac{[A_0]}{4}\right)^{1-n}}{[A_0]^{1-n} - \left(\dfrac{[A_0]}{2}\right)^{1-n}} = \dfrac{1-(2^2)^{n-1}}{1-2^{n-1}}$

$= 1 + 2^{n-1}$

7. $t_{1/2} = C \cdot (C_0)^{1-n} \Rightarrow \ln t_{1/2} = \ln C + (1-n) \cdot \ln C_0$

8. $K' = K \cdot [H^+]$

On doubling $[H^+]$, K' will double but K will remain unchanged.

9. Theory based

10. (a) For steady state, $\dfrac{6.93 \times 10^{-6}}{80} = \dfrac{0.693}{100} \times [SO_3]$

$\therefore\ [SO_3] = 1.25 \times 10^{-5}$ M

(b) $n_{eq}\ SO_3 = n_{eq}\ NaOH \Rightarrow 1.25 \times 10^{-5} \times 10^3 \times 2$
$= V_{NaOH} \times 1$

$\therefore\ V_{NaOH} = 2.5 \times 10^{-2}$ L = 25 ml

(c) Mole of SO_3 needed $= \dfrac{980 \times 10^3}{98} = 10^4$

$\therefore$ Air needed $= \dfrac{10^4}{1.25 \times 10^{-5}} = 8 \times 10^8$ L

(d) 1000 days = 10 $t_{1/2}$

$\therefore\ [SO_3] = \dfrac{1.25 \times 10^{-5}}{2^{10}} \approx 1.25 \times 10^{-8}$ M

11.
$$\begin{array}{llll} & 3A(g) & \longrightarrow\ 2B(g) & +\ \ 2C(s) \\ t = 0 & 6 \text{ atm} & 0 & - \\ t = 20 \text{ min} & (6-x) \text{ atm} & \frac{2}{3}x \text{ atm} & 0.05 \text{ atm} \\ t = \infty & \approx 0 & 4 \text{ atm} & 0.05 \text{ atm} \end{array}$$

But from question, $P_\infty = 4.05$ atm and hence, $(4.05 - 4) = 0.05$ atm is the vapour pressure of $C(s)$.

Now, $P_{20} = (6-x) + \dfrac{2}{3}x + 0.05 = 5.05 \Rightarrow x = 2$

$\therefore\ t = 20 \text{ min} = t_{1/2}$

12. $-\dfrac{d\theta}{dt} = K \cdot \theta \Rightarrow Kt = \ln\dfrac{\theta_0}{\theta}$

(a) $t = \dfrac{1}{K} \cdot \ln\dfrac{\theta_0}{\theta} = \dfrac{1}{0.04} \cdot \ln\dfrac{596}{298} = 17.5$ sec

(b) $t = \dfrac{1}{0.04} \cdot \ln\dfrac{1192}{298} = 35$ sec

13. (a)
$$\begin{array}{lccc} & A\ + & B \longrightarrow & 2C \\ t = 0 & 2a & a & \\ t = t & 2a - x & a - x & \end{array}$$

As [A] ≠ [B] throughout, the overall reaction is not first-order.

(b) $r = K[A]^{-1}[B]^2 = K' \cdot [B]^2 \Rightarrow t_{1/2} = \dfrac{1}{K'[B_0]}$

(c) $r = K[A]^{-1}[B]^2 = K''\,[A]^{-1}$

(d) As [A] = [B] = stoichiometric ratio, then the mole ratio will remain constant throughout.

14. $A \xrightarrow{K_1} P\ ;\ t_{1/2} = \dfrac{0.693}{K_1}$

$B \xrightarrow{K_2} Q\ ;\ t_{1/2} = \dfrac{1}{K_2[B_0]} = \dfrac{1}{K_2}$

From question, $\dfrac{0.693}{K_1} = \dfrac{1}{K_2} \quad \Rightarrow K_2 > K_1$

15.
$$\begin{array}{lcc} & A_4 \longrightarrow & 4A \\ t = 0 & a\text{M} & 0 \\ t = 30 \text{ min} & (a-x)\text{ M} & 4x\text{M} \end{array}$$

As $a - x = 4x \Rightarrow x = \dfrac{a}{5}$

$\therefore$ Percentage reaction at $t = 30$ min

$= \dfrac{x}{a} \times 100 = 20\%$

Now, $30 = \dfrac{t_{1/2}}{\log 2} \cdot \log\dfrac{a}{a-x} \Rightarrow t_{1/2} = 90$ min

16. (a) $\Delta_r \text{H} = \sum \Delta_f \text{H}_{\text{Products}} - \sum \Delta_f \text{H}_{\text{Reactants}}$

$= 2 \times (-1263) - [(-2238) + (-285)] = -3$ KJ/mol

(b) Can not confirm because in aqueous medium, there is no combustion.

(d) Concentration in G.P. in equal time interval.

17. $n = 1 \Rightarrow t_{100\%} = \dfrac{1}{K} \cdot \ln\dfrac{[A_0]}{0} = \text{Infinite}$

$n \neq 1 \Rightarrow t_{100\%} = \dfrac{[A_0]^{1-n} - (0)^{1-n}}{K(1-n)} = \dfrac{[A_0]^{1-n}}{K(1-n)}$ if $n < 1$

$= \text{Infinite}$ if $n > 1$

18. $\dfrac{[B]}{[C]} = \dfrac{K_1}{K_2} = \dfrac{1}{2} \Rightarrow [C] > [B]$

Hence, after long time, the solution will be dextrorotatory.

Now, $K = K_1 + K_2 = 6.93 \times 10^{-2} + 13.86 \times 10^{-2}$
$= 3 \times 6.93 \times 10^{-2}\ \text{min}^{-1}$

$\therefore\ t_{1/2} = \dfrac{\ln 2}{K} = \dfrac{0.693}{3 \times 6.93 \times 10^{-2}} = \dfrac{10}{3}$ min

	$A \longrightarrow$	B	$A \longrightarrow$	C
$t = 0$	2M	0	2M	0
$t = t$	$2 - (x + y)$M	xM	$2 - (x + y)$M	yM

From question, $x + y = 1.5$ and $\dfrac{x}{y} = \dfrac{1}{2}$

$\therefore\ x = 0.5,\ y = 1.0$

Hence, total rotation $= 0.5 \times 60° + 0.5 \times (-72°)$
$+ 1.0 \times 42° = 36°$

19. $[B] : [C] : [D] = 1 \times 3K : 2 \times 2K : 3 \times K = 3 : 4 : 3$

	$A \longrightarrow$	B	$A \longrightarrow$	$2C$	$A \longrightarrow$	$3D$
$t = 0$	1M	0	1M	0	1M	0
$t = t$	$1 - (x + y + z)$	xM	$1 - (x + y + z)$	$2y$M	$1 - (x + y + z)$	$3z$M
$t = \infty$	$1 - (a + b + c)$	aM	$1 - (a + b + c)$	$2b$M	$1 - (a + b + c)$	$3c$M

