Chemical Kinetics

## 3.1 Rate of a Chemical Reaction

SA I (2 marks)

1. In the given reaction, $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$ the rate of formation of NH_3 is 3.6×10^{-4} mol L^{-1} s^{-1}.
   Calculate the
   (i) rate of reaction and
   (ii) rate of disappearance of $H_{2(g)}$.
   (Term-II, 2021-22) [Ap]

2. The following reaction was carried out in water :
   $Br_2 + 2I^- \longrightarrow 2Br^- + I_2$
   The initial concentration of I^- was 0.30 M and the concentration after 10 minutes reduced to 0.28 M. Calculate the ratio of disappearance of I^- and production of I_2. (2021 C)

3. In the given reaction, $A + 3B \rightarrow 2C$, the rate of formation of C is 2.5×10^{-4} mol $L^{-1} s^{-1}$.
   Calculate the
   (i) rate of reaction, and
   (ii) rate of disappearance of B. (2020) [U]

4. For the reaction, $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$, the rate of formation of $NO_{2(g)}$ is 2.8×10^{-3} M s^{-1}. Calculate the rate of disappearance of $N_2O_{5(g)}$. (2018)

3.2 Factors Influencing Rate of a Reaction

MCQ

5. The following experimental rate data were obtained for a reaction carried out at 25°C:
   $$A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$$
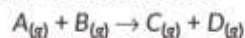
Initial $[A_{(g)}]$ / mol dm^{-3}	Initial $[B_{(g)}]$/ mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
3.0×10^{-2}	2.0×10^{-2}	1.89×10^{-4}
3.0×10^{-2}	4.0×10^{-2}	1.89×10^{-4}
6.0×10^{-2}	4.0×10^{-2}	7.56×10^{-4}

What are the orders with respect to $A_{(g)}$ and $B_{(g)}$?

	Order with respect to $A_{(g)}$	Order with respect to $B_{(g)}$
(a)	Zero	Second
(b)	First	Zero
(c)	Second	Zero
(d)	Second	First

(2023)

6. **Assertion (A)** : The molecularity of the reaction $H_2 + Br_2 \longrightarrow 2HBr$ appears to be 2.
   Reason (R) : Two molecules of the reactants are involved in the given elementary reaction.
   (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
   (b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
   (c) Assertion (A) is true, but Reason (R) is false.
   (d) Assertion (A) is false, but Reason (R) is true.
   (2023)

7. **Assertion** : Order of reaction is applicable to elementary as well as complex reactions.
   Reason : For a complex reaction molecularity has no meaning.
   (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A)
   (b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A)
   (c) Assertion (A) is true, but Reason (R) is false.
   (d) Assertion (A) is false, but Reason (R) is true.
   (2023)

8. **Assertion (A)** : The molecularity of the reaction $H_2 + Br_2 \rightarrow 2HBr$ appears to be 2.
   Reason (R) : Two molecules of the reactants are involved in the given elementary reaction.
   (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
   (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
   (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
   (d) Assertion (A) is incorrect, but Reason (R) is correct statement. (2020)

VSA (1 mark)

9. Calculate the overall order of the reaction whose rate law expression was predicted as :
   Rate = $k[NO]^{3/2} [O_2]^{1/2}$. (2020) [U]

10. Define the rate constant.
    (1/5, Foreign 2015, Delhi 2015C)

11. Define the specific rate of reaction. (AI 2014C) [R]

12. Define rate of reaction. Write two factors that affect the rate of reaction. (Term-II, 2021-22, AI 2015)

13. Write two differences between 'order of reaction' and 'molecularity of reaction'.
(Term-II, 2021-22C, Delhi 2014)

14. For a reaction

$$2H_2O_2 \xrightarrow[\text{Alkaline medium}]{I^-} 2H_2O + O_2$$

the proposed mechanism is as given below :

(1) $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ (slow)

(2) $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ (fast)

(i) Write rate law for the reaction.

(ii) Write the overall order of reaction.

(iii) Out of steps (1) and (2), which one is rate determining step? (Delhi 2019) Ap

15. For a reaction : $2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$;
Rate = k

(i) Write the order and molecularity of this reaction.

(ii) Write the unit of k. (Delhi 2016)

16. For a reaction : $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$; Rate = k

(i) Write the order and molecularity of this reaction

(ii) Write the unit of k. (AI 2016)

17. For a reaction $A + B \rightarrow P$, the rate is given by
Rate = $k[A][B]^2$

(i) How is the rate of reaction affected if the concentration of B is doubled?

(ii) What is the overall order of reaction if A is present in large excess? (2/5, Delhi 2015)

18. Write units of rate constants for zero order and for the second order reactions if the concentration is expressed in mol L^{-1} and time in second. (AI 2015C)

19. (i) For a reaction, $A + B \rightarrow$ Product, the rate law is given by, Rate = $k[A]^1[B]^2$. What is the order of the reaction?

(ii) Write the unit of rate constant 'k' for the first order reaction. (Delhi 2014C) U

20. A reaction is of second order with respect to its reactant. How will its reaction rate be affected if the concentration of the reactant is (i) doubled (ii) reduced to half ? (AI 2014C)

21. Following data were obtained for the given reaction : $X + Y \longrightarrow$ Product

Exp.	[X]/M	[Y]/M	Initial Rate M min^{-1}
1	0.1 M	0.2 M	0.05
2	0.2 M	0.2 M	0.10
3	0.1 M	0.1 M	0.05

(i) Find the order of reaction with respect to X and Y.

(ii) Write the rate law expression.

(iii) Find the rate constant. (2021C) Ev

22. How will the rate of the reaction be affected when

(a) surface area of the reactant is reduced,

(b) catalyst is added in a reversible reaction, and

(c) temperature of the reaction is increased?
(2020)

23. The following data were obtained for the reaction :
$A + 2B \longrightarrow C$

Experiment	[A]/M	[B]/M	Initial rate of formation of C/M min^{-1}
1	0.2	0.3	4.2×10^{-2}
2	0.1	0.1	6.0×10^{-3}
3	0.4	0.3	1.68×10^{-1}
4	0.1	0.4	2.40×10^{-2}

(a) Find the order of reaction with respect to A and B.

(b) Write the rate law and overall order of reaction.

(c) Calculate the rate constant (k). (2019) An

24. A reaction is second order in A and first order in B.

(i) Write the differential rate equation.

(ii) How is the rate affected on increasing the concentration of A three times?

(iii) How is the rate affected when the concentration of both A and B are doubled? (2018 C)

3.3 Integrated Rate Equations

25. The order of the reaction
$$H_{2(g)} + Cl_{2(g)} \xrightarrow{h\nu} 2HCl_{(g)} \text{ is}$$
(a) 2 (b) 1 (c) 0 (d) 3
(2023)

26. The half-life period for a zero order reaction is equal to

(a) $\dfrac{0.693}{k}$ (b) $\dfrac{2k}{[R]_0}$ (c) $\dfrac{2.303}{k}$ (d) $\dfrac{[R]_0}{2k}$

(where $[R]_0$ is initial concentration of reactant and k is rate constant.) (2020) An

27. Assertion (A) : Hydrolysis of an ester follows first order kinetics.

Reason (R) : Concentration of water remains nearly constant during the course of the reaction.

(a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

VSA (1 mark)

28. For a reaction $R \rightarrow P$, half-life $(t_{1/2})$ is observed to be independent of the initial concentration of reactants. What is the order of reaction?
(Term-II, 2021-22, Delhi 2017)

29. Write the slope value obtained in the plot of $\ln[R]$ vs. time for a first order reaction. *(One word, 2020)*

30. Write the slope value obtained in the plot of $\log [R_o]/[R]$ vs. time for a first order reaction.
(2020) An

31. Define the following term :

Pseudo first order reaction
(NCERT Exemplar, 1/2, Delhi 2014)

SA I (2 marks)

32. Answer the following questions (Do any two) :
    (a) Identify the order of reaction from the following unit for its rate constant : $L\ mol^{-1}\ s^{-1}$
    (b) The conversion of molecules A to B follow second order kinetics. If concentration of A is increased to three times, how will it affect the rate of formation of B?
    (c) Write the expression of integrated rate equation for zero order reaction.
(Term II, 2021-22) U

33. Analyse the given graph, drawn between concentration of reactant vs. time.
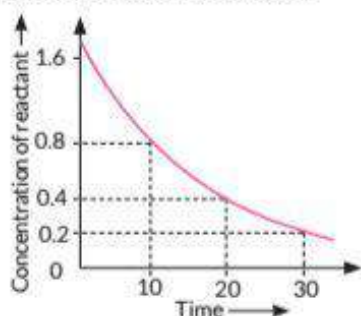
(a) Predict the order of reaction.
(b) Theoretically, can the concentration of the reactant reduce to zero after infinite time. Explain. *(2020)* Ev

34. Define rate constant and give the mathematical relation between rate constant and half-life period for a first order reaction. *(2020C)* R

35. Define order of reaction. Predict the order of reaction in the given graphs :

(a) $t_{1/2}$ (b) $t_{1/2}$
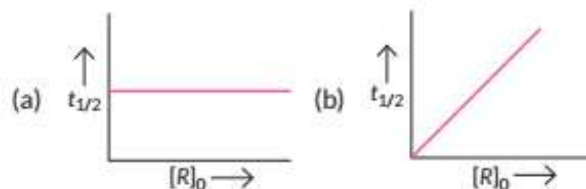
where $[R]_0$ is the initial concentration of reactant and $t_{1/2}$ is half-life. *(2019)* Ev

36. For a reaction, $C_2H_{4(g)} + H_{2(g)} \longrightarrow C_2H_{6(g)}$,

rate $= 5.5 \times 10^{-14} [C_2H_4]$.
    (a) Write the unit of rate constant.
    (b) Calculate its half-life $(t_{1/2})$. *(2019 C)*

37. For a chemical reaction $R \rightarrow P$, the variation in the concentration $[R]$ vs. time (t) plot is given as

    (i) Predict the order of the reaction.
    (ii) What is the slope of the curve?
(2/5, AI 2019, AI 2014)
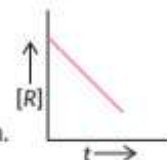
38. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.
(NCERT, AI 2017C)

39. Define half-life of a reaction. Write the expression of half-life for
    (i) zero order reaction and
    (ii) first order reaction. *(Foreign 2014)*

