CHAPTER 18

CHEMICAL KINETICS

FACT/DEFINITION TYPE QUESTIONS

1. The term – dc/dt in a rate equation refers to :
(a) the conc. of a reactant
(b) the decrease in conc. of the reactant with time
(c) the velocity constant of reaction
(d) None of these

2. The rate law for the single- step reaction $2A + B \longrightarrow 2C$, is given by:
(a) rate = k [A].[B] (b) rate = k $[A]^2$.[B]
(c) rate = k [2A].[B] (d) rate = k $[A]^2.[B]^o$

3. Rate of which reaction increases with temperature :
(a) of any type of reactions
(b) of exothemic reactions
(c) of endothemic reactions
(d) of none

4. In a slow reaction, rate of reaction generally .... with time:
(a) decreases
(b) increases
(c) sometimes increases and sometimes decreases.
(d) remains constant

5. The rate of a chemical reaction tells us about,
(a) the reactants taking part in reaction
(b) the products formed in the reaction
(c) how slow or fast the reaction is taking place
(d) None of the above

6. For the reaction $2A + B \rightarrow 3C + D$
which of the following does not express the reaction rate ?
(a) $-\frac{d[B]}{dt}$ (b) $\frac{d[D]}{dt}$
(c) $-\frac{1}{2}\frac{d[A]}{dt}$ (d) $-\frac{1}{3}\frac{d[C]}{dt}$

7. Consider the reaction
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
The equality relationship between $\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is
(a) $+\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$
(b) $+\frac{d[NH_3]}{dt} = -\frac{3}{2}\frac{d[H_2]}{dt}$
(c) $\frac{d[NH_3]}{dt} = -\frac{d[H_2]}{dt}$
(d) $\frac{d[NH_3]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$

8. For the reaction $2A + B \rightarrow 3C + D$
which of the following does not express the reaction rate ?
(a) $-\frac{d[B]}{dt}$ (b) $\frac{d[D]}{dt}$
(c) $-\frac{1}{2}\frac{d[A]}{dt}$ (d) $-\frac{1}{3}\frac{d[C]}{dt}$

9. Which of the following reaction does not occur fastly ?
(a) Precipitation of AgCl by mixing aqueous solutions of $AgNO_3$ and NaCl.
(b) Burning of gasoline
(c) Rusting of iron
(d) Burning of LPG for cooking

10. Chemical kinetics is a study to find out
(a) the feasibility of a chemical reaction
(b) extent to which a reaction will proceed
(c) speed of a reaction
(d) All of the above

11. Rate of a reaction can be defined as
(a) the rate of decrease in concentration of any one of the reactants
(b) the rate of increase in concentration of any one of the products
(c) the rate of decrease in concentration of any one of the reactants or the rate of increase in concentration of any one of the products
(d) the sum of rate of decrease in concentration of all the reactants or the rate of increase in concentration of all the products

12. The rate of reaction
(a) increases as the reaction proceeds
(b) decreases as the reaction proceeds
(c) remains the same as the reaction proceeds
(d) may decrease or increase as the reaction proceeds

13. The unit of rate of reaction is
(a) mole/dm^3 (b) mole/pound
(c) mole/dm^3 sec (d) mole/cm^3

14. In the rate equation, when the conc. of reactants is unity then rate is equal to
(a) specific rate constant
(b) average rate constant
(c) instantaneous rate constant
(d) None of above

15. The rate of reaction between two specific time intervals is called
(a) instantaneous rate (b) average rate
(c) specific rate (d) ordinary rate

16. Instantaneous rate of a chemical reaction is
(a) rate of reaction in the beginning
(b) rate of reaction at the end
(c) rate of reaction at a given instant
(d) rate of reaction between two specific time intervals

17. At the beginning the decrease in the conc. of reactants is
(a) slow (b) moderate
(c) rapid (d) None of above

18. The average rate and instantaneous rate of a reaction are equal
(a) at the start
(b) at the end
(c) in the middle
(d) when two rate have time interval equal to zero

19. The rate of reaction depends upon the
(a) volume (b) force
(c) pressure (d) conc. of reactants

20. For the following reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$, the rate law is: Rate = k $[NO_2]^2$. If 0.1 mole of gaseous carbon monoxide is added at constant temperature to the reaction mixture which of the following statements is true?
(a) Both k and the reaction rate remain the same
(b) Both k and the reaction rate increase
(c) Both k and the reaction rate decrease
(d) Only k increases, the reaction rate remain the same

21. 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 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.

22. The rate of the reaction $2NO + Cl_2 \longrightarrow 2NOCl$ 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 concentration of NO.
(b) increasing the temperature.
(c) increasing the concentration of the Cl_2
(d) doing all of the above

23. Order of reaction can be
(a) 0 (b) fraction
(c) whole number (d) integer, fraction, zero

24. Units of rate constant of first and zero order reactions in terms of molarity M unit are respectively
(a) sec^{-1}, $Msec^{-1}$ (b) sec^{-1}, M
(c) $Msec^{-1}$, sec^{-1} (d) M, sec^{-1}.

25. A reaction involving two different reactants can never be
(a) bimolecular reaction (b) second order reaction
(c) first order reaction (d) unimolecular reaction

26. $3A \rightarrow B + C$, 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

27. For the following homogeneous reaction,
$A + B \xrightarrow{k} C$
the unit of rate constant is
(a) sec^{-1} (b) sec^{-1} mol L^{-1}
(c) sec^{-1} mol^{-1} L (d) sec^{-1} mol^{-2} L^2

28. Order of reaction is decided by
(a) temperature
(b) mechanism of reaction as well as relative concentration of reactants
(c) molecularity
(d) pressure

29. Velocity constant k of a reaction is affected by
(a) change in the concentration of the reactant
(b) change of temperature
(c) change in the concentration of the product
(d) None of the above

30. The rate constant for the reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$ is 3.10×10^{-5} sec^{-1}. If the rate is 2.4×10^{-5} mol $litre^{-1}$ sec^{-1} then the concentration of N_2O_5 (in mol $litre^{-1}$) is :
(a) 0.04 (b) 0.8
(c) 0.07 (d) 1.4

31. A zero order reaction is one whose rate is independent of
(a) the concentration of the reactants
(b) the temperature of reaction
(c) the concentration of the product
(d) the material of the vessel in which reaction is carried out

32. 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
(a) $(m+n)$ (b) $(n-m)$
(c) $2^{(n-m)}$ (d) $\frac{1}{2^{(m+n)}}$

33. In the reaction $2A + B \rightarrow A_2B$, if the concentration of A is doubled and that of B is halved, then the rate of the reaction will:

(a) increase 2 times (b) increase 4 times
(c) decrease 2 times (d) remain the same

34. 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

35. If the rate of a gaseous reaction is independent of pressure, the order of reaction is:

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

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

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

37. In a reaction, when the concentration of reactant is increased two times, the increase in rate of reaction was four times. Order of reaction is :

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

38. For the reaction $A + 2B \rightarrow C$, rate is given by $R = [A][B]^2$ then the order of the reaction is

(a) 3 (b) 6
(c) 5 (d) 7

39. 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}

40. Which one of the following reactions is a true first order reaction?

(a) Alkaline hydrolysis of ethyl acetate
(b) Acid catalyst hydrolysis of ethyl acetate
(c) Decomposition of N_2O
(d) Decomposition of gaseous ammonia on a hot platinum surface

41. For a reaction $A + B \longrightarrow C + 2D$, experimental results were collected for three trials and the data obtained are given below:

Trial	[A], M	[B], M	Initial Rate, M s^{-1}
1	0.40	0.20	5.5×10^{-4}
2	0.80	0.20	5.5×10^{-4}
3	0.40	0.40	2.2×10^{-3}

The correct rate law of the reaction is

(a) rate $= k[A]^0 [B]^2$ (b) rate $= k[A][B]^2$
(c) rate $= k[A][B]$ (d) rate $= k[A][B]^0$

42. The rate law for the reaction $xA + yB \longrightarrow mP + nQ$ is Rate $= k[A]^c[B]^d$. What is the total order of the reaction?