As $a : 2b : 3c = 3 : 4 : 3$ and $a + b + c = 1$

$[C] = 2b = 0.67$ M

As $[A_0] = 1$ M, $[B] \neq 1$M

20. For $S_N 1$ path : $r_1 = (3 \times 10^{-4}\ \text{s}^{-1})\ [\text{RX}]$

For $S_N 2$ path : $r_2 = (5 \times 10^{-4}\ \text{M}^{-1}\ \text{s}^{-1})\ [\text{RX}][\bar{\bar{N}}u]$

(a) $[\bar{\bar{N}}u] = 0.1$ M, then $r_1 > r_2$

(b) $[\bar{\bar{N}}u] = 1.0$ M, then $r_1 < r_2$

(c) $[\bar{\bar{N}}u] = 0.6$ M, then $r_1 = r_2$

(d) $[\bar{\bar{N}}u] = 0.4$ M, then $\dfrac{r_1}{r_2} = \dfrac{2}{3}$

$\therefore$ Percentage product by $S_N 1 = \dfrac{2}{2+3} \times 100 = 40\%$

21. $-\dfrac{d[A]}{dt} = +\dfrac{d[B]}{dt}$ always

22. As mole is not changing, $C_A + C_B + C_C = C_{A_0}$

Now, $\dfrac{C_B}{C_{A_0} - C_A} = \dfrac{C_B}{C_B + C_C} = \dfrac{K_1}{K_1 + K_2}$

23. Informative

24. Theoretical

25. Increase in temperature will result in greater increase in the rate of reaction A → B than B → C.

26. Informative

27. Informative

28. $K_1 = K_2 \Rightarrow -\dfrac{14000}{RT} + 5 = -\dfrac{20000}{RT} + 10$

$\Rightarrow T = \dfrac{1200}{8.314} K$

Now, $\dfrac{P_{A_2}}{P_{B_3}} = \dfrac{1 \times e^{-K_1 t}}{1 \times e^{-K_2 t}} = \dfrac{1}{1}$

Now, initial pressure

$$P_0 = \frac{(1+1) \times 0.0821 \times \dfrac{1200}{8.314}}{100} = 0.237 \text{ atm}$$

As number of moles will increase on reaction, the total pressure can never be less than 0.2 atm

Now, $\dfrac{P_A}{P_B} = \dfrac{2K_1}{3K_2} = \dfrac{2}{3}$

29. $\dfrac{1}{K} \cdot \dfrac{dK}{dT} = \dfrac{d(\ln K)}{dT} = \dfrac{1.25 \times 10^6}{T^3} = \dfrac{E_a}{RT^2}$

$\therefore\ E_a = \dfrac{1.25 \times 10^6 R}{T} = \dfrac{1.25 \times 10^6 \times 2}{250} = 10^4$ cal/mol

30. $\Delta H = E_{a_f} - E_{a_b}$

$\Rightarrow -2 = E_{a_f} - 8$

$\Rightarrow E_{a_f} = 6$ kcal/mol

Now, the fraction of molecules crossing energy barrier $= e^{-E_a/RT}$

and $K_{\text{eq}} = e^{-\Delta H/Rt}$

Section C (Comprehensions)

Comprehension I

1. The overall reaction is first-order.

2. $\dfrac{K_1}{2} = \dfrac{K_2}{4} = \dfrac{K_3}{1} \Rightarrow 2K_1 = K_2 = 4K_3$

3. $$\begin{array}{cccc} 2N_2O_5 & \longrightarrow 4NO_2 & + & O_2 \\ 2 \times 108 \text{ gm} & 4 \times 46 \text{ gm} & & 32 \text{ gm} \\ 108 \text{ gm} & 92 \text{ gm} & & 16 \text{ gm} \end{array}$$

Comprehension II

4. $CO(g) + Cl_2(g) \longrightarrow COCl_2\,(g)$

$$r_{COCl_2} = +\frac{d[COCl_2]}{dt} = K_5 \cdot [COCl][Cl_2] \qquad (1)$$

Now, for steady state of COCl, $+\dfrac{d[COCl]}{dt} = 0$

or $K_3\,[Cl][CO] - K_4\,[COCl] - K_5\,[COCl][Cl_2] = 0$

$$\therefore\ [COCl] = \frac{K_3[Cl][CO]}{K_4 + K_5[Cl_2]} \qquad (2)$$

$\therefore$ For steady state of Cl, $\dfrac{d[Cl]}{dt} = 0$

or $2K_1[Cl_2] - 2K_2[Cl]^2 - K_3[Cl][CO] + K_4[COCl] + K_5[COCl][Cl_2] = 0$

$$\therefore\ [Cl] = \left(\frac{K_1[Cl_2]}{K_2}\right)^{1/2} \qquad (3)$$

From (1), (2), (3), $r_{COCl_2} = \dfrac{K_1^{1/2} K_5 K_3 [CO][Cl_2]^{3/2}}{K_2^{1/2}(K_4 + K_5[Cl_2])}$

5. $r_4 >> r_5$

or $K_4\,[COCl] >> K_5\,[COCl][Cl_2]$

or $K_4 >> K_5\,[Cl_2]$

$$\therefore\ r_{COCl_2} = \frac{K_1^{1/2} K_3 K_5 [CO][Cl_2]^{3/2}}{K_2^{1/2}(K_4 + K_5[Cl_2])} \approx \frac{K_1^{1/2} K_3 K_5 [CO][Cl_2]^{3/2}}{K_2^{1/2} K_4}$$

6. $A_{\text{overall}} = \dfrac{A_1^{1/2} \cdot A_3 \cdot A_5}{A_2^{1/2} \cdot A_4}$

7. $E_{a_{\text{overall}}} = \dfrac{1}{2} E_{a_1} + E_{a_3} + E_{a_5} - \dfrac{1}{2} E_{a_2} - E_{a_4}$

Comprehension III

For steady state of Br, $+\dfrac{d[Br]}{dt} = 0$

or, $2K_1[Br_2] - K_2[Br][H_2] + K_3[H][Br_2] + K_4[H][HBr] - 2K_5[Br]^2 = 0 \qquad (1)$

For steady state of H, $+\dfrac{d[H]}{dt} = 0$

or, $K_2[Br][H_2] - K_3[H][Br_2] - K_4[H][HBr] = 0 \qquad (2)$

8. From (1) and (2), $[Br] = \left(\dfrac{K_1[Br_2]}{K_5}\right)^{1/2}$

9. $$[H] = \frac{K_2[Br][H_2]}{K_3[Br_2] + K_4[HBr])} = \frac{K_2 \cdot K_1^{1/2} \cdot [Br_2]^{1/2} \cdot [H_2]}{K_5^{1/2}(K_3[Br_2] + K_4[HBr])}$$