SA II (3 marks)

40. (a) For the reaction
    $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$ at 318 K
    Calculate the rate of reaction if rate of disappearance of $N_2O_{5(g)}$ is $1.4 \times 10^{-3}\ M\ s^{-1}$.
    (b) For a first order reaction derive the relationship $t_{99\%} = 2t_{90\%}$ *(2023)*

41. A first order reduction takes 30 minutes for 75% decomposition. Calculate $t_{1/2}$.
Given : $[\log 2 = 0.3, \log 3 = 0.48, \log 4 = 0.6, \log 5 = 0.7]$
(Term-II, 2021-22) Ap

42. Observe the graph shown in figure and answer the following questions :
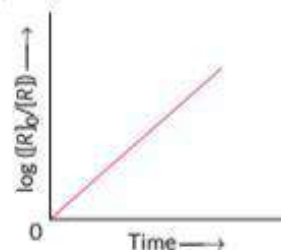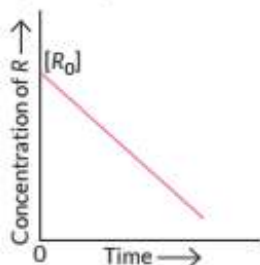

    (a) What is the order of the reaction?
    (b) What is the slope of the curve?
    (c) Write the relationship between k and $t_{1/2}$ (half life period). *(Term II, 2021-22)* Ap

43. A first order reaction is 50% complete in 40 minutes. Calculate the time required for the completion of 90% of reaction.
[Given : log 2 = 0.3010, log 10 = 1]
(Term-II, 2021-22)

44. The variation in the concentration (R) vs. time (t) plot is given below. Answer the following questions on the basis of the given figure :

(i) Predict the order of the reaction.
(ii) What is the slope of the curve?
(iii) What are the units of the rate constant k?
(Term-II, 2021-22C) (Ev)

45. A first order reaction has a rate constant 4.9×10^{-3} s^{-1}. How long will 4 g of this reactant take to reduce to 3 g ? [log 4 = 0.6020, log 3 = 0.4771]
(2020C)

46. A first order reaction is 40% complete in 80 minutes. Calculate the value of rate constant (k). In what time will the reaction be 90% completed?
[Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021, log 5 = 0.6771, log 6 = 0.7782]
(2020)

47. The decomposition of NH_3 on platinum surface is zero order reaction. If rate constant (k) is 4×10^{-3} M s^{-1}, how long will it take to reduce the initial concentration of NH_3 from 0.1 M to 0.064 M?
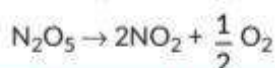(Delhi 2019)

48. A first order reaction takes 30 minutes for 20% decomposition. Calculate $t_{1/2}$.
[log 2 = 0.3010]
(3/5, AI 2019)

49. Following data are obtained for the reaction :
$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2} O_2$$

t/s	0	300	600
[N$_2$O$_5$]/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(a) Show that it follows first order reaction.
(b) Calculate the half-life.
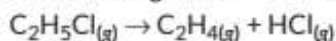(Given : log 2 = 0.3010, log 4 = 0.6021)
(Delhi 2017) (An)

50. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed.
(Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021)
(AI 2017) (An)

51. For the first order thermal decomposition reaction, the following data were obtained :
$$C_2H_5Cl_{(g)} \rightarrow C_2H_{4(g)} + HCl_{(g)}$$

Time/sec	Total pressure/atm
0	0.30
300	0.50

Calculate the rate constant.
(Given : log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)
(AI 2016)

52. A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction. (log 2 = 0.3010)
(3/5, Delhi 2015) (An)

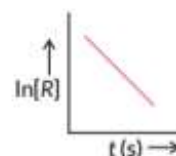53. A first order reaction takes 10 minutes for 25% decomposition. Calculate $t_{1/2}$ for the reaction.
(Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021)
(3/5, Foreign 2015)

54. For a chemical reaction $R \longrightarrow P$, the variation in the concentration, ln [R] vs. time (s) plot is given as
(i) Predict the order of the reaction.
(ii) What is the slope of the curve?
(iii) Write the unit of the rate constant for this reaction.
(3/5, Foreign 2015)

55. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its $1/10^{th}$ value?
(AI 2015C)

56. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume :
$$SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$$
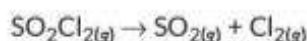
Experiment	Time/s	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.
(Given : log 4 = 0.6021, log 2 = 0.3010)
(Delhi, AI, Foreign 2014) (Ev)

57. Hydrogen peroxide, $H_2O_{2(aq)}$ decomposes to $H_2O_{(l)}$ and $O_{2(g)}$ in a reaction that is first order in H_2O_2 and has a rate constant $k = 1.06 \times 10^{-3}$ min^{-1}.
(i) How long will it take for 15% of a sample of H_2O_2 to decompose?
(ii) How long will it take for 85% of the sample to decompose?
(Delhi 2014C) (Ev)

The following questions are case based questions. Read the case carefully and answer the questions that follow.

58. The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. Mathematical representation of rate of reaction is given by rate law. Rate constant and order of a reaction can be determined from rate law or its integrated rate equation.

(i) What is average rate of reaction?

(ii) Write two factors that affect the rate of reaction.

(iii) (1) What happens to rate of reaction for zero order reaction?

(2) What is the unit of k for zero order reaction?

OR

(iii) (1) For a reaction $P + 2Q \longrightarrow$ Products Rate $= k[P]^{1/2}[Q]^1$. What is the order of the reaction?

(2) Define pseudo first order reaction with an example. *(2023)*

59. Read the passage given below and answer the questions that follow :

The rate law for a chemical reaction relates the reaction rate with the concentrations or partial pressures of the reactants. For a general reaction, $aA + bB \rightarrow C$, with no intermediate steps in its reaction mechanism, meaning that it is an elementary reaction, the rate law is given by $r = k[A]^x[B]^y$, where $[A]$ and $[B]$ express the concentrations of A and B in moles per litre. Exponents x and y vary for each reaction and are determined experimentally. The value of k varies with conditions that affect reaction rate, such as temperature, pressure, surface area, etc. The sum of these exponents is known as overall reaction order. A zero order reactions has constant rate that is independent of the concentration of the reactions. A first order reaction depends on the concentration of only one reactant. A reaction is said to be second order when the overall order is two. Once we have determined the order of the reaction, we can go back and plug in one set of our initial values and solve for k.

(i) Calculate the overall order of a reaction which has the following rate expression : Rate $= k[A]^{1/2}[B]^{3/2}$

(ii) What is the effect of temperature on rate of reaction?

(iii) What is meant by rate of a reaction?

(iv) (a) A first order reaction takes 77.78 minutes for 50% completion. Calculate the time required for 30% completion of this reaction. (log 10 = 1, log 7 = 0.8450)

OR

(b) A first order reaction has a rate constant 1×10^{-3} per sec. How long will 5 g of this reactant take to reduce to 3 g? (log 3 = 0.4771 ; log 5 = 0.6990) *(Term II, 2021-22)* [Ev]

60. Read the following passage and answer the questions that follow :

The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. A number of factors such as temperature, concentration of reactants, catalyst affect the rate of reaction. Mathematical representation of rate of a reaction is given by rate law :

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

x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of $x + y$ gives the overall order of a reaction.

When a sequence of elementary reactions gives us the products, the reactions are called complex reactions. Molecularity and order of an elementary reaction are same. Zero order reaction are relatively uncommon but they occur under special conditions. All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

(a) What is the effect of temperature on the rate constant of a reaction?

(b) For a reaction $A + B \rightarrow$ Product, the rate law is given by, Rate $= k[A]^2[B]^{1/2}$. What is the order of the reaction?

(c) How order and molecularity are different for complex reactions?

(d) A first order reaction has a rate constant 2×10^{-3} s^{-1}. How long will 6 g of this reactant take to reduce to 2 g?

OR

The half life for radioactive decay of ^{14}C is 6930 years. An archaeological artifact containing wood had only 75% of the ^{14}C found in a living tree. Find the age of the sample.

[log 4 = 0.6021; log 3 = 0.4771; log 2 = 0.3010; log 10 = 1] *(Term II, 2021-22)* [Cr]

61. (a) A first order reaction is 25% complete in 40 minutes. Calculate the value of rate constant. In what time will the reaction be 80% completed ?

(b) Define order of reaction. Write the condition under which a bimolecular reaction follows first order kinetics. *(2020)* [U]

62. (a) Visha plotted a graph between concentration of R and time for a reaction $R \rightarrow P$. On the basis of this graph, answer the following questions :
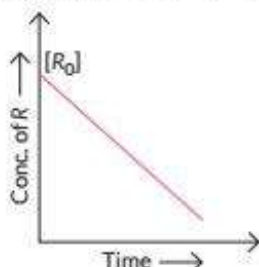
(i) Predict the order of reaction.
(ii) What does the slope of the line indicate?
(iii) What are the units of rate constant?

