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Tel: 49842349/ 49842350

Edited By

Sanjay Kumar Vishwakarma
Diksha Jhanwar

Typeset By

DISHA DTP Team

Write To Us At

feedback_disha@aiets.co.in

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CONTENTS

Class XI

Class XII

3

Chemical Kinetics

1. A reaction, $3X(g) \rightarrow 2Y(g) + Z(g)$ takes place in a closed vessel. What is the rate of formation of Y (in mol L^{-1}) if the rate of disappearance of X is 7.2×10^{-3} mol L^{-1} s^{-1}?

(a) 3.6×10^{-3} (b) 4.8×10^{-3}
(c) 2.4×10^{-3} (d) 1.2×10^{-3}

2. Consider a gas phase reaction which occurs in a closed vessel

$2A \rightarrow 4B + C$

The concentration of B is found to be increased by 5×10^{-3} mol L^{-1} in 10 seconds.

The rate of disappearance of A (in mol L^{-1} s^{-1}) is

(a) 4.75×10^{-4} (b) 7.5×10^{-4}
(c) 1.25×10^{-4} (d) 2.5×10^{-4}

3. Consider the reaction carried out at T(K)

$A(g) + B(g) \rightarrow C(g)$

The rate law for this reaction is $r = k[A]^1 [B]^2$. The concentration of A in experiment 2 and rate in experiment 3 shown as x and z in the table, x and z are respectively

Experiment	$\frac{[A]}{\text{mol } L^{-1}}$	$\frac{[B]}{\text{mol } L^{-1}}$	Initial rate (mol. $L^{-1}s^{-1}$)
1	0.05	0.05	R
2	x	0.05	2R
3	0.20	0.10	z

(a) $x = 0.10$ $z = 8R$ (b) $x = 0.05$ $z = 4R$
(c) $x = 0.10$ $z = 16R$ (d) $x = 0.20$ $z = 16R$

4. A first order reaction has the rate constant of 1.15×10^{-3} s^{-1}. The time required to reduce 10 g of reactant to 6 g is $x \times 10^2$ sec. What is the approximate value of x?

($\log 5 = 0.7, \log 3 = 0.48$)

(a) 2.2 (b) 3.3 (c) 4.4 (d) 1.1

5. The rate constant, k of a zero order reaction $\xrightarrow[1130K]{Pt} 2NH_3(g)\, N_2(g) + 3H_2(g)$ is $y \times 10^{-4}$ mol L^{-1} s^{-1}. The rate of formation of hydrogen (in mol L^{-1} s^{-1}) is

(a) $y \times 10^{-4}$ (b) $2y \times 10^{-4}$
(c) $3y \times 10^{-4}$ (d) $\frac{y}{3} \times 10^{-4}$

6. For the reaction $2A + 3B + \frac{3}{2}C \rightarrow 3P$, which statement is **correct** ?

(a) $\frac{dn_A}{dt} = \frac{3}{2}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$

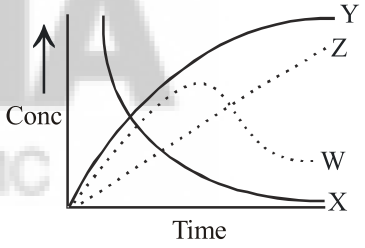
(b) $\frac{dn_A}{dt} = \frac{dn_B}{dt} = \frac{dn_C}{dt}$

(c) $\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{4}{3}\frac{dn_C}{dt}$

(d) $\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$

7. For the reaction A + B $\longrightarrow$ C + D. The variation of the concentration of the products is given by the curve

Tricky



(a) Z (b) Y (c) W (d) X

8. A possible mechanism for the gaseous reaction $2H_2 + 2NO \rightarrow 2H_2O + N_2$ is

Step 1: $2NO \rightleftharpoons N_2O_2$

Step 2: $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)

Step 3: $N_2O + H_2 \rightarrow N_2 + H_2O$

The rate law for this reaction is

(a) $R = k[NO]^2 [H_2]^2$ (b) $R = k[NO] [H_2]^2$
(c) $R = k[NO]^{1/2} [H_2]$ (d) $R = k[NO]^2 [H_2]$

9. The rate law for the decomposition of hydrogen iodide is $-\frac{d[HI]}{dt} = k[HI]^2$. The units of rate constant k are

(a) L mol^{-1} s^{-1} (b) L^{-1} mol s^{-1}
(c) L^2 mol^{-2} s^{-1} (d) $L^{1/2}$ $mol^{-1/2}$ s^{-1}

10. What is the concentration (in mol L^{-1}) of the product after 20 s in the following reaction. Given that $A \rightarrow 3B$, rate = $k[A]^\circ$

Time(s)	**Concentration of the reactant (mol L^{-1})**
0	0.1
15	0.05
20	0.1-x

(a) 6.6×10^{-2} (b) 1.32×10^{-1}
(c) 1.98×10^{-1} (d) 2.2×10^{-2}

11. The rate constant for a zero order reaction $A \rightarrow$ products is 0.0030 mol L^{-1} s^{-1}. How long it will take for the initial concentration of A to fall from 0.10 M to 0.075M?

Tricky

(a) 10s (b) 20s
(c) 8.33s (d) 1.33s

12. For the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, the experimental data suggest, rate = $k[H_2][Br_2]^{1/2}$. The molecularity and order of the reaction are respectively

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

13. For a chemical reaction $t_{1/2}$ is 2.5 hours at room temperature. How much of the reactant will be left after 7.5 hours if initial weight of reactant was 160 g?

Critical Thinking

(a) 10 g (b) 40 g (c) 80 g (d) 20 g

14. A following mechanism has been proposed for a reaction

$2A + B \rightarrow D + E$
$A + B \rightarrow C + D$ (slow)
$A + C \rightarrow E$ (fast)

The rate law expression for the reaction is:

(a) $r = k[A]^2[B]$ (b) $r = k[A][B]$
(c) $r = k[A]^2$ (d) $r = k[A][C]$

15. For a first order reaction, a plot of log (a – x) against time is a straight line with a negative slope equal to

(a) $\frac{-k}{2.303}$ (b) $-2.303\,k$
(c) $\frac{2.303}{k}$ (d) $-\frac{E_a}{2.303\,R}$

16. Rate constants in the following reaction are

Reaction 1 : $A \xrightarrow{\text{catalyst 1}} P_1, k_1 = 1 s^{-1}$

Reaction 2 :

$A \xrightarrow{\text{catalyst 2}} P_2, k_2 = 0.1\ L\ mol^{-1} s^{-1}$

Reaction 3 :

$A \xrightarrow{\text{catalyst 3}} P_3, k_3 = 0.01\ L^2\ mol^{-2} s^{-1}$

The correct relations between the rate of the reactions at 1 M of A are

Critical Thinking

(a) $r_1 = \frac{r_3}{100}, r_2 = \frac{r_3}{10}$

(b) $r_1 = \frac{r_2}{10}, r_2 = \frac{r_3}{10}$

(c) $r_1 = 100r_3, r_2 = \frac{r_3}{10}$

(d) $r_1 = 10r_2, r_3 = \frac{r_2}{10}$

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

Critical Thinking

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

18. The reaction $2A \rightarrow 2B + C$ has a rate constant of $1.2 \times 10^{-2} s^{-1}$. Which of the following is correct?

(a) Plot of [A] vs "$\frac{1}{t}$" will be straight line
(b) Plot of $\frac{1}{[A]}$ vs t^2 will be a straight line
(c) Plot of ln[A] vs t will be a straight line
(d) Plot of [A] vs t^2 will be a straight line

19. Which statement among the following is incorrect?

(a) Unit of rate of disappearance is M s^{-1}.
(b) Unit of rate of reaction is M s^{-1}.
(c) Unit of rate constant k depends upon order of reaction.
(d) Unit of rate constant k for a first order reaction is M s^{-1}.

20. For a reaction $A + B \to P$, the following data are provided

Tricky

Entry	[A] in M	[B] in M	Initial rate (M/ s)
1	0.02	0.02	2×10^{-2}
2	0.02	0.04	4×10^{-2}
3	0.02	0.04	8×10^{-2}

The rate constant for this reaction in standard unit is

(a) 5 (b) 1.2
(c) 2.4×10^{-4} (d) 50

21. The rate law for the reaction below is given by the expression k [A][B]

A + B → Product

If the concentration of B is increased from 0.1 to 0.3 mole, keeping the value of A at 0.1 mole, the rate constant will be:

(a) 3k (b) 9k (c) k/3 (d) k

22. The order of a reaction, with respect to one of the reacting component Y, is zero. It implies that:

(a) the reaction is going on at a constant rate
(b) the rate of reaction does not vary with temperature
(c) the reaction rate is independent of the concentration of Y
(d) the rate of formation of the activated complex is zero

23. **Statement I :** Molecularity is defined as the number of reacting species taking part in a complex reaction,

Statement II : Molecularity helps in understanding the mechanism of reaction.

(a) Both statement I and II are correct.
(b) Both statement I and II are incorrect.
(c) Statement I is correct but statement II is incorrect.
(d) Statement II is correct but statement I is incorrect.

24. **Assertion :** The order of a reaction can have fractional value.

Reason : The order of a reaction cannot be written from balanced equation of a reaction.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If the Assertion is incorrect and Reason is correct.

