CHAPTER

4

Chemical Kinetics

4.1 Rate of a Chemical Reaction

1. For the chemical reaction,

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

the correct option is

(a) $3\frac{d[H_2]}{dt} = 2\frac{d[NH_3]}{dt}$

(b) $-\frac{1}{3}\frac{d[H_2]}{dt} = -\frac{1}{2}\frac{d[NH_3]}{dt}$

(c) $-\frac{d[N_2]}{dt} = 2\frac{d[NH_3]}{dt}$

(d) $-\frac{d[N_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$ *(NEET 2019)*

2. The rate of the reaction : $2N_2O_5 \longrightarrow 4NO_2 + O_2$ can be written in three ways.

$$\frac{-d[N_2O_5]}{dt} = k[N_2O_5]$$

$$\frac{d[NO_2]}{dt} = k'[N_2O_5]; \quad \frac{d[O_2]}{dt} = k''[N_2O_5]$$

The relationship between k and k' and between k and k'' are

(a) $k' = 2k, k'' = k$ (b) $k' = 2k, k'' = k/2$

(c) $k' = 2k, k'' = 2k$ (d) $k' = k, k'' = k$

(Mains 2011)

3. For the reaction $N_2O_{5(g)} \rightarrow 2NO_{2(g)} + 1/2O_{2(g)}$ the value of rate of disappearance of N_2O_5 is given as 6.25×10^{-3} mol $L^{-1}s^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as :

(a) 6.25×10^{-3} mol L^{-1} s^{-1} and 6.25×10^{-3} mol L^{-1} s^{-1}

(b) 1.25×10^{-2} mol L^{-1} s^{-1} and 3.125×10^{-3} mol L^{-1} s^{-1}

(c) 6.25×10^{-3} mol L^{-1} s^{-1} and 3.125×10^{-3} mol L^{-1} s^{-1}

(d) 1.25×10^{-2} mol L^{-1} s^{-1} and 6.25×10^{-3} mol L^{-1} s^{-1} *(2010)*

4. For the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$, if $\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$ mol $L^{-1}s^{-1}$, the value of $\frac{-d[H_2]}{dt}$ would be

(a) 4×10^{-4} mol L^{-1} s^{-1} (b) 6×10^{-4} mol L^{-1} s^{-1}

(c) 1×10^{-4} mol L^{-1} s^{-1} (d) 3×10^{-4} mol L^{-1} s^{-1}

(2009)

5. In the reaction,

$BrO_{3\,(aq)}^{-} + 5Br_{(aq)}^{-} + 6H_{(aq)}^{+} \longrightarrow 3Br_{2(l)} + 3H_2O_{(l)}$

The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as

(a) $\frac{d[Br_2]}{dt} = -\frac{5}{3}\frac{d[Br^-]}{dt}$ (b) $\frac{d[Br_2]}{dt} = \frac{5}{3}\frac{d[Br^-]}{dt}$

(c) $\frac{d[Br_2]}{dt} = \frac{3}{5}\frac{d[Br^-]}{dt}$ (d) $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

(2009)

6. Consider the reaction :

$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

The equality relationship between $\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is

(a) $\frac{d[NH_3]}{d\ dt} = -\frac{d[H_2]}{dt}$

(b) $\frac{[NH_3]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$

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

(d) $+\frac{d[NH_3]}{dt} = -\frac{3}{2}\frac{d[H_2]}{dt}$ *(2006)*

7. For the reaction, $2A + B \longrightarrow 3C + D$, which of the following does not express the reaction rate?

(a) $-\frac{d[A]}{2dt}$ (b) $-\frac{d[C]}{3dt}$

(c) $-\frac{d[B]}{dt}$ (d) $\frac{d[D]}{dt}$ *(2006)*

8. $3A \longrightarrow 2B$, rate of reaction $\frac{+d[B]}{dt}$ is equal to

(a) $-\frac{3}{2}\frac{d[A]}{dt}$ (b) $-\frac{2}{3}\frac{d[A]}{dt}$

(c) $-\frac{1}{3}\frac{d[A]}{dt}$ (d) $+2\frac{d[A]}{dt}$ *(2002)*

9. For the reaction,

$H^+ + BrO_3^- + 3Br^- \text{——} 5Br_2 + H_2O$

which of the following relations correctly represents the consumption and formation of products?

(a) $\frac{d[Br^-]}{dt} = -\frac{3}{5}\frac{d[Br_2]}{dt}$ (b) $\frac{d[Br^-]}{dt} = -\frac{3}{5}\frac{d[Br_2]}{dt}$

(c) $\frac{d[Br^-]}{dt} = -\frac{5}{3}\frac{d[Br_2]}{dt}$ (d) $\frac{d[Br^-]}{dt} = -\frac{5}{3}\frac{d[Br_2]}{dt}$ *(2000)*

10. For the reaction $H_{2(g)} + I_{2(g)}\ 2HI_{(g)}$, the rate of reaction is expressed as

(a) $\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[I_2]}{\Delta t} = -\frac{\Delta[HI]}{\Delta t}$

(b) $-\frac{\Delta[I_2]}{\Delta t} = -\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$

(c) $\frac{\Delta[I_2]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[HI]}{2\Delta t}$

(d) none of these. *(1997)*

4.2 Factors Influencing Rate of a Reaction

11. Mechanism of a hypothetical reaction,
$X_2 + Y_2 \longrightarrow 2XY$, is given below:
(i) $X_2 \longrightarrow X + X$ (fast)
(ii) $X + Y_2$ □ $XY + Y$ (slow)
(iii) $X + Y \longrightarrow XY$ (fast)
The overall order of the reaction will be
(a) 2 (b) 0
(c) 1.5 (d) 1 *(NEET 2017)*

12. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first-order reaction. It is because the
(a) rate is proportional to the surface coverage
(b) rate is inversely proportional to the surface coverage
(c) rate is independent of the surface coverage
(d) rate of decomposition is very slow.
(NEET-II 2016)

13. The rate constant of the reaction $A \longrightarrow B$ is 0.6×10^{-3} mol L^{-1} s^{-1}. If the concentration of A is 5 M, then concentration of B after 20 minutes is
(a) 3.60 M (b) 0.36 M
(c) 0.72 M (d) 1.08 M *(2015)*

14. For a reaction between A and B the order with respect to A is 2 and the order with respect to B is 3. The concentrations of both A and B are doubled, the rate will increase by a factor of
(a) 12 (b) 16
(c) 32 (d) 10
(Karnataka NEET 2013)

15. In a reaction, $A + B \longrightarrow$ product, rate is doubled when the concentration of B is doubled, and rate increases by a factor of 8 when the concentration of both the reactants (A and B) are doubled, rate law for the reaction can be written as
(a) rate = $k[A][B]^2$ (b) rate = $k[A]^2[B]^2$
(c) rate = $k[A][B]$ (d) rate = $k[A]^2[B]$
(2012)

16. Which one of the following statements for the order of a reaction is incorrect?
(a) Order can be determined only experimentally.
(b) Order is not influenced by stoichiometric coefficient of the reactants.
(c) Order of a reaction is sum of power to the concentration terms of reactants to express the rate of reaction.
(d) Order of reaction is always whole number.
(2011)

17. The unit of rate constant for a zero order reaction is
(a) mol L^{-1} s^{-1} (b) L mol^{-1} s^{-1}
(c) L^2 mol^{-2} s^{-1} (d) s^{-1} *(Mains 2011)*

18. During the kinetic study of the reaction, $2A + B \rightarrow C + D$, following results were obtained :

Run	[A]/ mol L^{-1}	[B]/ mol L^{-1}	Initial rate of formation of D/mol L^{-1} min^{-1}
I.	0.1	0.1	6.0×10^{-3}
II.	0.3	0.2	7.2×10^{-2}
III.	0.3	0.4	2.88×10^{-1}
IV.	0.4	0.1	2.40×10^{-2}

Based on the above data which one of the following is correct?
(a) Rate = $k[A]^2[B]$ (b) Rate = $k[A][B]$
(c) Rate = $k[A]^2[B]^2$ (d) Rate = $k[A][B]^2$
(2010)

19. For the reaction, $A + B \rightarrow$ products, it is observed that

(i) on doubling the initial concentration of A only, the rate of reaction is also doubled and

(ii) on doubling the initial concentration of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate of this reaction is given by

(a) rate = $k[A][B]^2$ (b) rate = $k[A]^2[B]^2$
(c) rate = $k[A][B]$ (d) rate = $k[A]^2[B]$ *(2009)*

20. The bromination of acetone that occurs in acid solution is represented by this equation.

$$CH_3COCH_{3(aq)} + Br_{2(aq)} \longrightarrow CH_3COCH_2Br_{(aq)} + H^+_{(aq)} + Br^-_{(aq)}$$

These kinetic data were obtained for given reaction concentrations.

Initial concentrations, *M*

$[CH_3COCH_3]$	$[Br_2]$	$[H^+]$
0.30	0.05	0.05
0.30	0.10	0.05
0.30	0.10	0.10
0.40	0.05	0.20

Initial rate, disappearance of Br_2, M s^{-1}

5.7×10^{-5}
5.7×10^{-5}
1.2×10^{-4}
3.1×10^{-4}

Based on these data, the rate equation is

(a) Rate = $k[CH_3COCH_3][Br_2][H^+]^2$
(b) Rate = $k[CH_3COCH_3][Br_2][H^+]$
(c) Rate = $k[CH_3COCH_3][H^+]$
(d) Rate = $k[CH_3COCH_3][Br_2]$ *(2008)*

21. The reaction of hydrogen and iodine monochloride is given as :

$$H_{2(g)} + 2ICl_{(g)} \longrightarrow 2HCl_{(g)} + I_{2(g)}$$

This reaction is of first order with respect to $H_{2(g)}$ and $ICl_{(g)}$, following mechanisms were proposed.

Mechanism *A* :

$$H_{2(g)} + 2ICl_{(g)} \longrightarrow 2HCl_{(g)} + I_{2(g)}$$

Mechanism *B* :

$H_{2(g)} + ICl_{(g)} \longrightarrow HCl_{(g)} + HI_{(g)}$; slow
$HI_{(g)} + ICl_{(g)} \longrightarrow HCl_{(g)} + I_{2(g)}$; fast

Which of the above mechanism(s) can be consistent with the given information about the reaction?