10. $$+\frac{d[HBr]}{dt} = K_2[Br][H_2] + K_3[H][Br_2] - K_4[H][HBr]$$
$$= 2K_3[H][Br_2] = \frac{2K_3 K_2 K_1^{1/2} [Br_2]^{3/2} [H_2]}{K_5^{1/2}(K_3[Br_2] + K_4[HBr])}$$

11. At $t = 0$, $[HBr] = 0$ and hence, initial rate is given by,

$$r_0 = \frac{2K_2 K_1^{1/2} [Br_2]^{1/2} [H_2]}{K_5^{1/2}}$$

Comprehension IV

12. $$K = \frac{1}{t}\cdot\ln\frac{[H_2O_2]_0}{[H_2O_2]_t} = \frac{1}{t}\cdot\ln\frac{V_0}{V_t}$$

For $t = 10$ min, $K_1 = \frac{1}{10}\cdot\ln\frac{25.6}{16} = \frac{\ln 1.6}{10}\,\text{min}^{-1}$

For $t = 20$ min, $K_2 = \frac{1}{20}\cdot\ln\frac{25.6}{10} = \frac{\ln 1.6}{10}\,\text{min}^{-1}$

As $K_1 = K_2$, order of reaction = 1

13. $$t_{1/2} = \frac{\ln 2}{K} = \frac{\log 2}{\left(\frac{\log 1.6}{10}\right)} = 15\,\text{min}$$

14. $$Kt = \ln\frac{[H_2O_2]_0}{[H_2O_2]_t} = \ln\frac{a}{a-x} = \ln\frac{1}{1-\frac{x}{a}}$$

or, $\frac{\ln 1.6}{10}\times 25 = \ln\frac{1}{1-\frac{x}{a}}$

$\Rightarrow \frac{x}{a} = \frac{11}{16}$

15. Order = 1, but molecularity = 2 (as per reaction).

Comprehension V

	$C_8H_{18}O_2(g)$	$\rightarrow 2CH_3COCH_3(g)$	$+\ C_2H_6(g)$
$t = 0$	800 torr	0	0
$t = t$	$(800 - x)$ torr	$2x$ torr	x torr

16. $P_{C_8H_{18}O_2} = 800\text{ torr} \xrightarrow{t=3\times t_{1/2}} 100\text{ torr}$

$\therefore\ t = 3 \times 80 = 240$ min

17. $P_{\text{acetone}} = 2x = 1200 \Rightarrow x = 600$

$\therefore\ P_{C_8H_{18}O_2} = 800\text{ torr} \xrightarrow{t=2\times t_{1/2}} 200\text{ torr}$

$\therefore\ t = 2 \times 80 = 160$ min

18. $800 - x = 700 \Rightarrow x = 100$

$\therefore\ P_{\text{total}} = (800 - x) + 2x + x = 1000$ torr

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Comprehension VI

19. From (1) and (2) data : order w.r.t OH = 1

From (2) and (3) data : order w.r.t H_2S = 1

$\therefore\ r = K[H_2S][OH]$

20. $$K = \frac{r}{[H_2S][OH]} = \frac{1.4\times10^{-6}\text{ M s}^{-1}}{(2.1\times10^{-8}\text{ M})\times(1.3\times10^{-8}\text{ M})}$$

$= 5.1 \times 10^{9}\ \text{M}^{-1}\ \text{s}^{-1}$

21. $r = K[H_2S][OH] = 5.1 \times 10^{9} \times (1.0 \times 10^{-8}) \times (1.7 \times 10^{-8})$

$= 8.67 \times 10^{-7}\ \text{M s}^{-1}$

22. $r = 8.67 \times 10^{-7} \times 0.1 = 8.67 \times 10^{-8}\ \text{mol s}^{-1}$

Comprehension VII

23. $$K = \frac{1}{t}\cdot\ln\frac{P_x{}^{\circ}}{P_x}$$

For $t = 100$ min, $K_1 = \frac{1}{100}\cdot\ln\frac{800}{400} = \frac{\ln 2}{100}\,\text{min}^{-1}$

For $t = 200$ min, $K_2 = \frac{1}{200}\cdot\ln\frac{800}{200} = \frac{\ln 2}{100}\,\text{min}^{-1}$

As $K_1 = K_2$, order of reaction = 1

24. $K = \frac{\ln 2}{100} = 6.93\times10^{-3}\ \text{min}^{-1}$

$\therefore\ K_{rxn} = \frac{K}{2} = 3.465\times10^{-3}\ \text{min}^{-1}$

25. Time for 87.5% reaction $= 3\times t_{1/2} = 3\times\frac{\ln 2}{6.93\times10^{-3}}$

$= 300$ min

26.

	$2X(g) \longrightarrow$	$3Y(g)$	$+$	$2Z(g)$
$t = 0$	800	0		0
$t = t$	$800 - x$ $= 700$	$\frac{3}{2}x$		x

$\therefore\ P_{\text{total}} = 800 + \frac{3}{2}x = 950$ torr

Comprehension VIII

27.
$$\begin{array}{lcccc} & A & + \; 2B & \longrightarrow C & + \; D \\ t=0 & a\text{ M} & b\text{ M} & 0 & 0 \\ t=t & (a-x)\text{ M} & (b-2x)\text{ M} & & \end{array}$$

$$\text{Now, } r = K \cdot C_B \Rightarrow -\frac{d[\text{A}]}{dt} = K(b-2x)$$

$$\Rightarrow \frac{dx}{dt} = K(b-2x)$$

$$\text{or, } \int_0^x \frac{dx}{b-2x} = K \cdot \int_0^t dt \Rightarrow x = \frac{b}{2}(1-e^{-2Kt})$$

$$\therefore C_A = a - x = a - \frac{b}{2}(1-e^{-2Kt})$$

28. For $C_A = \frac{a}{2}$,

$$\frac{a}{2} = a - \frac{b}{2}(1-e^{-2Kt})$$

$$\therefore (t_{1/2})_A = \frac{1}{2K} \cdot \ln\frac{b}{b-a}$$

29. For $(t_{1/2})_A = (t_{1/2})_B, \frac{[A]}{[B]} = \frac{a}{b} = \frac{1}{2}$

Comprehension IX

30. $r_{rxn} = -\frac{1}{n_1} \cdot \frac{dn_A}{dt} = K \cdot n_A \Rightarrow n_A = n_A{}^{\circ} \cdot e^{-n,\,kt}$