25. Match Column-I with Column-II.

	Column-I		**Column-II**
(A)	Number of collisions per second per unit volume of the reaction mixture.	(p)	Effective collisions.
(B)	Fraction of molecules with energies equal to or greater than E_a	(q)	Collision frequency
(C)	Molecules for which Rate = $Z_{AB} e^{-E_a/RT}$ shows significant deviations	(r)	$e^{-E_a/RT}$
(D)	Collision in which, molecules collide with sufficient K.E. and proper orientation.	(s)	Complex molecules

(a) A – (q), B – (r), C – (s), D – (p)
(b) A – (r), B – (q), C – (s), D – (p)
(c) A – (q), B – (s), C – (r), D – (p)
(d) A – (q), B – (r), C – (p), D – (s)

26. For a reaction, the rate constant is expressed as $k = Ae^{-40000/T}$. The energy of the activation is

(a) 40000 cal (b) 88000 cal
(c) 80000 cal (d) 8000 cal

27. A catalyst lowers the activation enegy of a reaction from 20 kJ mol^{-1} to 10 kJ mol^{-1}. The temperature at which the uncatalyzed reaction will have the same rate as that of the catalyzed at 27 °C is

(a) – 123 °C (b) 327 °C
(c) 32.7 °C (d) + 23 °C

28. Find the correct equation among the following.

(a) $\ln k - \ln A = \dfrac{E_a}{RT}$ (b) $k = \dfrac{AE_a}{RT}$

(c) $\ln k + \ln A = \dfrac{E_a}{RT}$ (d) $\dfrac{E_a}{RT} = \ln A - \ln k$

29. If benzene diazonium chloride undergoes first order decomposition at T(K) with a rate constant of 6.93×10^{-2} min^{-1}, the time for completion of 90% of the reaction (in min) is (nearest integer) (log 2 = 0.30, log 3 = 0.477)

(a) 15 (b) 30 (c) 33 (d) 43

30. The time required for completion of 93.75% of a first order reaction is x minutes. The half life of it (in minutes) is
(a) x/8 (b) x/2 (c) x/4 (d) x/3

31. A $\rightarrow$ products, is a first order reaction. The time required to decompose A to half its initial amount is 60 minutes. The rate constant of the reaction (in s^{-1}) is
(a) 1.05×10^{-2} (b) 1.15×10^{-2}
(c) 1.25×10^{-4} (d) 1.92×10^{-4}

32. In the reaction, A $\rightarrow$ products, If the concentration of the reactant is doubled rate of the reaction remains unchanged. The order of the reaction with respect to A is
(a) 1 (b) 2 (c) 0.5 (d) 0

33. The half-life of a reaction is inversely proportional to the square of the initial concentration of the reactant. Then the order of the reaction is
(a) 0 (b) 1 (c) 2 (d) 3

34. For a reaction $A \xrightarrow{K_1} B \xrightarrow{K_2} C$
If the rate of formation of B is set to be zero then the concentration of B is given by :
(a) $K_1K_2[A]$ (b) $(K_1 - K_2)[A]$
(c) $(K_1 + K_2)[A]$ (d) $(K_1/K_2)[A]$

35. In a reaction, 2A $\rightarrow$ products, the concentration of A decreases from 0.50 M to 0.38 M in 10 min. What is the rate of reaction (in M s^{-1}) during this interval?
(a) 0.012 (b) 0.024
(c) 2×10^{-3} (d) 2×10^{-4}

36. **Assertion:** The rate of the reaction is the rate of change of concentration of a reactant or a product.
Reason: Rate of reaction remains constant during the course of reaction.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If the Assertion is incorrect and Reason is correct.

37. A reaction takes place in various steps. The rate constant for first, second, third and fifth steps are k_1, k_2, k_3 and k_5 respectively. The overall rate constant is given by $k = \frac{k_2}{k_3}\left(\frac{k_1}{k_5}\right)^{1/2}$
If activation energy are 40, 60, 50 and 10 kJ/mol respectively, the overall energy of activation (kJ/mol) is :
Toughnut
(a) 10 (b) 20
(c) 25 (d) none of these

38. The rate of reaction is doubled for every 10°C rise in temperature. The increase in reaction rate as a result of temperature rise from 10°C to 100°C is
(a) 112 (b) 512 (c) 400 (d) 614

39. For the reaction system :
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO, the rate of reaction will
(a) diminish to one-eighth of its initial value
(b) increase to eight times of its initial value
(c) increase to four times of its initial value
(d) diminish to one-fourth of its initial value

40. For a zero-order reaction, the correct expression for rate constant (k) at half-life time ($t_{1/2}$) is (R_0 = initial concentration of reactant)
(a) $k = \frac{2.303}{t_{1/2}} \log \frac{[R_0]}{\frac{[R_0]}{2}}$
(b) $k = \frac{2.303}{t} \log \frac{[R_0]}{[R_0]}$
(c) $k = \frac{[R_0] - \frac{1}{2}[R_0]}{t_{1/2}}$
(d) $k = \frac{2.303}{(t_2 - t_1)} \log [R_0]$

41. For the reaction A + B $\rightarrow$ C, the following data were obtained

Exp	**Initial concentration**		**Initial rate**
	[A] M	**[B] M**	**(M min^{-1})**
1.	0.1	0.1	1.0×10^{-4}
2.	0.1	0.3	9.0×10^{-4}
3.	0.3	0.3	2.7×10^{-3}

The order of reaction with respect to A and B are respectively
(a) 1, 2 (b) 2, 1
(c) 1.5, 1.5 (d) 0, 3

42. For a reaction, the threshold energy is 75 kJ/mole. If the internal energy of the reactants is 20 kJ/mole, the activation energy (in kJ/mole) is
(a) 55 (b) 20 (c) 75 (d) 95

43. The graph obtained between ln k (k = Rate constant) on y-axis 1/T on x-axis is a straight line. The slope of it is -4×10^4k. The activation energy of the reaction (in kJ mol^{-1})is ($R = 8.3\ J\ K^{-1}\ mol^{-1}$)
(a) 166 (b) 332 (c) 765 (d) 382

44. For a reaction, activation energy (E_a) = 0 and rate constant $(k) = 3.2 \times 10^6\ s^{-1}$ at 300 K. What is the value of the rate constant at 310 K
(a) $3.2 \times 10^{-12}\ s^{-1}$ (b) $3.2 \times 10^6\ s^{-1}$
(c) $6.4 \times 10^{12}\ s^{-1}$ (d) $6.4 \times 10^6\ s^{-1}$

45. The minimum energy a molecule should possess in order to enter into a fruitful collision is known as
(a) reaction energy (b) collision energy
(c) activation energy (d) threshold energy

46. In the Arrhenius plot of ln k Vs $\frac{1}{T}$, a linear plot is obtained with a slope of -2×10^4 K. The energy of activation of the reaction (in kJ $mole^{-1}$) is (R value is $8.3\ J\ K^{-1}\ mol^{-1}$) Toughnut
(a) 83 (b) 166 (c) 249 (d) 332

47. A + 2B → C, the rate equation for this reaction is given as Rate = K[A][B].
If the concentration of A is kept the same but that of B is doubled what will happen to the rate itself ?
(a) halved (b) the same
(c) doubled (d) quadrupled

48. **Assertion:** The order w.r.t a reactant may be negative.
Reason: In some cases, the rate of reaction decreases as the concentration of the reactant increases.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If the Assertion is incorrect and Reason is correct.

49. A chemical reaction was carried out at 300 K and 280 K. The rate constants were found to be k_1 and k_2 respectively. then
(a) $k_2 = 4k_1$ (b) $k_2 = 2k_1$
(c) $k_2 = 0.25\ k_1$ (d) $k_2 = 0.5\ k_1$

50. **Statement I :** $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a.
Statement II : E_a can be calculated as follows

$$\log\frac{k_1}{k_2} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

(a) Both statement I and II are correct.
(b) Both statement I and II are incorrect.
(c) Statement I is correct but statement II is incorrect.
(d) Statement II is correct but statement I is incorrect.

51. Rate constant $k = 1.2 \times 10^3\ mol^{-}\ 1\ L\ s^{-1}$ and $E_a = 2.0 \times 10^2\ kJ\ mol^{-1}$. When T → ∞:
(a) $A = 2.0 \times 10^2\ kJ\ mol^{-1}$
(b) $A = 1.2 \times 10^3\ mol^{-1}\ L\ s^{-1}$
(c) $A = 1.2 \times 10^3\ mol\ L^{-1}\ s^{-1}$
(d) $A = 2.4 \times 10^3\ kJ\ mol^{-1}\ s^{-1}$

52. Which of the following reactions is **not** of the first order?
(a) Inversion of sucrose in the presence of acid
(b) Acid-catalyzed hydrolysis of ethyl acetate
(c) Hydrolysis of tertiary butyl halide using alkali
(d) Oxidation of I^- ion by $S_2O_8^{2-}$ ion

53. In the reaction A → B + C, rate constant is 0.001 Ms^{-1}. If we start with 1 M of A then conc. of A and B after 10 minutes are respectively.
(a) 0.5 M, 0.5 M (b) 0.6 M, 0.4 M
(c) 0.4 M, 0.6 M (d) 0.6 M 0.5 M

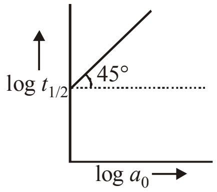
54. At 30°C, the half life for the decomposition of AB_2 is 200 s and is independent of the initial concentration of AB_2. The time required for 80% of the AB_2 to decompose is (Given: log 2 = 0.30; log 3 = 0.48)
(a) 200 s (b) 323 s (c) 467 s (d) 532 s

55. In a reaction at 27ºC, 10^{-3}% reactant molecules manage to cross over the barrier of transition state. The energy of these molecules in excess of the average value will be ($R = 2$ cal $K^{-1}\ mol^{-1}$) :

Toughnut

(a) 6.91 $k$cal mol^{-1} (b) 3.00 $k$cal mol^{-1}
(c) 4.15 $k$cal mol^{-1} (d) 5.10 $k$cal mol^{-1}

56. For a reaction $A \rightarrow$ Products, a plot of log $t_{1/2}$ versus log a_0 is shown in the figure. If the initial concentration of A is represented by a_0, the order of the reaction is



(a) one (b) zero (c) two (d) three

57. The rate constant, k for a first order reaction, $C_2H_5I(g) \rightarrow C_2H_4(g) + HI(g)$ is xs^{-1}at 600 K and $4x\ s^{-1}$ at 700 K.
The energy of activation of the reaction (in kJ mol^{-1}) is

(a) 48.16 (b) 58.16 (c) 38.16 (d) 28.16

58. For zero order reaction, a plot of $t_{1/2}$ *versus* $[A]_0$ will be

(a) a straight line passing through the origin and slope = k
(b) a horizontal line (parallel to x-axis)
(c) a straight line with slope $-k$
(d) a straight line passing through origin and slope = $\frac{1}{2k}$

59. **Assertion :** For each ten degree rise of temperature the specific rate constant is nearly doubled.
Reason : Energy-wise distribution of molecules in a gas is an experimental function of temperature.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If the Assertion is incorrect and Reason is correct.

60. For a zero order reaction $A \rightarrow$ product, a plot of [A] (on y-axis) and time (on x-axis) gave a straight line with slope equal to -3×10^{-3} M min^1 and intercept equal to 2×10^{-2} M (on y-axis). What is the rate constant (in M min^{-1}) of this reaction?

