Chapter 18. Chemical Kinetics

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

2. 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)

3. 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)

4. 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)

5. 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)

6. 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)*

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

8. 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)*

9. 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)

10. For a reaction between A and B the order with respect to A is 2 and the other 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)

11. 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)

12. In a reaction, $A + B \rightarrow$ 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)

13. 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)*

14. 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) $\ln \dfrac{k_2}{k_1} = -\dfrac{E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

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

   (c) $\ln \dfrac{k_2}{k_1} = -\dfrac{E_a}{R}\left(\dfrac{1}{T_2} + \dfrac{1}{T_1}\right)$

   (d) $\ln \dfrac{k_2}{k_1} = \dfrac{E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$ *(Mains 2012)*

15. 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)*

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

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

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

   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)*

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. 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)*

19. 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)*

20. 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)*

21. 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)*

22. For the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$, if

   $$\dfrac{d[NH_3]}{dt} = 2\times10^{-4} \text{ mol } L^{-1}s^{-1}, \text{ the value of}$$

   $$\dfrac{-d[H_2]}{dt} \text{ would be}$$

   (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)*

23. In the reaction,
   $BrO_{3(aq)}^- + 5Br_{(aq)}^- + 6H^+ \rightarrow 3Br_{2(l)} + 3H_2O_{(l)}$.
   The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as

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

(b) $\dfrac{d[\text{Br}_2]}{dt} = \dfrac{5}{3}\dfrac{d[\text{Br}^-]}{dt}$

(c) $\dfrac{d[\text{Br}_2]}{dt} = \dfrac{3}{5}\dfrac{d[\text{Br}^-]}{dt}$

(d) $\dfrac{d[\text{Br}_2]}{dt} = -\dfrac{3}{5}\dfrac{d[\text{Br}^-]}{dt}$ *(2009)*

24. 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)

25. 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)

26. The bromination of acetone that occurs in acid solution is represented by this equation.
$\text{CH}_3\text{COCH}_{3(aq)} + \text{Br}_{2(aq)} \rightarrow$
   $\text{CH}_3\text{COCH}_2\text{Br}_{(aq)} + \text{H}^+_{(aq)} + \text{Br}^-_{(aq)}$
These kinetic data were obtained for given reaction concentrations.

Initial concentrations, *M*

[CH$_3$COCH$_3$]	[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$_2$, Ms^{-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 $= k\,[\text{CH}_3\text{COCH}_3][\text{Br}_2][\text{H}^+]^2$
(b) Rate $= k\,[\text{CH}_3\text{COCH}_3][\text{Br}_2][\text{H}^+]$
(c) Rate $= k\,[\text{CH}_3\text{COCH}_3][\text{H}^+]$
(d) Rate $= k\,[\text{CH}_3\text{COCH}_3][\text{Br}_2]$ *(2008)*

27. 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) $\dfrac{1000}{2.303}$ K

(c) 1000 K   (d) $\dfrac{2000}{2.303}$ K   *(2008)*

28. 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)

29. 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) $\dfrac{\log 2}{k}$ (b) $\dfrac{\log 2}{k\sqrt{0.5}}$

(c) $\dfrac{\ln 2}{k}$ (d) $\dfrac{0.693}{0.5k}$ *(2007)*

30. The reaction of hydrogen and iodine monochloride is given as:
   $\text{H}_{2(g)} + 2\text{ICl}_{(g)} \rightarrow 2\text{HCl}_{(g)} + \text{I}_{2(g)}$
This reaction is of first order with respect to $\text{H}_{2(g)}$ and $\text{ICl}_{(g)}$, following mechanisms were proposed.
Mechanism A :
   $\text{H}_{2(g)} + 2\text{ICl}_{(g)} \rightarrow 2\text{HCl}_{(g)} + \text{I}_{2(g)}$
Mechanism B :
   $\text{H}_{2(g)} + \text{ICl}_{(g)} \rightarrow \text{HCl}_{(g)} + \text{HI}_{(g)}$; slow
   $\text{HI}_{(g)} + \text{ICl}_{(g)} \rightarrow \text{HCl}_{(g)} + \text{I}_{2(g)}$; 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)*