(a) A and B both (b) Neither A nor B
(c) A only (d) B only *(2007)*

22. The rate of reaction between two reactants A and B decreases by a factor of 4 if the concentration of reactant B is doubled. The order of this reaction with respect to reactant B is

(a) 2 (b) –2
(c) 1 (d) –1 *(2005)*

23. If the rate of the reaction is equal to the rate constant, the order of the reaction is

(a) 0 (b) 1
(c) 2 (d) 3 *(2003)*

24. $2A + B \rightarrow C$, It would be a zero order reaction when

(a) the rate of reaction is proportional to square of concentration of A
(b) the rate of reaction remains same at any concentration of A
(c) the rate remains unchanged at any concentration of B and C
(d) the rate of reaction doubles if concentration of B is increased to double. *(2002)*

25. For the reaction; $2N_2O_5 \longrightarrow 4NO_2 + O_2$ rate and rate constant are 1.02×10^{-4} and 3.4×10^{-5} sec^{-1} respectively, then concentration of N_2O_5 at that time will be

(a) 1.732 (b) 3
(c) 1.02×10^{-4} (d) 3.4×10^5 *(2001)*

26. The experimental data for the reaction, $2A + B_2 \longrightarrow 2AB$ is

Experiment	**$[A]$**	**$[B_2]$**	**Rate (mole s^{-1})**
1	0.50	0.50	1.6×10^{-4}
2	0.50	1.00	3.2×10^{-4}
3	1.00	1.00	3.2×10^{-4}

The rate equation for the above data is

(a) rate = $k[A]^2[B]^2$ (b) rate = $k[A]^2[B]$
(c) rate = $k[B_2]$ (d) rate = $k[B_2]^2$ *(1997)*

27. The given reaction,

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

is an example of

(a) third order reaction
(b) first order reaction
(c) second order reaction
(d) none of these. *(1996)*

28. The data for the reaction $A + B \rightarrow C$, is

Exp.	**$[A]_0$**	**$[B]_0$**	**Initial rate**
1	0.012	0.035	0.10
2	0.024	0.070	0.80
3	0.024	0.035	0.10
4	0.012	0.070	0.80

The rate law corresponds to the above data is

(a) rate = $k[A][B]^3$ (b) rate = $k[A]^2[B]^2$
(c) rate = $k[B]^3$ (d) rate = $k[B]^4$. *(1994)*

4.3 Integrated Rate Equations

29. The rate constant for a first order reaction is 4.606×10^{-3} s^{-1}. The time required to reduce 2.0 g of the reactant to 0.2 g is
(a) 100 s (b) 200 s
(c) 500 s (d) 1000 s *(NEET 2020)*

30. If the rate constant for a first order reaction is k, the time (t) required for the completion of 99% of the reaction is given by
(a) $t = 2.303/k$ (b) $t = 0.693/k$
(c) $t = 6.909/k$ (d) $t = 4.606/k$
(NEET 2019)

31. A first order reaction has a rate constant of 2.303×10^{-3} s^{-1}. The time required for 40 g of this reactant to reduce to 10 g will be
[Given that $\log_{10} 2 = 0.3010$]
(a) 230.3 s (b) 301 s
(c) 2000 s (d) 602 s
(Odisha NEET 2019)

32. The correct difference between first and second order reactions is that
(a) the rate of a first-order reaction does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations
(b) the half-life of a first-order reaction does not depend on $[A]_0$; the half-life of a second-order reaction does depend on $[A]_0$
(c) a first-order reaction can be catalysed; a second-order reaction cannot be catalysed
(d) the rate of a first-order reaction does depend on reactant concentrations; the rate of a second-order reaction does not depend on reactant concentrations. *(NEET 2018)*

33. When initial concentration of the reactant is doubled, the half-life period of a zero order reaction
(a) is halved (b) is doubled
(c) is tripled (d) remains unchanged.
(NEET 2018)

34. A first order reaction has a specific reaction rate of 10^{-2} sec^{-1}. How much time will it take for 20 g of the reactant to reduce to 5 g?
(a) 138.6 sec (b) 346.5 sec
(c) 693.0 sec (d) 238.6 sec *(NEET 2017)*

35. The rate of first-order reaction is 0.04 mol L^{-1} s^{-1} at 10 seconds and 0.03 mol L^{-1} s^{-1} at 20 seconds after initiation of the reaction. The half-life period of the reaction is
(a) 44.1 s (b) 54.1 s
(c) 24.1 s (d) 34.1 s *(NEET-I 2016)*

36. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is
(a) second
(b) more than zero but less than first
(c) zero (d) first. *(2015, Cancelled)*

37. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. The order of reaction is
(a) 1 (b) 2 (c) 3 (d) 0
(Karnataka NEET 2013)

38. The half-life of a substance in a certain enzyme-catalysed reaction is 138 s. The time required for the concentration of the substance to fall from 1.28 mg L^{-1} to 0.04 mg L^{-1} is
(a) 414 s (b) 552 s
(c) 690 s (d) 276 s *(Mains 2011)*

39. Half-life period of a first order reaction is 1386 seconds. The specific rate constant of the reaction is
(a) 0.5×10^{-2} s^{-1} (b) 0.5×10^{-3} s^{-1}
(c) 5.0×10^{-2} s^{-1} (d) 5.0×10^{-3} s^{-1} *(2009)*

40. If 60% of a first order reaction was completed in 60 minutes, 50% of the same reaction would be completed in approximately (log 4 = 0.60, log 5 = 0.69)
(a) 45 minutes (b) 60 minutes
(c) 40 minutes (d) 50 minutes. *(2007)*

41. In a first-order reaction, $A \rightarrow B$, if k is rate constant and initial concentration of the reactant A is 0.5 M, then the half-life is
(a) $\frac{\log 2}{k}$ (b) $\frac{\log 2}{k\sqrt{0.5}}$
(c) $\frac{\ln 2}{k}$ (d) $\frac{0.693}{0.5k}$ *(2007)*