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

61. What will be the overall order of a reaction for which the rate expression is given as

Rate = $k[A]^{\frac{1}{2}}[B]^{\frac{3}{2}}$

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

62. Consider the consecutive reactions :

Tricky

$$A \xrightarrow{k=2\times10^{-5}s^{-1}} B \xrightarrow{k=8\times10^{-6}s^{-1}} C \xrightarrow{k=3\times10^{-3}s^{-1}} D$$

The rate determining step of the reaction is :

(a) $A \rightarrow B$ (b) $C \rightarrow D$
(c) $B \rightarrow C$ (d) $A \rightarrow D$

63. In the reaction of formation of sulphur trioxide by contact process $2SO_2 + O_2 \rightleftharpoons 2SO_3$ the rate of reaction was measured as $\frac{d[O_2]}{dt} = -2.5\times10^{-4}\,mol\ L^{-1}s^{-1}$. The rate of reaction is terms of $[SO_2]$ in mol $L^{-1}\ s^{-1}$ will be:

(a) -1.25×10^{-4} (b) -2.50×10^{-4}
(c) -3.75×10^{-4} (d) -5.00×10^{-4}

64. For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$, the rate equation can be expressed in two ways $-\frac{d[N_2O_5]}{dt} = k[N_2O_5]$ and $+\frac{d[NO_2]}{dt} = k'[N_2O_5]$
k and k′ are related as:

(a) $k = k'$ (b) $2k = k'$
(c) $k = 2k'$ (d) $k = 4k'$

65. The reaction $2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2$ is

(a) bimolecular and of second order
(b) unimolecular and of first order
(c) bimolecular and of first order
(d) bimolecular and of zero order

66. For a reaction of order n, the unit of the rate constant is :

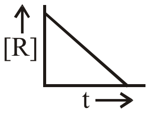
(a) $mol^{1-n}\ L^{1-n}\ s$ (b) $mol^{1-n}\ L^{2n}\ s^{-1}$
(c) $mol^{1-n}\ L^{n-1}s^{-1}$ (d) $mol^{1-n}\ L^{1-n}\ s^{-1}$

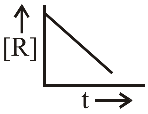
67. The activation energy of the reaction, $A + B \rightarrow C + D + 38$ kcal is 20 kcal. What would be the activation energy of the following reaction.

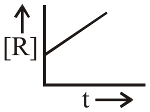
$$C + D \rightarrow A + B$$

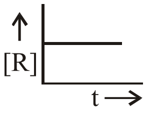
(a) 20 kcal (b) –20 kcal
(c) 18 kcal (d) 58 kcal

68. The plot that represents the zero order reaction is:
[R] = Concentration

(a) 

(b) 

(c) 

(d) 

69. Which of the following will react at the highest rate?

Critical Thinking

(a) 1 mole of A and 1 mole of B in a 1-L vessel
(b) 2 mole of A and 2 mole of B in a 2-L vessel
(c) 3 mole of A and 3 mole of B in a 3-L vessel
(d) All would react at the same rate

70. In the reaction, $A + 2B \longrightarrow 6C + 2D$, If the initial rate $-\dfrac{d[A]}{dt}$ at t = 0 is 2.6×10^{-2} M sec^{-1}, what will be the value of $\dfrac{d[B]}{dt}$ at t = 0?

(a) 8.5×10^{-2} M sec^{-1} (b) 2.5×10^{-2} M sec^{-1}
(c) 5.2×10^{-2} M sec^{-1} (d) 7.5×10^{-2} M sec^{-1}

71. The plot of concentration of the reactant Vs time for a reaction is a straight line with a negative slope. The reaction follows a rate equation of

Tricky

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

72. The reaction $L \longrightarrow M$ is started with 10.0 g of L. After 30 and 90 minutes 5.0 g and 1.25 g of L respectively are left. The order of the reaction is
(a) 0 (b) 1 (c) 2 (d) 3

73. Rate of a reaction can be expressed by Arrhenius equation as: $k = Ae^{-E_a/RT}$
In this equation, E_a represents
(a) the total energy of the reacting molecules at a temperature, T
(b) the fraction of molecules with energy greater than the activation energy of the reaction
(c) the energy below which all the colliding molecules will react
(d) the energy below which colliding molecules will not react

74. Match Column-I with Column-II.

	Column-I		Column-II
(A)	Catalyst alters the rate	(p)	cannot be fraction or zero of reaction
(B)	Molecularity	(q)	proper orientation is not there always.
(C)	Second half life of first order reaction	(r)	by lowering the activation energy
(D)	Energetically favourable	(s)	is same as the first reactions are sometimes slow

(a) A – (q), B – (r), C – (s), D – (p)
(b) A – (r), B – (s), C – (p), D – (q)
(c) A – (r), B – (p), C – (s), D – (q)
(d) A – (p), B – (r), C – (s), D – (q)

75. A reaction rate constant is given by

Tricky

$k = 1.2 \times 10^{14} e^{-25000/RT} \text{sec}^{-1}$. It means
(a) log *k* versus log T will give a straight line with a slope as –25000
(b) log *k* versus T will give a straight line with slope as 25000
(c) log *k* versus 1/T will give a straight line with slope as –25000/R
(d) log *k* versus 1/T will give a straight line

76. The rate constant of a zero order reaction is 2.0×10^{-2} mol L^{-1} s^{-1}. If the concentration of the reactant after 25 seconds is 0.5 M. What is the initial concentration?
(a) 0.5 M (b) 1.25 M
(c) 12.5 M (d) 1.0 M

77. Consider the following statements:

Critical Thinking

I. Increase in concentration of reactant increases the rate of a zero order reaction.
II. Rate constant *k* is equal to collision frequency *A* if $E_a = 0$.
III. Rate constant *k* is equal to collision frequency *A* if $E_a = \infty$.
IV. ln *k* Vs T is a straight line.
V. In *k* Vs 1/T is a straight line.

Correct statements are
(a) I and IV (b) II and V
(c) III and IV (d) II and III

78. A reaction which is of first order w.r.t. reactant A, has a rate constant 6 min^{-1}. If we start with [A] = 0.5 mol L^{-1}, when would [A] reach the value of 0.05 mol L^{-1}
(a) 0.384 min (b) 0.15 min
(c) 3 min (d) 3.84 min

79. A first order reaction is half-completed in 45 minutes. How long does it need for 99.9% of the reaction to be completed?
(a) 20 hours (b) 10 hours
(c) $7\frac{1}{2}$ hours (d) 5 hours

80. The rate constant of a reaction is 0.0693 min^{-1}. Starting with 10 mol, the rate of the reaction after 10 min is
(a) 0.0693 mol min^{-1}
(b) 0.0693×2 mol min^{-1}
(c) 0.0693×5 mol min^{-1}
(d) $0.0693 \times (5)^2$ mol min^{-1}

81. The time taken for 90% of a first order reaction to complete is approximately
(a) 1.1 times that of half-life
(b) 2.2 times that of half-life
(c) 3.3 times that of half-life
(d) 4.4 times that of half-life

82. **Statement I :** Reactions with the molecularity three are very rare and slow to proceed.
Statement II : Complex reactions involving more than three molecules take place in more than one step.
(a) Both statement I and II are correct.
(b) Both statement I and II are incorrect.
(c) Statement I is correct but statement II is incorrect.
(d) Statement II is correct but statement I is incorrect.

83. A first order reaction is 50% completed in 20 minutes at 27°C and in 5 minutes at 47°C. The energy of activation of the reaction is :

Toughnut

(a) 43.85 kJ/mol (b) 55.14 kJ/mol
(c) 11.97 kJ/mol (d) 6.65 kJ/mol

84. For the first order reaction $A \rightarrow B + C$ is carried out at 27°C. If 3.8×10^{-16} % of the reactant molecules exists in the activated state, the E_a (activation energy) of the reaction is:
(a) 12 kJ/mol (b) 831.4 kJ/mol
(c) 100 kJ/mol (d) 88.57 kJ/mol

85. The velocity of a reaction is doubled for every 10°C rise in temp. If the temp. is raised to 50°C from 0 °C the reaction velocity increases by about
(a) 12 times (b) 16 times
(c) 32 times (d) 50 times

86. Which of the following statements is incorrect?
(a) Activation energy for the forward reaction is equals to activation energy for the reverse reaction
(b) For a reversible reaction, an increase in temperature increases the reaction rate for both the forward and the backward reaction
(c) The larger the initial reactant concentration for a second order reaction, the shorter is its half-life.
(d) When Δt is infinitesimally small, the average rate equals the instantaneous rate

87. The reason for almost doubling the rate of reaction on increasing the temperature of the reaction system by 10°C is
(a) The value of threshold energy increases
(b) Collision frequency increases
(c) The fraction of the molecule having energy equal to threshold energy or more increases
(d) Activation energy decreases.

88. A catalyst lowers the activation energy of a certain reaction from 83.314 to 75 kJ mol^{-1} at 500 K. What will be the rate of reaction as compared to uncatalysed reaction? Assume other things being equal.
(a) Double (b) 28 times
(c) 7.38 times (d) 7.38×10^3 times

89. 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

90. 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

91. 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?

Toughnut

(a) 2 hours (b) 1 hour
(c) 0.5 hour (d) 0.25 hour

92. The rate of a reaction increases four-fold when the concentration of reactant is increased 16 times. If the rate of reaction is 4×10^{-6} mol L^{-1} s^{-1} when the concentration of the reactant is 4×10^{-4} mol L^{-1}. The rate constant of the reaction will be

Toughnut

(a) 2×10^{-4} $\text{mol}^{1/2}$ $L^{-1/2}$ s^{-1}
(b) 1×10^{-2} s^{-1}
(c) 2×10^{-4} $\text{mol}^{-1/2}$ $L^{1/2}$ s^{-1}
(d) 25 mol^{-1} L min^{-1}

93. The half life for the virus inactivation if in the beginning 1.5% of the virus is inactivated per minute is (Given: The reaction is of first order)

(a) 76 min (b) 66 min
(c) 56 min (d) 46 min

94. For a chemical reaction A + B → Product, the order is 1 with respect to A and B.

Rate mol $L^{-1}s^{-1}$	[A] mol L^{-1}	[B] mol L^{-1}
0.10	20	0.5
0.40	x	0.5
0.80	40	y

What is the value of x and y?