(b) A first order reaction takes 25 minutes for 25% decomposition. Calculate $t_{1/2}$.
[Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021] *(2020)*

63. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained :

t/s	0	30	60
$[CH_3COOCH_3]$/mol L^{-1}	0.60	0.30	0.15

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.
(ii) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
(Given : log 2 = 0.3010, log 4 = 0.6021) *(Delhi 2015)*

3.4 Temperature Dependence of the Rate of a Reaction

MCQ

64. Which of the following is affected by catalyst?
(a) ΔH (b) ΔG (c) E_a (d) ΔS *(2023)*

65. A biochemical reaction was carried out in the absence of enzyme and the rate of reaction was found to be 10^{-6} min^{-1}. If the same reaction is now carried out in the presence of enzyme, then the E_a for the reaction will be
(a) same
(b) greater than 10^{-6} min^{-1}
(c) lower than 10^{-6} min^{-1}
(d) data insufficient, E_a cannot be predicted. *(2020C) U*

VSA (1 mark)

66. Will the rate constant of the reaction depend upon T if the E_{act} (activation energy) of the reaction is zero? *(One word, 2020)*

67. What is the effect of adding a catalyst on
(a) activation energy (E_a), and
(b) Gibbs energy (ΔG) of a reaction? *(AI 2017) Ap*

68. Define the following :
Energy of activation of reaction. *(1/5, Foreign 2015, AI 2014C)*

SA I (2 marks)

69. What happens to the rate constant k and activation energy E_a as the temperature of a chemical reaction is increased? Justify. *(2023)*

70. Draw the plot of ln k vs $1/T$ for a chemical reaction. What does the intercept represent? What is the relation between slope and E_a? *(2/5, AI 2019)*

71. How does a change in temperature affect the rate of a reaction? How can this effect on the rate constant of reaction be represented quantitatively? *(AI 2014C)*

SA II (3 marks)

72. The rate constant for the first order decomposition of N_2O_5 is given by the following equation :
$$k = (2.5 \times 10^{14} \text{ s}^{-1}) e^{(-25000 \text{ K})/T}$$
Calculate E_a for this reaction and rate constant if its half-life period be 300 minutes. *(2020) Ap*

73. The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of activation (E_a) of the reaction assuming that it does not change with temperature.
[R = 8.314 J K^{-1} mol^{-1}, log 4 = 0.6021] *(NCERT, 3/5, AI 2019)*

74. The rate constant of a first order reaction increases from 2×10^{-2} to 6×10^{-2} when the temperature changes from 300 K to 320 K. Calculate the energy of activation.
(Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021) *(2019 C)*

75. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction. (Given : log 2 = 0.3010, log 4 = 0.6021, R = 8.314 J K^{-1} mol^{-1}) *(2018)*

76. The rate constant for the first order decomposition of H_2O_2 is given by the following equation :
$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} K$$
Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes.
(Given : R = 8.314 J K^{-1} mol^{-1}) *(Delhi 2016) An*

77. The rate constant of a first order reaction increases from 2×10^{-2} to 4×10^{-2} when the temperature changes from 300 K to 310 K. Calculate the energy of activation (E_a). (log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)   (Delhi 2015)

78. The rate constants of reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} respectively. Calculate the value of activation energy, E_a ($R = 8.314$ J K^{-1} mol^{-1}).   (Delhi 2015C)

79. For a decomposition reaction, the values of k at two different temperatures are given below:
$k_1 = 2.15 \times 10^{-8}$ L/(mol.s) at 650 K
$k_2 = 2.39 \times 10^{-8}$ L/(mol.s) at 700 K

Calculate the value of E_a for the reaction.
($R = 8.314$ J K^{-1} mol^{-1})   (AI 2014C)

3.5 Collision Theory of Chemical Reactions

80. (a) The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its $\frac{1}{16}$ th value?
    (b) Write two factors that affect the rate of a chemical reaction.
    (c) Write two conditions for the collisions to be effective collisions.   (2020)

CBSE Sample Questions

3.2 Factors Influencing Rate of a Reaction

MCQ

1. For the reaction, $A + 2B \rightarrow AB_2$, the order w.r.t. reactant A is 2 and w.r.t. reactant B is zero. What will be change in rate of reaction if the concentration of A is doubled and B is halved?
    (a) Increases four times
    (b) Decreases four times
    (c) Increases two times
    (d) No change   (2022-23)

SA I (2 marks)

2. Explain how and why will the rate of reaction for a given reaction be affected when
    (a) a catalyst is added
    (b) the temperature at which the reaction was taking place is decreased?   (2022-23)

3. For a reaction the rate law expression is represented as follows :
    Rate = $k [A][B]^{1/2}$
    (i) Interpret whether the reaction is elementary or complex. Give reason to support your answer.
    (ii) Write the units of rate constant for this reaction if concentration of A and B is expressed in moles/L.   (2020-21) [Ap]

4. The following results have been obtained during the kinetic studies of the reaction :
    $P + 2Q \rightarrow R + 2S$

Exp.	Initial P (mol/L)	Initial Q (mol/L)	Initial Rate of Formation of R (M min^{-1})
1.	0.10	0.10	3.0×10^{-4}
2.	0.30	0.30	9.0×10^{-4}
3.	0.10	0.30	3.0×10^{-4}
4.	0.20	0.40	6.0×10^{-4}

Determine the rate law expression for the reaction.   (2020-21) [Ev]

3.3 Integrated Rate Equations

MCQ

5. Which radioactive isotope would have the longer half-life ^{15}O or ^{19}O? (Given rate constants for ^{15}O and ^{19}O are 5.63×10^{-3} s^{-1} and $k = 2.38 \times 10^{-2}$ s^{-1} respectively.)
    (a) ^{15}O
    (b) ^{19}O
    (c) Both will have the same half-life
    (d) None of the above, information given is insufficient   (2022-23)

SA I (2 marks)

6. A first-order reaction takes 69.3 min for 50% completion. What is the time needed for 80% of the reaction to get completed?
    (Given : log 5 = 0.6990, log 8 = 0.9030, log 2 = 0.3010)   (2022-23)

7. The C-14 content of an ancient piece of wood was found to have three tenths of that in living trees.

How old is that piece of wood? ($\log 3 = 0.4771$, $\log 7 = 0.8540$, Half-life of C-14 = 5730 years)

(2020-21)

LA (5 marks)

8. Read the passage given below and answer the questions that follow.

Are these nuclear reactions going on in our bodies?

There are nuclear reactions constantly occurring in our bodies, but there are very few of them compared to the chemical reactions, and they do not affect our bodies much. All of the physical processes that take place to keep a human body running are chemical processes. Nuclear reactions can lead to chemical damage, which the body may notice and try to fix.

The nuclear reaction occurring in our bodies is radioactive decay. This is the change of a less stable nucleus to a more stable nucleus. Every atom has either a stable nucleus or an unstable nucleus, depending on how big it is and on the ratio of protons to neutrons. The ratio of neutrons to protons in a stable nucleus is thus around 1:1 for small nuclei ($Z < 20$). Nuclei with too many neutrons, too few neutrons, or that are simply too big are unstable. They eventually transform to a stable form through radioactive decay. Wherever there are atoms with unstable nuclei (radioactive atoms), there are nuclear reactions occurring naturally. The interesting thing is that there are small amounts of radioactive atoms everywhere: in your chair, in the ground, in the food you eat, and yes, in your body.

The most common natural radioactive isotopes in humans are carbon-14 and potassium-40. Chemically, these isotopes behave exactly like stable carbon and potassium. For this reason, the body uses carbon-14 and potassium-40 just like it does normal carbon and potassium; building them into the different parts of the cells, without knowing that they are radioactive. In time, carbon-14 atoms decay to stable nitrogen atoms and potassium-40 atoms decay to stable calcium atoms. Chemicals in the body that relied on having a carbon-14 atom or potassium-40 atom in a certain spot will suddenly have a nitrogen or calcium atom. Such a change damages the chemical. Normally, such changes are so rare, that the body can repair the damage or filter away the damaged chemicals.

The natural occurrence of carbon-14 decay in the body is the core principle behind carbon dating. As long as a person is alive and still eating, every carbon-14 atom that decays into a nitrogen atom is replaced on average with a new carbon-14 atom. But once a person dies, he stops replacing the decaying carbon-14 atoms. Slowly the carbon-14 atoms decay to nitrogen without being replaced, so that there is less and less carbon-14 in a dead body. The rate at which carbon-14 decays is constant and follows first order kinetics. It has a half - life of nearly 6000 years, so by measuring the relative amount of carbon-14 in a bone, archeologists can calculate when the person died. All living organisms consume carbon, so carbon dating can be used to date any living organism, and any object made from a living organism. Bones, wood, leather, and even paper can be accurately dated, as long as they first existed within the last 60,000 years. This is all because of the fact that nuclear reactions naturally occur in living organisms.

(*Source: The textbook Chemistry: The Practical Science by Paul B. Kelter, Michael D. Mosher and Andrew Scott states*)

(a) Why is carbon -14 radioactive while carbon-12 not? (Atomic number of carbon: 6)

(b) Researchers have uncovered the youngest known dinosaur bone, dating around 65 million years ago. How was the age of this fossil estimated?

(c) Which are the two most common radioactive decays happening in human body?

(d) Suppose an organism has 20 g of carbon-14 at its time of death. Approximately how much carbon-14 remains after 10,320 years? (Given antilog 0.517 = 3.289)
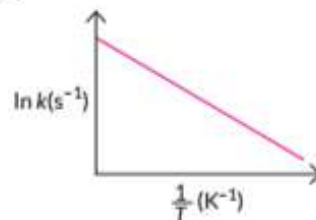
OR

Approximately how old is a fossil with 12 g of carbon-14 if it initially possessed 32 g of carbon-14? (Given log 2.667 = 0.4260)

(Term II, 2021-22)

3.4 Temperature Dependence of the Rate of a Reaction

MCQ

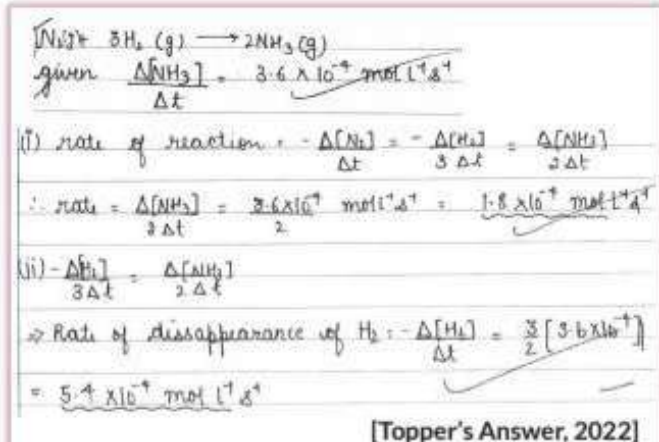9. Arrhenius equation can be represented graphically as follows :

The (i) intercept and (ii) slope of the graph are

(a) (i) $\ln A$ (ii) E_a/R
(b) (i) A (ii) E_a
(c) (i) $\ln A$ (ii) $-E_a/R$
(d) (i) A (ii) $-E_a$

(2022-23)

Detailed SOLUTIONS

1.