(a) (x + y) (b) (m + n)
(c) (c + d) (d) x/y

43. What is order with respect to A, B, C, respectively

[A]	[B]	[C]	rate (M/sec.)
0.2	0.1	0.02	8.08×10^{-3}
0.1	0.2	0.02	2.01×10^{-3}
0.1	1.8	0.18	6.03×10^{-3}
0.2	0.1	0.08	6.464×10^{-2}

(a) –1, 1, 3/2 (b) –1, 1, 1/2
(c) 1, 3/2, –1 (d) 1, –1, 3/2

44. Select the rate law that corresponds to the data shown for the following reaction :

$$A + B \longrightarrow C$$

Expt. No.	*(A)*	*(B)*	*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

(a) Rate $= k[B]^3$ (b) Rate $= k[B]^4$
(c) Rate $= k[A][B]^3$ (d) Rate $= k[A]^2[B]^2$

45. The order of a reaction with rate equal to $k[A]^{3/2}[B]^{-1/2}$ is :

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

46. For the reaction,

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} \text{products}$$

The rate is governed by expression

$$\frac{dx}{dt} = k[\text{acetone}][H^+]$$

The order w.r.t. I_2 is:

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

47. The rate constant of a reaction is 3.00×10^3 L mol^{-1} sec^{-1}. The order of this reaction will be:

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

48. 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 $= k[A][B]^2$

49. 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) $1, \frac{1}{2}$

50. The chemical reaction $2O_3 \longrightarrow 3O_2$ proceeds as follows:

$O_3 \xrightarrow{\text{Fast}} O_2 + O$; $O + O_3 \xrightarrow{\text{Slow}} 2O_2$ the rate law expression should be

(a) $r = k[O_3]^2$ (b) $r = k[O_3]^2[O_2]^{-1}$

(c) $r = k^3[O_3][O_2]^2$ (d) $r = [O_3][O_2]^2$

51. Nitrogen monoxide, NO, reacts with hydrogen, H_2, according to the following equation:

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

If the mechanism for this reaction were,

$2NO(g) + H_2(g) \rightarrow N_2(g) + H_2O_2(g)$; slow

$H_2O_2(g) + H_2(g) \rightarrow 2H_2O(g)$; fast

Which of the following rate laws would we expect to obtain experimentally?

(a) Rate = $k[H_2O_2][H_2]$ (b) Rate = $k[NO]^2[H_2]$

(c) Rate = $k[NO]^2[H_2]^2$ (d) Rate = $k[NO][H_2]$

52. Which of the following is not a first order reaction ?

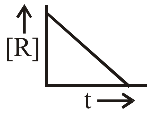
(a) Hydrogenation of ethene

(b) Natural radioactive decay of unstable nuclei

(c) Decomposition of HI on gold surface

(d) Decomposition of N_2O

53. The plot that represents the zero order reaction is :

(a)


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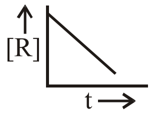

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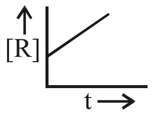

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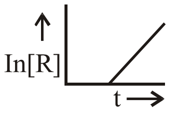


54. The plot of concentration of the reactant vs time for a reaction is a straight line with a negative slope. The reaction follows a rate equation

(a) zero order (b) first order

(c) second order (d) third order

55. 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

56. 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) $t_{\frac{1}{2}} = \frac{k}{a}$

57. Half life of a first order reaction is 4s and the initial concentration of the reactant is 0.12 M. The concentration of the reactant left after 16 s is

(a) 0.0075 M (b) 0.06 M

(c) 0.03 M (d) 0.015 M

58. 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) 2 hours (b) 1 hour

(c) 0.5 hour (d) 0.25 hour

59. 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

60. The rate constant for a first order reaction whose half-life, is 480 seconds is :

(a) 2.88×10^{-3} sec^{-1} (b) 2.72×10^{-3} sec^{-1}

(c) 1.44×10^{-3} sec^{-1} (d) 1.44 sec^{-1}

61. The rate constant of a first order reaction is $6.9 \times 10^{-3} s^{-1}$. How much time will it take to reduce the initial concentration to its 1/8th value?

(a) 100 s (b) 200 s

(c) 300 s (d) 400 s

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

(a) 8 min (b) 16 min

(c) 20 min (d) 24 min

63. Point out the wrong statement:

For a first order reaction

(a) time for half-change ($t_{1/2}$) is independent of initial concentration

(b) change in the concentration unit does not change the rate constant (k)

(c) time for half-change × rate constant = 0.693

(d) the unit of k is mole^{-1} min^{-1}

64. $t_{\frac{1}{4}}$ 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 $t_{\frac{1}{4}}$ can be written as

(a) 0.75/*k* (b) 0.69/*k*

(c) 0.29/*k* (d) 0.10/*k*

65. In a first-order reaction A → B, if k is rate constant and inital concentration of the reactant A is 0.5 M, then the half-life is

(a) $\frac{\log 2}{k}$ (b) $\frac{\log 2}{k\sqrt{0.5}}$

(c) $\frac{\ln 2}{k}$ (d) $\frac{0.693}{0.5k}$

66. Consider the reaction, 2A + B → products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is
(a) s^{-1} (b) $L\ mol^{-1}\ s^{-1}$
(c) no unit (d) $mol\ L^{-1}\ s^{-1}$.

67. The decomposition of N_2O_5 occurs as
$2N_2O_5 \longrightarrow 4NO_2 + O_2$ and follows Ist order kinetics, hence:
(a) the reaction is unimolecular
(b) the reaction is bimolecular
(c) $t_{1/2} \propto a^0$
(d) None of these

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

69. 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) $-\frac{E_a}{2.303\ R}$

70. In a reaction $A \rightarrow$ Products, when start is made from 8.0×10^{-2} M of A, half-life is found to be 120 minute. For the initial concentration 4.0×10^{-2} M, the half-life of the reaction becomes 240 minute. The order of the reaction is :
(a) zero (b) one
(c) two (d) 0.5

71. The value of rate constant of a pseudo first order reaction __________.
(a) depends on the concentration of reactants present in small amount.
(b) depends on the concentration of reactants present in excess.
(c) is independent on the concentration of reactants.
(d) depends only on temperature.

72. In the Haber process for the manufacture of ammonia the following catalyst is used
(a) Platinized asbestos
(b) Iron with molybdenum as promoter
(c) Copper oxide
(d) Alumina

73. 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) $269\ kJ\ mol^{-1}$ (b) $34.7\ kJ\ mol^{-1}$
(c) $15.1\ kJ\ mol^{-1}$ (d) $342\ kJ\ mol^{-1}$

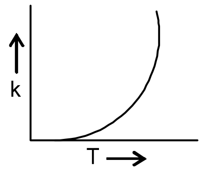
74. A reaction having equal energies of activation for forward and reverse reaction has :
(a) $\Delta G = 0$ (b) $\Delta H = 0$
(c) $\Delta H = \Delta G = \Delta S = 0$ (d) $\Delta S = 0$

75. In an exothermic reaction if ΔH is the enthalpy then activation energy is
(a) more than ΔH (b) less than ΔH
(c) equal to ΔH (d) none of the above

76. 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 $8.3\ J\ K^{-1}\ mol^{-1}$)
(a) 83 (b) 166
(c) 249 (d) 332

77. 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

78. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is

(a)


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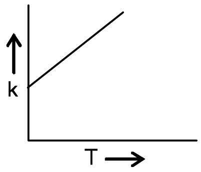

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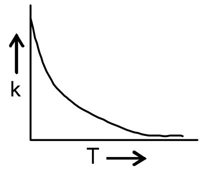

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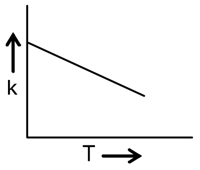


79. If the activation energy for the forward reaction is 150 kJ mol^{-1} and that of the reverse reaction is 260 kJ mol^{-1}, what is the enthalpy change for the reaction ?
(a) $410\ kJ\ mol^{-1}$ (b) $-110\ kJ\ mol^{-1}$
(c) $110\ kJ\ mol^{-1}$ (d) $-410\ kJ\ mol^{-1}$

80. Activation energy of a chemical reaction can be determined by
(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

81. In respect of the equation $k = Ae^{-E_a/RT}$ in chemical kinetics, which one of the following statements is correct ?
(a) A is adsorption factor
(b) E_a is energy of activation
(c) R is Rydberg's constant
(d) k is equilibrium constant

82. 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

83. The minimum energy required for the reacting molecules to undergo reaction is :

(a) potential energy (b) kinetic energy

(c) thermal energy (d) activation energy

84. 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

85. 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

86. The activation energy for a reaction is 9.0 kcal/mol. The increase in the rate constant when its temperature is increased from 298K to 308K is

(a) 63% (b) 50%

(c) 100% (d) 10%

87. 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

88. A catalyst

(a) increases the rate of reaction by decreasing ΔG of a reaction.