(a) 80 and 2 (b) 40 and 4
(c) 160 and 4 (d) 80 and 4

95. Integrated rate law equation for a first order gas phase reaction is given by (where P_i is initial pressure and P_t is total pressure at time t)

(a) $k = \frac{2.303}{t} \times \log \frac{(2P_i - P_i)}{P_i}$

(b) $k = \frac{2.303}{t} \times \frac{P_i}{(2P_i - P_t)}$

(c) $k = \frac{2.303}{t} \times \log \frac{2P_i}{(2P_i - P_t)}$

(d) $k = \frac{2.303}{t} \times \log \frac{P_i}{(2P_i - P_t)}$

96. The rate constant of a reaction with a virus is $3.3 \times 10^{-4}\ s^{-1}$. Time required for the virus to become 75% inactivated is

(a) 35 min (b) 70 min
(c) 105 min (d) 17.5 min

97. The activation energy for a simple chemical reaction $A \rightarrow B$ is E_a in forward direction. The activation energy for reverse reaction

(a) is always double of E_a
(b) is negative of E_a
(c) is always less than E_a
(d) can be less than or more than E_a

98. The rate equation for a reaction,

$N_2O \longrightarrow N_2 + 1/2O_2$

is Rate = $k[N_2O]^0 = k$. If the initial concentration of the reactant is *a* mol Lit^{-1}, the half-life period of the reaction is

(a) $t_{\frac{1}{2}} = \frac{a}{2k}$ (b) $-t_{\frac{1}{2}} = ka$

(c) $t_{\frac{1}{2}} = \frac{a}{k}$ (d) $t_{\frac{1}{2}} = \frac{k}{a}$

99. A student has studied the decomposition of a gas AB_3 at 25°C. He obtained the following data.

p(mm Hg)	50	100	200	400
Relative $t_{1/2}$(s)	4	2	1	0.5

The order of the reaction is

(a) 0.5 (b) 2
(c) 1 (d) 0 (zero)

100. The slope in Arrhenius plot, is equal to:

(a) $-\frac{E_a}{2.303R}$ (b) $\frac{E_a}{R}$

(c) $-\frac{R}{2.303E_a}$ (d) None of these

101. The rate constant for a first order reaction whose half life is 480 sec, is :

(a) $1.44 \times 10^{-3}\ sec^{-1}$ (b) $1.44 \times sec^{-1}$
(c) $0.72 \times 10^{-3}\ sec^{-1}$ (d) $2.88 \times 10^{-3}\ sec^{-1}$

102. The hypothetical reaction **Toughnut**

$A_2 + B_2 \longrightarrow 2AB$; follows the following mechanism $A_2 \xrightarrow{\text{Fast}} A + A$,

$A + B_2 \xrightarrow{\text{Slow}} AB + B$, $A + B \xrightarrow{\text{Fast}} AB$.

The order of the overall reaction is

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

103. For an exothermic reaction, the energy of activation of the reactants is

(a) equal to the energy of activation of products
(b) less than the energy of activation of products
(c) greater than the energy of activation of products
(d) sometimes greater and sometimes less than that of the products

104. The activation energies of the forward and backward reactions in the case of a chemical reaction are 30.5 and 45.4 kJ/mol respectively. The reaction is :

(a) exothermic
(b) endothermic
(c) neither exothermic nor endothermic
(d) independent of temperature

105. In the presence of an acid, the initial concentration of cane sugar was reduced from 0.20 to 0.10 M in 5 hours and from 0.2 to 0.05 M in 10 hours. The reaction is of : **Tricky**

(a) Zero order (b) First order
(c) Second order (d) Third order

106. A radioactive isotope having a half - life period of 3 days was received after 12 days. If 3g of the isotope is left in the container, what would be the initial mass of the isotope?

(a) 12g (b) 36g (c) 48g (d) 24g

107. For the exothermic reaction $A + B \rightarrow C + D, \Delta H$ is the heat of reaction and E_a is the energy of activation. The energy of activation for the formation of A + B will be

(a) E_a (b) ΔH
(c) $E_a + \Delta H$ (d) $\Delta H - E_a$

108. In a reversible reaction the energy of activation of the forward reaction is 50 kcal. The energy of activation for the reverse reaction will be

(a) < 50 kcal
(b) either greater than or less than 50 kcal
(c) 50 kcal
(d) > 50 kcal

109. Activation energy of a chemical reaction can be determined by **Critical Thinking**

(a) evaluating rate constant at standard temperature
(b) evaluating velocities of reaction at two different temperatures
(c) evaluating rate constants at two different temperatures
(d) changing concentration of reactants

110. $A \rightarrow B, \Delta H = -10 \text{kJ mol}^{-1}, E_{a(f)} = 50 \text{ kJ mol}^{-1}$, then E_a of $B \rightarrow A$ will be

(a) 40 kJ mol^{-1} (b) 50kJ mol^{-1}
(c) – 50kJ mol^{-1} (d) 60 kJ mol^{-1}

111. Half life periods for a reaction at initial concentrations of 0.1 M and 0.01 M are 5 and 50 minutes, respectively. The order of reaction is

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

112. The activation energy for a reaction which doubles the rate when the temperature is raised from 298 K to 308 K is **Critical Thinking**

(a) 59.2 kJ mol^{-1} (b) 39.2 kJ mol^{-1}
(c) 52.9 kJ mol^{-1} (d) 29.5 kJ mol^{-1}

113. $t_{1/4}$ can be taken as the time taken for the concentration of a reactant to drop to $\frac{3}{4}$ of its initial value. If the rate constant for a first order reaction is *k*, the $t_{1/4}$ can be written as **Toughnut**

(a) 0.75/*k* (b) 0.69/*k*
(c) 0.29/*k* (d) 0.10/*k*

114. The half life period for catalytic decomposition of AB_3 at 50 mm Hg is 4 hrs and at 100 mm Hg it is 2 hrs. The order of reaction is

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

115. A reaction proceeds by first order, 75% of this reaction was completed in 32 min. The time required for 50% completion is **Critical Thinking**

(a) 8 min (b) 16 min
(c) 20 min (d) 24 min

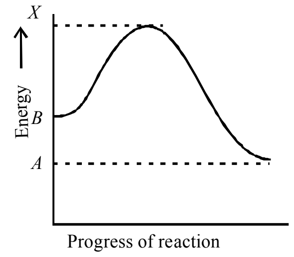
116. For a reaction $A + 2B \rightarrow C$, the amount of C formed by starting the reaction with 5 moles of A and 8 moles of B is

(a) 5 mol (b) 8 mol
(c) 16 mol (d) 4 mol

117. The rate of a first order reaction doubles when the temperature changes from 300 K to 310 K. The activation energy of the reaction (in kJ mol^{1}) is ($R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}, \log 2 = 0.3$)

(a) 43.33 (b) 53.33
(c) 63.33 (d) 73.33

118. Consider the energy diagram of a reaction : $B \rightarrow A$. On the basis of given diagram, select the correct code for matching Column-I and Column-II.



Column-I	Column-II
(A) X – A	(p) Enthalpy of reaction
(B) X – B	(q) Energy of transition state

(C)	A – B	(r)	Activation energy of forward reaction
(D)	X	(s)	Activation energy of backward reaction

(a) A – (s), B – (r), C – (q), D – (p)
(b) A – (q), B – (r), C – (p), D – (s)
(c) A – (r), B – (s), C – (p), D – (q)
(d) A – (s), B – (r), C – (p), D – (q)

119. A reaction having equal energies of activation for forward and reverse reaction has :

(a) $\Delta G = 0$
(b) $\Delta H = 0$
(c) $\Delta H = \Delta G = \Delta S = 0$
(d) $\Delta S = 0$

120. The rate coefficient (k) for a particular reactions is 1.3×10^{-4} M^{-1} s^{-1} at 100°C, and 1.3×10^{-3} M^{-1} s^{-1} at 150°C. What is the energy of activation (E_a) (in kJ) for this reaction? (R = molar gas constant = 8.314 JK^{-1} mol^{-1})

Toughnut

(a) 16 (b) 60 (c) 99 (d) 132

Numeric Value Questions

121. The following data was obtained for chemical reaction given below at 975 K.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

	[NO] mol L^{-1}	$[H_2]$ mol L^{-1}	Rate mol $L^{-1}s^{-1}$
(A)	8×10^{-5}	8×10^{-5}	7×10^{-9}
(B)	24×10^{-5}	8×10^{-5}	2.1×10^{-8}
(C)	24×10^{-5}	32×10^{-5}	8.4×10^{-8}

The order of the reaction with respect to NO is _______.

122. $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(s)$

This reaction was studied at –10 ºC and the following data was obtained

run	$[NO]_0$	$[Cl_2]_0$	r_0
1	0.10	0.10	0.18
2	0.10	0.20	0.35
3	0.20	0.20	1.40

$[NO]_0$ and $[Cl_2]_0$ are the initial concentrations and r_0 is the initial reaction rate.

The overall order of the reaction is ________.

123. The rection $2A + B_2 \rightarrow 2AB$ is an elementary reaction. For a certain quantity of reactants. If the volume of the reaction vessel is reduced by a factor of 3, the rate of the reaction increases by a factor of _______.

124. $2NO + 2H_2 \rightarrow N_2 + 2H_2O$

The above reaction has been studied at 800°C. The related data are given in the table below

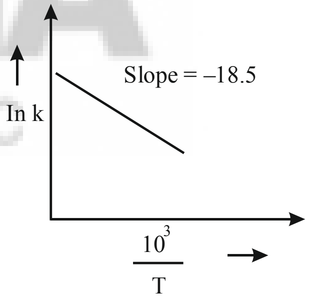
Reaction serial number	Initial pressure of H_2/kP_a	Initial pressure of NO/kP_a	Initial rate $\left(\frac{-dp}{dt}\right)/(kP_a/s)$
1	65.6	40.0	0.135
2	65.6	20.1	0.033
3	38.6	65.6	0.214
4	19.2	65.6	0.106

The order of the reaction with respect to NO is____.

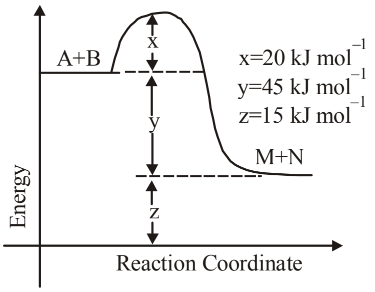
125. If 75% of a first order reaction was completed in 90 minutes, 60% of the same reaction would be completed in approximately (in minutes) ____________.

(Take : log 2 = 0.30; log 2.5 = 0.40)

126. The rate constants for decomposition of acetaldehyde have been measured over the temperature range 700 –1000 K. The data has been analysed by plotting In k vs $\frac{10^3}{T}$ graph.The value of activation energy for the reaction is___ kJ mol^{-1}. (Nearest integer) (Given : R = 8.31 J K^{-1} mol^{-1})



127. According to the following figure, the magnitude of the enthalpy change of the reaction $A + B \rightarrow M + N$ in kJ mol^{-1} is equal to _________. (Integer answer)



128. For following reactions:

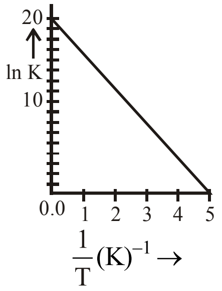
$$A \xrightarrow{700\,K} \text{Product}$$

$$A \xrightarrow[\text{catalyst}]{500\,K} \text{Product}$$

it was found that the E_a is decrease by 30 kJ/mol in the presence of catalyst. If the rate remains unchanged, the activation energy for catalysed reaction is (Assume pre exponential factor is same):

129. The activation energy of one of the reactions in a biochemical process is 532611 J mo1^{-1}. When the temperature falls from 310 K to 300 K, the change in rate constant observed is $k_{300} = x \times 10^{-3}\, k_{310}$. The value of x is ________.
[Given: 1n10 = 2.3 , R = 8.3 J K^{-1} mo1^{-1}]

130. For a reaction, given below is the graph of ln k vs $\frac{1}{T}$. The activation energy for the reaction is equal to _______ cal mol^{-1}.
(Given : R = 2 cal K^{-1} mol^{-1})