42. For a first order reaction $A \longrightarrow B$ the reaction rate at reactant concentration of 0.01 M is found to be 2.0×10^{-5} mol L^{-1} s^{-1}. The half-life period of the reaction is
(a) 30 s (b) 220 s
(c) 300 s (d) 347 s *(2005)*

43. The rate of a first order reaction is 1.5×10^{-2} mol L^{-1} min^{-1} at 0.5 M concentration of the reactant. The half-life of the reaction is
(a) 0.383 min (b) 23.1 min
(c) 8.73 min (d) 7.53 min *(2004)*

44. The reaction $A \rightarrow B$ follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 hour. What is the time taken for conversion of 0.9 mole of A to produce 0.675 mole of B ?
(a) 1 hour (b) 0.5 hour
(c) 0.25 hour (d) 2 hours *(2003)*

45. For a first-order reaction, the half-life period is independent of
(a) first power of final concentration
(b) cube root of initial concentration
(c) initial concentration
(d) square root of final concentration. *(1999)*

4.4 Temperature Dependence of the Rate of a Reaction

46. For a reaction, activation energy $E_a = 0$ and the rate constant at 200 K is $1.6 \times 10^6\ s^{-1}$. The rate constant at 400 K will be
[Given that gas constant $R = 8.314\ J\ K^{-1}\ mol^{-1}$]
(a) $3.2 \times 10^4\ s^{-1}$ (b) $1.6 \times 10^6\ s^{-1}$
(c) $1.6 \times 10^3\ s^{-1}$ (d) $3.2 \times 10^6\ s^{-1}$
(Odisha NEET 2019)

47. The addition of a catalyst during a chemical reaction alters which of the following quantities?
(a) Enthalpy (b) Activation energy
(c) Entropy (d) Internal energy
(NEET-I 2016)

48. The activation energy of a reaction can be determined from the slope of which of the following graphs?
(a) $\ln k$ *vs* $\frac{1}{T}$ (b) $\frac{T}{\ln k}$ *vs* $\frac{1}{T}$
(c) $\ln k$ *vs* T (d) $\frac{\ln k}{T}$ *vs* T
(2015, Cancelled)

49. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20 °C to 35 °C? ($R = 8.314\ J\ mol^{-1} K^{-1}$)
(a) $34.7\ kJ\ mol^{-1}$ (b) $15.1\ kJ\ mol^{-1}$
(c) $342\ kJ\ mol^{-1}$ (d) $269\ kJ\ mol^{-1}$
(NEET 2013)

50. In a zero-order reaction, for every 10 °C rise of temperature, the rate is doubled. If the temperature is increased from 10 °C to 100 °C, the rate of the reaction will become
(a) 256 times (b) 512 times
(c) 64 times (d) 128 times. *(2012)*

51. Activation energy (E_a) and rate constants (k_1 and k_2) of a chemical reaction at two different temperatures (T_1 and T_2) are related by
(a) $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
(b) $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
(c) $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} + \frac{1}{T_1}\right)$
(d) $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ *(Mains 2012)*

52. The rate of the reaction,
$2NO + Cl_2 \rightarrow 2NOCl$ is given by the rate equation, rate $= k[NO]^2[Cl_2]$. The value of the rate constant can be increased by
(a) increasing the temperature
(b) increasing the concentration of NO
(c) increasing the concentration of the Cl_2
(d) doing all of these. *(Mains 2010)*

53. The rate constants k_1 and k_2 for two different reactions are $10^{16} \cdot e^{-2000/T}$ and $10^{15} \cdot e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is
(a) 2000 K (b) $\frac{1000}{2.303}$ K
(c) 1000 K (d) $\frac{2000}{2.303}$ K *(2008)*

54. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $k = A \times e^{-E^*/RT}$. Activation energy (E^*) of the reaction can be calculated by plotting
(a) k *vs* T (b) k *vs* $\frac{1}{\log T}$
(c) $\log k$ *vs* $\frac{1}{T}$ (d) $\log k$ *vs* $\frac{1}{\log T}$ *(2003)*

55. The activation energy for a simple chemical reaction A B is E_a in forward direction. The activation energy for reverse reaction
(a) is negative of E_a
(b) is always less than E_a
(c) can be less than or more than E_a
(d) is always double of E_a. *(2003)*

56. When a biochemical reaction is carried out in laboratory, outside the human body in absence of enzyme, then rate of reaction obtained is 10^{-6} times, the activation energy of reaction in the presence of enzyme is
(a) $6/RT$ (b) P is required
(c) different from E_a obtained in laboratory
(d) can't say anything. *(2001)*

57. How enzymes increases the rate of reactions?
(a) By lowering activation energy
(b) By increasing activation energy
(c) By changing equilibrium constant
(d) By forming enzyme substrate complex *(2000)*

58. Activation energy of a chemical reaction can be determined by
(a) evaluating rate constants at two different temperatures
(b) evaluating velocities of reaction at two different temperatures
(c) evaluating rate constant at standard temperature
(d) changing concentration of reactants. (1998)

59. By the action of enzymes, the rate of biochemical reaction
(a) does not change
(b) increases
(c) decreases
(d) either (a) or (c).
(1994)

4.5 Collision Theory of Chemical Reactions

60. An increase in the concentration of the reactants of a reaction leads to change in
(a) activation energy
(b) heat of reaction
(c) threshold energy
(d) collision frequency.
(NEET 2020)