$N_2 + 3H_2 (g) \longrightarrow 2NH_3 (g)$

given $\dfrac{\Delta[NH_3]}{\Delta t} = 3.6 \times 10^{-4}$ mol L^{-1}s^{-1}

(i) rate of reaction $= -\dfrac{\Delta[N_2]}{\Delta t} = -\dfrac{\Delta[H_2]}{3\Delta t} = \dfrac{\Delta[NH_3]}{2\Delta t}$

$\therefore$ rate $= \dfrac{\Delta[NH_3]}{2\Delta t} = \dfrac{3.6\times 10^{-4}}{2}$ mol L^{-1}s^{-1} = 1.8×10^{-4} mol L^{-1}s^{-1}

(ii) $-\dfrac{\Delta[H_2]}{3\Delta t} = \dfrac{\Delta[NH_3]}{2\Delta t}$

$\Rightarrow$ Rate of disappearance of $H_2 = -\dfrac{\Delta[H_2]}{\Delta t} = \dfrac{3}{2}[3.6\times 10^{-4}]$

$= 5.4 \times 10^{-4}$ mol L^{-1}s^{-1}

[Topper's Answer, 2022]

2. $Br_2 + 2I^- \longrightarrow 2Br^- + I_2$

According to rate law expression

$-\dfrac{d[Br_2]}{dt} = -\dfrac{1}{2}\dfrac{d[I^-]}{dt} = +\dfrac{1}{2}\dfrac{d[Br^-]}{dt} = +\dfrac{d[I_2]}{dt}$

$-\dfrac{d[I_2]}{dt} = \dfrac{0.30 - 0.28}{10} = 0.002$ M min^{-1}

Now, $-\dfrac{1}{2}\dfrac{d[I^-]}{dt} = +\dfrac{d[I_2]}{dt}$

or $\dfrac{d[I_2]}{dt} = \dfrac{1}{2} \times 0.002$ M min^{-1} = 0.001 M min^{-1}

Ratio of disappearance of I^- and production of I_2 = $\dfrac{0.002}{0.001} = \dfrac{2}{1}$ i.e., 2 : 1.

3. Given, $\dfrac{d[C]}{dt} = 2.5 \times 10^{-4}$ mol L^{-1}s^{-1}

According to rate law expression,

$-\dfrac{d[A]}{dt} = -\dfrac{1}{3}\dfrac{d[B]}{dt} = \dfrac{1}{2}\dfrac{d[C]}{dt}$

(i) Rate of reaction = $\dfrac{1}{2}\dfrac{d[C]}{dt}$

$= \dfrac{1}{2} \times 2.5 \times 10^{-4}$ mol L^{-1}s^{-1} = 1.25×10^{-4} mol L^{-1}s^{-1}

(ii) Rate of disappearance of B = $-\dfrac{d[B]}{dt} = \dfrac{3}{2}\dfrac{d[C]}{dt}$

$= \dfrac{3}{2} \times 2.5 \times 10^{-4}$ mol L^{-1}s^{-1} = 3.75×10^{-4} mol L^{-1}s^{-1}

Concept Applied 🎯

⮕ For expressing the rate of a reaction where stoichiometric coefficients of reactants and products are not equal to one, the rate of disappearance or appearance is divided by the respective stoichiometric coefficients.

4. Given, $\dfrac{d[NO_2]}{dt} = 2.8 \times 10^{-3}$ Ms^{-1}

According to rate law expression,

$-\dfrac{1}{2}\dfrac{d[N_2O_5]}{dt} = \dfrac{1}{4}\dfrac{d[NO_2]}{dt} = \dfrac{d[O_2]}{dt}$

$\therefore -\dfrac{d[N_2O_5]}{dt} = \dfrac{2}{4} \times 2.8 \times 10^{-3}$

$\dfrac{-d[N_2O_5]}{dt} = \dfrac{1}{2} \times 2.8 \times 10^{-3} = 1.4 \times 10^{-3}$ Ms^{-1}

5. (c) : Rate = $k[A]^x[B]^y$

From exp (1), $1.89 \times 10^{-4} = k(3.0 \times 10^{-2})^x (2.0 \times 10^{-2})^y$ ...(i)

From exp (2), 1.89×10^{-4}
$= k (3.0 \times 10^{-2})^x (4.0 \times 10^{-2})^y$...(ii)

Dividing (ii) by (i), we get $1 = (2)^y$

$\therefore \boxed{y = 0}$

From exp (3),
$7.56 \times 10^{-4} = k(6.0 \times 10^{-2})^x (4.0 \times 10^{-2})^y$ ...(iii)

Dividing (iii) by (ii), we get

$\dfrac{7.56 \times 10^{-4}}{1.89 \times 10^{-4}} = \dfrac{(6.0 \times 10^{-2})^x}{(3.0 \times 10^{-2})^x}$

$4 = (2)^x$

$(2)^2 = (2)^x$

$\boxed{x = 2}$

Rate = $k[A]^2[B]^0$

6. (a) : The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called the molecularity of a reaction. Thus, for the reaction, $H_2 + Br_2 \longrightarrow 2HBr$, the molecularity will be 2 as two molecules of reactants are involved in elementary reaction.

7. (b) : Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction, molecularity has no meaning.

8. (a) : Molecularity is two because two molecules of the reactants are involved in the given elementary reaction.

9. Given, rate = $k[NO]^{3/2}[O_2]^{1/2}$

$\therefore$ Overall order = $\dfrac{3}{2} + \dfrac{1}{2} = \dfrac{4}{2} = 2$

10. Rate constant is the proportionality factor in the rate law expression for a chemical reaction. It is defined as the rate of a chemical reaction for which the concentration of each of the reacting species is unity.

11. At a given temperature, rate is equal to the rate constant of reaction when concentration of the reactant

in unity. Thus rate constant is also known as specific reaction rate.

In the case of two reactants, the reaction may be written as:

$$A + B \rightarrow \text{Products}$$

$$r = \frac{dx}{dt} = k\, C_A C_B$$

where all the terms have their usual meaning.

If $C_A = C_B = 1$ then $r = k$.

12. Change in concentration (*i.e.*, either decrease in concentration of reactant or increase in concentration of product) per unit time is called rate of reaction.

Following factors affect the rate of a chemical reaction:

(i) Concentration of reactants : Higher the concentration of reactants, faster would be the rate of reaction.

Rate $= k\, C^n$, where $C =$ concentration of reactant.

(ii) Temperature : The rate of reaction increases with the temperature. For every 10°C rise in temperature rate of reaction increases 2 to 3 times.

13. Differences between order and molecularity of a reaction are the following :

Order of a reaction	Molecularity of a reaction
1. It is the sum of powers of the concentration of the reactants in the rate law expression.	It is the number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.
2. It can be zero or even a fraction.	It is always a whole number.

Key Points 💡

⮞ Generally, in a complex reaction the order of reaction is equal to the molecularity of the slowest step.

14. (i) Rate $= k[H_2O_2][I^-]$

(ii) Overall order of reaction is 2.

(iii) Step (1) being the slow step is the rate determining step of the reaction.

Concept Applied 🎯

⮞ Slowest step of the mechanism is always the rate determining step.

15. (i) The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.

In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration.

However, two molecules of ammonia react to give products thus, the molecularity is two.

(ii) For a zero order reaction, unit of rate constant is $\text{mol L}^{-1} \text{s}^{-1}$.

16. (i) Experimentally, it is found that the rate of reaction is independent of the concentration of H_2 and Cl_2. Hence, it is a zero order reaction.

Molecularity $= 2$

(ii) Unit of $k = \text{mole litre}^{-1} \text{sec}^{-1}$

Concept Applied 🎯

⮞ Rate $= k[\text{conc}]^n$

$k = \dfrac{\text{Rate}}{[\text{Conc}]^n} \Rightarrow$ unit of $k = \dfrac{\text{Mol L}^{-1} \text{s}^{-1}}{[\text{Mol L}^{-1}]^n}$

Where $n =$ order of reaction.

17. (i) From the rate law equation, order of reaction w.r.t. B is 2. Hence, if concentration of B is doubled, rate will become four times.

(ii) If A is present in large excess, rate of reaction will be independent of concentration of A and hence, order of reaction will be 2.

18. Unit of rate constant (k), for zero order reaction.

Rate $= k[A]^0 \Rightarrow k = \text{mol L}^{-1} \text{s}^{-1}$

Unit of rate constant (k), for second order reaction

Rate $= k[A]^2 \Rightarrow k = \text{L mol}^{-1} \text{s}^{-1}$

19. (i) Order of reaction is sum of powers of concentration terms,

∴ Order of reaction $= 1 + 2 = 3$

(ii) Unit of rate constant for first order reaction is s^{-1}.

20. Let the concentration of the reactant $[A] = a$

Order of reaction $= 2$

So rate of reaction $= k[A]^2 = ka^2$ ...(1)

(i) Given that concentration of the reactant is doubled

So, $[A] = 2a$,

Putting the value in equation (i) we get

New rate of reaction, $R_1 = k(2a)^2 = 4ka^2$

Hence, rate of reaction will increase to 4 times.

(ii) Given that concentration of the reactant is reduced to half

So, $[A] = (1/2)a$

Putting the value in equation (1), we get

New rate of reaction $R_2 = k((1/2)a)^2 = (1/4)ka^2$

Hence, rate of reaction will reduce to 1/4.

21. Let the rate law expression is $r = k[X]^a[Y]^b$

Given, $r_1 = k(0.1)^a (0.2)^b = 0.05$ ...(i)

$r_2 = k(0.2)^a (0.2)^a = 0.10$ ...(ii)

$r_3 = k(0.1)^a (0.1)^b = 0.05$ ...(iii)

From eqn. (i) and (ii), $\dfrac{r_2}{r_1} = \dfrac{0.10}{0.05} = 2^a \Rightarrow a = 1$

From eqn. (ii) and (iii), $\dfrac{r_1}{r_3} = \dfrac{0.05}{0.05} = 2^b \Rightarrow b = 0$

(i) Order w.r.t. X is one and w.r.t. Y is zero.

(ii) The rate law expression is $r = k[X]^1[Y]^0 = k[X]$

(iii) From the rate law, $k = \dfrac{\text{Rate}}{[X]} = \dfrac{0.05}{0.1} = 5 \times 10^{-3}\ min^{-1}$

22. (a) For a reaction involving a solid reactant or catalyst, the smaller is the particle size *i.e.*, greater is the surface area, the faster is the reaction. Therefore, on reducing the surface area, rate of reaction is reduced.

(b) A catalyst generally increases the speed of a reaction without itself being consumed in the reaction. For a reversible reaction catalyst increases the speed of reaction in both forward and reverse reaction, which helps in attaining the equilibrium faster.