(b) increases the rate of reaction by increasing ΔG of a reaction.

(c) increases the rate of reaction by decreasing activation energy of the forward reaction.

(d) increases the rate of reaction by providing an alternative pathway via an intermediate with lower activation energy.

89. Which of the following statements best describes how a catalyst works?

(a) A catalyst changes the potential energies of the reactants and products.

(b) A catalyst decreases the temperature of the reaction which leads to a faster rate.

(c) A catalyst lowers the activation energy for the reaction by providing a different reaction mechanism.

(d) A catalyst destroys some of the reactants, which lowers the concentration of the reactants.

90. In terms of the 'Collision Theory of Chemical Kinetics', the rate of a chemical reaction is proportional to

(a) the change in free energy per second

(b) the change in temperature per second

(c) the number of collisions per second

(d) the number of products molecules

91. According to collision theory, which of the following is NOT a true statement concerning a catalyst?

(a) A catalyst changes the temperature of reaction.

(b) The mechanism of a reaction will change when a catalyst is added.

(c) A catalyst provides a different activation energy for a reaction.

(d) A catalyst changes the speed of a reaction, but not the equilibrium constant.

92. Which of the following influences the rate of a chemical reaction performed in solution?

(a) Temperature

(b) Activation energy

(c) Presence of a catalyst

(d) All of the above influence the rate

93. How can be activation energy for a reaction be determined graphically?

(a) Plot *k versus T*, the slope of the line will be equal to E_a

(b) Plot $1/[A]_t$ *versus t*, the slope of the line will be equal to E_a

(c) Plot ln $[A]_t$ *versus t*, the slope of the line will be equal to $-E_a$

(d) Plot ln *k versus* $1/T$, the slope of the line will be equal to $-E_a/R$

94. The Arrhenius equation expressing the effect of temperature on the rate constant of the reaction is

(a) $k = e^{-E_a/RT}$ (b) $k = \frac{E_a}{RT}$

(c) $k = \log_e \frac{E_a}{RT}$ (d) $k = Ae^{-E_a/RT}$

95. In Arrhenius plot, intercept is equal to

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

(c) ln k (b) $\log_{10}a$

96. 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) $k_1 = 4k_1$ (b) $k_2 = 2k_1$

(c) $k_2 = 0.25\,k_1$ (d) $k_2 = 0.5\,k_1$

97. For a first order reaction, the plot of log K against 1/T is a straight line. The slope of the line is equal to

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

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

98. Collision theory is applicable to

(a) first order reactions (b) zero order reactions

(c) bimolecular reactions (d) intra-molecular reactions

99. According to the collision theory of reaction rates, the rate of reaction increases with temperature due to

(a) greater number of collision

(b) higher velocity of reacting molecules

(c) greater number of molecules having the activation energy

(d) decrease in the activation energy

100. Which of the following has been used to explain the subject of chemical kinetics

(a) Collision theory of bimolecular reactions

(b) The activated complex theory

(c) Arrhenius equation

(d) All of these

101. A catalyst increases rate of reaction by

(a) decreasing enthalpy

(b) decreasing internal energy

(c) decreasing activation energy

(d) increasing activation energy

102. Activation energy of the reaction is

(a) the energy released during the reaction

(b) the energy evolved when activated complex is formed

(c) minimum amount of energy needed to overcome the potential barrier

(d) the energy needed to form one mole of the product

103. In a reaction, the threshold energy is equal to

(a) activation energy + normal energy of reactants

(b) activation energy - normal energy of reactants

(c) normal energy of reactants - activation energy

(d) average kinetic energy of molecules of reactants

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

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

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

105. Consider an endothermic reaction X → Y with the activation energies E_b and E_f for the backward and forward reactions, respectively. In general

(a) there is no definite relation between E_b and E_f

(b) $E_b = E_f$

(c) $E_b > E_f$

(d) $E_b < E_f$

106. The energies of activation for forward and reverse reactions for $A_2 + B_2 \rightleftharpoons 2AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1}. The enthalpy change of the reaction ($A_2 + B_2 \rightarrow 2AB$) in the presence of a catalyst will be (in kJ mol^{-1})

(a) 20 (b) 300

(c) 120 (d) 280

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 most cases, for a rise of 10K temperature the rate constant is doubled to tribled. This is due to the reason that

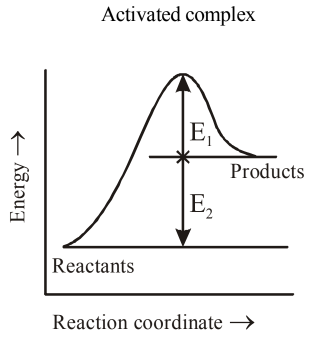
(a) collision frequency increases by a factor of 2 to 3.

(b) fraction of molecules possessing threshold energy increases by a factor of 2 to 3

(c) Activation energy is lowered by a factor of 2 to 3.

(d) none of these

109. Consider Fig. and mark the correct option.



(a) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.

(b) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant.

(c) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product.

(d) Activation energy of backward reaction is E_1 and product is more stable than reactant.

110. Activation energy of a chemical reaction can be determined by ____________

(a) determining the rate constant at standard temperature.

(b) determining the rate constants at two temperatures.

(c) determining probability of collision.

(d) using catalyst.

111. According to which theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision ?

(a) Arrhenius theory
(b) Activated complex theory
(c) Collision theory
(d) Both (a) and (c)

STATEMENT TYPE QUESTIONS

112. Consider the following reaction :

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

(i) Rate of reaction with respect to NH_3 will be $-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t}$

(ii) For the given reaction $-\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$

(iii) For the given reaction $-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t}$

(iv) For the given reaction,

$$\text{Rate} = -\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{4\Delta[NO]}{\Delta t} = \frac{6\Delta[H_2O]}{\Delta t}$$

Which of the following is the correct code for the statements above.

(a) TTTT (b) TFTF
(c) FTFT (d) TFFT

113. Which of the following statement(s) is/are correct?

(i) Rate of reaction decreases with passage of time as the concentration of reactants decrease.

(ii) For a reaction

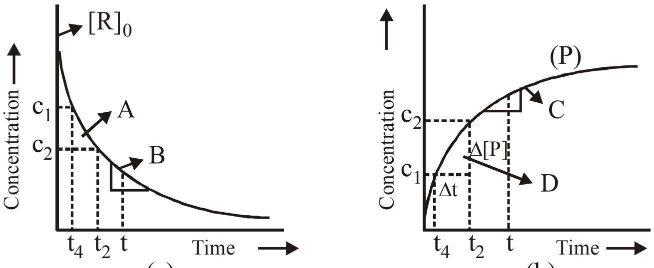
$$pP + qQ \longrightarrow rR + sS$$

$\text{Rate} = k[P]^x[Q]^y$ where $x = p$ and $y = q$

(iii) Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stichiometric coefficient of the reacting species in a balanced chemical equation.

(a) (i) and (iii) (b) (i) and (ii)
(c) (ii) and (iii) (d) (i) only

114. Study the following graphs and choose the correct option



(a) (b)

(i) in fig. a, A represents average rate and B represents instantaneous rate

(ii) in fig. b, D represents average rate and C represents instantaneous rate

(iii) fig. a, A represents instantaneous rate and B represents average rate

(iv) fig. b, C represents average rate and D represents instantaneous rate

(a) (i) and (ii) are correct (b) (ii) and (iv) are correct
(c) (i) and (iv) are correct (d) (ii) and (iii) are correct

115. Choose correct option based on following statements. Here T stands for true statement and F for false statement.

(i) Molecularity is defined as the number of reacting species taking part in a complex reaction,

(ii) Molecularity helps in understanding the mechanism of reaction.