31.
$$\begin{array}{lcc} & n_1A \longrightarrow & n_2A \\ t=0 & a\text{ mole} & 0 \\ t=t & (a-x)\text{mole} & \frac{n_2}{n_1} \cdot x\text{ mole} \\ & = a \cdot e^{-n,\,kt} & \end{array}$$

$$\therefore x = a(1-e^{-n,\,kt})$$

$$\text{Now, } \frac{V_2}{V_1} = \frac{n_{\text{final}}}{n_{\text{initial}}} = \frac{(a-x) + \frac{n_2}{n_1} \cdot x}{a}$$

$$\text{or, } \frac{V_2}{V_0} = \frac{a + x\left(\frac{n_2}{n_1} - 1\right)}{a} = 1 + \left(\frac{n_2}{n_1} - 1\right) \cdot (1 - e^{-n,\,kt})$$

$$\therefore V_2 = V_0\left[\frac{n_2}{n_1} + \left(1 - \frac{n_2}{n_1}\right)e^{-n,\,kt}\right]$$

32. If $n_1 = 1$, $n_2 = 2$, then $V_2 = V_0\,(2 - e^{-kt})$

$$\text{Now, } [A] = \frac{n_A}{V_2} = \frac{n_A{}^{\circ} \cdot e^{-kt}}{V_0 \cdot (2-e^{-kt})} = [A_0] \cdot \left(\frac{e^{-kt}}{2-e^{-kt}}\right)$$

Comprehension X

33. $\int_0^f \frac{df}{1-f} = K \cdot \int_0^t dt$

$$\Rightarrow t = -\frac{\ln(1-f)}{K}$$

$$\text{Now, } K = \frac{-(-3)}{200} = \frac{3}{200}\text{ hr}^{-1}$$

$$\therefore t_{1/2} = \frac{\ln 2}{K} = \frac{0.693}{\left(\frac{3}{200}\right)} = 46.2\text{ hr}$$

34. $t = -\frac{\ln(1-f)}{K} \Rightarrow f = 1 - e^{-Kt} = 1 - e^{-3t/200}$

Comprehension XI

35. Unit of $K = \text{s}^{-1} \Rightarrow$ order $= 1$

36. $K_B = \frac{10}{100} \times K = \frac{10}{100} \times 1.5 \times 10^{-4} = 1.5 \times 10^{-5}\text{ s}^{-1}$

Comprehension XII

37. $[A]=[A_0]\cdot e^{-K_1t}=(1.0\,\text{M})\times e^{-0.04\times 25}=0.368\text{ M}$

38. $[B]=\dfrac{K_1[A_0]}{K_2-K_1}(e^{-K_1t}-e^{-K_2t})$

$$=\frac{0.04\times(1.0\,\text{M})}{0.06-0.04}(e^{-0.04\times 25}-e^{-0.06\times 25})$$

$=0.29\text{ M}$

39. $[C]=[A_0]-[A]-[B]=1.0-0.368-0.29=0.342\text{ M}$

40. $t_{\max}=\dfrac{\ln\left(\dfrac{K_2}{K_1}\right)}{K_2-K_1}=\dfrac{\ln\left(\dfrac{3}{2}\right)}{0.06-0.04}=20\text{ min}$

41. $[B]_{\max}=[A_0]\left(\dfrac{K_2}{K_1}\right)^{\frac{-K_2}{K_2-K_1}}=(1.0\text{ M})\times\left(\dfrac{3}{2}\right)^{\frac{-0.06}{0.06-0.04}}$

$=0.3\text{ M}$

42. $[A]=[B]=[C]=\dfrac{[A_0]}{3}$

Now, $t=\dfrac{1}{K_1}\cdot\ln\dfrac{[A_0]}{[A]}=\dfrac{\ln 3}{K_1}=\dfrac{1.1}{0.04}=27.5\text{ min}$

43. $-\dfrac{d[A]}{dt}=+\dfrac{d[C]}{dt}\Rightarrow K_1\,[A]=K_2\,[B]\Rightarrow t=20\text{ min}$

$\therefore\ [A]=[A_0]\cdot e^{-K_1t}=(1.0\text{ M})\cdot \text{e}^{-0.04\times 20}=0.45\text{M}$

44. $(r_C)_{\max}=K_2\,[B]_{\max}=0.06\times 0.3=1.8\times 10^{-2}\text{ M/ min}$

Comprehension XIII

	A	$\rightleftharpoons$	B
$t=0$	0.15 M		0
$t=10$	$(0.15-x)$ M $=0.125$ M		x M $=0.025$ M
$t=t_{\text{eq}}$	$(0.15-x_{\text{eq}})$ M $=0.10$ M		x_{eq} M $=0.05$ M

Now, $K_{eq}=\dfrac{K_f}{K_b}=\dfrac{0.05}{0.10}=\dfrac{1}{2}$ (1)

and $t_{1/2}=\dfrac{\ln 2}{K_f+K_b}\Rightarrow 10\,\text{min}=\dfrac{0.693}{K_f+K_b}$ (2)

45. From (1) and (2), $K_f=2.31\times 10^{-2}\text{ min}^{-1}$

46. From (1), $K_b=4.62\times 10^{-2}\text{ min}^{-1}$

47. $K_{eq}=0.5$

48. $t_{1/2}=10\text{ min}$

Comprehension XIV

49. $E_{a(\text{overall})}=\dfrac{K_1\cdot E_{a_1}+K_2\cdot E_{a_1}}{K_1+K_2}$

or, $10.5=\dfrac{K_1\times 12+K_2\times 9}{K_1+K_2}\Rightarrow K_1=K_2$

or, $A_1\cdot e^{-E_{a_1}/RT}=A_2\cdot e^{-E_{a_2}/RT}$

or, $\dfrac{E_{a_1}-E_{a_2}}{RT}=\ln\dfrac{A_1}{A_2}$

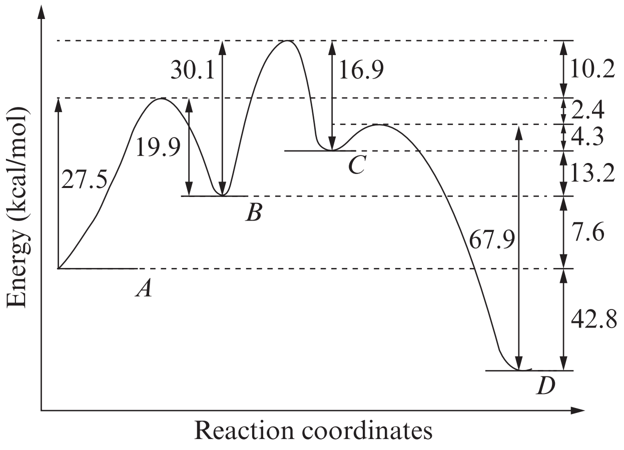
$\Rightarrow\dfrac{(12-9)\times 10^3}{2\times T}=\ln\dfrac{2\times 10^{14}}{2\times 10^{14}\times e^{-2}}$