(c) The rate of reaction increases with increase in temperature. In most of the cases, the rate of reaction becomes nearly double for every 10°C rise of temperature. In some cases, reactions do not take place at room temperature but takes place at higher temperature.

23. (a) Let rate $= k[A]^x[B]^y$

$4.2 \times 10^{-2} = k(0.2)^x(0.3)^y$ ...(i)
$6.0 \times 10^{-3} = k(0.1)^x(0.1)^y$ ...(ii)
$1.68 \times 10^{-1} = k(0.4)^x(0.3)^y$ ...(iii)
$2.40 \times 10^{-2} = k(0.1)^x(0.4)^y$ ...(iv)

Dividing eqn. (iii) by (i),

$\dfrac{1.68 \times 10^{-1}}{4.2 \times 10^{-2}} = \dfrac{(0.4)^x}{(0.2)^x}$

or $4 = 2^x \Rightarrow x = 2$

Dividing eqn. (iv) by (ii),

$\dfrac{2.40 \times 10^y}{6.0 \times 10^y} = \dfrac{(0.4)^y}{(0.1)^y}$ or $4 = 4^y \Rightarrow y = 1$

Hence, order of the reaction w.r.t. A is 2 and w.r.t. B is 1.

(b) Rate $= k[A]^2[B]^1$
Overall order of reaction $= 2 + 1 = 3$

(c) From experiment 1,
$4.2 \times 10^{-2} = k(0.2)^2(0.3)$
or $4.2 \times 10^{-2} = k \times 0.012$
or $k = 3.5$

24. Since the reaction is second order w.r.t. A and first order w.r.t. B.

(i) Differential rate equation is
Rate $= k[A]^2[B]$

(ii) The new concentration of A $= [3A]$
∴ New rate $= k[3A]^2[B] = 9k[A]^2[B]$
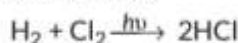∴ New rate $= 9$ times of the original rate

(iii) New concentration of A $= [2A]$
New concentration of B $= [2B]$
∴ New rate $= k[2A]^2[2B] = 8k[A]^2[B]$
∴ New rate $= 8$ times of the original rate.

25. (c): Photochemical combination of hydrogen and chlorine to give hydrogen chloride is called zero order reaction because rate of reaction is independent of concentration of the reactants.

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

26. (d): For zero order reaction rate constant is given by:

$k = \dfrac{[R]_0 - [R]}{t}$, At $t = t_{1/2}$, $[R] = \dfrac{[R]_0}{2}$

$k = \dfrac{[R]_0 - \dfrac{[R]_0}{2}}{t_{1/2}} \Rightarrow k = \dfrac{[R]_0}{2t_{1/2}} \Rightarrow t_{1/2} = \dfrac{[R]_0}{2k}$

In zero order reaction, $t_{1/2}$ is directly proportional to $[R]_0$.

27. (a): Hydrolysis of an ester is a pseudo first order reaction.

28. Half-life of first order reaction is independent of the initial concentration of reactants.

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

29. Slope $= -k$

Answer Tips 🖊

⮕ The straight line graph is represented by the equation $y = mx + c$, where m represents the slope of the graph.
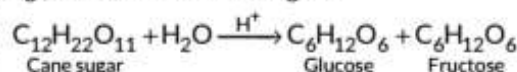
30. For first order reaction

$k = \dfrac{2.303}{t} \log \dfrac{[R_0]}{[R]}$

$\log \dfrac{[R_0]}{[R]} = \dfrac{kt}{2.303}$

Plotting $\log [R_0]/[R]$ vs t will give a straight line with slope $\dfrac{k}{2.303}$.

31. Those reactions which are not truly of the first order but under certain conditions become reactions of the first order are called *pseudo first order reactions*.
e.g., inversion of cane sugar :

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Rate $= k[C_{12}H_{22}O_{11}]^1[H_2O]^0$

32. (a) Unit of rate constant $(k) = (mol\ L^{-1})^{1-n}\ s^{-1}$
or $(bar)^{1-n}\ s^{-1}$
For, $n = 2$, $k = mol^{-1}\ L\ s^{-1}$. Thus, this reaction is a second order reaction.

(b) For the reaction, $A \longrightarrow B$
Rate $= R = k[A]^2$ (As reaction is of second order.)
$R' = k[3A]^2 \Rightarrow R' = 9k[A]^2$
$\dfrac{R'}{R} = 9$

So, rate of reaction becomes 9 times by increasing concentration of A to three times.

(c) Integrated rate equation for zero order reaction is :
$[A]_t = -kt + [A]_0$

33. (a) The reaction is of first order.

(b) The rate of first order reactions and the concentration of the reactant vary exponentially with time. Hence, theoretically it will take infinite time for the reaction to go to completion (though after a finite period, the concentration becomes nearly zero).

34. Rate constant is the proportionality factor in the rate law expression for a chemical reaction. It is defined as the rate of a chemical reaction for which the concentration of each of the reacting species is unity.

Half-life of first order reaction is independent of the initial concentration of reactants.

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

35. The sum of the exponents (powers) to which the molar concentrations in the rate law equation are raised to express the observed rate of the reaction is called the order of reaction.

(a) For first order reaction, $t_{1/2} = k[R_0]^0 = k$

Thus, $t_{1/2}$ is independent of initial concentration. Hence, plot of $t_{1/2}$ vs. $[R_0]$ will be a horizontal line.

(b) For zero order reaction, $t_{1/2} = k[R_0]$

Hence, plot of $t_{1/2}$ vs. $[R_0]$ will be linear passing through the origin and having slope = k.

Key Points 💡

➲ $t_{1/2} \propto \dfrac{1}{[R_0]^{(n-1)}}$

where, n = order of reaction

36. (a) Given, rate = $5.5 \times 10^{-14} [C_2H_4]$

This implies that it is a first order reaction as rate depends on $[C_2H_4]$ only.

Hence, unit of rate constant is s^{-1} or $time^{-1}$.

(b) For a first order reaction, $t_{1/2} = \dfrac{0.693}{k}$

or $t_{1/2} = \dfrac{0.693}{5.5 \times 10^{-14}} = 1.26 \times 10^{13}$ sec

37. (i) The reaction is of zero order.
   (ii) Slope of the curve = $-k$

Concept Applied 🎯

➲ For zero order reaction,
   $[R]_t = -kt + [R]_0$

38. For first order reaction, $t = \dfrac{2.303}{k} \log \dfrac{[R_0]}{[R_t]}$

For 99% completion of reaction
$t = t_{0.99}, [R]_0 = 1, [R]_t = (1 - 0.99) = 0.01 = 10^{-2}$

$t_{0.99} = \dfrac{2.303}{k} \log \dfrac{1}{10^{-2}} = \dfrac{2.303}{k} \log 10^2 = \dfrac{2.303}{k} \times 2$ ...(i)

For 90% completion of reaction
$t = t_{0.90}, [R]_0 = 1, [R]_t = (1-0.9) = 0.1 = 10^{-1}$

$t_{0.90} = \dfrac{2.303}{k} \log \dfrac{1}{10^{-1}} = \dfrac{2.303}{k} \log 10 = \dfrac{2.303}{k}$ ...(ii)

Comparing equations (i) and (ii), $t_{0.99} = 2 \times t_{0.90}$

39. The time taken for half of the reaction to complete, i.e., the time in which the concentration of a reactant is reduced to half of its original value is called half life period of the reaction.

(i) For zero order reaction rate constant is given by:

$k = \dfrac{[R]_0 - [R]}{t}$, At $t = t_{1/2}, [R] = \dfrac{[R]_0}{2}$

$k = \dfrac{[R]_0 - \dfrac{[R]_0}{2}}{t_{1/2}} \Rightarrow k = \dfrac{[R]_0}{2 t_{1/2}} \Rightarrow t_{1/2} = \dfrac{[R]_0}{2k}$

For zero order reaction, $t_{1/2}$ is directly proportional to $[R]_0$.

(ii) For first order reaction,

$k = \dfrac{2.303}{t} \log \dfrac{[R]_0}{[R]}$, At $t = t_{1/2}, [R] = \dfrac{[R]_0}{2}$

∴ $k = \dfrac{2.303}{t_{1/2}} \log \dfrac{[R]_0}{[R]_0/2}$ or, $t_{1/2} = \dfrac{2.303}{k} \log 2$

$t_{1/2} = \dfrac{2.303 \times 0.3010}{k} \Rightarrow t_{1/2} = \dfrac{0.693}{k}$

For first order reaction, $t_{1/2}$ is independent of initial concentration.

40. (a) Given: $\dfrac{-d[N_2O_5]}{dt} = 1.4 \times 10^{-3} Ms^{-1}$

According to rate law expression,

$-\dfrac{1}{2} \dfrac{d[N_2O_5]}{dt} = \dfrac{1}{4} \dfrac{d[NO_2]}{dt} = \dfrac{d[O_2]}{dt}$

Rate of reaction $= \dfrac{1}{2} \dfrac{d[N_2O_5]}{dt} = \dfrac{1}{2} \times 1.4 \times 10^{-3} Ms^{-1}$

$= 7 \times 10^{-4} Ms^{-1}$

(b) For first order reaction, $t = \dfrac{2.303}{k} \log \dfrac{[R_0]}{[R_t]}$

For 99% completion of reaction
$t = t_{0.99}, [R]_0 = 1, [R]_t = (1 - 0.99) = 0.01 = 10^{-2}$

$t_{0.99} = \dfrac{2.303}{k} \log \dfrac{1}{10^{-2}} = \dfrac{2.303}{k} \log 10^2 = \dfrac{2.303}{k} \times 2$ ...(i)

For 90% completion of reaction
$t = t_{0.90}, [R]_0 = 1, [R]_t = (1-0.9) = 0.1 = 10^{-1}$

$t_{0.90} = \dfrac{2.303}{k} \log \dfrac{1}{10^{-1}} = \dfrac{2.303}{k} \log 10 = \dfrac{2.303}{k}$ ...(ii)

Comparing equations (i) and (ii), $t_{0.99} = 2 \times t_{0.90}$

41.

order of rxⁿ = 1st
Given, for 75% completion / decomposition
i.e. $\dfrac{[A]_t}{[A]_0} = \dfrac{1}{4}$ $t = 30$ mins

$K = \dfrac{2.303}{t} \log_{10}\left(\dfrac{A_0}{A_t}\right)$

$K = \dfrac{2.303 \times \log_{10} 4}{30 \text{ mins}}$

$t_{1/2} = \dfrac{0.693}{k}$ or $\dfrac{\ln 2}{k}$ $\left[t_{1/2} = \dfrac{2.303}{k} \times \log_{10}\left(\dfrac{A_0}{A_t}\right)$ or $A_0/A_t = 2\right]$

$t_{1/2} = \dfrac{0.693 \times 30 \text{ mins}}{2.303 \times 2 \log_{10} 2}$ ($\log_{10} 4 = 2 \log_{10} 2$)

$= \dfrac{0.693 \times 30 \text{ mins}}{2 \times 0.693}$ = [15 mins]

[Topper's Answer, 2022]

42. (a) This graph represents first order reaction.