ANSWER KEY

1.	(d)	**2.**	(b)	**3.**	(b)	**4.**	(d)	**5.**	(d)	**6.**	(c)	**7.**	(b)	**8.**	(b)	**9.**	(a)	**10.**	(b)
11.	(c)	**12.**	(a)	**13.**	(c)	**14.**	(c)	**15.**	(d)	**16.**	(d)	**17.**	(a)	**18.**	(d)	**19.**	(a)	**20.**	(c)
21.	(d)	**22.**	(b)	**23.**	(a)	**24.**	(b)	**25.**	(b)	**26.**	(c)	**27.**	(a)	**28.**	(c)	**29.**	(c)	**30.**	(d)
31.	(d)	**32.**	(b)	**33.**	(b)	**34.**	(a)	**35.**	(c)	**36.**	(d)	**37.**	(a).	**38.**	(c)	**39.**	(b)	**40.**	(a)
41.	(c)	**42.**	(d)	**43.**	(b)	**44.**	(a)	**45.**	(c)	**46.**	(b)	**47.**	(b)	**48.**	(a)	**49.**	(a)	**50.**	(b)
51.	(b,d)	**52.**	(a)	**53.**	(b)	**54.**	(c)	**55.**	(c)	**56.**	(c)	**57.**	(a)	**58.**	(a)	**59.**	(b)	**60.**	(d)

Hints & Explanations

1. (d) : For the given chemical reaction,

$$\text{Rate of reaction} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$$

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

$$-\frac{1}{2}\underbrace{\frac{d[N_2O_5]}{dt}}_{k} = +\frac{1}{4}\underbrace{\frac{d[NO_2]}{dt}}_{k'} = +\underbrace{\frac{d[O_2]}{dt}}_{k''}$$

$$\frac{1}{2}k = \frac{1}{4}k' = k'',\ k' = 2k;\ k'' = \frac{1}{2}k$$

3. (b) : $N_2O_{5(g)} \rightarrow 2NO_{2(g)} + 1/2O_{2(g)}$

For the given reaction the rate is written as

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

Given that $\frac{-d[N_2O_5]}{dt} = 6.25 \times 10^{-3}\ \text{mol L}^{-1}\text{s}^{-1}$

$$\therefore \frac{d[NO_2]}{dt} = 2 \times 6.25 \times 10^{-3} = 1.25 \times 10^{-2}\ \text{mol L}^{-1}\text{s}^{-1}$$

and $\frac{d[O_2]}{dt} = \frac{6.25 \times 10^{-3}}{2}$

$$= 3.125 \times 10^{-3}\ \text{mol L}^{-1}\text{s}^{-1}$$

4. (d) : For reaction, $N_2 + 3H_2 \rightarrow 2NH_3$

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

Given, $\frac{d[NH_3]}{dt} = 2 \times 10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}$

$$\therefore -\frac{d[H_2]}{dt} = \frac{3}{2}\frac{d[NH_3]}{dt} = \frac{3}{2} \times 2 \times 10^{-4}$$

$$\Rightarrow -\frac{d[H_2]}{dt} = 3 \times 10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}$$

5. (d) : For the given reaction,

$$BrO_3^-{}_{(aq)} + 5Br^-{}_{(aq)} + 6H^+{}_{(aq)} \rightarrow 3Br_{2(l)} + 3H_2O_{(l)}$$

Rate of reaction in terms of Br_2 and Br^- is,

$$\text{Rate} = \frac{1}{3}\frac{d[Br_2]}{dt} = -\frac{1}{5}\frac{d[Br^-]}{dt}$$

$$\therefore \frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$$

6. (c) : $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

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

$$\text{Hence, } +\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$$

7. (b) : $2A + B \rightarrow 3C + D$

$$\text{rate} = \frac{-d[A]}{2dt} = -\frac{d[B]}{dt} = \frac{d[C]}{3dt} = \frac{d[D]}{dt}$$

Negative sign shows the decrease in concentration

8. (b) : $3A \rightarrow 2B$

Rate of the reaction $= \frac{1}{2}\frac{d[B]}{dt} = -\frac{1}{3}\frac{d[A]}{dt}$

$$\Rightarrow \frac{d[B]}{dt} = -\frac{2}{3}\frac{d[A]}{dt}$$

9. (a) : Rate of reaction $= -\frac{1}{3}\frac{d[\mathrm{Br}^-]}{dt} = +\frac{1}{5}\frac{d[\mathrm{Br}_2]}{dt}$

$$\Rightarrow \frac{d[\mathrm{Br}^-]}{dt} = -\frac{3}{5}\frac{d[\mathrm{Br}_2]}{dt}$$

10. (b) : For $H_{2(g)} + I_{2(g)} \square\ 2HI_{(g)}$, the rate of reaction is

$$-\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[I_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

Negative sign shows disappearance of reactant and positive sign shows the appearance of product.

11. (c) : Note : Correct the reactions given in question as

$X_2 \quad X + X$ (fast)

$X + Y_2 \longrightarrow XY + Y$ (slow)

Slow step is the rate determining step.

Rate $= k[X][Y_2]$ ...(i)

Equilibrium constant for fast step, $K = \frac{[X]^2}{[X_2]}$

$[X] = \sqrt{K[X_2]}$

By substituting $[X]$ in equation (i), we get

Rate $= k\sqrt{K[X_2]}\,[Y_2] = k'[X_2]^{1/2}[Y_2]$

$\therefore$ Order of reaction $= \frac{1}{2} + 1 = \frac{3}{2} = 1.5$

12. (a) : At low pressure, rate is proportional to the surface coverage and is of first order while at high pressure, it follows zero order kinetics due to complete coverage of surface area.