$\therefore\ T=750\ K$

50. Above 750 K, Y will be the major product and below 750 K, Z will be the major product as $E_{a_1}>E_{a_2}$.

51. Reactions with higher E_a are more sensitive towards temperature change.

Comprehension XV



52. C → D [E_a : A $\xrightarrow{27.5}$ B $\xrightarrow{30.1}$ C $\xrightarrow{4.3}$ D]

53. C → B [E_a : D $\xrightarrow{67.9}$ C $\xrightarrow{16.9}$ B $\xrightarrow{19.9}$ A]

54. C → D [Lowest E_a]

55. B → C [Highest E_a]

56. D → C [Highest E_a]

Section D (Assertion – Reason)

1. Molecularity can never be fractional.
2. $t_{100\%} = \dfrac{[A_0]^{1-n}}{K(1-n)}$ when $n < 1$

   = Infinite when $n \geq 1$
3. For a particular step, rates always increase with increase in temperature.
4. Relative increase in rate constant with increase in temperature is higher for the reaction with higher activation energy.
5. $\Delta H = E_{a_f} - E_{a_b}$
6. Theoretical
7. For zero order reaction : $t_{1/2} = \dfrac{[A_0]}{2K}, t_{100\%} = \dfrac{[A_0]}{K}$
8. Order is in dependent from stoichiometry of reaction.
9. $t_{1/2} = \dfrac{[A_0]}{2K}$
10. Theoretical

Section E (Column Match)

1. Informative
2. Informative
3. Theoretical
4. Theoretical
5. Theoretical
6. Theoretical
7. Theoretical
8. Theoretical
9.

(P) $a \xrightarrow[= 18\text{ sec}]{t_{1/3}} \dfrac{2a}{3} \xrightarrow[= 18\text{ sec}]{t_{1/3}} \dfrac{4a}{9} \xrightarrow[= 18\text{ sec}]{t_{1/3}} \dfrac{8a}{27}$

$t_{19/27} = 54$ sec

(Q) $a \xrightarrow[= 16\text{ sec}]{t_{1/4}} \dfrac{3a}{4} \xrightarrow[= 16\text{ sec}]{t_{1/4}} \dfrac{9a}{16}$

$t_{7/16} = 32$ sec

(R) $K = \dfrac{1}{4}\left[\dfrac{1}{2a/3} - \dfrac{1}{a}\right] = \dfrac{1}{56}\left[\dfrac{1}{a-x} - \dfrac{1}{a}\right] \Rightarrow x = \dfrac{7}{8}a$

(S) $K = \dfrac{a-\dfrac{2a}{3}}{18} = \dfrac{x}{30} \Rightarrow x = \dfrac{5}{9}a$

(T) $K = \dfrac{a-\dfrac{a}{2}}{16} = \dfrac{x}{28} \Rightarrow x = \dfrac{7}{8}a$

10. (A) $\dfrac{d[C]}{dt} = K_2[B]$

For $\left(\dfrac{d[C]}{dt}\right)_{\max}$, $[B]$ should be maximum and hence

$$t = \frac{\ln\left(\dfrac{K_2}{K_1}\right)}{K_2 - K_1} = \frac{\ln 2}{K_1} \qquad \text{(when } K_2 = 2K_1\text{)}$$

Now, $(t_{1/2})_A = \dfrac{\ln 2}{K_1}$

(B) Rate of formation of B is maximum at $t = 0$, at which $[B] = [C] = 0$

Now, $[B] = [C]$

$$\frac{K_1[A_0]}{K_2 - K_1}(e^{-K_1 t} - e^{-K_2 t})$$

$$= [A_0]\left[1 - \frac{K_2 \cdot e^{-K_1 t} - K_1 \cdot e^{-K_2 t}}{K_2 - K_1}\right]$$

or, $e^{-K_1 t} - e^{-2K_1 t} = 1 - \dfrac{2K_1 \cdot e^{-K_1 t} - K_1 \cdot e^{-2K_1 t}}{K_1}$

(when $K_2 = 2K_1$)

or, $K_1 \cdot e^{-K_1 t} - K_1 \cdot e^{-2K_1 t}$

$= K_1 - 2K_1 \cdot e^{-K_1 t} - K_1 \cdot e^{-2K_1 t}$

$\therefore\ t = \dfrac{\ln 2}{K_1}$

(C) [A] = [B]

$$[A_0] \cdot e^{-K_1 t} = \frac{K_1[A_0]}{K_2 - K_1}(e^{-K_1 t} - e^{-K_2 t})$$

$$\frac{K_2 - K_1}{K_1} = 1 - e^{(K_1 - K_2)t}$$

$$\therefore\ t = \frac{1}{K_1 - K_2} \cdot \ln \frac{2K_1 - K_2}{K_1}$$

Section F (Subjective)

Single Digit Integer Type

1. ii, iv, v

2. Theoretical

3. $\dfrac{K_{\text{BrO}^-}}{3} = \dfrac{K_{\text{BrO}_3^-}}{1} = \dfrac{K_{\text{Br}^-}}{2}$

$\therefore\ K_{\text{BrO}_3^-} = a = \dfrac{0.06}{3} = 0.02\ \text{M}^{-1}\text{s}^{-1}$

and $K_{\text{Br}^-} = b = \dfrac{2}{3} \times 0.06 = 0.04\ \text{M}^{-1}\text{s}^{-1}$

4. $\dfrac{7.2 \times 10^{-15}}{3600}\ \text{M s}^{-1} = K \times (2 \times 10^{-8}\ \text{M})^2$

$K = \dfrac{1}{200}\ \text{M}^{-1}\ \text{s}^{-1} = 5\ \text{ml mol}^{-1}\ \text{s}^{-1}$

5. $-\dfrac{dP}{dt} = K \cdot P_{\text{NO}}^a \cdot P_{\text{H}_2}^b$

$\dfrac{1.5}{0.25} = \left(\dfrac{372}{152}\right)^a \Rightarrow a = 2$

and $\dfrac{1.60}{0.79} = \left(\dfrac{289}{144}\right)^b \Rightarrow b = 1$

6. $\dfrac{0.1}{0.4} = \dfrac{0.20}{x} \Rightarrow x = 0.8$

$\dfrac{0.1}{0.8} = \dfrac{0.2 \times 0.05}{0.4 \times y} \Rightarrow y = 0.2$

7. $t = \dfrac{1}{K} \cdot \ln \dfrac{[\text{Cr}^{3+}]_0}{[\text{Cr}^{3+}]}$

$= \dfrac{1}{9 \times 10^{-5}\ \text{s}^{-1}} \cdot \ln \dfrac{100}{100 - 80}$

$= 1.8 \times 10^4\ \text{sec} = 5\ \text{hrs}$

8. (i) Addition of NaOH will decrease $[\text{H}_3\text{O}^+]$.

(ii) Addition of water will decrease the concentration of both.