31. Consider the reaction: $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}$
The equality relationship between

$\dfrac{d[\text{NH}_3]}{dt}$ and $-\dfrac{d[\text{H}_2]}{dt}$ is

(a) $\dfrac{d[\text{NH}_3]}{dt} = -\dfrac{d[\text{H}_2]}{dt}$

(b) $\dfrac{d[\text{NH}_3]}{dt} = -\dfrac{1}{3}\dfrac{d[\text{H}_2]}{dt}$

(c) $+\dfrac{d[\text{NH}_3]}{dt} = -\dfrac{2}{3}\dfrac{d[\text{H}_2]}{dt}$

(d) $+\dfrac{d[\text{NH}_3]}{dt} = -\dfrac{3}{2}\dfrac{d[\text{H}_2]}{dt}$ *(2006)*

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

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

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

33. 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)*

34. For a first order reaction $A \rightarrow B$ 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)*

35. 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)*

36. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $k = A \cdot e^{-E^*/RT}$. Activation energy (E^*) of the reaction can be calculated by plotting

(a) $k\ vs\ T$ (b) $k\ vs\ \dfrac{1}{\log T}$

(c) $\log k\ vs\ \dfrac{1}{T}$ (d) $\log k\ vs\ \dfrac{1}{\log T}$

(2003)

37. 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)*

38. 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)*

39. The activation energy for a simple chemical reaction $A \rightleftharpoons B$ 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)*

40. $2A \rightarrow B + C$ 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)*

41. $3A \rightarrow 2B$, rate of reaction $\dfrac{+d[B]}{dt}$ is equal to

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

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

42. When a bio-chemical 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)*

43. For the reaction; $2N_2O_5 \rightarrow 4NO_2 + O_2$ 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)

44. 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)

45. For the reaction $H^+ + BrO_3^- + 3Br^- \rightarrow 5Br_2 + H_2O$ which of the following relation correctly represents the consumption and formation of products.

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

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

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

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

46. 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)

47. 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)

48. The experimental data for the reaction,
  $2A + B_2 \rightarrow 2AB$ 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)

49. For the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2 HI_{(g)}$, the rate of reaction is expressed as
  (a) $\dfrac{\Delta[H_2]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[I_2]}{\Delta t} = -\dfrac{\Delta[HI]}{\Delta t}$
  (b) $-\dfrac{\Delta[I_2]}{\Delta t} = -\dfrac{\Delta[H_2]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[HI]}{\Delta t}$
  (c) $\dfrac{\Delta[I_2]}{\Delta t} = \dfrac{\Delta[H_2]}{\Delta t} = \dfrac{\Delta[HI]}{2\Delta t}$
  (d) none of these.   *(1997)*

50. The given reaction
  $2 FeCl_3 + SnCl_2 \rightarrow 2 FeCl_2 + SnCl_4$
  is an example of
  (a) third order reaction
  (b) first order reaction
  (c) second order reaction
  (d) none of these.   *(1996)*

51. 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)

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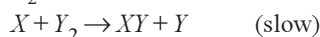 (c) decreases
  (d) either (a) or (c).   *(1994)*

Answer Key

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

EXPLANATIONS

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

$X_2 \rightleftharpoons X + X$ (fast)

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

Slow step is the rate determining step.

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

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

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

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 = $\dfrac{1}{2} + 1 = \dfrac{3}{2} = 1.5$

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

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

$10^{-2} = \dfrac{2.303}{t}\log\dfrac{20}{5}$

$10^{-2} = \dfrac{2.303 \times 0.6020}{t}$

$t = 138.6$ sec

3. (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.