13. (c) : Reaction is of zero order as the unit of rate constant is mol L^{-1} s^{-1}.

Concentration of $B = k \times t$

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

14. (c) : $\text{Rate}_1 = k[A]^2[B]^3$

$\text{Rate}_2 = k[2A]^2[2B]^3$

$\text{Rate}_2 = 32k[A]^2[B]^3$

$\therefore$ $\text{Rate}_2 = 32(\text{Rate}_1)$

15. (d) : [*A*] [*B*] Rate

$x \quad y \quad R$ ...(i)

$x \quad 2y \quad 2R$ ...(ii)

$2x \quad 2y \quad 8R$ ...(iii)

Let the rate law ; rate $= k[A]^a[B]^b$

From data given, $(x)^a(y)^b = R$ ...(iv)

$(x)^a(2y)^b = 2R$ ...(v)

Dividing eqn. (v) by (iv),

$$\frac{(2y)^b}{(y)^b} = \frac{2R}{R} \Rightarrow (2)^b = 2 = 2^1$$

Thus, $b = 1$

From data of (iii) experiment,

$(2x)^a(2y)^b = 8R$ ...(vi)

From eqn. (v) and (vi),

$$\frac{(2x)^a}{(x)^a} = \frac{8R}{2R} \Rightarrow (2)^a = 4 = 2^2$$

Thus, $a = 2$. By replacing the values of a and b in rate law; rate $= k[A]^2[B]$

16. (d) : Order of a reaction is not always whole number. It can be zero, or fractional also.

17. (a) : Rate $= k[A]^0$

mol L^{-1} $s^{-1} = k$

Thus, the unit of rate constant is mol L^{-1} s^{-1}.

18. (d) : Let the rate of reaction be given by :

rate $= k[A]^a[B]^b$.

Now consider II and III where $[A]$ is constant.

$$\frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{[0.3]^a[0.2]^b}{[0.3]^a[0.4]^b}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^b \Rightarrow b = 2$$

Now consider I and IV,

$$\frac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}} = \frac{[0.1]^a[0.1]^b}{[0.4]^a[0.1]^b}$$

$$\frac{1}{4} = \left(\frac{1}{4}\right)^a \Rightarrow a = 1$$

$\therefore$ Rate $= k[A][B]^2$

19. (a) : $R = k[A]^m[B]^n$ ...(i)

$2R = k[2A]^m[B]^n$ ...(ii)

$8R = k[2A]^m[2B]^n$ ...(iii)

from (i), (ii) and (iii), $m = 1$, $n = 2$

So, rate $= k[A][B]^2$

20. (c) : From the first two experiments, it is clear that when concentration of Br_2 is doubled, the initial rate of disappearance of Br_2 remains unaltered. So, order of reaction with respect to Br_2 is zero. Thus, the probable rate law for the reaction will be : $k[CH_3COCH_3][H^+]$

21. (d) : The slow step is the rate determining step and it involves 1 molecule of $H_{2(g)}$ and 1 molecule of $ICl_{(g)}$. Hence, the rate will be,

$r = k[H_{2(g)}]\,[ICl_{(g)}]$

i.e., the reaction is 1st order with respect to $H_{2(g)}$ and $ICl_{(g)}$.

22. (b) : Rate of reaction $= k\,[A]^\alpha[B]^\beta$

$\alpha \rightarrow$ order of reaction *w.r.t.* A

$\beta \rightarrow$ order of reaction *w.r.t.* B

$r_1 = k[A]^{\alpha}[B]^{\beta}$

$r_2 = r_1/4 = k[A]^{\alpha}[2B]^{\beta}$

$$\frac{r_1}{r_2} = \frac{k[A]^{\alpha}[B]^{\beta}}{k[A]^{\alpha}[2B]^{\beta}} \Rightarrow 4 = \left(\frac{1}{2}\right)^{\beta} \Rightarrow \beta = -2$$

23. (a) : $A \rightarrow$ products

If $-\frac{dx}{dt} = k$, it means $-\frac{dx}{dt} = k[A]^0 = k$

Hence, order of reaction must be zero.

24. (b) : $2A \rightarrow B + C$

The rate equation of this reaction may be expressed as $r = k[A]^0$, Order = 0, $r = k$

∴ The rate is independent of concentration of the reactant A.

25. (b) : $2N_2O_5 \rightarrow 4NO_2 + O_2$

This is a first order reaction.

∴ rate = $k[N_2O_5]$;

$[N_2O_5] = \text{rate}/k = \frac{1.02 \times 10^{-4}}{3.4 \times 10^{-5}} = 3$

26. (c) : For the reaction, $2A + B_2$ □ $2AB$,

Rate $\propto [A]^x[B_2]^y$.

On substituting the given data, we get

From experiment 1,

$1.6 \times 10^{-4} \propto [0.50]^x [0.50]^y$ ...(i)

From experiment 2,

$3.2 \times 10^{-4} \propto [0.50]^x [1.00]^y$ ...(ii)

From experiment 3,

$3.2 \times 10^{-4} \propto [1.00]^x [1.00]^y$ ...(iii)

On dividing equation (iii) by (ii), we get ,

$$1 = \left[\frac{1.00}{0.50}\right]^x \Rightarrow 1 = 2^x \Rightarrow 2^0 = 2^x \Rightarrow x = 0$$

Now, divide equation (ii) by equation (i) we get,

$$2 = \left[\frac{1.00}{0.50}\right]^y \Rightarrow 2 = 2^y \Rightarrow y = 1$$

Thus, rate equation is :

Rate = $k[A]^0[B_2]^1 = k[B_2]$

27. (a) : For a general reaction,

$xA + yB + zC \rightarrow$ product, the order of reaction is $x + y + z$. Since three molecules undergo change in concentration, therefore it is a third order reaction.