(b) Slope of the curve is $\dfrac{k}{2.303}$

(c) $t_{1/2} = \dfrac{0.693}{k}$

43. $t_{1/2}$ or $t_{50\%} = 40$ min

$k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{40} = 0.0173\ \text{min}^{-1}$

$t_{90\%} = \dfrac{2.303}{k}\log\dfrac{100}{100-90} = \dfrac{2.303}{0.0173}\log 10 = 133\ \text{min}$

44. (i) The reaction is of zero order.

(ii) Slope of the curve = $-k$

(iii) Unit of rate constant, k, for zero order reaction is $\text{mol L}^{-1}\text{s}^{-1}$.

45. $t = \dfrac{2.303}{k}\log\dfrac{A_0}{A_t}$

$t = \dfrac{2.303}{4.9\times 10^{-3}}\log\dfrac{4}{3}$

$t = 58.75\ \text{s}$

46. According to the 1st order kinetics,

$k = \dfrac{2.303}{t}\log\dfrac{[A]_0}{[A]_t}$

or, $k = \dfrac{2.303}{80}\log\dfrac{100}{60} = 6.386\times 10^{-3}\ \text{min}^{-1}$

Time required for 90% completion of the reaction,

$t = \dfrac{2.303}{k}\log\dfrac{100}{10} = \dfrac{2.303}{6.386\times 10^{-3}}\log 10 = 360.63\ \text{minutes.}$

47. For a zero order reaction, $k = \dfrac{1}{t}([A]_0 - [A])$

$\Rightarrow t = \dfrac{1}{4\times 10^{-3}}\times(0.1-0.064) = 9\ \text{s}$

48. For a first order reaction, $k = \dfrac{2.303}{t}\log\dfrac{[R]_0}{[R]}$

$k = \dfrac{2.303}{30}\log\dfrac{100}{100-20} = \dfrac{2.303}{30}\times 0.097 = 7.4\times 10^{-3}\ \text{min}^{-1}$

$t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{7.4\times 10^{-3}} = 93.65\ \text{min}$

49. (a) The formula of rate constant for first order reaction is

$k = \dfrac{2.303}{t}\log\dfrac{[A]_0}{[A]_t}$

$k_1 = \dfrac{2.303}{300\ \text{s}}\log\dfrac{(1.6\times 10^{-2})\text{mol L}^{-1}}{(0.8\times 10^{-2})\ \text{mol L}^{-1}} = 2.3\times 10^{-3}\ \text{s}^{-1}$

Similarly, $k_2 = \dfrac{2.303}{600\ \text{s}}\log\dfrac{(1.6\times 10^{-2})\text{mol L}^{-1}}{(0.4\times 10^{-2})\ \text{mol L}^{-1}}$

$= 2.3\times 10^{-3}\ \text{s}^{-1}$

Unit and magnitude of rate constant shows the given reaction is of first order.

(b) The formula for half-life for first order reaction is

$t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{2.3\times 10^{-3}\ \text{s}^{-1}} = 301.30\ \text{s}$

50. According to the 1st order kinetics

$k = \dfrac{2.303}{t}\log\dfrac{[A_0]}{[A_t]}$

$\Rightarrow k = \dfrac{2.303}{20\ \text{min}}\log\dfrac{[100]}{[75]} \Rightarrow k = 0.014\ \text{min}^{-1}$

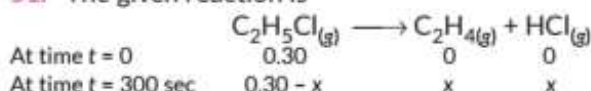Similarly, for 2nd process, $0.014 = \dfrac{2.303}{t}\log\left(\dfrac{100}{25}\right)$

$t = 99\ \text{min}$

51. The given reaction is

$$C_2H_5Cl_{(g)} \longrightarrow C_2H_{4(g)} + HCl_{(g)}$$

At time $t = 0$	0.30	0	0
At time $t = 300$ sec	0.30 – x	x	x

Total pressure = $0.30 - x + x + x = 0.50$ atm

or $0.30 + x = 0.50$

$\therefore x = 0.50 - 0.30 = 0.20$

$\therefore$ Initial pressure, $P_0 = 0.30$ atm

Pressure of C_2H_5Cl after 300 sec,

$P_t = 0.30 - 0.20 = 0.10$ atm

Using formula for first order reaction,

$k = \dfrac{2.303}{t}\log\dfrac{P_0}{P_t}$

$k = \dfrac{2.303}{300}\log\dfrac{0.30}{0.10}$

$k = \dfrac{2.303}{300}\log 3 = \dfrac{2.303\times 0.4771}{300} = 3.66\times 10^{-3}\ \text{sec}^{-1}$

52. $t_{50\%}$ or $t_{1/2} = 30$ minutes

$\Rightarrow k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{30} = 0.0231\ \text{min}^{-1}$

$t_{90\%} = \dfrac{2.303}{k}\log\dfrac{100}{100-90} = \dfrac{2.303}{0.0231}\log 10$

$= 99.69$ minutes

53. For a first order reaction,

$k = \dfrac{2.303}{t}\log\dfrac{[R]_0}{[R]} = \dfrac{2.303}{10}\log\dfrac{100}{100-25}$

$k = \dfrac{2.303}{10}\times 0.124 = 0.003$

$\therefore t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{0.003} = 23.1\ \text{min}$

54. (i) The reaction is of 1st order.

(ii) For first order reaction

$\ln[R] = -kt + \ln[R]_0$

comparing eqn. $y = mx + c$

we get a straight line with slope $= -k$ and intercept equal to $\ln[R]_0$.

(iii) Unit of rate constant for first order reaction

$$\frac{mol\,L^{-1}}{s} \times \frac{1}{(mol\,L^{-1})^1} = s^{-1}$$

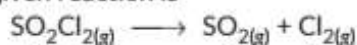**55.** $t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]}$

$\Rightarrow k = 60\,s^{-1}, [R] = \dfrac{1}{10}[R]_0$

$t = \dfrac{2.303}{60} \log \dfrac{[R]_0}{\dfrac{[R]_0}{10}} \Rightarrow t = \dfrac{2.303}{60} \log 10$

$\Rightarrow t = \dfrac{2.303 \times 1}{60} = 0.0384$ second

56. The given reaction is

$$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$

At $t = 0$ 0.4 atm   0   0

At time t (0.4 − x) atm   x atm   x atm

Total pressure at time t will be

$P_t = (0.4 - x) + x + x = 0.4 + x$

$x = (P_t - 0.4)$

Pressure of SO_2Cl_2 at time t will be

$p_{SO_2Cl_2} = 0.4 - x = 0.4 - (P_t - 0.4) = 0.8 - P_t$

At time $t = 100$ s, $P_t = 0.7$ atm

$\therefore \quad p_{SO_2Cl_2} = 0.8 - 0.7 = 0.1$ atm

According to first order kinetic equation

$k = \dfrac{2.303}{t} \log \dfrac{p_{SO_2Cl_2\,(initial)}}{p_{SO_2Cl_2\,(after\;reaction)}}$

$= \dfrac{2.303}{100} \log \left(\dfrac{0.4}{0.1}\right) = 1.3 \times 10^{-2}\,s^{-1}$

57. (i) $t = \dfrac{2.303}{k} \log \dfrac{[A]_0}{[A]}$

Given $k = 1.06 \times 10^{-3}\,min^{-1}$, $\dfrac{[A]_0}{[A]} = \dfrac{100}{85}$

$t = \dfrac{2.303}{1.06 \times 10^{-3}\,min^{-1}} \log \dfrac{100}{85}$

$t = \dfrac{2303}{1.06}[2 \log 10 - \log 85]$ min

$t = \dfrac{2303}{1.06}[2 \times 1 - 1.9294] = \dfrac{2303 \times 0.0706}{1.06}$

$t = 153.39$ min $= 153.4$ min

(ii) Given $k = 1.06 \times 10^{-3}\,min^{-1}$, $\dfrac{[A]_0}{[A]} = \dfrac{100}{15}$

$t = \dfrac{2.303}{1.06 \times 10^{-3}\,min^{-1}} \log \dfrac{100}{15}$

$= \dfrac{2303}{1.06}[2 \log 10 - \log 15]$ min

$= \dfrac{2303}{1.06}[2 \times 1 - 1.1761] = \dfrac{2303 \times 0.8239}{1.06}$ min $= 1790$ min

58. (i) Average rate of reaction : Ratio of change in concentration and time required for the change is average rate of reaction.

$r_{av} = \dfrac{\Delta x}{\Delta t} = \dfrac{\text{Change in concentration}}{\text{Time required for the change}}$

(ii) Two factors that affect rate of reaction are:

(a) Nature of reactants

(b) Temperature

(iii) (1) The rate of reaction of a zero order reaction is proportional to zero power of the concentration of reactants. Rate of reaction for zero order reaction is given as :

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

(2) Units of k for zero order reaction is $mol\,L^{-1}s^{-1}$.

OR

(iii) (1) $P + 2Q \longrightarrow$ Products

Rate $= k[P]^{1/2}\,[Q]^1$

Order of reaction $= \dfrac{1}{2} + 1 = 3$

(2) The reactions which are of second order but behave like first order reactions are called pseudo first order reactions e.g., during hydrolysis of ethyl acetate (ester) with water, the concentration of water does not alter much during the reaction. So, in the rate equation, the rate of change in water concentration (the reactant which is in excess) can be taken as constant hence the reaction behaves as first order reaction.