ANSWER KEY

1	(b)	**14**	(b)	**27**	(b)	**40**	(c)	**53**	(c)	**66**	(c)	**79**	(c)	**92**	(a)	**105**	(b)	**118**	(d)
2	(d)	**15**	(a)	**28**	(d)	**41**	(a)	**54**	(c)	**67**	(d)	**80**	(c)	**93**	(d)	**106**	(c)	**119**	(b)
3	(c)	**16**	(d)	**29**	(c)	**42**	(a)	**55**	(a)	**68**	(b)	**81**	(c)	**94**	(a)	**107**	(c)	**120**	(b)
4	(c)	**17**	(c)	**30**	(c)	**43**	(b)	**56**	(b)	**69**	(d)	**82**	(a)	**95**	(d)	**108**	(b)	**121**	(1)
5	(c)	**18**	(c)	**31**	(d)	**44**	(b)	**57**	(a)	**70**	(c)	**83**	(b)	**96**	(b)	**109**	(c)	**122**	(3)
6	(c)	**19**	(d)	**32**	(d)	**45**	(d)	**58**	(d)	**71**	(a)	**84**	(c)	**97**	(d)	**110**	(d)	**123**	(27)
7	(b)	**20**	(d)	**33**	(d)	**46**	(b)	**59**	(a)	**72**	(d)	**85**	(c)	**98**	(a)	**111**	(b)	**124**	(2)
8	(d)	**21**	(d)	**34**	(d)	**47**	(c)	**60**	(a)	**73**	(d)	**86**	(a)	**99**	(b)	**112**	(c)	**125**	(60)
9	(a)	**22**	(c)	**35**	(d)	**48**	(a)	**61**	(a)	**74**	(c)	**87**	(b)	**100**	(a)	**113**	(c)	**126**	(154)
10	(c)	**23**	(d)	**36**	(c)	**49**	(c)	**62**	(c)	**75**	(c)	**88**	(c)	**101**	(a)	**114**	(c)	**127**	(45)
11	(c)	**24**	(b)	**37**	(c)	**50**	(c)	**63**	(d)	**76**	(d)	**89**	(d)	**102**	(d)	**115**	(b)	**128**	(75)
12	(a)	**25**	(a)	**38**	(b)	**51**	(b)	**64**	(b)	**77**	(b)	**90**	(b)	**103**	(b)	**116**	(d)	**129**	(1)
13	(d)	**26**	(c)	**39**	(b)	**52**	(d)	**65**	(c)	**78**	(a)	**91**	(b)	**104**	(a)	**117**	(b)	**130**	(8)

Hints & Solutions

1. **(b)** $-\frac{1}{3}\frac{d[X]}{dt} = \frac{1}{2}\frac{d[Y]}{dt} = \frac{d[Z]}{dt}$

$\Rightarrow \frac{d[Y]}{dt} = \frac{2}{3}\frac{d[X]}{dt} = \frac{2}{3} \times 7.2 \times 10^{-3}$

$= 4.8 \times 10^{-3}$ mol L^{-1} S^{-1}

2. **(d)** $\frac{1}{2}\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt} \Rightarrow \frac{d[A]}{dt} = \frac{1}{2} \times \frac{d[B]}{dt}$

$\Rightarrow \frac{1}{2} \times \frac{5 \times 10^{-3}}{10} = 2.5 \times 10^{-4}$ Ms^{-1}.

3. **(c)** According to the rate law:-

When $[A]_2 = 4\,[A]_1$ and $[B]_2 = 2\,[B]_1$

rate $= r = z = k\,[4A]\,[2B]^2$

$= k \times 4 \times 4 \times [A]_1\,[B]_1 = 16\,R$.

And when [B] is kept constant, and $[A]_2 = x$

$\Rightarrow$ rate $= r_2 = 2\,R = 2k\,(0.05)\,(0.05)^2$

$= k\,(0.10)\,(0.05)^2 = k\,(x)\,(0.05)^2$

Thus, x = 0.10.

4. **(c)** Order = 1, $k = 1.15 \times 10^{-3}\ S^{-1}, C_1 = 10, C_2 = 6$

$$\Rightarrow t = \frac{2.303}{k}\log\frac{C_1}{C_2} = \frac{2.303}{1.15\times10^{-3}}\log\frac{10}{6}$$

$$= 444.27 \cong 4.4 \times 10^2$$

Thus, x = 4.4

5. **(c)** $r = K\,[NH_3]^{\circ} = K = y \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$

Now, $\frac{1}{3}\frac{d[H_2]}{dt} = r$

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

6. **(c)** For a given reaction,

$$rate = -\frac{1}{2}\frac{dn_A}{dt} = -\frac{1}{3}\frac{dn_B}{dt} = -\frac{2}{3}\frac{dn_C}{dt}$$

$$rate = \frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{4}{3}\frac{dn_C}{dt}$$

7. **(b)** The curve Y shows the exponential increase in concentration of products with time.

8. **(d)** Step 1 : $2\,NO \underset{}{\overset{k_1}{\rightleftharpoons}} N_2O_2$

Step 2 : $N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$ (slow)

Step 3 : $N_2O + H_2 \rightarrow N_2 + H_2O$

As slowest step is the rate determining step. So, rate of reaction will be given as,

Rate = $k_2\,[N_2O_2]\,[H_2]$ ...(i)

From the equilibrium step,

$[N_2\,O_2] = k_1\,[NO]^2$ ...(ii)

Now, substitute equation (ii) in equation (i), we get

Rate = $k_1\,k_2\,[NO]^2\,[H_2]$

Since k_1, k_2 both are constants, put $k_1, k_2 = k$ in the above equation rate = $k\,[NO]^2\,[H_2]$

9. **(a)** From the rate law,

$$units = \frac{\left(mol\ L^{-1}s^{-1}\right)}{\left(mol\ L^{-1}\right)^2} = L\ mol^{-1-}\ s^{-1}.$$

10. **(c)** $-\frac{d[A]}{dt} = \frac{1}{3}\frac{d[B]}{dt} = k$

(zero order reaction)

From the table, it is found that $t_{1/2} = 15s$

$$\therefore \quad 1 = \frac{[A]_0}{2t_{1/2}} = \frac{0.1}{2\times15} = \frac{1}{300}$$

Now, $[B]_{20} - [B]_0 = 3k\,(t_{20} - t_0)$

$$\text{or} \quad [B]_{20} = \frac{3}{300}\times 20 = 2\times10^{-1}\ mol\ L^{-1}$$

(close to option (c))

11. **(c)** The rate equation for zero order reaction, $[A]_t = [A]_0 - kt$ or, $0.075 = 0.1 - 0.003\,t$ or

$$t = (0.1 - 0.075)/0.003 = \frac{0.025}{0.003} = \frac{25}{3} = 8.33\ s$$

12. **(a)** The order of reaction is $\frac{3}{2}$ and molecularity is 2.

13. **(d)** Using the relation

$[A] = [A]_0 (1/2)^n$ [n = number of half-lives]

$T = n \times t_{1/2}$

Here, $n = \frac{7.5}{2.5} = 3$

$$\therefore [A] = 160 \times \left(\frac{1}{2}\right)^3 = 160 \times \frac{1}{8} = 20g$$

14. **(b)** From slow reaction

Rate = k [A] [B]

15. **(a)** $t = \frac{2.303}{k}\log\frac{a}{a-x}$

$$\text{or} \quad t = \frac{2.303}{k}\log a - \frac{2.303}{k}\log(a-x)$$

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

16. **(d)** The unit of rate constant indicates the order of reaction

$$k = -\left(\frac{d[A]}{dt}\right)\Big/[A]^n$$

$\Rightarrow$ $mol\ L^{-1}s^{-1}/mol^n L^{-n} = mol^{1-n}\,L^{n-1}\,s^{-1}$

$n = 1, k = s^{-1}$; $n = 2, k = mol^{-1}\,Ls^{-1}$; $n = 3, k = mol^{-2}\,L^2s^{-1}$.

$\therefore$ Reaction 1 : 1st order, Reaction 2 : 2nd order, Reaction 3 : 3rd order

$\therefore$ $r_1 = k_1[A]$ $r_2 = k_2[A]^2$ $r_3 = k_3[A]^3$

$= 1$ $= 0.1 \times 1^2$ $= 0.01 \times 1^3$

$= 10r_2$ $= \frac{1}{10} = \frac{r_1}{10}$ $= \frac{1}{100} = \frac{r_1}{100}$

$= 100r_3$ $\therefore r_2 = 10r_3$ $\therefore r_1 = 100r_3$

17. **(c)** $Rate_1 = k\,[A]^n\,[B]^m$; $Rate_2 = k\,[2A]^n\,[½B]^m$

$$\therefore \frac{Rate_2}{Rate_1} = \frac{k[2A]^n[½B]^m}{k[A]^n[B]^m}$$

$= [2]^n\,[½]^m = 2^n.2^{-m} = 2^{n-m}$

18. **(c)** $K = 1.2 \times 10^{-2}\ s^{-1}$; This is a 1st order reaction. Hence, $[A] = [A]_0\,e^{-kt}$; $\ln[A] = \ln[A]_0 - kt$

$\therefore$ ln[A] vs t is a straight line with negative slope (k).

19. **(d)** k depends on order of reaction and unit of k for 1st order reaction is s^{-1}.

20. **(d)** $A + B \rightarrow P$

According to rate law expression

$$\text{Rate} = k[A]^{\alpha}[B]^{\beta} \text{ (K is constant)} \qquad ...(i)$$

Taking ratio of (1) and (2) entry.

$$\Rightarrow \frac{4 \times 10^{-2}}{2 \times 10^{-2}} = \frac{[0.04]^{\beta}[0.02]^{\alpha}}{[0.02]^{\beta}[0.02]^{\alpha}}$$

$$2 = [2]^{\beta} \Rightarrow [2]^{1} = [2]^{\beta}$$

Order w.r.t $[B] = \beta = 1$

Taking ratio of (2) and (3) entry,

$$\frac{8 \times 10^{-2}}{4 \times 10^{-2}} = \frac{[0.04]^{\alpha}[0.04]^{\beta}}{[0.02]^{\alpha}[0.04]^{\beta}}$$

Order w.r.t [A]

$$[2] = [2]^{\alpha} \Rightarrow \alpha = 1 = 2 \times 10^{-2} = k[A]^{1}[B]^{1}$$

$$k = \frac{2 \times 10^{-2}}{0.02 \times 0.02} = \frac{2 \times 10^{-2} \times 10^{4}}{4} = \frac{100}{2} = 50$$

21. **(d)** Rate constant is independent of concentration

22. **(c)** Let us consider a reaction,

$$xX + yY \longrightarrow aA + bB$$

rate $= [X]^{x}[Y]^{y}$

It is given that order of reaction w.r.t. component Y is zero.