(iii) Acetic acid is a weak acid and hence, $[\text{H}_3\text{O}^+]$ will decrease.

(iv) Increase in temperature increases the reaction rate.

9. Time for certain progress of reaction, $t \,\alpha\, [A_0]^{1-n}$

$$\frac{1\times10^{-3}}{0.25\times10^{-3}} = \left(\frac{0.02}{0.04}\right)^{1-n} \Rightarrow n = 3$$

10.

$$\begin{array}{lcc} & C_4H_8 \longrightarrow & 2C_2H_4 \\ t=0 & a \text{ mole} & 0 \\ t=t & (a-x) \text{ mole} & 2x \text{ mole} \end{array}$$

As, $a - x = 2x \Rightarrow x = \dfrac{a}{3}$

Now,

$$t = \frac{t}{K}\cdot\ln\frac{a}{a-x} = \frac{1}{\frac{25}{18}\times10^{-5}\ \text{s}^{-1}}\times\ln\frac{a}{a-\frac{a}{3}} = 2\text{hrs}$$

11. For 2% reaction, we may assume that rate is almost constant.

$$r = K[A] \Rightarrow \frac{2}{100}\times[A]\ \text{min}^{-1} = K[A]$$
$$\Rightarrow K = 0.02\ \text{min}^{-1}$$

12. $H_2O_2\,(aq) \longrightarrow H_2O(l) + \frac{1}{2}\,O_2(g)$

$\Delta H = (-287) - (-187) = -100$ KJ/mol

Moles of H_2O_2 reacted per sec $= 7.5\times10^{-4}\times0.02\times2$
$= 3\times10^{-5}$

$\therefore$ Heat produced per sec $= 3\times10^{-5}\times(100\times10^3)$
$= 3$ J

13.

$$t = \frac{1}{K}\cdot\ln\frac{a}{a-x} = \frac{1}{\left(\frac{4.5}{3.1536}\times10^{-8}\ \text{s}^{-1}\right)}\cdot\ln\frac{100}{40}$$

$$= \frac{0.9\times3.1536\times10^8}{4.5\times3.1536\times10^7}\text{Year} = 2 \text{ Years}$$

14. $t_{1/2} = \dfrac{0.693}{6.93\times10^{-4}} = 1000$ sec

$$\begin{array}{lcc} & A \longrightarrow & nB \\ t=0 & a \text{ mole} & 0 \\ t=1000 \text{ sec} & \frac{a}{2} \text{ mole} & \frac{n\cdot a}{2} \text{ mole} \end{array}$$

Now, $\dfrac{\frac{a}{2}+\frac{n\cdot a}{2}}{a} = 3 \Rightarrow n = 5$

15. $r = K[\text{ester}][H^+]^x = k_1[\text{ester}]$

$K_1 = K\cdot[H^+]^x$

$$\frac{1.0}{10} = \left(\frac{10^{-3}}{10^{-2}}\right)^x \Rightarrow x = 1$$

and $K_1 = \dfrac{K_1}{[H^+]} = \dfrac{1.0\times10^{-3}}{10^{-3}} = 1 = y$

16. $t_{3/4} = 2\times t_{1/2}$ and hence, $a = 1$.

Now, $t_{1/2} = \dfrac{\ln 2}{K} = \dfrac{\ln 2}{K[H^+]^b}$

$$\frac{1.0}{0.5} = \left(\frac{0.02}{0.01}\right)^b \Rightarrow b = 1$$

17. Concentrations are in G.P. and hence, order = 1.

18.

$$\begin{array}{lcccc} & A_2B_3(aq) \longrightarrow & 2A^{3+}\,(aq) & + & 3\,B^{2-}\,(aq) \\ t=0 & a \text{ mole} & 0 & & 0 \\ t=10\text{ min} & a-x & 2x & & 3x \end{array}$$

Now, $\pi = CRT = \rho gh \Rightarrow$ total mole $\alpha\, h$

$$\therefore\ \frac{a}{a+4x} = \frac{2}{6} \Rightarrow t = 10 \text{ min} = t_{1/2}$$

Now, at $t = t_{3/4} = 2\times t_{1/2} = 20$ min, $x = \dfrac{3a}{4}$

$$\therefore\ \frac{a}{a+\left(4\times\frac{3a}{4}\right)} = \frac{2}{h} \Rightarrow h = 8 \text{ mm}$$

$$\pi = x = \rho gh = \left(1.0\frac{\text{gm}}{\text{cm}^3}\right)\times\left(1000\frac{\text{cm}}{\text{s}^2}\right)\times(0.8\text{ cm})$$

$$= 800\frac{\text{dyne}}{\text{cm}^2} = 80 \text{ pascal}$$

Now, $\dfrac{x}{y} = \dfrac{80}{20} = 4$

19. $[A]^4 = \dfrac{1}{t+1} \Rightarrow 4[A]^3\cdot\dfrac{d[A]}{dt} = -\dfrac{1}{(t+1)^2} = -[A]^8$

$$\therefore\ -\frac{d[A]}{dt} = \frac{[A]^5}{4} = \frac{(0.2)^5}{4} = 8\times10^{-5}\ \text{M s}^{-1}$$

20.

$$\begin{array}{lcc} & A \longrightarrow & 2B \\ t=0 & a \text{ mole} & 0 \\ t=t & (a-x) \text{ mole} & 2x \text{ mole} \end{array}$$

From mass conservation, $a\times M_0 = (a+x)\times M_t$

$$\therefore\ x = \frac{a(M_0 - M_t)}{M_t}$$

If the reaction is zero order, then

$$K = \frac{a-(a-x)}{t} = \frac{x}{t} = \frac{a(M_0 - M_t)}{t\cdot M_t}$$

For $t = 10$ min, $K = \dfrac{a(42-35)}{10\times 35} = \dfrac{a}{50}$

For $t = 20$ min, $K = \dfrac{a(42-30)}{20\times 30} = \dfrac{a}{50}$

As K values are same, the reaction is of zero-order.

21. $r = K[A]^n$ and $2r = K(4[A])^n \Rightarrow n = \dfrac{1}{2}$

$\therefore\ t_{1/2}\ \alpha\, [A_0]^{1-n} = [A_0]^{1/2}$

Next $t_{1/2}$ will be $\dfrac{1}{\sqrt{2}}$ times of previous one and hence, $t = \dfrac{8\sqrt{2}}{\sqrt{2}} = 8$ hr.