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$
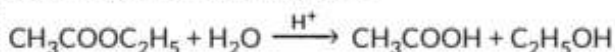
Rate $= k'[CH_3COOC_2H_5][H_2O]$ the term $[H_2O]$ can be taken as constant. Hence, the rate equation becomes Rate $= k[CH_3COOC_2H_5]$ where $k = k'[H_2O]$.

59. (i) Rate $= k[A]^{\frac{1}{2}}[B]^{\frac{3}{2}}$

Because reaction is an elementary reaction, hence order of reaction will be $\dfrac{1}{2} + \dfrac{3}{2} = 2$

(ii) Rate of reaction increases with increase in temperature.

(iii) Rate of reaction is the rate of change in concentration of a reactant or product in unit time.

(iv) (a) For a first order reaction,

$t_{1/2} = \dfrac{0.693}{k} = 77.78$ min

$k = 8.90 \times 10^{-3}\,min^{-1}$

Time required for 30% completion,

$t = \dfrac{2.303}{k} \log \left(\dfrac{100}{70}\right) = \dfrac{2.303}{8.90 \times 10^{-3}\,min^{-1}} \log 1.43$

$t = 40$ min

(b) Given :

For first order reaction, $k = 1 \times 10^{-3}$ sec^{-1}

$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A]}$$

$$t = \frac{2.303}{1 \times 10^{-3} sec^{-1}} \log\left(\frac{5}{3}\right) = \frac{2.303 \times 0.2219}{1 \times 10^{-3} sec^{-1}} = 511.03 \text{ sec}$$

60. (a) The rate of reaction is nearly doubled with a rise in temperature by 10°C for a chemical reaction. The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation :

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

where
$k \rightarrow$ Rate constant
$A \rightarrow$ Arrhenius factor
$R \rightarrow$ Gas constant
$T \rightarrow$ Temperature
$E_a \rightarrow$ Energy of activation for the reaction.

(b) Rate $= k[A]^2[B]^{1/2}$

As order of reaction is sum of powers of concentration represented in rate law, order of the given reaction will be $2 + \frac{1}{2} = \frac{5}{2} = 2.5$

(c) Differences between order and molecularity of a reaction are the following :

Order of a reaction	Molecularity of a reaction
1. It is the sum of powers of the concentration of the reactants in the rate law expression.	It is the number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.
2. It can be zero or even a fraction.	It is always a whole number.

(d) Given that, reaction is of first order,

$k = 2 \times 10^{-3}$ sec^{-1}

$[A]_0 = 6$ g, $[A]_t = 2$ g

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t} \Rightarrow t = \frac{2.303}{2 \times 10^{-3}} \times \log\left(\frac{6}{2}\right)$$

$t = 1.15 \times 10^3 \times (0.4771)$

$t = 0.5486 \times 10^3$ sec $= 548.6$ s

Given that, $t_{1/2} = 6930$ years

$[A]_t = 0.75 \quad [A]_0 = 1$

$$t_{1/2} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{6930}$$

$k = 1 \times 10^{-4}$ year^{-1}

$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A]} = \frac{2.303}{10^{-4}} \times \log\left[\frac{1}{0.75}\right]$$

$$t = 2.303 \times 10^4 \times \log\left(\frac{100}{75}\right) = 2.303 \times 10^4 \times \log\left(\frac{4}{3}\right)$$

$t = 2.303 \times 10^4 \times (\log 4 - \log 3)$

$t = 2.303 \times 10^4 \times (0.6021 - 0.4771)$

$t = 0.2878 \times 10^4 \Rightarrow t = 2878$ years

61. (a) $t = 40$ minutes

$[A_0] = 100 \quad [A_t] = 75$

For first order reaction

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A_t]} = \frac{2.303}{40} \log\left(\frac{100}{75}\right)$$

$$= \frac{2.303}{40} \log \frac{4}{3} = \frac{2.303}{40} (\log 4 - \log 3)$$

$$= \frac{2.303}{40} (0.6020 - 0.4771)$$

$k = 7.19 \times 10^{-3}$ min^{-1}

$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A_t]}$$
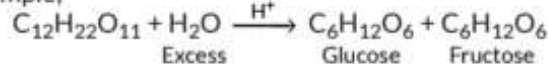
For 80% completion $[A_0] = 100, \quad [A_t] = 20$

$$t = \frac{2.303}{7.19 \times 10^{-3}} \log \frac{100}{20} = \frac{2.303}{7.19 \times 10^{-3}} \times 0.6990$$

$t = 223.8$ minute

(b) Order of reaction : The sum of exponents (powers) to which the molar concentration in the rate law equation are raised to express the observed rate of the reaction is called the order of reaction.

If one of the reactant is taken in large excess then its concentration will not affect the rate of reaction, thus the bimolecular reaction will follows first order kinetics. Example,

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
$$\text{Excess} \qquad \text{Glucose} \quad \text{Fructose}$$

Rate $= k[C_{12}H_{22}O_{11}]$

62. (a) (i) The reaction is of 1st order.

(ii) For first order reaction

$\ln[R] = -kt + \ln[R]_0$

comparing eqn. $y = mx + c$

we get a straight line with slope $= -k$ and intercept equal to $\ln[R]_0$.

(iii) Unit of rate constant for first order reaction

$$\frac{molL^{-1}}{s} \times \frac{1}{(molL^{-1})^1} = s^{-1}$$

(b) For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{25} \log \frac{100}{100 - 25}$$

$$k = \frac{2.303}{25} \times 0.125 = 0.0115$$

$$\therefore \quad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0115} = 60.26 \text{ min}$$

63. (i) For a first order reaction, $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$

When $t = 30$ s

$$k = \frac{2.303}{30} \log \frac{0.60}{0.30} = \frac{2.303}{30} \times 0.3010 = 0.0231 \text{ s}^{-1}$$

When $t = 60$ s

$$k = \frac{2.303}{60}\log\left(\frac{0.60}{0.15}\right) = \frac{2.303}{60}\times 0.6021 = 0.0231\ s^{-1}$$

As the value of k is constant at different time intervals, the reaction is first order w.r.t. ester when $[H_2O]$ is constant. Hence, it is pseudo first order reaction.

(ii) Average rate $= -\dfrac{C_2 - C_1}{t_2 - t_1} = \dfrac{-(0.15 - 0.30)}{60 - 30}$

$$= \frac{0.15}{30} = 5\times 10^{-3}\ mol\ L^{-1}s^{-1}$$

64. **(c)**: In the presence of a catalyst, the reaction follows a path of lower activation energy.

65. **(d)**: Data is insufficient, E_a can't be predicted.

66. No

67. (a) A catalyst lowers the activation energy (E_a) by providing an alternate pathway or reaction mechanism.
(b) Catalyst does not affect the Gibbs energy (ΔG) of a reaction.

68. The minimum extra energy which must be supplied to the reactants to enable them to cross over the potential energy barrier between reactants and products is called activation energy. It is denoted by E_a.

$$E_a = E_T - E_R$$

69. The rate constant of a chemical reaction is nearly doubled with a rise in temperature by $10°$.
The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation :

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

where $k \rightarrow$ Rate constant
$A \rightarrow$ Arrhenius factor
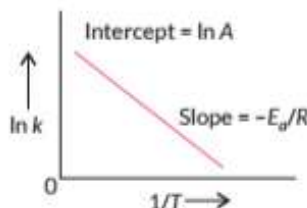$R \rightarrow$ Gas constant
$T \rightarrow$ Temperature
$E_a \rightarrow$ Energy of activation for the reaction.
With increase in temperature, activation energy decreases.
Activation energy = Threshold energy − Average energy possessed by molecules.

70. $\boxed{\ln k = -\dfrac{E_a}{RT} + \ln A}$

Intercept = $\ln A$

Slope = $-\dfrac{E_a}{R}$

Key Points
➔ Arrhenius equation : $k = Ae^{-E_a/RT}$

71. The rate of reaction is nearly doubled with a rise in temperature by $10°C$ for a chemical reaction.
The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation :

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

where $k \rightarrow$ Rate constant
$A \rightarrow$ Arrhenius factor
$R \rightarrow$ Gas constant
$T \rightarrow$ Temperature
$E_a \rightarrow$ Energy of activation for the reaction.

72. $k = (2.5 \times 10^{14})\ e^{\frac{-25000}{T}}$

Comparing it with the Arrhenius equation
$k = Ae^{-E_a/RT}$
We get $A = 2.5 \times 10^{14}\ s^{-1}$

$$\frac{E_a}{R} = 25000$$

or $E_a = 25000\ K \times 8.314\ J\ K^{-1}\ mol^{-1} = 207850\ J\ mol^{-1}$

For a first order reaction, $t_{1/2} = \dfrac{0.693}{k}$

or, $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{300} = 2.31\times 10^{-3}\ min^{-1}$

Concept Applied 🎯
➔ In order to calculate E_a in J/mol, the value of R should be taken as 8.314 J/mol K.

73. Since the rate of a reaction quadruples when temperature changes from 293 K to 313 K,
∴ $k_2 = 4k_1$
$T_1 = 293$ K and $T_2 = 313$ K
According to Arrhenius equation

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

Putting the values,

$$\log\frac{4k_1}{k_1} = \frac{E_a}{2.303\times 8.314\ JK^{-1}\ mol^{-1}}\left[\frac{(313-293)K}{293K\times 313K}\right]$$

$$0.6021 = \frac{E_a \times 20K}{2.303\times 8.314\ J\ K^{-1}\ mol^{-1}\times 293K\times 313K}$$

∴ $E_a = \dfrac{0.6021\times 2.303\times 8.314\times 293\times 313}{20}\ Jmol^{-1}$

$= 52863.3\ J\ mol^{-1} = 52.86\ kJ\ mol^{-1}$

74. Given, $T_1 = 300$ K, $T_2 = 320$ K
$k_1 = 2\times 10^{-2}$, $k_2 = 6\times 10^{-2}$, $E_a = ?$
Using Arrhenius equation,