(iii) Reactions with the molecularity three are very rare and slow to proceed.

(iv) Complex reactions involving more than three molecules take place in more than one step.

(a) TTTF (b) TFTF
(c) FTTF (d) FTTT

116. Read the following statements

(i) Order of reaction can be fractional or zero.

(ii) Molecularity of a reaction can be fractional but cannot be zero.

(iii) Slowest step in the complex reaction is considered as a rate determining step.

(iv) Units of rate constant for second order reaction are mol L s^{-1}.

(v) Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions.

Which of the following is the correct code for the statements above ?

(a) TTFFT (b) TFTFT
(c) FFFTT (d) FTTFF

117. Consider the following statements with respect of zero order reaction

(i) The rate of the reaction is independent of reactant concentration

(ii) The rate of the reaction is independent of temperature

(iii) The rate constant of the reaction is independent of temperature

(iv) The rate constant of the reaction is independent of reactant concentration

Choose the correct statement(s).

(a) (i) only (b) (i) and (ii) only
(c) (iii) and (iv) only (d) (i) and (iv)only

118. Which of the following statement(s) is/are correct ?

(i) For a zero order reaction concentration [R] vs time (t) gives a straight line plot

(ii) For a first order reaction $\log\frac{[R]_0}{[R]}$ does not vary linearly with time.

(iii) Inversion of cane sugar is a pseudo first order reaction.

(a) (i) and (iii) (b) (i) only
(c) (ii) and (iii) (d) (iii) only

119. At high pressure the following reaction is of zero order.

$$2NH_3(g) \xrightarrow[\text{Platinum catalyst}]{1130\text{ K}} N_2(g) + 3H_2(g)$$

Which of the following statements are correct for above reaction?

(i) Rate of reaction = Rate constant

(ii) Rate of reaction depends on concentration of ammonia.

(iii) Rate of decomposition of ammonia will remain constant until ammonia disappears completely.

(iv) Further increase in pressure will change the rate of reaction.

(a) (i), (iii) and (iv) (b) (i), (ii) and (iii)

(c) (ii) and (iv) (d) (i), (ii) and (iv)

120. Consider the following statements:

(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) lnk vs T is a straight line.

(v) lnk 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)

121. According to collision theory, not all collisions between molecules lead to reaction. Which of the following statements provide reasons for the same ?

(i) The total energy of the two colliding molecules is less than some minimum amount of energy.

(ii) Molecules cannot react with each other unless a catalyst is present.

(iii) Molecules that are improperly oriented during collision will not react.

(iv) Molecules in different states of matter cannot react with each other.

(a) (i) and (ii) (b) (i) and (iii)

(c) (ii) and (iii) (d) (i) and (iv)

122. Consider the following statements

(i) Rate constant for every physical and chemical change gets doubled with 10°C rise in temperature

(ii) On taking log both side Arrhenius equation will become

$$\log k = -\frac{Ea}{RT} + \log A$$

(iii) The energy required to form activated complex is known as activation energy

Which of the following is the correct code for statements above?

(a) TTT (b) FTT

(c) FTF (d) TFT

123. Read the following statements.

(i) $e^{-E_a/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a.

(ii) E_a can be calculated as follows

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

(iii) Catalyst can alter a reaction both ways means it can either decrease on increase rate of reaction

(iv) A catalyst always decreases the activation energy of the reaction but does not alter Gibb's energy.

(v) A catalyst does not alter equilibrium constant rather, it helps in attaining the equilibrium faster.

Which of the following is the correct codes for above statements ?

(a) TTTFF (b) TFFTT

(c) TFFTF (d) FTFTT

124. The following statement(s) is (are) correct :

(i) A plot of log k_p versus 1/T is linear

(ii) A plot of log [X] versus time is linear for a first order reaction, X → P

(iii) A plot of log p versus 1/T is linear at constant volume

(iv) A plot of p versus 1/V is linear at constant temperature

(a) (i) only (b) (ii) only

(c) (i) and (iv) (d) (i), (ii) and (iv)

MATCHING TYPE QUESTIONS

125. Match the columns

	Column-I		Column-II
(A)	Mathematical expression for rate of reaction	(p)	rate constant
(B)	Rate of reaction for zero order reaction is equal to	(q)	rate law
(C)	Units of rate constant for zero order reaction is same as that of	(r)	order of slowest step
(D)	Order of a complex reaction is determined by	(s)	rate of reaction

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

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

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

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

126. Match the columns

	Column-1		Column-II
(A)	Zero order reaction	(p)	L $mole^{-1}$ sec^{-1}
(B)	First order reaction	(q)	mole L^{-1} sec^{-1}
(C)	Second order reaction	(r)	sec^{-1}

(a) A – (q), B – (r) ,C – (p)

(b) A – (q), B – (p) ,C – (r)

(c) A – (p), B – (q) ,C – (r)

(d) A – (p), B – (r) ,C – (q)

127. Match the columns

	Column-I		**Column-II**
(A)	The decomposition of gaseous ammonia on a hot platinum surface	(p)	Zero order reaction
(B)	The thermal decomposition of HI on gold surface	(q)	Pseudo first order reaction.
(C)	All natural and artificial radioactive decay of unstable nuclei	(r)	Zero order reaction at high pressure
(D)	Inversion of cane sugar	(s)	First order reaction.

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

128. Match the columns.

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

(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)

129. Match the columns

	Column - I		**Column - II**
(A)	$k = \frac{[R_0]-[R]}{t}$	(p)	$k = \frac{2.303}{t_{1/2}}\log 2$
(B)	$k = \frac{2.303}{t}\log\frac{[R_0]}{[R]}$	(q)	Rate constant for zero order reaction
(C)	Value of k for first order reaction when $t = t_{\frac{1}{2}}$ and $[R] = \frac{[R]_0}{2}$	(r)	$k = \frac{[R]_0}{2t_{1/2}}$
(D)	Value of k for zero order reaction when $t = t_{1/2}$ and $[R] = \frac{[R]_0}{2}$	(s)	Rate constant for first order reaction

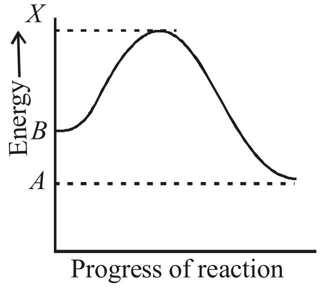
(a) A – (s), B – (q), C – (p), D – (r)
(b) A – (q), B – (s), C – (p), D – (r)
(c) A – (q), B – (p), C – (s), D – (r)
(d) A – (q), B – (s), C – (p), D – (t)

130. Match the columns

	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)

131. 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)

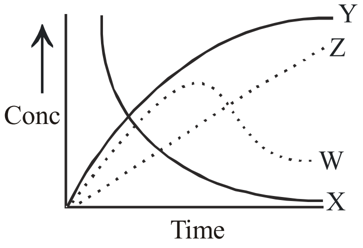
CRITICAL THINKING TYPE QUESTIONS

132. In the following reaction, how is the rate of appearance of underlined product related to the rate of disappearance of the underlined reactant ?

$$BrO_3^-(aq) + 5\underline{Br}^-(aq) + 6H^+ \longrightarrow 3\underline{Br}_2(l) + 3H_2O(l)$$

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

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



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

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

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

$$\frac{d[NO_2]}{dt} = k'\,[N_2O_5]$$

$$\frac{d[O_2]}{dt} = k''\,[N_2O_5]$$

The relationship between k and k' and between k and k″ are:

(a) $k' = 2k\,;\ k' = k$ (b) $k' = 2k\,;\ k'' = k/2$
(c) $k' = 2k\,;\ k'' = 2k$ (d) $k' = k\,;\ k'' = k$

135. $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$

Rate law for above reaction will be

Rate = $k[CHCl_3][Cl_2]^{\frac{1}{2}}$

On the basis of information provided which of the following option will be correct ?

(a) Rate law for any chemical reaction can be predicted accurately by looking at balanced chemical equation.
(b) Rate law for a chemical reaction has to determine experimentally.
(c) Either determined experimentally or obtained from balanced chemical reaction, rate law will be same.
(d) None of the above is correct.