Hence, rate $= [X]^{x}$

i.e., rate becomes independent of the concentration of Y.

23. **(d)** Molecularity is defined as the number of reacting species taking part in an elementary reaction.

24. **(b)** The order of a reaction can have fractional value. The order of a reaction can not be written from balanced equation of a reaction because its value changes with pressure, temperature and concentration. It can only be determined experimentally.

25. **(a)** The fraction of molecules having equal or more energy to E_a is obtained from Maxwell-Boltzmann distribution curve. For complex molecules, all collisions does not happen in proper orientation. So, increase in concentration of the reactant may not increase the rate of reaction for such complex.

26. **(c)** $k = Ae^{-E_a/RT}$

$$\therefore \frac{-E_a}{R} = -40000$$

$$\therefore E_a = 40000 \times 2 = 80000 \text{ cal}$$

27. **(b)** $\frac{E'_a}{T_1} = \frac{E'_a}{T_2} = \frac{10}{300} = \frac{20}{T_2}$

$$\therefore T_2 = 600\text{ K} = 327°\text{C}$$

28. **(d)** The temperature dependence of the rate of a chemical reaction can be explained by Arrhenius equation, $k = A \,.\, e^{E_a/RT}$

Taking ln on both side

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

29. **(c)** for a first order reaction ;

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

Now, for 90% completion, a = 100 and a – x = 100 – 90 = 10.

$$\Rightarrow t = \frac{2.303}{6.93 \times 10^{-2}}\log\frac{100}{10} = 33.23 \text{ min.}$$

30. **(c)** A → Products

$t = 0 \; A_0$

$t = t \; A_t = 1 - 0.9375 = 0.0625$

$$\therefore A_t = A_0 e^{-kt}$$

$$\text{or,} \quad \ln\left(\frac{A_t}{A_0}\right) = -kt$$

$$\Rightarrow kt = \ln\left(\frac{A_0}{A_t}\right)$$

$$\text{or,} \quad k = \frac{1}{x}\ln\left(\frac{1}{0.0625}\right) = \frac{2.77}{x}$$

$$\therefore t_{1/2} = \frac{0.693}{k} = 0.25x = \frac{x}{4}$$

31. **(d)** $A \longrightarrow$ products; 1st order reaction

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60 \times 60} = 1.92 \times 10^{-4} s^{-1}$$

32. **(d)** $r_1 = k[A]^n$ and $r_2 = k[2A]^n$

$\because \; r_1 = r_2 \quad \therefore \; k[A]^n = k(2[A])^n$

or, $2^n = 1$

or, $2^n = 2^{\circ} \Rightarrow n = 0$

It is a zero order reaction.

33. **(d)** $t_{1/2} \propto \frac{1}{a^2}$

We know that $t_{1/2} \propto \frac{1}{a^{n-1}}$

i.e. $n = 3$

Thus reaction is of 3rd order.

34. **(d)** Rate of formation of B is

$$\frac{d[B]}{dt} = K_1[A] - K_2[B] = 0$$

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

35. **(d)** Rate of reaction $= \frac{d[A]}{dt}$

Given, $[A]_{initial} = 0.50$ M; $[A]_{final} = 0.38$ M

$dt = 10$ min $= 600$ sec

$d[A] = 0.12$

Rate $= \frac{0.12}{600} = 2 \times 10^{-4}\,M\,s^{-1}$.

36. **(c)** Rate of reaction does not remain constant during the complete reaction because rate depends upon the concentration of reactants which decreases with time.

37. **(c)** $k = A.e^{-E_a/(RT)}$

$\therefore$ Effective overall energy of activation

$$E_a = E_a(2) - E_a(3) + \frac{1}{2}E_a(1) - \frac{1}{2}E_a(5)$$

$$= 60 - 50 + \frac{1}{2} \times 40 - \frac{1}{2} \times 10 = 25 \text{ kJ/mol}$$

38. **(b)** As the rate of reaction get doubled for every 10°C rise in temperature. Hence the increase in reaction rate as a result of temperature rise from 10°C to 100°C is equal to $= 2^9 = 512$

39. **(b)** $r = k\,[O_2][NO]^2$. When the volume is reduced to 1/2, the conc. will double

$\therefore$ New rate $= k\,[2O_2][2\,NO]^2 = 8\,k\,[O_2][NO]^2$

The new rate increases to eight times of its initial.

40. **(c)** For zero-order reaction, integrated rate equation is given as:

$$k = \frac{[R_0] - [R]}{t}$$

k = rate constant

where, $[R_0]$ = initial concentration and $[R]$ = concentration at time (t)

When, $t = t_{1/2}$, then $[R] = \frac{[R_0]}{2}$

Thus, $k = \dfrac{[R_0] - \frac{1}{2}[R_0]}{t_{1/2}}$

Hence, option (c) is the correct answer.

41. **(a)** When initial concentration of A is kept constant and that of B is changed (tripled), the rate of the reaction increases by 9 times.

Thus, the order of the reaction will be α with respect to B.

When the concentration of B is kept constant and that of A is increased by 3 times, the rate of the reaction increases by 3 times too.

Thus, the order of the reaction is 1 with respect to A.

42. **(a)** Threshold energy = Activation energy + energy possessed by reacting species

$75 = E_a + 20$ or, $E_a = 75 - 20 = 55$ kJ/mol

43. **(b)** The equation for the corresponding graph is :-

$$\ln K = -\frac{E_a}{RT} + \ln A$$

where $-\frac{E_a}{R}$ is the slope and ln A is the y-intercept.

$\Rightarrow$ Slope $= -4 \times 10^4\,K = -\frac{E_a}{R}$

$\Rightarrow$ $E_a = 4 \times 10^4 \times R = 4 \times 10^4 \times 8.3$

$= 332\,000\,J = 332$ kJ.

44. **(b)** When $E_a = 0$, rate constant is independent of temperature.

45. **(d)** The definition of threshold energy.

46. **(b)** $k = Ae^{-E_a/RT}$

$\ln k = \ln A - E_a/RT$

For ln k Vs 1/T

$\ln A$ = intercept $- E_a/R$ = slope $= -2 \times 10^4$ K

$\therefore E_a = 8.3 \times 2 \times 10^4\,J\,mol^{-1}$

$= 16.6 \times 10^4\,J\,mol^{-1}$ or $166\,kJ\,mol^{-1}$

47. **(c)** Rate $= k\,[A][B] = R$

$R' = k\,[A][2B]$

$$\frac{R}{R'} = \frac{k[A][B]}{k[A][2B]} = \frac{k[A][B]}{2k[A][B]}$$

$\Rightarrow 2R = R'$ i.e., rate become doubles.

48. **(a)** If on increasing concentration, rate of reaction decreases then the order of reaction will be negative.

49. **(c)** The rate constant doubles for 10° C rise in temperature.

For 20° C rise, the rate constant will be 4 times

$\therefore k_1 = 4k_2$ or $k_2 = 0.25\,k_1$

50. **(c)** Correct formula for calculation of E_a is

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

51. **(b)** $k = Ae^{-Ea/RT}$

If $T \xrightarrow{\quad} \infty, k = A$

52. **(d)** It is a second order reaction, first order both w.r.t $S_2O_8^{2-}$ and I^-.

$\therefore\ r = k[S_2O_8^{2-}][I^-]$

All other options are of first order reaction.

53. **(c)** $[A]_t = [A] - kt = 1 - 0.001 \times 10 \times 60 = 0.4\text{ M}$

$[B]_t = 0.001 \times 10 \times 60 = 0.6\text{ M}$

54. **(c)** For Ist order reaction

$$k = \frac{2.303}{t}\log\frac{a_o}{0.2a_o} \text{ also } t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{200} \Rightarrow \frac{0.693}{200} = \frac{2.303}{t}\log\frac{1}{0.2}$$

$$t = \frac{2.303}{0.693} \times 200 \log\frac{1}{0.2} = 466.675 \approx 467\text{ sec}$$

55. **(a)** $e^{-E_a/RT} = 10^{-3}\% = 10^{-5}$;

$E_a = 2.303 \times 2 \times 300 \times 5$ cal

$= 6.91\ k\,cal\ \text{mol}^{-1}$

56. **(b)** Plot given is for zero order reaction.

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

$$\log\left(\frac{4x}{x}\right) = \frac{E_a}{2.303(8.314)}\left(\frac{700 - 600}{700 \times 600}\right)$$

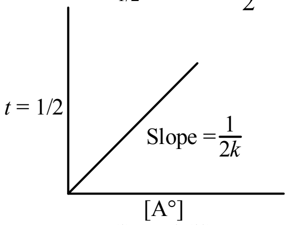
$$0.602 = \frac{E_a}{19.147}\left(2.38 \times 10^{-4}\right)$$

$\Rightarrow$ $E_a = 48548.3\text{ J} = 48.54\text{ kJ H' } 48.16\text{ kJ}$.

58. **(d)** For zero order reaction,

$[A] = [A_0] - kt$ …(i)

When $t = t_{1/2}$, $[A] = \frac{[A_0]}{2}$ …(ii)



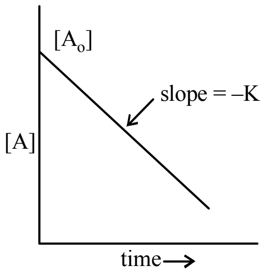
From eqs. (i) and (ii)

$$\frac{[A_0]}{2} = [A_0] - kt_{1/2} \Rightarrow t_{1/2} = \frac{[A_0]}{2k}$$

Plot of $t_{1/2}$ *versus* $[A_0]$ will be straight line.

59. **(a)** Assertion is correct as for every 10 ºC rise in temperature, the specific rate constant, *k* nearly doubles. (Although it is not correct for all reactions.

60. **(a)**



$A \rightarrow$ product

Rate constant = k

$K = -$ slope $- (-3 \times 10^{-3}) = 3 \times 10^{-3}$.

61. **(a)** The overall order of the reaction is $= \frac{1}{2} + \frac{3}{2} = \frac{4}{2} = 2$

Given rate expression is for second order reaction.

62. **(c)** The slowest step determines the rate.