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

or $\log\dfrac{6\times 10^{-2}}{2\times 10^{-2}} = \dfrac{E_a}{2.303\times 8.314}\left[\dfrac{1}{300} - \dfrac{1}{320}\right]$

or $\log 3 = \dfrac{E_a}{2.303\times 8.314}\times\left[\dfrac{320-300}{320\times 300}\right]$

or $E_a = \dfrac{0.4771\times 2.303\times 8.314\times 320\times 300}{20}$

$= 43848\ J\ mol^{-1} = 43.85\ kJ\ mol^{-1}$

75. $(t_{1/2})_1 = 40$ min, $(t_{1/2})_2 = 20$ min
$T_1 = 300$ K, $T_2 = 320$ K

$E_a = ?$

For 1st order reaction,

$$k_1 = \frac{0.693}{(t_{1/2})_1} = \frac{0.693}{40} = 0.017 \, min^{-1}$$

$$k_2 = \frac{0.693}{(t_{1/2})_2} = \frac{0.693}{20} = 0.034 \, min^{-1}$$

From Arrhenius equation,

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

$$\log \frac{0.034}{0.017} = \frac{E_a}{2.303 \times 8.314}\left[\frac{20}{320 \times 300}\right]$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 320 \times 300}{20}$$

$E_a = 27663.8 \, J/mol = 27.6 \, kJ/mol$

76. For first order reaction, $t_{1/2} = \dfrac{0.693}{k}$

$t_{1/2} = 200 \, min = 200 \times 60 = 12000 \, s$

$$\Rightarrow \quad k = \frac{0.693}{12000 \, s} = 5.8 \times 10^{-5} \, s^{-1}$$

Also, for first order decomposition of H_2O_2, rate constant is

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} K$$

Comparing the above equation with the Arrhenius equation,

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

or $\quad \dfrac{E_a}{2.303\,RT} = \dfrac{1 \times 10^4}{T}$

$\Rightarrow \quad E_a = 2.303 \times 8.314 \times 1.0 \times 10^4 = 1.91 \times 10^5 \, J\,mol^{-1}$

77. Given, $T_1 = 300 \, K$, $T_2 = 310 \, K$

$k_1 = 2 \times 10^{-2}$, $k_2 = 4 \times 10^{-2}$, $E_a = ?$

Using Arrhenius equation,

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

or $\quad \log \dfrac{4 \times 10^{-2}}{2 \times 10^{-2}} = \dfrac{E_a}{2.303 \times 8.314}\left[\dfrac{1}{300} - \dfrac{1}{310}\right]$

or $\quad \log 3 = \dfrac{E_a}{2.303 \times 8.314} \times \left[\dfrac{320 - 300}{320 \times 300}\right]$

or $\quad E_a = \dfrac{0.301 \times 2.303 \times 8.314 \times 310 \times 300}{10}$

$\qquad = 53598 \, J\,mol^{-1} = 53.6 \, kJ\,mol^{-1}$

78. $k_1 = 0.02 \, s^{-1}$, $k_2 = 0.07 \, s^{-1}$

$T_1 = 500 \, K$, $T_2 = 700 \, K$

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

$$\log \frac{0.07}{0.02} = \frac{E_a}{2.303\,R}\left[\frac{700 - 500}{700 \times 500}\right]$$

$$E_a = \frac{0.544 \times 2.303 \times 8.314 \times 700 \times 500}{200}$$

$\qquad = 18228.07 \, J\,mol^{-1} = 18.23 \, kJ\,mol^{-1}$

79. $\log \dfrac{k_2}{k_1} = \dfrac{E_a}{2.303\,R}\left(\dfrac{T_2 - T_1}{T_1 T_2}\right)$

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

$$E_a = \frac{2.303 \times 8.314 \times 650 \times 700}{700 - 650} \times \log \frac{2.39 \times 10^{-8}}{2.15 \times 10^{-8}}$$

$$E_a = \frac{19.147 \times 650 \times 700}{50} \, (\log 2.39 - \log 2.15) \, J\,mol^{-1}$$

$\qquad = 174237.7 \, (0.3783 - 0.3324) \, J\,mol^{-1}$

$\qquad = 174237.7 \times 0.0459 \, J\,mol^{-1} = 7997.51 \, J\,mol^{-1}$

80. (a) $\quad t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]}$

$\Rightarrow \quad k = 60 \, s^{-1}$, $[R] = \dfrac{1}{16}[R]_0$

$$t = \frac{2.303}{60} \log \frac{[R]_0}{\frac{[R]_0}{16}} \quad \Rightarrow \quad t = \frac{2.303}{60} \log 16$$

$\Rightarrow \quad t = \dfrac{2.303 \times 1.20}{60} = 0.046 \, second$

(b) Following factors affect the rate of a chemical reaction :

(i) **Concentration of reactants :** Higher the concentration of reactants, faster would be the rate of reaction.

Rate $= k\,C^n$, where $C = $ concentration of reactant.

(ii) **Temperature :** The rate of reaction increases with the temperature. For every $10°C$ rise in temperature rate of reaction increases 2 to 3 times.

(c) Two conditions for the collisions to be effective collisions are:

(i) Colliding molecules must have energy greater than the threshold energy.

(ii) Colliding molecules must have proper orientations at the time of collision.

1. (a): Rate $= [A]^2[B]^0 \Rightarrow$ Rate $= [A]^2$

If $[A]$ is doubled then, Rate $= [2A]^2$ become $4[A]^2 = 4$ Rate

Rate of reaction increases 4 times.

Note : Order of B is not mentioned in question. (1)

2. (a) The rate of reaction will increase. The catalyst decreases the activation energy of the reaction therefore the reaction becomes faster. (1)

(b) The rate of reaction will decease. At lower temperatures, the kinetic energy of molecules decrease

thereby, the collisions decrease resulting in lowering of rate of reaction. (1)

3. (i) Rate = $k[A][B]^{1/2}$ (1/2)

∴ Order of reaction = 1 + 1/2 = 1.5

Molecularity of the reaction cannot be 1.5. (1/2)

Since the reaction occurs in steps hence, it is a complex reaction.

(ii) Units of $k = mol^{-1/2} L^{1/2} s^{-1}$ (1)

4. Given reaction, $P + 2Q \rightarrow R + 2S$

Exp.	Initial P (mol/L)	Initial Q (mol/L)	Initial Rate of Formation of R (M min^{-1})
1.	0.10	0.10	3.0×10^{-4}
2.	0.30	0.30	9.0×10^{-4}
3.	0.10	0.30	3.0×10^{-4}
4.	0.20	0.40	6.0×10^{-4}

Let rate of this reaction, $r = k[P]^x [Q]^y$

Then, $\dfrac{r_1}{r_3} = \dfrac{3.0 \times 10^{-4}}{3.0 \times 10^{-4}} = \dfrac{k(0.10)^x(0.10)^y}{k(0.10)^x(0.30)^y}$

$\Rightarrow 1 = \left(\dfrac{1}{3}\right)^y \Rightarrow y = 0$ (1/2)

Again from $\dfrac{r_2}{r_3} = \dfrac{9.0 \times 10^{-4}}{3.0 \times 10^{-4}} = \dfrac{k(0.30)^x(0.30)^y}{k(0.10)^x(0.30)^y}$ (1/2)

$\Rightarrow 3.0 = (3)^x \Rightarrow x = 1$

Hence, the expression for rate law is, $r = k[P]$ (1)

5. (a): The rate constant for the decay of O-15 is less than that for O-19. Therefore, the rate of decay of O-15 will be slower and will have a longer half life. (1)

6. Half life, $t_{1/2} = 0.693/k$

$k = 0.693/69.3 = 1/100 = 0.01$ min^{-1} (1/2)

For first order reaction,

$k = \dfrac{2.303}{t} \log \dfrac{[R_o]}{R}$ (1/2)

$t = \dfrac{2.303}{0.01} \log \dfrac{100}{20}$

$t = 230.3 \log 5$ (log 5 = 0.6990) (1/2)

$t = 160.9$ min (1/2)

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

$k = 0.693/5730$ years^{-1} (1/2)

$t = \dfrac{2.303}{k} \log \dfrac{C_0}{C_t}$ (1/2)

Let $C_0 = 1$, $C_t = 3/10$,

so, $\dfrac{C_0}{C_t} = \dfrac{1}{3/10} = \dfrac{10}{3} \Rightarrow t = \dfrac{2.303}{0.693} \times 5730 \log \dfrac{10}{3}$ (1/2)

$t = 19042 (1 - 0.4771) = 9957$ years (1/2)

8. (a) Ratio of neutrons to protons in carbon-14 is 2.3: 1 which makes it unstable whereas in carbon-12 this ratio is 1 : 1, i.e., number of neutrons and protons are equal. Hence C-12 nucleus is stable. (1)

(b) The age of fossils can be estimated with the help of C-14 decay. All living organisms have C-14 which continously decays. Once the organism dies, the decayed C-14 cannot be replaced back. (1)

(c) Carbon-14 atoms decay to stable nitrogen atoms and potassium-40 atoms decay to stable calcium atoms.

$^{14}_{6}C \longrightarrow \,^{14}_{7}N + \,^{0}_{-1}e$ (1)

β decay

$^{40}_{19}K \longrightarrow \,^{40}_{20}Ca + \,^{0}_{-1}e$

β decay
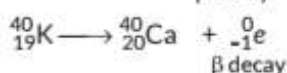
(d) $C_0 = 20$ g and $C_t = ?$

$t = 10320$ years, $k = \dfrac{0.693}{t_{1/2}} = 0.693/6000$

(half-life given in passage)

$t = \dfrac{2.303}{k} \log \dfrac{C_0}{C_t}$ (1/2)

$10320 = \dfrac{2.303}{\dfrac{0.693}{6000}} \log \dfrac{20}{C_t}$ (1/2)

$0.517 = \log \dfrac{20}{C_t} \Rightarrow$ antilog $0.517 = \log \dfrac{20}{C_t}$ (1/2)

$3.289 = \dfrac{20}{C_t} \Rightarrow C_t = 6.089$ g (1/2)

OR

$C_0 = 32$ g and $C_t = 12$ g

$t = ? k = 0.693/6000$ (half life given in passage)

$t = (2.303/k) \log (C_0/C_t)$ (1/2)

$t = 2.303 / (0.693/6000) \log (32/12)$ (1/2)

$t = \dfrac{2.303 \times 6000}{0.693} \log 2.667$ (1/2)

$t = \dfrac{2.303 \times 6000 \times 0.4260}{0.693} = 8494.64$ years (1/2)

9. (c) : $k = Ae^{-E_a/RT}$

$\ln k = \ln A - \dfrac{E_a}{RT}$

Comparing with $y = mx + c$

$m = -\dfrac{E_a}{RT}$ = Slope

Intercept = $c = \ln A$ (1)