28. (c) : $A + B \rightarrow C$

Let rate = $k[A]^x[B]^y$

where order of reaction is $(x + y)$.

Putting the values of exp. 1, 2, and 3, we get following equations.

$0.10 = k[0.012]^x[0.035]^y$ ...(i)

$0.80 = k[0.024]^x[0.070]^y$ ...(ii)

$0.10 = k[0.024]^x[0.035]^y$ ...(iii)

Dividing (ii) by (iii), we get

$$\frac{0.80}{0.10} = \left(\frac{0.070}{0.035}\right)^y \Rightarrow 2^y = 8 \Rightarrow y = 3$$

Keeping $[A]$ constant, $[B]$ is doubled, rate becomes 8 times.

Dividing eq. (iii) by eq. (i), we get

$$\frac{0.10}{0.10} = \left(\frac{0.024}{0.012}\right)^x \Rightarrow 2^x = 1 \Rightarrow x = 0$$

Keeping $[B]$ constant, $[A]$ is doubled, rate remains unaffected. Hence, rate is independent of $[A]$.

rate $\propto [B]^3$.

29. (c) : For a first order reaction,

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

$$\Rightarrow t = \frac{2.303}{4.606 \times 10^{-3}\ \text{s}^{-1}}\log\left(\frac{2}{0.2}\right) = \frac{2.303 \times 10^3}{4.606} = 500\ \text{s}$$

30. (d) : For 1st order reaction,

$$t = \frac{2.303}{k}\log\frac{a}{a-x} = \frac{2.303}{k}\log\frac{100}{100-99}$$

$$= \frac{2.303}{k}\log 10^2 = \frac{2.303}{k} \times 2 \times \log 10 = \frac{4.606}{k}$$

31. (d) : For a first order reaction, $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t}$

$$2.303 \times 10^{-3} = \frac{2.303}{t}\log\frac{40}{10}$$

$$t = \frac{1}{10^{-3}}\log 2^2 = \frac{2}{10^{-3}}\log 2 = \frac{2}{10^{-3}} \times 0.3010 = 602\ \text{s}$$

32. (b) : For the first order reaction, $t_{1/2} = \frac{0.693}{k}$ which is independent of initial concentration $[A]_0$.

For second order reaction, $t_{1/2} = \frac{1}{k[A]_0}$

Half-life depends on initial concentration of reactant.

33. (b) : $(t_{1/2})_{zero} = \frac{[A]_0}{2k}$

As the half-life of a zero order reaction is directly proportional to initial concentration.

∴ If $[A]_0$ = doubled then, $t_{1/2}$ = doubled.

34. (a) : For a first order reaction,

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]_t} \quad \text{or} \quad 10^{-2} = \frac{2.303}{t}\log\frac{20}{5}$$

$$10^{-2} = \frac{2.303 \times 0.6020}{t} \quad \text{or } t = 138.6\ \text{sec}$$

35. (c) : For a first order reaction, $A \rightarrow$ Products and for concentration of the reactant at two different times,

$$k = \frac{2.303}{t_2 - t_1} \log \frac{[A]_1}{[A]_2}$$

$$\therefore k = \frac{2.303}{t_2 - t_1} \log \frac{(\text{rate})_1}{(\text{rate})_2} \qquad (\because \text{rate} \propto [A])$$

$$k = \frac{2.303}{(20-10)} \log\left(\frac{0.04}{0.03}\right) = 0.0287 \text{ sec}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287 \text{ sec}^{-1}} = 24.14 \text{ sec}$$

36. (d) : Half-life period of a first order reaction is independent of initial concentration,

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

37. (a) : As $t_{75\%} = 2 \times t_{50\%}$, the order of the reaction is one.

38. (c) : Fall of concentration from 1.28 mg L^{-1} to 0.04 mg L^{-1} requires 5 half-lives.

$\therefore$ Time required $= 5 \times t_{1/2} = 5 \times 138 = 690$ s

39. (b) : Given, $t_{1/2} = 1386$ s

For a first order reaction,

$$t_{1/2} = \frac{0.693}{k} \quad (k = \text{rate constant})$$

$$\Rightarrow 1386 = \frac{0.693}{k} \quad \Rightarrow k = 5 \times 10^{-4} \text{ s}^{-1} = 0.5 \times 10^{-3} \text{ s}^{-1}$$

40. (a) : For a first order reaction,

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

$$k = \frac{2.303}{60} \log \frac{100}{40} = \frac{2.303}{60} \times \log 2.5 = 0.0153$$

$$\text{Again, } t_{1/2} = \frac{2.303}{k} \log \frac{100}{50} = \frac{2.303}{0.0153} \times \log 2 = 45.31 \text{ min.}$$

41. (c) : For a 1st order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$\text{At } t_{1/2},\ k = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{a - \frac{a}{2}}$$

$$\text{or } t_{1/2} = \frac{2.303}{k} \log_{10} 2 = \frac{\ln 2}{k}$$

42. (d) : $A \longrightarrow B$

Rate of reaction $= 2 \times 10^{-5}$ mol L^{-1} s^{-1}

$\Rightarrow$ order of reaction is $n = 1$, rate $= k[A]^n = k[A]$

k is the rate constant.