63. **(d)** From rate law

$$-\frac{1}{2}\frac{dSO_2}{dt} = -\frac{dO_2}{dt} = \frac{1}{2}\frac{dSO_3}{dt}$$

$$\therefore\ -\frac{dSO_2}{dt} = -2 \times \frac{dO_2}{dt}$$

$= -2 \times 2.5 \times 10^{-4} = -5 \times 10^{-4}$ mol L^{-1} s^{-1}

64. **(b)** Rate of disappearance of reactant = Rate of appearance of products

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

$$\frac{1}{2}k[N_2O_5] = \frac{1}{4}k'[N_2O_5]$$

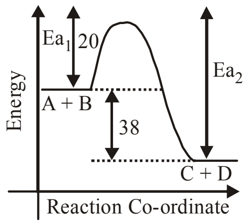
$$\frac{k}{2} = \frac{k'}{4};\ \therefore\ k' = 2k$$

65. **(c)** It is bimolecular first order reaction since Rate $\propto$ $[N_2O_5]$

66. **(c)** Rate = $k[A]^n$ comparing units

$$\frac{(\text{mol}/\text{L})}{\text{sec}} = k\left(\frac{\text{mol}}{\text{L}}\right)^n \Rightarrow k = \text{mol}^{(1-n)}\,\text{L}^{(n-1)}\,\text{s}^{-1}$$

67. **(d)** $E_{a_2} = 58$



68. **(b)** $[R] = [R_D] - k_t$

69. **(d)** Since all have same concentration of reactants, all would react at same time.

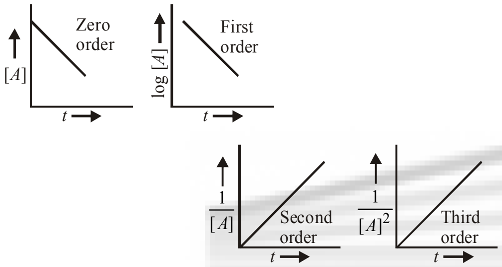
70. **(c)** Rate of reaction

$$= \frac{\text{Rate of disappearance / appearance}}{\text{Stoichiometric coefficient}}$$

$$= -\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt} = 2.6 \times 10^{-2}$$

$$= -\frac{1}{2}\frac{d[B]}{dt} \Rightarrow 5.2 \times 10^{-2} = -\frac{d[B]}{dt}$$

71. **(a)** Plots of conc. [A] Vs time, t



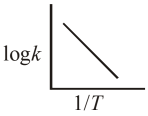
72. **(d)** After every 30 minutes the amount is reduced to $\frac{1}{2}$ therefore $t_{1/2}$ is 30 minutes. In 90 minutes the amount is reduced to $\frac{1}{8}$ i.e. $\frac{1}{2^n}$. Here $n = 3$. True for 1st order reaction.

73. **(d)** In Arrhenius equation $k = Ae^{-E_a/RT}$, E_a is the energy of activation, which is required by the colliding molecules to react resulting in the formation of products.

74. **(c)** A reaction cannot happen without the involvement of the molecule $t_{1/2}$ for 1st order reaction is independent of concentration of the reactant. Proper orientation during collision leads to the effective collision resulting into product.

75. **(c)** $k = 1.2 \times 10^{14} e^{-25000/RT}\ \text{sec}^{-1}$ or

$$\log k = \log 1.2 \times 10^{14} - \frac{25000}{R} \cdot \frac{1}{T}$$



Equation of straight line slope $= -\frac{25000}{R}$

76. **(d)** For a zero order reaction

$$\text{Rate constant} = k = \frac{[R]_0 - [R]}{t}$$

$$2 \times 10^{-2} = \frac{[R]_0 - 0.5}{25}$$

$a - 0.5 = 0.5$; $[R]_0 = 1.0$ M

77. **(b)** According to Arrhenius equation, $k = Ae^{-Ea/RT}$

$\therefore$ when $E_a = 0, k = A$

Also $\ln k$ vs 1/T is a straight line with slope $= -E_a/R$.

$\therefore$ Statements (ii) and (v) are correct.

78. **(a)** $t = \frac{2.303}{k} \log \frac{a}{a - x}$

$$= \frac{2.303}{6} \log \frac{0.5}{0.05} = 0.384 \text{ min}.$$

79. **(c)** $k = \frac{0.693}{45}$ further

$$t = \frac{2.303}{0.693} \times 45 \log \frac{100}{100 - 99.9}$$

$$= \frac{2.303 \times 45 \times 3}{0.693} = 7\frac{1}{2} \text{ hours}.$$

80. **(c)** $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0693} = 10$ min

Reactant after 10 min = 5 mol

$$\text{Rate}\left(\frac{dx}{dt}\right) = k[A] = 0.0693 \times 5 \text{ mol min}^{-1}$$

81. **(c)** $t_{90\%} = \frac{2.303}{k} \log \frac{100}{100 - 90}$ (I)

$$t_{50\%} = \frac{2.303}{k} \log \frac{100}{100 - 50} \quad \text{(II)}$$

$$\text{Dividing } \frac{t_{90\%}}{t_{50\%}} = \frac{\log 10}{\log 2}$$

$\therefore t_{90\%} = 3.3 t_{50\%}$

82. **(a)** Effective collision is the deciding factor for complex reactions.

83. **(b)** $k_{1(300)} = \frac{0.693}{20}$; $k_{2(320)} = \frac{0.693}{5}$

$$\ln \frac{k_{2(320)}}{k_{1(300)}} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$E_a = \frac{2.303\, RT_1T_2}{(T_2 - T_1)} \log\frac{k_2}{k_1}$$

$$= \frac{2.303 \times 8.314}{20 \times 1000} \times 300 \times 320 \log 4 = 55.14\,\text{kJ/mol}$$

84. **(c)** $e^{-\frac{E_a}{RT}} = 3.8 \times -\frac{10^{-16}}{100}$

$$-\frac{E_a}{RT} = \ln 3.8 \times 10^{-18}$$

$E_a = 100$ kJ/mol

85. **(c)** There are 5 tens hence $(2)^5 = 32$.

86. **(a)** $E_a(\text{F.R.}) \neq E_a(\text{B.R.})$ E_a can be calculated.

87. **(b)** When the temperature is increased, energy in form of heat is supplied which increases the kinetic energy of the reacting molecules. this will increase the number of collisions and ultimately the rate of reaction will be enhanced.

88. **(c)** $\frac{k_2}{k_1} = \frac{Ae^{-E_{a_2}/RT}}{Ae^{-E_{a_1}/RT}} = e^{(E_{a_1} - E_{a_2})/RT}$

$$2.303 \log\frac{k_2}{k_1} = \frac{E_{a_1} - E_a}{RT}$$

$$= \frac{(83.314 - 75) \times 10^3}{8.314 \times 500} = 2$$

$$\log k_2 = \frac{2}{2.303} = 0.868$$

Taking Antilog; $k_2 = 7.38$

89. **(d)** Given [A] = 0.01 M

Rate = 2.0×10^{-5} mol L^{-1} s^{-1}

For a first order reaction

Rate = k[A]

$$k = \frac{2.0 \times 10^{-5}}{[0.01]} = 2 \times 10^{-3}$$

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

90. **(b)** For a first order reaction, A → Products

$$r = k[A] \text{ or } k = \frac{r}{[A]} \Rightarrow k = \frac{1.5 \times 10^{-2}}{0.5} = 3 \times 10^{-2}$$

Further, $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3 \times 10^{-2}} = 23.1$

91. **(b)** $A \rightarrow B$ For a first order reaction

Given $a = 0.8$ mol, $(a - x) = 0.8 - 0.6 = 0.2$

$$k = \frac{2.303}{1} \log\frac{0.8}{0.2} \text{ or } k = 2.303 \log 4$$

again $a = 0.9$, $a - x = 0.9 - 0.675 = 0.225$

$$k = \frac{2.303}{t} \log\frac{0.9}{0.225}$$

$$2.303 \log 4 = \frac{2.303}{t} \log 4$$

Hence $t = 1$ hour

92. **(a)** Rate $\propto \sqrt{\text{Concentration}}$

$$= k\sqrt{\text{Concentration}}$$

$$k = \frac{\text{Rate}}{(\text{Concentration})^{1/2}}$$

$$= \frac{4 \times 10^{-6}}{(4 \times 10^{-4})^{1/2}} = \frac{4 \times 10^{-6}}{2 \times 10^{-2}}$$

$= 2 \times 10^{-4}$ mol$^{1/2}$ L$^{-1/2}$ s^{-1}

93. **(d)** For the first order reaction for small finite change

$$k_1 = \frac{1}{[A]} \frac{\Delta[A]}{\Delta t} \Rightarrow \frac{\Delta[A]/[A]}{\Delta t} = 1.5\%\ \text{min}^{-1}$$

$= 0.015$ min^{-1}

$$t_{1/2} = \frac{0.693}{0.015 \text{ min}^{-1}} = 46.2 \text{ min} \approx 46 \text{ min}$$

94. **(a)** $r = K[A]^1[B]^1$

$0.1 = K(20)^1 (0.5)^1$ ... (i)

$0.40 = K(x)^1 (0.5)^1$ ... (ii)

$0.80 = K(40)^1 (y)^1$ ... (iii)

From (i) and (ii)

$x = 80$

From (i) and (iii)

$y = 2$

95. **(d)**

$$\begin{array}{ccccc} A(g) & \rightarrow & B(g) & + & C(g) \\ P_i & & 0 & & 0 \\ P_i - x & & x & & x \end{array}$$

$P_t = P_i + x$

$P_i - x = P_i - P_t + P_i = 2P_i - P_t$

$$k = \frac{2.303}{t} \log\frac{P_i}{2P_i - P_t}$$

96. **(b)** $t_{1/2} = \frac{0.693}{k} = 2100 \text{ s} = 35 \text{ min}$

$t_{75\%} = 2t_{1/2} = 2 \times 35 = 70$ min

97. **(d)** The activation energy of reverse reaction will depend upon whether the forward reaction is exothermic or endothermic.

As $\Delta H = E_a$ (forward reaction) – E_a (backward reaction)

For exothermic reaction

$\Delta H = -ve$

$\therefore -\Delta H = E_a(f) - E_a(b)$

or $E_a(f) = E_a(b) - \Delta H$; $E_a(f) < E_a(b)$

for endothermic reaction

$\Delta H = +ve$

$\therefore \Delta H = E_a(f) - E_a(b)$ or $E_a(f) = \Delta H + E_a(b)$

$\therefore \quad E_a(f) > E_a(b)$.

98. **(a)** For a zero order reaction

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

99. **(b)** $t_{1/2} \propto (P_0)^{1-n}$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{(P_0)^{1-n}}{(P_0)_2^{1-n}} \Rightarrow \left(\frac{4}{2}\right) = \left(\frac{50}{100}\right)^{1-n}$$

$$\Rightarrow \quad 2 = \left(\frac{1}{2}\right)^{1-n} \quad \Rightarrow \quad 2 = (2)^{n-1}$$

$$\Rightarrow \quad n - 1 = 1 \quad \Rightarrow \quad n = 2$$

100. **(a)** Arrhenius equation is given by

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

Taking log on both sides, we get

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

Arrhenius plot a graph between $\log k$ and $\frac{1}{T}$ whose slope is $\frac{-E_a}{2.303R}$.