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

$$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$$

The reaction is of first order with respect to $H_2(g)$ and ICI(g), following mechanisms were proposed.

Mechanism A:

$$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$$

Mechanism B:

$$H_2(g) + ICl(g) \longrightarrow HI(g); \text{slow}$$

$$HI(g) + ICl(g) \longrightarrow HCl(g) + I_2(g); \text{fast}$$

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

137. The hypothetical reaction $A_2 + B_2 \longrightarrow 2AB$; 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

138. The initial rates of reaction $3A + 2B + C \longrightarrow$ Products, at different initial concentrations are given below:

Initial rate, Ms^{-1}	**$[A]_0$, M**	**$[B]_0$, M**	**$[C]_0$, M**
5.0×10^{-3}	0.010	0.005	0.010
5.0×10^{-3}	0.010	0.005	0.015
1.0×10^{-2}	0.010	0.010	0.010
1.25×10^{-3}	0.005	0.005	0.010

The order with respect to the reactants, A, B and C are respectively

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

139. The rate law for the reaction $2X + Y \rightarrow Z$ is Rate = k[X][Y]. The correct statement with regard to this relation is

(a) the rate of the reaction is independent of [X] and [Y]
(b) for this reaction $t_{1/2}$ is independent of initial concentrations of reactant
(c) the rate of formation of Z is twice the rate of disappearance of X
(d) the rate of disappearance of X is equal to rate of disappearance of Y

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

$$CH_3COCH_3\,(aq) + Br_2\,(aq) \rightarrow CH_3COCH_2Br\,(aq) + H^+\,(aq) + Br^-\,(aq)$$

These kinetic data were obtained for given reaction concentrations.

Initial Concentrations, M			**Initial rate, disappearance of Br_2, Ms^{-1}**
$[CH_3COCH_3]$	**$[Br_2]$**	**$[H^+]$**	
0.30	0.05	0.05	5.7×10^{-5}
0.30	0.10	0.05	5.7×10^{-5}
0.30	0.10	0.10	1.2×10^{-4}
0.40	0.05	0.20	3.1×10^{-4}

Based on given data, the rate equations is:

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

141. Consider a reaction $aG + bH \rightarrow$ Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is

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

142. Diazonium salt decomposes as

$$C_6H_5N_2^+Cl^- \rightarrow C_6H_5Cl + N_2$$

At 0°C, the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is

(a) a first order reaction
(b) a second order reaction
(c) independent of the initial concentration of the salt
(d) a zero order reaction

143. Consider the following reaction at 25°C:

$(CH_3)_3COH(l) + HCl(aq) \rightarrow (CH_3)_3CCl(l) + H_2O(l)$

The experimentally determined rate law for this reaction indicates that the reaction is of first order in $(CH_3)_3COH$ and that the reaction is of first order overall. Which of the following would produce an increase in the rate of this reaction?

(a) Increasing the concentration of $(CH_3)_3COH$
(b) Increasing the concentration of HCl
(c) Decreasing the concentration of HCl
(d) Decreasing the concentration of $(CH_3)_3CCl$

144. The following data pertains to reaction between A and B :

S. No.	$[A]$ mol L^{-1}	$[B]$ mol L^{-1}	Rate (mol L^{-1} time^{-1})
1	1.0×10^{-2}	2.0×10^{-2}	2.0×10^{-4}
2	2.0×10^{-2}	2.0×10^{-2}	4.0×10^{-4}
3	2.0×10^{-2}	4.0×10^{-2}	8.0×10^{-4}

Which of the following inference(s) can be drawn from the above data ?

(i) Rate constant of the reaction is 1.0×10^{-4}.
(ii) Rate law of the reaction is : rate = $k[A][B]$
(iii) Rate of reaction increases four times on doubling the concentration of both the reactants.

Select the correct answer using the codes given below :

(a) (i), (ii) and (iii) (b) (i) and (ii)
(c) (ii) and (iii) (d) (iii) only

145. The decomposition of ammonia on tungsten surface at 500 K follows zero order kinetics. The half-life period of this reaction is 45 minutes when the initial pressure is 4 bar. The half-life period (minutes) of the reaction when the initial pressure is 16 bar at the same temperature is

(a) 120 (b) 60
(c) 240 (d) 180

146. A substance 'A' decomposes by a first order reaction starting initially with [A] = 2.00 M and after 200 min, [A] becomes 0.15 M. For this reaction $t_{1/2}$ is

(a) 53.72 min (b) 50.49 min
(c) 48.45 min (d) 46.45 min

147. If half-life of a substance is 5 yrs, then the total amount of substance left after 15 years, when initial amount is 64 grams is

(a) 16 grams (b) 2 grams
(c) 32 grams (d) 8 grams.

148. In a 1st order reaction, reactant concentration C varies with time t as :

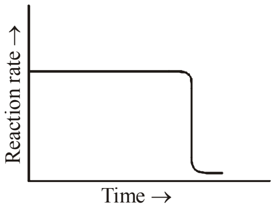
(a) $\frac{1}{C}$ increases linearly with t
(b) $\log C$ decreases linearly with t
(c) C decreases with $\frac{1}{t}$
(d) $\log C$ decreases with $\frac{1}{t}$

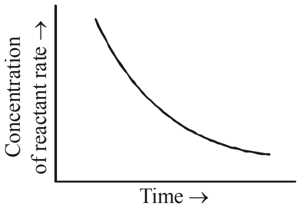
149. For the first order reaction

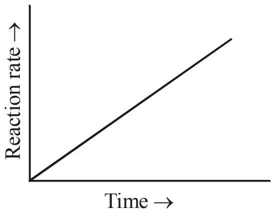
$C_2H_4O(g) \rightarrow CH_4(g) + CO(g)$, the initial pressure of $C_2H_4O(g)$ is 80 torr and total pressure at the end of 20 minutes is 120 torr. The time needed for 75% decomposition of C_2H_4O would be :

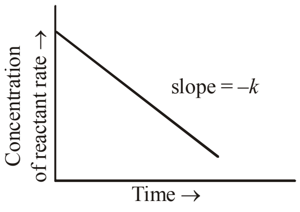
(a) 20 minutes (b) 40 minutes
(c) 80 minutes (d) 120 minutes

150. Which of the following graph(s) is/are correct for a zero order reaction?

(i)


(iii)


(iii)


(iv)


(a) (ii) and (iii) (b) (i), (ii) and (iii)
(c) (ii), (iii) and (iv) (d) (i) and (iv)

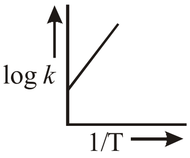
151. The integrated rate equations can be determined for
(a) zero order reactions
(b) first order reactions
(c) second order reactions
(d) Both (a) and (b)

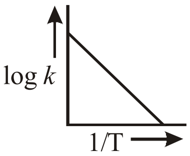
152. In a zero-order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, the rate of the reaction will become :
(a) 256 times (b) 512 times
(c) 64 times (d) 128 times

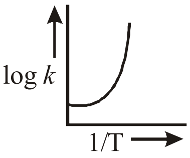
153. For a first order reaction A→P, the temperature (T) dependent rate constant (*k*) was found to follow the equation $\log k = -(2000)\frac{1}{T} + 6.0$. The pre-exponential factor A and the activation energy E_a, respectively, are
(a) $1.0 \times 10^6\ s^{-1}$ and $9.2\ kJ\ mol^{-1}$
(b) $6.0\ s^{-1}$ and $16.6\ kJ\ mol^{-1}$
(c) $1.0 \times 10^6\ s^{-1}$ and $16.6\ kJ\ mol^{-1}$
(d) $1.0 \times 10^6\ s^{-1}$ and $38.3\ kJ\ mol^{-1}$

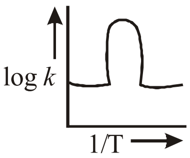
154. The activation energies of two reactions are E_1 and E_2 ($E_1 > E_2$). If the temperature of the system is increased from T_1 to T_2, the rate constant of the reactions changes from k_1 to k_1' in the first reaction and k_2 to k_2' in the second reaction. Predict which of the following expression is correct?
(a) $\frac{k_1'}{k_1} = \frac{k_2'}{k_2}$ (b) $\frac{k_1'}{k_1} > \frac{k_2'}{k_2}$
(c) $\frac{k_1'}{k_1} < \frac{k_2'}{k_2}$ (d) $\frac{k_1'}{k_1} = \frac{k_2'}{k_2} = 1$