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

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

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

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

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

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

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

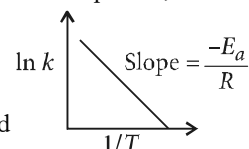$\therefore$ Concentration of $B = k \times t$

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

7. (a) : According to Arrhenius equation,

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

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

Hence, if $\ln k$ is plotted

against $1/T$, slope of the line will be $-\dfrac{E_a}{R}$.

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

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

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

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

or $T_2 = 35 + 273 = 308$ K

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

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

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

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

10. (c) : Rate$_1 = k[A]^2 [B]^3$

Rate$_2 = k[2A]^2[2B]^3$

Rate$_2 = 32k[A]^2[B]^3$

$\therefore$ Rate$_2 = 32$(Rate$_1$)

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

12. (d) :

$[A]$	$[B]$	Rate	
x	y	R	... (i)
x	$2y$	$2R$	... (ii)
$2x$	$2y$	$8R$	... (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),

$\dfrac{(2y)^b}{(y)^b} = \dfrac{2R}{R}$ or $(2)^b = 2$

Thus $b = 1$

From data of (iii) experiment,

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

From eqn. (v) and (vi),

$$\frac{(2x)^a}{(x)^a} = \frac{8R}{2R} \quad \text{or} \quad (2)^a = 4$$

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

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

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

14. (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

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

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

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

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

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

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

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

17. (a) : The units are mol L^{-1} s^{-1}.

18. (c) : Fall of concentration from 1.28 mg L^{-1} to 0.04 mg L^{-1} requires 5 half-lives.
∴ Time required $= 5 \times t_{1/2} = 5 \times 138 = 690$ s

19. (b) : $N_2O_{5(g)} \rightarrow 2NO_{2(g)} + 1/2O_{2(g)}$
For the given reaction the rate law may be written as :

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

given that $\dfrac{-d[N_2O_5]}{dt} = 6.25 \times 10^{-3}$ mol L^{-1} 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 $\dfrac{d[O_2]}{dt} = \dfrac{6.25 \times 10^{-3}}{2} = 3.125 \times 10^{-3}$ molL^{-1}s^{-1}

20. (d) : Let the rate of reaction be given by :
rate $= k[A]^a[B]^b$.
Now consider II and III where $[A]$ is constant.

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

$$\frac{1}{4} = \left(\frac{1}{2}\right)^b$$
$b = 2$
Now consider I and IV

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

$$\frac{1}{4} = \left(\frac{1}{4}\right)^a$$
$a = 1$ ∴ Rate $= k[A][B]^2$

21. (a) : Rate constant is independent of the initial concentration of the reactants. It has a constant value at fixed temperature. Hence the value of rate constant can be increased by increasing the temperature.

22. (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, $\dfrac{d[NH_3]}{dt} = 2 \times 10^{-4}$ mol L^{-1} s^{-1}

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

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

23. (d) : For the given reaction,
$BrO_{3(aq)}^- + 5Br^-_{(aq)} + 6H^+ \rightarrow 3Br_{2(l)} + 3H_2O_{(l)}$
Rate of reaction in terms of Br_2 and Br^- is,

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

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

24. (b) : Given, $t_{1/2} = 1386$ s
For a first order reaction,

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

$$\Rightarrow 1386 = \frac{0.693}{k}$$

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

25. (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 $= k[A][B]^2$

26. (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. The probable rate law for the reaction will be : $k[CH_3COCH_3][H^+]$

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

The temperature at which $k_1 = k_2$ will be

$$10^{16}e^{-2000/T} = 10^{15}e^{-1000/T}$$

$$\Rightarrow \frac{e^{-2000/T}}{e^{-1000/T}} = \frac{10^{15}}{10^{16}}$$

$$\Rightarrow e^{\frac{-1000}{T}} = 10^{-1} \Rightarrow \log_e e^{\frac{-1000}{T}} = \log_e 10^{-1}$$

$$\Rightarrow 2.303\log_{10} e^{\frac{-1000}{T}} = 2.303 \times \log_{10} 10^{-1}$$

$$\Rightarrow \frac{-1000}{T} \times \log_{10} e = -1 \quad \therefore \quad T = \frac{1000}{2.303} \text{ K}$$

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

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

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

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

$$= 45.31 \text{ min.}$$

29. (c) : For a 1st order kinetics,

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

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

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

30. (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 $ICl_{(g)}$.