101. **(a)** $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{480} = 1.44 \times 10^{-3} s^{-1}$

102. **(d)** $A_2 + B_2 \longrightarrow 2AB$;

$A_2 \longrightarrow A + A$ (Fast);

$A + B_2 \longrightarrow AB + B$ (Slow)

Rate law $= k[A][B_2]$ put value of $[A]$ from Ist reaction since A is intermediate $\sqrt{k[A_2]} = A$

$\therefore$ Rate law equation $= K\sqrt{k[A_2]}[B_2]$

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

103. **(b)** Activation energy of reactant is less than the energy of activation of products.

104. **(a)** Exothermic because of activation energy $E_b > E_f$

105. **(b)** $k_1 = \frac{1}{5} \text{In} \frac{0.2}{0.1}$; $k_2 = \frac{1}{10} \text{In} \frac{0.2}{0.05}$; $k_1 = k_2$.

106. **(c)** Given $t_{1/2} = 3$

Total time T = 12

No. of half lives $(n) = \frac{12}{3} = 4 \Rightarrow \left(\frac{1}{2}\right)^n = \frac{N}{N_o}$

$$\therefore \quad \left(\frac{1}{2}\right)^4 = \frac{3}{N} \Rightarrow \frac{3}{N} = \frac{1}{16} \quad N = 48 \text{ g}$$

107. **(c)** For the exothermic reaction the energy of products is always less than the reactants. If E_a is the energy of activation for the forward reaction, the energy of activation for backward reaction is $E_a + \Delta H$

108. **(b)** $\Delta H = E_a(f) - E_a(b)$

Thus energy of activation for reverse reaction depend upon whether reaction is exothermic or endothermic.

If reaction is exothermic,

$\Delta H = -ve$, $E_a(b) > E_a(f)$

If reaction is endothermic,

$\Delta H = +ve$ $E_a(b) < E_a(f)$

109. **(c)** We know that the activation energy of chemical reaction is given by formula $= \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$, where k_1 is the rate constant at temperature T_1 and k_2 is the rate constant at temperature T_2 and E_a is the activation energy. Therefore activation energy of chemical reaction is determined by evaluating rate constant at two different temperatures.

110. **(d)** $A \longrightarrow B, \Delta H = -10 \text{ kJ mol}^{-1}$

It is an exothermic reaction.

$E_{a(b)} = E_{a(f)} - (\Delta H)$

$= 50 - (-10) = 60$ kJ

111. **(b)** $\frac{(t_{1/2})_2}{(t_{1/2})_2} = \left(\frac{a_1}{a_2}\right)^{1-n}$

$$\left(\frac{0.1}{0.01}\right) = \left(\frac{5}{50}\right)^{1-n} \Rightarrow (10) = \left(\frac{1}{10}\right)^{1-n} \Rightarrow n = 2$$

112. **(c)** Activation energy can be calculated from the equation.

$$\frac{\log K_2}{\log K_1} = \frac{-E_a}{2.303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Given $\frac{\log K_2}{\log K_1} = 2$ $T_2 = 308$ K; $T_1 = 298$ K

$$\therefore \;\; \log 2 = \frac{-E_a}{2.303 \times 8.314}\left(\frac{1}{308} - \frac{1}{298}\right)$$

$E_a = 52.9$ kJ mol^{-1}

113. (c) $t_{1/4} = \frac{2.303}{k}\log\frac{1}{3/4} = \frac{2.303}{k}\log\frac{4}{3}$

$$= \frac{2.303}{k}(\log 4 - \log 3) = \frac{2.303}{k}(2\log 2 - \log 3)$$

$$= \frac{2.303}{k}(2 \times 0.301 - 0.4771) = \frac{0.29}{k}$$

114. (c) $t_{1/2} \propto \frac{1}{(p)^{n-1}}$ where n is the order of reaction

$$\frac{2}{4} = \left(\frac{50}{100}\right)^{n-1} \text{ or } \frac{1}{2} = \left(\frac{1}{2}\right)^{n-1}$$

$n - 1 = 1; n = 2$

115. (b) Given: 75% reaction gets completed in 32 min

Thus, $k = \frac{2.303}{t}\log\frac{a}{(a-x)}$

$$= \frac{2.303}{32}\log\frac{100}{(100-75)}$$

$$= \frac{2.303}{32}\log 4 = 0.0433 \text{ min}^{-1}$$

Now we can use this value of k to get the value of time required for 50% completion of reaction

$$t = \frac{2.303}{k}\log\frac{a}{(a-x)} = \frac{2.303}{0.0433}\log\frac{100}{50}$$

$$= \frac{2.303}{0.0433}\log 2 = 16 \text{ min}$$

116. (d) $A + 2B \longrightarrow C$

1 mole of A reacts with 2 moles of B to give 1 mol of C.

∴ 5 moles of A would react with 10 moles of B to give 5 moles of C.

But, only 8 moles of B are available

∴ B acts as a limiting reagent.

2 moles of B gives 1 mole of C

∴ 8 moles of B will give 1/2 × 8 = 4 moles of C.

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

$$\log(2) = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$$

$$= \frac{E_a}{19.15}(0.0001075)$$

$\Rightarrow$ $E_a = 53441.86$ J mol^{-1}

$= 53.442$ kJ mol$^{-1} \approx 53.33$ kJ mol^{-1}

118. (d) Energy profile diagram indicate the kinetic and thermodynamic feasibility of reaction.

119. (b) $\Delta H = E_a(f) - E_a(b) = 0$

120. (b) According to Arrhenius equation

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

$$\log\frac{1.3 \times 10^{-3}}{1.3 \times 10^{-4}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{373} - \frac{1}{423}\right]$$

$$1 = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{373} - \frac{1}{423}\right]$$

$E_a = 60$ kJ / mol

121. (1) Rate = k $[NO]^x [H_2]^y$

$7 \times 10^{-9} = k \times (8 \times 10^{-5})^x (8 \times 10^{-5})^y$ ...(i)

$2.1 \times 10^{-8} = k \times (24 \times 10^{-5})^x (8 \times 10^{-5})^y$ ...(ii)

Now dividing equation (i) by equation (ii):

$$\frac{7 \times 10^{-9}}{2.1 \times 10^{-8}} = \left(\frac{8 \times 10^{-5}}{24 \times 10^{-5}}\right)^x$$

$$\frac{1}{3} = \left(\frac{1}{3}\right)^x \Rightarrow x = 1$$

122. (3) General form of rate law,

Rate $(r) = k[NO]^x[Cl_2]^y$

Using for all 3 exp.

$(r_1)\; 0.18 = k[0.10]^x[0.10]^y$ . . . (i)

$(r_2)\; 0.35 = k[0.10]^x[0.20]^y$ . . . (ii)

$(r_3)\; 1.40 = k[0.20]^x[0.20]^y$ . . . (iii)

From reaction (i) and (ii),

$$\frac{0.18}{0.35} = \frac{[0.10]^x\,[0.10]^y}{[0.10]^x\,[0.20]^y}$$

$$\Rightarrow \frac{0.18}{0.35}=\left(\frac{1}{2}\right)^y \Rightarrow \left(\frac{1}{2}\right)^1=\left(\frac{1}{2}\right)^y$$

∴ Order w.r.t. $[Cl_2]=y=1$

From reaction (ii) and (iii),

$$\frac{0.35}{1.40}=\frac{[0.10]^x\,[0.20]^y}{[0.20]^x\,[0.20]^y}$$

$$\Rightarrow \frac{0.35}{1.40}=\left(\frac{1}{2}\right)^x \Rightarrow \left(\frac{1}{2}\right)^2=\left(\frac{1}{2}\right)^x$$

∴ Order w.r.t. [NO], $x=2$

Now, $r=k[NO]^2[Cl_2]^1$

∴ Overall order of reaction = 2 + 1 = 3

123. (27) $2A+B_2 \longrightarrow 2AB$

Rate of reaction is $r=k\cdot[A]^2[B_2]$

The conc. of A and B_2 will become 3 times as the volume of reaction vessel is reduced by a factor of 3 and hence, the rate becomes $3^2 \times 3 = 27$ times of initial rate.

124. (2) When initial pressure of NO increases by a factor of 2 ($2 \times 20.1 \approx 40$) then initial rate increases by a factor of 4 ($4 \times 0.033 \approx 0.135$). Therefore, order of reaction w.r.t. NO = 2.

125. (60)

$$t=\frac{2.303}{k}\log\left[\frac{100}{100-x\%}\right]$$

$$t_{75\%}=\frac{2.303}{k}\log\left[\frac{100}{25}\right]=90$$

$$t_{60\%}=\frac{2.303}{k}\log\left[\frac{100}{40}\right]$$

$$\frac{t_{75\%}}{t_{60\%}}=\frac{2\log 2}{\log 2.5}\Rightarrow\frac{90}{t_{60\%}}=\frac{2\times 0.3}{0.4}$$

$$\Rightarrow t_{60\%}=\frac{90\times 4}{6}=60\text{ min.}$$

126. (154) $\ln k=\ln A-\dfrac{E_a}{10^3RT}\times 10^3$

$$=\ln A+\frac{10^3}{T}\left[-\frac{E_a}{10^3\,R}\right]$$

From the graph, $\dfrac{-E_a}{10^3\times R}=-18.5$

$E_a=153.735=154$ kJ/mol

127. (45) ΔH = Energy of products – Energy of reactants

$=Z-(Z+Y)=15-(15+45)=-45$

$|\Delta H|=45$ kJ/mol

128. (75) $A \xrightarrow{700K(k_1)} \text{Product}$

$A \xrightarrow[\text{Catalyst}]{500K(k_2)} \text{Product}$

Given: $k_1=k_2$

$$Ae^{-\frac{E_{a_1}}{RT_1}}=Ae^{-\frac{E_{a_2}}{RT_2}}$$

$$\frac{E_{a_1}}{T_1}=\frac{E_{a_2}}{T_2}$$

Given, $E_{a_2}=E_{a_1}-30 \Rightarrow E_{a_1}=E_{a_2}+30$

$$\frac{E_{a_2}+30}{700}=\frac{E_{a_2}}{500}\Rightarrow E_{a_2}=75\text{ kJ / mol}$$

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

$$\ln\left(\frac{k_2}{k_1}\right)=\frac{532611}{8.3}\times\left(\frac{10}{310\times 300}\right)$$

where k_2 is at 310 K & k_1 is at 300 K

$$\ln\left(\frac{k_2}{k_1}\right)=6.9=3\times\ln 10$$

$$\ln\frac{k_2}{k_1}=\ln 10^3$$

$k_2=k_1\times 10^3 \Rightarrow k_1=k_2\times 10^{-3}$. So $x=1$

130. (8) $k=Ae^{-E_a/RT}$

Taking ln both sides;

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

$y=mx+c$

$$\text{Slope}=\frac{E_a}{R}=\frac{20}{5}$$

$E_a=4R=8$ cal/mol