155. A graph plotted between log k vs 1/T for calculating activation energy is shown by

(a) 

(b) 

(c) 

(d) 

156. The rate constant, the activation energy and the arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} s^{-1}$, $104.4\ kJ\ mol^{-1}$ and $6.0 \times 10^{14}\ s^{-1}$ respectively. The value of the rate constant as $T \to \infty$ is
(a) $2.0 \times 10^{18}\ s^{-1}$ (b) $6.0 \times 10^{14}\ s^{-1}$
(c) Infinity (d) $3.6 \times 10^{30}\ s^{-1}$

157. Collision theory is used to explain how chemical species undergo a reaction. Using this theory and the kinetic molecular model, which of the following does NOT influence the rate of a chemcial reaction?
(a) The temperature of the system
(b) The geometry or orientation of the collision
(c) The velocity of the reactants at the point of collision
(d) All of the above influence the rate

158. The activation energy for a hypothetical reaction, A → Product, is 12.49 kcal/mole. If temperature is raised from 295 to 305, the rate of reaction increased by
(a) 60% (b) 100%
(c) 50% (d) 20%

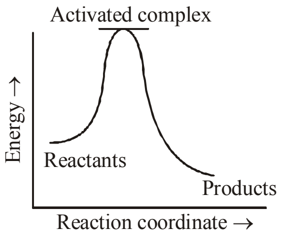
159. A reactant (A) froms two products :

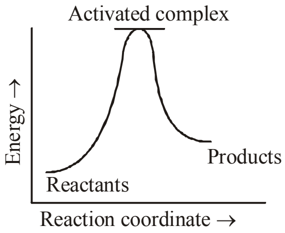
$$A \xrightarrow{k_1} B, \text{ Activation Energy } E_{a_1}$$

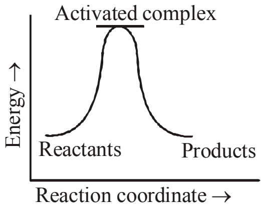
$$A \xrightarrow{k_2} C, \text{ Activation Energy } E_{a_2}$$

If $E_{a_2} = 2\,E_{a_1}$, then k_1 and k_2 are related as :
(a) $k_2 = k_1 e^{Ea_1/RT}$ (b) $k_2 = k_1 e^{Ea_2/RT}$
(c) $k_1 = Ak_2 e^{Ea_1/RT}$ (d) $k_1 = 2k_2 e^{Ea_2/RT}$

160. Which of the following graph(s) represents exothermic reaction?

(A) 

(B) 

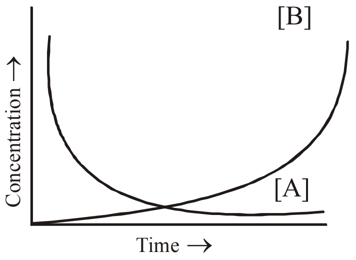
(C) 

(a) (A) only (b) (B) only
(c) (C) only (d) (A) and (B)

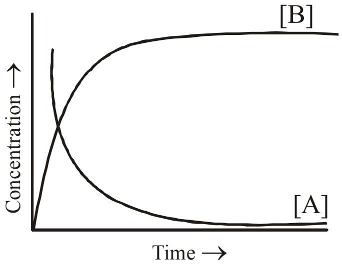
161. Which of the following statements is **not** correct for the catalyst?
(a) It catalyses the forward and backward reaction to the same extent.
(b) It alters ΔG of the reaction.
(c) It is a substance that does not change the equilibrium constant of a reaction.
(d) It provides an alternate mechanism by reducing activation energy between reactants and products.

162. Consider the reaction A *f* B. The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?

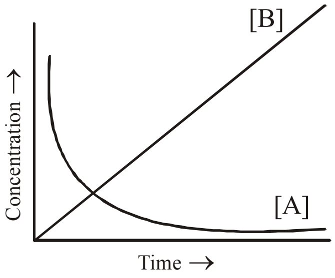
(a)



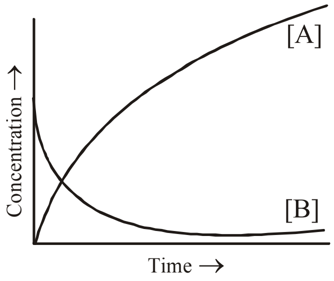
(b)



(c)



(d)



163. During decomposition of an activated complex.

(i) energy is always released
(ii) energy is always absorbed
(iii) energy does not change
(iv) reactants may be formed

(a) (i), (ii) and (iii) (b) (i) and (iv)
(c) (ii) and (iii) (d) (ii), (iii) and (iv)

164. Which of the following statements is incorrect ?

(a) Energy is always released when activated complex decomposes to form products.
(b) Peak of the energy distribution curve corresponds to the most probable potential energy.
(c) Peak of the energy distribution curve corresponds to the most probable kinectic energy.
(d) When the temperature is raised maximum of energy distribution curve moves to higher energy value and broadens out.

HINTS AND SOLUTIONS

FACT/DEFINITION TYPE QUESTIONS

1. **(b)** **2.** **(b)** **3.** **(a)** **4.** **(a)** **5.** **(c)**

6. **(d)** In the given options $-\frac{d[C]}{3dt}$ will not represent the reaction rate. It should not have –ve sign as it is product.

since $\frac{1}{3}\frac{dC}{dt}$ show the rate of formation of product C which will be positive.

7. **(a)** If we write rate of reaction in terms of concentration of NH_3 and H_2, then

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

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

8. **(d)** In the given options $-\frac{d[C]}{3.dt}$ will not represent the reaction rate. It should not have –ve sign as it is product.

since $\frac{1}{3}\frac{dC}{dt}$ show the rate of formation of product C which will be positive.

9. **(c)** Rusting of iron is a slow change.

10. **(c)** The feasibility of a chemical reaction can be predicted by thermodynamics. Extent to which a reaction will proceed can be determined from chemical equilibrium. Speed of a reaction i.e. time taken by a reaction to reach equilibrium, can be predicted by chemical kinetics

11. **(c)** **12.** **(d)** **13.** **(c)** **14.** **(a)** **15.** **(b)**

16. **(c)** **17.** **(c)** **18.** **(d)**

19. **(d)** The rate of a reaction is the speed at which the reactants are converted into products. It depends upon the concentration of reactants. e.g for the reaction

$$A + B \longrightarrow \text{Product}; \qquad r \propto [A][B]$$

20. **(a)** k remains constant at constant temperature and CO does not effect the rate of reaction.

21. **(d)** order of reaction may be zero, whole number or fractional.

22. **(b)** $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

Rate $= k\,[NO]^2\,[Cl]$

The value of rate constant can be increased by increasing the temperature.

23. **(d)** Order of reaction is equal to the number of molecules whose concentration is changing with time. It can be zero or in fractions or an integer.

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

rate $= k[A]^o$ i.e. rate $= k$

hence unit of $k = M.sec^{-1}$

For a first order reaction.

rate $= k\,[A]$

$k = M.sec^{-1}/M = sec^{-1}$

25. **(d)** The reaction involving two different reactant can never be unimolecular.

26. **(b)** For reaction $3A \longrightarrow B + C$

If it is zero order reaction $r = k\,[A]^0$, i.e the rate remains same at any concentration of 'A'. i.e independent upon concentration of A.

27. **(c)** $k = (mol\ lit^{-1})^{1-n}\ time^{-1}$. For given reaction $n = 2$. $\therefore k = mol^{-1}\ lit\ sec^{-1}$

28. **(b)** The order of a chemical reaction is given by concentration of reactants appearing in the lowest step.

29. **(b)** Velocity constant 'k' is characteristic constant of a reaction and depends only on temperature and catalyst.