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

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

Hence $\dfrac{d[NH_3]}{dt} = -\dfrac{2}{3}\dfrac{d[H_2]}{dt}$

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

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

Negative sign shows the decrease in concentration.

33. (b) : Rate of reaction $= k[A_0]^{\alpha}[B_0]^{\beta}$

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

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

$[B] = [2B_0]$

$$\frac{r_1}{r_2} = \frac{k[A_0]^{\alpha}[B_0]^{\beta}}{[A_0]^{\alpha}[2B_0]^{\beta}}; \quad 4 = \left(\frac{1}{2}\right)^{\beta} = \beta = -2$$

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

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

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

$k \rightarrow$ rate or velocity constant

$[A] = 0.01$ M

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

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

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

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

For first order reaction,

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

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

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

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

Hence order of reaction must be zero.

38. (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.

39. (c) : Activation energy is the minimum amount of energy required to convert reactant into product. It is affected by the presence of catalyst.

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

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

$\therefore$ The rate is independent of concentration.

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

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

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

42. (c) : For a given chemical reaction,

$k = Ae^{-E_a/RT}$ (Arrhenius equation)

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

This is a first order reaction.

∴   rate = k [N$_2$O$_5$] ;

$$[\text{N}_2\text{O}_5] = \text{rate}/k = \frac{1.02 \times 10^{-4}}{3.4 \times 10^{-5}} = 3$$

44. (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.

45. (a) : $-\dfrac{1}{3}\dfrac{d[\text{Br}^-]}{dt} = +\dfrac{1}{5}\dfrac{d[\text{Br}_2]}{dt}$ = rate of reaction

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

46. (c) : For the first order reaction, rate constant is given by $k_1 = \dfrac{1}{t}\ln\dfrac{a}{a-x}$

a = initial concentration, x = concentration at t time
At $t = t_{1/2}$, $x = a/2$

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

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

47. (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 J K^{-1} mole^{-1}
k_1 and k_2 are rate constants of the reaction at two different temperatures T_1 and T_2 respectively.
Therefore, $t_{1/2}$ is independent of initial concentration.

48. (c) : For the reaction $2A + B_2 \rightleftharpoons 2AB$,
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 ,

$1 = \left[\dfrac{1.00}{0.50}\right]^x$ or, $1 = 2^x$ or $2^0 = 2^x$ or $x = 0$

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

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

Thus rate equation is : Rate = $k[A]^0 [B_2]^1 = k[B_2]$.

49. (b) : For H$_{2(g)}$ + I$_{2(g)} \rightleftharpoons$ 2HI$_{(g)}$, the rate of reaction is

$$-\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{I}_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[\text{HI}]}{\Delta t}$$

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

50. (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.

51. (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 (i), we get

$\dfrac{0.80}{0.10} = \left(\dfrac{0.070}{0.035}\right)^y$

$\Rightarrow 2^y = 8 \Rightarrow y = 3.$
Keeping [A] constant, [B] is doubled, rate becomes 8 times.
Dividing eq. (iii) by eq. (i), we get

$\dfrac{0.10}{0.10} = \left(\dfrac{0.024}{0.012}\right)^x$

$\Rightarrow 2^x = 1$ $x = 0.$
Keeping [B] constant, [A] is doubled, rate remains unaffected. Hence rate is independent of [A].
rate $\propto [B]^3$.

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