$[A] = 0.01$ M

$$\Rightarrow k = \frac{2 \times 10^{-5}}{0.01} = 2 \times 10^{-3},\ k = \frac{0.693}{t_{1/2}}$$

$$t_{1/2} = \frac{0.693}{2 \times 10^{-3}} = 346.5 \approx 347 \text{ s}$$

43. (b) : Rate $\left(\frac{dx}{dt}\right) = kC$

i.e., $1.5 \times 10^{-2} = k \times 0.5$ or, $k = \frac{1.5 \times 10^{-2}}{0.5}$

For first order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693 \times 0.5}{1.5 \times 10^{-2}} = 23.1 \text{ min}$$

44. (a) :

In case I		In case II	
$A \rightarrow$	B	$A \rightarrow$	B
0.8	0	0.9	0
0.2	0.6	0.225	0.675
1	3	1	3

The time taken for the completion of same fraction of change is independent of initial concentration.

45. (c) : For the first order reaction, rate constant is given by, $k = \frac{1}{t} \ln \frac{a}{a-x}$

a = initial concentration, $(a - x)$ = concentration at t time

At $t = t_{1/2}$, $x = a/2$

$$\Rightarrow k_1 = \frac{1}{t_{1/2}} \ln \frac{a}{a - a/2} \Rightarrow k_1 = \frac{1}{t_{1/2}} \ln 2$$

$$\Rightarrow k_1 = \frac{0.693}{t_{1/2}}$$

Therefore, $t_{1/2}$ is independent of initial concentration.

46. (b) : According to Arrhenius equation,

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

$$\log \frac{k_2}{1.6 \times 10^6} = 0;\ \frac{k_2}{1.6 \times 10^6} = 1$$

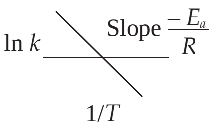
$k_2 = 1.6 \times 10^6 \text{ s}^{-1}$

47. (b) : A catalyst provides an alternate path to the reaction which has lower activation energy.

48. (a) : According to Arrhenius equation,

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

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



Hence, if ln k is plotted against $1/T$, slope of the line will be $-\frac{E_a}{R}$.

49. (a) : $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$k_2 = 2k_1$, $T_1 = 20 + 273 = 293$ K

or $T_2 = 35 + 273 = 308$ K

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

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{293} - \frac{1}{308}\right)$$

$$0.3010 = \frac{E_a}{19.147} \times \frac{\square 15}{293 \times 308}$$

$E_a = 34673\ \text{J mol}^{-1} = 34.7\ \text{kJ mol}^{-1}$

50. (b) : At 10°C rise, rate increases by 2.

$$\frac{r_{100°\text{C}}}{r_{10°\text{C}}} = 2^{\left(\frac{100-10}{10}\right)} = 2^9 = 512\ \text{times}$$

51. (b, d) : $k_1 = Ae^{-E_a/RT_1}$, $k_2 = Ae^{-E_a/RT_2}$

$\ln k_1 = \ln A - E_a/RT_1$ ...(i)

$\ln k_2 = \ln A - E_a/RT_2$ ...(ii)

From eq.(i) and (ii), we have

$$\ln k_2 - \ln k_1 = \ln A - \frac{E_a}{RT_2} - \ln A + \frac{E_a}{RT_1}$$

$$\Rightarrow \ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Rightarrow \ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

52. (a) : Rate constant is independent of the initial concentration of the reactants. It has a constant value at fixed temperature. According to Arrhenius equation, the value of rate constant can be increased by increasing the temperature.

53. (b) : $k_1 = 10^{16}\, e^{-2000/T}$, $k_2 = 10^{15}\, e^{-1000/T}$

When, $k_1 = k_2$, $10^{16}\, e^{-2000/T} = 10^{15} e^{-1000/T}$

or $10e^{-2000/T} = e^{-1000/T}$

Taking natural logarithm of both sides, we get

$$\ln 10 - \frac{2000}{T} = \frac{-1000}{T}$$

or $$2.303 - \frac{2000}{T} = \frac{-1000}{T}$$

or $\frac{1000}{T} = 2.303$ or $T = \frac{1000}{2.303}\ \text{K}$

54. (c) : On plotting $\log k$ *vs* $1/T$, we get a straight line, the slope indicates the value of activation energy.

55. (c) : Activation energy is the minimum amount of energy required to convert reactant into product. Activation energy for reverse reaction can be less than or more than E_a depending whether the reaction is exothermic or endothermic.

56. (c) : According to $k = Ae^{-E_a/RT}$ (Arrhenius equation), the activation energy of a reaction in the presence of enzyme is different from E_a obtained in laboratory.

57. (a) : Enzymes act like catalyst in biochemical reactions. Presence of an enzyme increases the rate of reaction by lowering the activation energy of the reactant.

58. (a) : According to Arrhenius equation :

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

where E_a = activation energy

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

k_1 and k_2 are rate constants of the reaction at two different temperatures T_1 and T_2 respectively.

59. (b) : Since the enzymes are regarded as biological catalysts, therefore their action increases the rate of biological reaction.

60. (d) : Collision frequency ∝ no. of reacting molecules or atoms

Higher the concentration of reactant molecules, higher is the probability of collision and so the collision frequency.