30. **(b)** Given $dx/dt = 2.400 \times 10^{-5}$ mol litre^{-1} sec^{-1}

$k = 3.10 \times 10^{-5}\ sec^{-1}$

For first order reaction

$$2N_2O_5 \longrightarrow 2NO_2 + O_2$$

$$\frac{dx}{dt} = k[N_2O_5]$$

or $2.4 \times 10^{-5} = 3.0 \times 10^{-5}\,[N_2O_5]$

or $[N_2O_5] = \frac{2.4\times10^{-5}}{3.0\times10^{-5}} = 0.8$ mol. litre^{-1}

31. **(a)** For zero order reaction, $\frac{dx}{dt} = k\,[\text{reactant}]^0$

Thus the rate of zero order reaction is independent of concentration of reactants.

32. **(c)** $\text{Rate}_1 = k\,[A]^n\,[B]^m$; $\text{Rate}_2 = k\,[2A]^n\,[½B]^m$

$$\therefore \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[2A]^n[½B]^m}{k[A]^n[B]^m} = [2]^n\,[½]^m = 2^n.2^{-m} = 2^{n-m}$$

33. **(a)** $2A + B \longrightarrow A_2B$

$r_1 = k[A]^2\,[B]$ ...(i)

When, $[A] = [2A]$, $[B] = \left[\frac{B}{2}\right]$

$$r_2 = k\left[2A\right]^2\left[\frac{B}{2}\right] = k\,4[A]^2\,\frac{[B]}{2}$$

$$= k\,2[A]^2[B] = 2r_1 \qquad \left(\because r_1 = k[A]^2[B]\right)$$

$\therefore$ Rate of reaction is increased two times.

34. **(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.

35. **(a)** rate $\propto [p_{\text{reactant}}]^0$
i.e., rate = k
So, the order of reaction will be zero.

36. **(b)** $\because\ r = k[A]^n$
if $n = 0$
$r = k[A]^0$
or $r = k$ thus for zero order reactions rate is equal to the rate constant.

37. **(c)** Since rate of reaction becomes four times on doubling concentration of reactant, it is second order reaction.

38. **(b)** Order is the sum of the power of the concentration terms in rate law expression.
Hence the order or reaction is = 1 + 2 = 3

39. **(a)** Rate = $k[A]^\circ$
Unit of k = mol L^{-1} sec^{-1}

40. **(c)** $N_2O \longrightarrow N_2 + \frac{1}{2}O_2$

$\frac{dx}{dt} \propto [N_2O]^1$

i.e. order of reaction = 1

41. **(a)** From the first set of data (i) and (ii) it is observed that on keeping concentration of [B] constant and on doubling the concentration of [A] rate does not changes hence order of reaction with respect to A is zero.
From the second set of data (i) and (iii) it is observed that rate becomes 4 times on doubling the concentration of [B] keeping [A] constant hence order with respect to [B] will be 2
rate = $k[A]^0 [B]^2$

42. **(c)** Order is the sum of the powers to which the concentration terms are raised in the rate equation.

43. **(d)** If rate = $k[A]^x [B]^y [C]^z$
From first two given data
$8.08 \times 10^{-3} = k [0.2]^x [0.1]^y [0.02]^z$ .... (1)
$2.01 \times 10^{-3} = k [0.1]^x [0.2]^y [0.02]^z$ .... (2)
Divide (1) by (2) we get, $4 = 2^x (1/2)^y$
Similarly, from second and third data
$(9)^y (9)^z = 3$
$2y + 2z = 1$.
From first and fourth data $4^z = 8 = 2^3$
$2z = 3$. So $z = 3/2, y = -1, x = 1$

44. **(a)** Let the rate law be $r = k [A]^x[B]^y$
Divide (3) by (1) $\frac{0.10}{0.10} = \frac{[0.024]^x[0.035]^y}{[0.012]^x[0.035]^y}$
$\therefore 1 = [2]^x, x = 0$
Divide (2) by (3) $\frac{0.80}{0.10} = \frac{[0.024]^x[0.070]^y}{[0.024]^x[0.035]^y}$
$\therefore 8 = (2)^y, y = 3$
Hence, rate equation, $R = k[A]^0[B]^3 = k[B]^3$

45. **(a)** Given $r = k [A]^{3/2} [B]^{-1/2}$
Order = $3/2 - 1/2 = \frac{3-1}{2} = \frac{2}{2} = 1$

46. **(b)** The order w.r.t. I_2 is zero because the rate is not dependent on the concentration of I_2.

47. **(c)** As we know that, units of rate constant.
= (unit of conc.)$^{1-n}$ (unit of time)$^{-1}$
= $(\text{mol L}^{-1})^{1-n} (\text{sec})^{-1}$
On comparing these units with the given units of rate constant, we get
$(\text{mol L}^{-1})^{1-n} (\text{sec})^{-1} = \text{L mol}^{-1} \text{sec}^{-1}$
$\Rightarrow \text{L}^{n-1} \text{mol}^{1-n} \text{sec}^{-1} = \text{L mol}^{-1} \text{sec}^{-1}$
On comparing the powers, we get
$n - 1 = 1 \Rightarrow n = 2$
So, reaction is of second order.

48. **(d)** In case of (II) and (III), keeping concentration of [A] constant, when the concentration of [B] is doubled, the rate quadruples. Hence it is second order with respect to B. In case of I & IV Keeping the concentration of [B] constant. when the concentration of [A] is increased four times, rate also increases four times. Hence, the order with respect to A is one. hence
Rate = $k [A] [B]^2$

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

50. **(b)** $O_3 \xrightarrow{\text{Fast}} O_2 + O;\ O + O_3 \xrightarrow{\text{Slow}} 2O_2$

$k = \frac{[O_2][O]}{[O_3]}$ (I) Rate = $k' [O_3][O]$ put [O] from (I)

$r = \frac{k'[O_3]K[O_3]}{[O_2]} = k[O_3]^2[O_2]^{-1}$

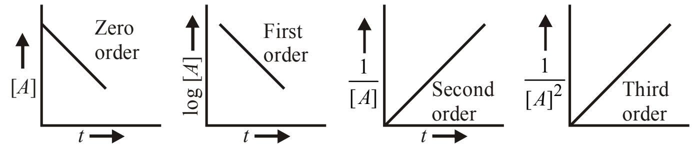
Note intermediates are never represented in rate law equation.

51. **(c)**

52. **(c)** Thermal decomposition of HI on gold surface is an example of zero order reaction.

53. **(c)** For zero order reaction,
rate, $r = k[R]^\circ$
$\Rightarrow \frac{dR}{dt} = k$
$\Rightarrow R = kt + R_0$
where R_0 is the concentration of reactant at time $t = 0$.
Thus [R] increases with time

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



55. **(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.

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

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

57. **(a)** $t_{1/2} = 4s$ $T = 16s$

$$n = \frac{T}{t_{1/2}} = \frac{16}{4} = 4 \qquad (\therefore T = n \times t_{1/2})$$

$$[A] = [A]_0\left(\frac{1}{2}\right)^n = 0.12 \times \left(\frac{1}{2}\right)^4 = \frac{0.12}{16} = 0.0075 \text{ M}$$

Where $[A]_0$ = initial concentration and [A] = concentration left after time t

58. **(b)** $A \to B$ 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

59. **(b)** For a first order reaction, A → products

$$r = k[\text{A}] \text{ or } k = \frac{r}{[\text{A}]}$$

$$\Rightarrow k = \frac{1.5 \times 10^{-2}}{0.5} = 3 \times 10^{-2}$$

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

60. **(c)** For first order reaction, $k = \frac{0.693}{t_{1/2}}$

where k = rate constant
$t_{1/2}$ = half life period = 480 sec.

$$\therefore k = \frac{0.693}{480} = 1.44 \times 10^{-3} \text{ sec}^{-1}$$

61. **(c)** $[\text{A}] = [\text{A}]_0\left(\frac{1}{2}\right)^n$

where $[\text{A}]_0$ = initial concentration

$$\frac{1}{8} = 1\left(\frac{1}{2}\right)^n ; n = 3$$

$$t_{1/2} = \frac{0.693}{6.9 \times 10^{-3}} = 100 \text{ sec}$$

$\therefore T = n \times t_{1/2} = 3 \times 100 = 300$ sec.