22. $$P_B = \frac{K_B\cdot P_A{}^{\circ}}{K_A+K_B+K_C}\cdot[1-e^{-(K_A+K_B+K_C)\cdot t}]$$

$$= \frac{2\times10^{-3}\times13.86}{6.93\times10^{-3}}[1-e^{-6.93\times10^{-3}\times100}] = 2\text{ atm}$$

23. $$\frac{K_{\text{I}}}{K_{\text{II}}} = \frac{A_{\text{I}}\cdot e^{-E_{a_{\text{I}}}/RT}}{A_{\text{II}}\cdot e^{-E_{a_{\text{II}}}/RT}} = \frac{A_{\text{I}}}{A_{\text{II}}}\cdot e^{-(E_{a_{\text{I}}}-E_{a_{\text{II}}})/RT}$$

$$= = 100\times e^{-4.606\times10^{3}/2\times500} = 1$$

24. Fraction of molecules having sufficient energy

$$= e^{-E_a/RT} = e^{-83.14\times10^{3}/8.314\times500} = 2\times10^{-9}$$

25. $$\ln\frac{K_2}{K_1} = \ln\frac{t_1}{t_2} = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

or, $$\ln\frac{1}{3} = \frac{E_a}{R}\left(\frac{1}{300}-\frac{1}{280}\right) \quad (1)$$

and $$\ln\frac{16}{t} = \frac{E_a}{R}\left(\frac{1}{300}-\frac{1}{330}\right) \quad (2)$$

From (1) and (2), $t = 4$ hrs

Four Digit Integer Type

1. $r = K[\text{O}_3]^2 = 5\times10^{-4}\times(2\times10^{-8})^2$
$= 2\times10^{-19}$ mol l^{-1} s^{-1}
$= 2\times10^{-19}\times6\times10^{23}\times10^{-3}\times60$
$= 7200$ molecules ml^{-1} min^{-1}

2. At $t = \infty$, P_{total} should be 400 mm, but as it is only 390 mm, some unreactive gas should also be present in the vessel. Let $P^{\circ}_{\text{C}_2\text{H}_5\text{Br}} = P_0$ mm then $P_{\text{unreactive}}$ gas $= (200 - P_0)$ mm.

$$\begin{array}{llll} & \text{C}_2\text{H}_5\text{Br(g)} \longrightarrow & \text{C}_2\text{H}_4\text{(g)} + & \text{HBr(g)} \\ t=0 & P_0 & 0 & 0 \\ t=t & P_0-x & x & x \\ t=\infty & 0 & P_0 & P_0 \end{array}$$

From question, $P_0 + P_0 + (200 - P_0) = 390$
$\Rightarrow P_0 = 190$

and $(P_0 - x) + x + x + (200 - P_0) = 342.5$
$\Rightarrow x = 142.5$

$\therefore$ Percentage C_2H_5 Br undecomposed

$$= \frac{P_0-x}{P_0} = 25\%$$

3. $t = \dfrac{t_{\text{gen}}}{\log 2}\cdot\log\dfrac{[A]}{[A_0]} \Rightarrow 96 = \dfrac{t_{\text{gen}}}{0.30}\cdot\log 3$

$\Rightarrow t_{\text{gen}} = 60$ hrs

4. $r = -\dfrac{dP_{\text{NO}}}{dt} = K'\cdot P_{\text{NO}}^2\cdot P_{\text{O}_2}$ and

$$K' = \frac{1.6\times10^5}{(0.08\times600)^2}\text{atm}^{-2}\text{s}^{-1}$$

$$\therefore\ r = \frac{1.6\times10^5}{48\times48}\times\left(\frac{190}{760}\right)^2\times\left(\frac{288}{760}\right)$$

$$= \frac{1250}{760}\text{atm s}^{-1} = 1250\text{ mm s}^{-1}$$

5. From the unit of rate constant, the process is zero order.

$$\therefore\ t_{100\%} = \frac{[\text{H}^+]_0}{K}$$

$$= \frac{\left(\dfrac{3\times10^{-7}}{0.05}\times1000\right)}{1.0\times10^{-7}} = 6\times10^4\text{ sec} = 1000\text{ min}$$

6. $K = \dfrac{1}{t}\ln\dfrac{[A_0]}{[A]} = \text{Constant}$

$$\therefore\ \frac{1}{100}\cdot\ln\frac{[A_0]}{[A_0]/3} = \frac{1}{t}\cdot\ln\frac{[A_0]}{[A_0]/9} \Rightarrow t = 200\text{ min}$$

7. $K = \dfrac{1}{t}\cdot\ln\dfrac{[A_0]}{[A]} = \text{Constant}$

$$\therefore \frac{1}{20}\cdot\ln\frac{500}{420}=\frac{1}{t}\cdot\ln\frac{100}{70}\ \Rightarrow t=40\text{ min}$$

8. $K=\frac{1}{t}\cdot\ln\frac{V_\infty}{V_\infty-V_t}=\text{Constant}$

$$\therefore \frac{1}{40}\cdot\ln\frac{80}{80-40}=\frac{1}{t}\cdot\ln\frac{80}{80-70}\ \Rightarrow t=120\text{ min}$$

9.

$$\begin{array}{lcccc}
 & 2\text{P} \longrightarrow & 4\text{Q} & +\ \text{R} + \text{S(l)} & \\
t=0 & P_0 & 0 & 0 & \\
t=30\text{ min} & P_0-x & 2x & \frac{x}{2} & \text{V.P.}=25 \\
t=60\text{ min} & P_0-y & 2y & \frac{y}{2} & \text{V.P.}=25 \\
t=\infty & 0 & 2P_0 & \frac{P_0}{2} & \text{V.P.}=25
\end{array}$$

From question, $2P_0+\frac{P_0}{2}+25=625 \Rightarrow P_0=240$

and $(P_0-x)+2x+\frac{x}{2}+25=445 \Rightarrow x=120$

Now, $\frac{1}{30}\cdot\ln\frac{P_0}{P_0-x}=\frac{1}{60}\cdot\ln\frac{P_0}{P_0-y}\ \Rightarrow y=180$

$\therefore\ P_{60}=(P_0-y)+2y+\frac{y}{2}+25=535\text{ mm}$

10. Initial moles of $NH_4NO_2=\frac{200\times0.02}{1000}=0.004$

and moles of N_2O formed

$$=\frac{\frac{(785-25)}{760}\times\frac{49.26}{1000}}{0.0821\times300}=0.002$$

$\therefore\ t_{\text{req}}=t_{1/2}=123$ min

11. For set 1 and 2, $r=K'[B]$ as $[A_0]>>[B_0]$

and $t_{1/2}=\frac{\ln2}{K'}=\frac{\ln2}{K[A_0]^2}\ \Rightarrow x=62.5$

For set 3 and 4, $r=K''[A]^2$ as $[B_0]>>[A_0]$

and $t_{1/2}=\frac{1}{K''[A_0]}=\frac{1}{K[B_0][A_0]}$

$\Rightarrow\ y=\frac{625}{2}=312.5$

$\therefore\ x+y=62.5+312.5=375$

12. $t=43.5\text{ min}=3t_{1/2}$

Hence, $P_{\text{ether}}=\frac{4}{2^3}=0.5\text{ atm}\ \Rightarrow \Delta P_{\text{ether}}=3.5\text{ atm}$

$\therefore\ P_{\text{final}}=0.5+3.5\times3=11\text{ atm}$

13. $\Delta t=\frac{t_{1/2}}{\ln2}\cdot\ln\frac{r_1}{r_2}\ \Rightarrow 12=\frac{t_{1/2}}{\ln2}\cdot\ln\left(\frac{0.04}{0.03}\right)$

$\therefore\ t_{1/2}=28\text{ min}=1680\text{ sec}$

14. $t=\frac{t_{1/2}}{\ln2}\cdot\ln\frac{V_\infty-V_0}{V_\infty-V_t}\Rightarrow 120=\frac{t_{1/2}}{\ln2}\cdot\ln\frac{60-20}{60-55}$

$\therefore\ t_{1/2}=40\text{ min}$ $\qquad ab=40$

Now, $\frac{[\text{HCl}]}{[\text{ester}]}=\frac{V_0}{V_\infty-V_0}\ \Rightarrow \frac{[\text{HCl}]}{6.0}=\frac{20}{60-20}$

$\Rightarrow[\text{HCl}]=3.0\text{ M}$

$\therefore\ cd=03$

15. $t_{1/2}=\frac{0.693}{1.386\times10^{-3}}=500\text{ sec}$

Let the initial moles of $A=x$, then after 500 sec,

$$\begin{array}{ccc}
\text{A} \longrightarrow & 2\text{B} & +\ \text{C} \\
x-\frac{x}{2} & 2\times\frac{x}{2} & \frac{x}{2} \\
=\frac{x}{2} & =x & =\frac{x}{2}
\end{array}$$

Total moles becomes $\left(\frac{x}{2}+x+\frac{x}{2}\right)=2x$. As moles becomes double, volume becomes double and hence,

$$[A]_{\text{req}}=\frac{0.1}{2\times2}=0.025\text{ M}=25\text{ millimole per litre}$$

16.

$$\begin{array}{lccc}
 & \text{A} \longrightarrow & 2\text{B} & +\ \text{C} \\
t=0 & 4a & 0 & 3a \\
t=t & 4a-x & 2x & 3a+x
\end{array}$$

From question $(4a-x)(40^\circ)+2x(10^\circ)+(3a+x)(-30^\circ)=0^\circ$

$\therefore\ x=\frac{7}{5}a$

Now, $t=\frac{1}{K}\cdot\ln\frac{4a}{4a-\frac{7}{5}a}=\frac{1}{0.001}\cdot\ln\frac{20}{13}=500\text{ min}$

17. Exp (1): $r = K'[B]^y$ as $[A_0] >> [B_0]$

$$\because t_{7/8} = 3\times t_{1/2} \Rightarrow y = 1$$

Exp (2): $r = K''[A]^x$ as $[A_0] << [B_0]$

$$\because t_{7/8} = 7\times t_{1/2} \Rightarrow x = 2$$

Now, for exp (2) and (3), $t_{1/2} = \dfrac{1}{K''[A_0]} = \dfrac{1}{K[B_0][A_0]}$

$\therefore\ a = \dfrac{10}{2\times 2} = 2.5$ and $b = 7\times 2.5 = 17.5$

And for exp (1) and (4), $t_{1/2} = \dfrac{\ln 2}{K'} = \dfrac{\ln 2}{K[A_0]}$

$\therefore\ c = 30\times 2 = 60$ and $d = 3\times 60 = 180$

18. Percentage yield

$$= \frac{K_2}{K_1+K_2}\times 100 = \frac{4.8}{3.2+4.8}\times 100 = 60\%$$

19.

$$\begin{array}{lcccccccc}
 & \text{A} & + & 2\text{B} & + & 3\text{C} & \rightleftharpoons & \text{D} \\
t = 0 & 1.0\text{ M} & & 1.0\text{ M} & & 1.0\text{ M} & & 0 \\
t = t & 1-x & & 1-2x & & 1-3x & & x \\
 & = 0.9 & & = 0.8 & & = 0.7 & & = 0.1 \\
 & & & & & \text{(given)} & &
\end{array}$$

$$\therefore\ r = 2\times 10^{-6}\times(0.9)^2 - \frac{1.4\times 10^{-6}\times(0.1)^2}{0.8\times 0.7}$$

$$= 1.595\times 10^{-6}$$

20. $[C] = 0.875 + 0.6 = 1.475$ M

21. $K_{eq} = \dfrac{K_f}{K_b} = \dfrac{[B]}{[A]} \Rightarrow \dfrac{1.38/300}{K_b} = \dfrac{0.1}{0.2}$

$$\Rightarrow K_b = \frac{1.38}{150}\ \text{min}^{-1}$$

Now, $t = \dfrac{1}{K_f + K_b}\cdot\ln\dfrac{x_{e,B}}{x_{e,B} - x_B}$

$$= \frac{1}{\frac{1.38}{300}+\frac{2.76}{300}}\cdot\ln\frac{0.1}{0.1-0.3\times\frac{25}{100}}$$

$$= \frac{300}{6\times\ln 2}\cdot\ln 4 = 100\text{ min}$$

22. For completion in 30 min, the rate should be increased by $\dfrac{4\times 60}{30} = 8$ times. Assuming temperature coefficient constant, the approximate temperature is $25 + \left(10\times\dfrac{8}{2}\right) = 55°\text{C}$.

23. $K_1 = K_2 \Rightarrow A_1\cdot e^{-E_{a_1}/RT} = A_2\cdot e^{-E_{a_2}/RT}$

$$\therefore\ \ln\frac{A_2}{A_1} = \frac{E_{a_2} - E_{a_1}}{RT}$$

$$\ln\frac{10^{14}}{10^{13}} = \frac{(171.39 - 152.30)\times 10^3}{8.3\times T}$$

or, $T = 1000\ K = 727°$ C

24. $t_{1/2} = \dfrac{\ln 2}{K} = \dfrac{\ln 2}{A\cdot e^{-E_a/RT}}$

$$\text{or, } 1\times 60 = \frac{0.7}{5\times 10^{13}\times e^{-149.4\times 10^3/8.3\times T}}$$

$\therefore\ T = 500$ K

25. $K_{\text{cat}} = K_{\text{uncat}}$

or, $A\cdot e^{-E_{a_{\text{cat}}}/RT_1} = A\cdot e^{-E_{a_{\text{uncat}}}/RT_2}$

or, $\dfrac{E_{a_{\text{cat}}}}{T_1} = \dfrac{E_{a_{\text{uncat}}}}{T_2} \Rightarrow \dfrac{E_{a_{\text{uncat}}} - 20}{400} = \dfrac{E_{a_{\text{uncat}}}}{500}$

$\therefore\ E_{a_{\text{uncat}}} = 100$ kJ/mol