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

$$\text{Thus, } k = \frac{2.303}{t}\log\frac{a}{(a-x)} = \frac{2.303}{32}\log\frac{100}{(100-75)}$$

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

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

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

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

63. **(d)** Unit of k for Ist order reaction is $(\text{Time})^{-1}$

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

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

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

65. **(c)** For a first order reaction

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

when $t = t_{1/2}$

$$k = \frac{2.303}{t_{1/2}}\log\frac{a}{a - a/2}$$

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

66. **(b)** Since doubling the concentration of B does not change half life, the reaction is of 1st order w.r.t. B.
Order of reaction with respect to A = 1 because rate of reaction doubles when concentration of A is doubled keeping concentration of B constant.
$\therefore$ Order of reaction = 1 + 1 = 2 and units of second order reaction are L mol^{-1} sec^{-1}.

67. **(c)** Half life time $(t_{1/2})$ for nth order reaction is given by,
$t_{1/2} \propto [a]^{1-n}$
where n is the order of reaction and a is concentration of reactant.

As decomposition of N_2O_5 follows 1st order kinetic. So,

$\Rightarrow t_{1/2} \propto [a]^{1-1} \quad \Rightarrow t_{1/2} \propto a^0$

68. (c) For a first order reaction

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

when $t = t_{½}$

$$k = \frac{2.303}{t_{½}}\log_{10}\frac{a}{a-a/2}$$

$$\text{or } t_{½} = \frac{2.303}{k}\log_{10} 2 = \frac{\ln 2}{k}$$

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

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

70. (c) $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1};\ \frac{120}{240} = \left(\frac{4\times10^{-2}}{8\times10^{-2}}\right)^{n-1};\ n = 2$

71. (b)

72. (b) In Haber's process, ammonia is manufactured from N_2 and H_2 using iron as catalyst with molybdenum as promoter at high temperature and pressure

$$N_2 + 3H_2 \xrightarrow[\text{Mo(catalytic promoter)}]{Fe_2O_3\text{ (catalyst)}} 2NH_3$$

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

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

$$0.3 = \frac{E_a}{2.303\times8.314} \times \frac{15}{293\times308}$$

$$E_a = \frac{0.3\times2.303\times8.314\times293\times308}{15}.$$

$= 34673\ \text{J mole}^{-1}$
$= 34.7\ \text{J mole}^{-1}$

74. (b) $\Delta H = E_{a_f} - E_{a_b} = 0$

75. (d) The activation energy depends upon the nature of chemical bonds undergoing rupture during chemical reaction and is independent of enthalpies of reactants and products.

76. (b) $k = Ae^{-E_a/RT}$
$\ln k = \ln A - E_a/RT$
For ln k vs 1/T
ln A = intercept
$-E_a/R = \text{slope} = -2 \times 10^4\ K$
$\therefore E_a = 8.3 \times 2 \times 10^4\ \text{J mol}^{-1}$
$= 16.6 \times 10^4\ \text{J mol}^{-1}$ or $166\ \text{kJ mol}^{-1}$

77. (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 $= 2^9 = 512$

78. (a) As per Arrhenius equation $(k = Ae^{-E_a/RT})$, the rate constant increases exponentially with temperature.

79. (b) For a reversible reaction,
$\Delta H = E_a\text{ (forward)} - E_a\text{ (backward)}$
$\Delta H = 150 - 260 = -110\ \text{kJ mol}^{-1}$

80. (c) We know that the activation energy of chemical reaction is given by formula $= \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$, 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.

81. (b) In equation $k = Ae^{-E_a/RT}$; A = Frequency factor k = velocity constant, R = gas constant and E_a = energy of activation

82. (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.

83. (d)

84. (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.

85. (a) Arrhenius equation is given by

$k = Ae^{-E_a/(2.303RT)}$

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 $\frac{-E_a}{2.303R}$.

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

$$\log\frac{k_2}{k_1} = \frac{9.0\times10^3}{2.303\times2}\left[\frac{308-298}{308\times298}\right]$$

$$\frac{k_2}{k_1} = 1.63;\ k_2 = 1.63k_1;$$

$$\text{Increase in } k_1 = \frac{k_2 - k_1}{k_1} \times 100$$

$$= \frac{1.63k_1 - k_1}{k_1} \times 100 = 63.0\%$$

87. (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, $\Delta H = -\text{ve}$, $E_{a(b)} > E_{a(f)}$

If reaction is endothermic, $\Delta H = +\text{ve}$ $E_{a(b)} < E_{a(f)}$

88. (d) **89. (c)** **90. (c)** **91. (a)** **92. (d)**

93. (d)

94. (d) $k = Ae^{-E_a/RT}$

95. (b) $\ln k = \ln A - \frac{E_a}{RT}$, intercept is ln A.

96. (c) The rate constant doubles for 10º C rise in temperature. For 20º C rise, the rate constant will be 4 times
$\therefore k_1 = 4k_2$ or $k_2 = 0.25\ K_1$

97. (d) $k = Ae^{-E_a/RT}$ $\log k = \log A - \frac{E_a}{2.303R}.\frac{1}{T}$

Equation of straight line slope = $\frac{-E_a}{2.303R}$.

98. (c) Applicable to bimolecular reactions.

99. (a)

100. (d) All the statements are correct (see text).

101. (c) Activation energy is lowered in presence of +ve catalyst.

102. (c)

103. (a) Threshold Energy = Energy of activation + Internal energy

104. (b) $k = Ae^{-E_a/RT}$ $\log k = \log A - \frac{E_a}{2.303R}.\frac{1}{T}$

Plot of log k Vs. $\frac{1}{T}$

Straight line Slope = $\frac{-E_a}{2.303R}$

105. (d) Enthalpy of reaction $(\Delta H) = E_{a\,(f)} - E_{a\,(b)}$
for an endothermic reaction $\Delta H = +\text{ve}$ hence for ΔH to be positive
$E_{a\,(b)} < E_{a\,(f)}$

106. (a) Presence of catalyst does not affect enthalpy change of reaction $\Delta H_R = E_f - E_b = 180 - 200 = -20$ kJ/mol

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) For a 10 K rise in temperature, collision frequency increases merely by 1 to 2% but the number of effective collisions increases by 100 to 200%.

109. (a) **110. (b)** **111. (c)**

STATEMENT TYPE QUESTIONS

112. (b) For the given reaction

$$4NH_3(g) + 5O_2(g) \xrightarrow{pt(s)} 4NO(g) + 6H_2O(g)$$

$$\text{Rate} = \frac{-1}{4}\frac{\Delta[NH_3]}{\Delta t} = \frac{-1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

113. (a) For given reaction x and y may or may not be equal to p and q respectively.

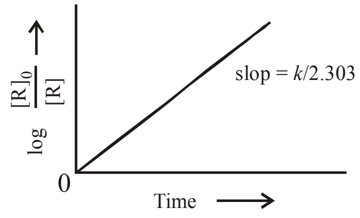
114. (a) Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur. Average rate cannot be used to predict the rate of a reaction at a particular instant as it would be constant for the time interval for which it is calculated. So, to express the rate at a particular moment of time we determine the instantaneous rate. It is obtained when we consider the average rate at the smallest time interval say dt (i.e. when it approaches zero).

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

116. (b) Molecularity cannot be fractional or zero. Correct units of rate constant for second order reaction are $mol^{-1}\,Ls^{-1}$.

117. (d) For zero order reaction, rate of reaction as well as rate constant are independent of reactant concentration.

118. (a) For a first order reaction $\log\frac{[R]_0}{[R]}$ varies linearly with time as shown below.



119. (a)

120. (b) According to Arrhenius equation, $k = Ae^{-E_a/RT}$
$\therefore$ when $E_a = 0$, $k = A$
Also ln k υs 1/T is a straight line with slope = $-E_a/R$.
$\therefore$ Statements (ii) and (v) are correct.

121. (b)

122. (b) Rate constant gets doubled with every 10°C in temperature for chemical change only not for physical change.

123. (b) Correct formula for calculation of E_a is

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

The word catalyst should not be used when the added substance reduces the rate of reaction. The substance is then called inhibiter.

124. (d) The relevant expressions are as follows.

$$\log K_p=-\frac{\Delta H}{R}\frac{1}{T}+I$$

$\log[X]=\log[X]_0+kt$

$P/T=\text{constant}$ (V constant)

$PV=\text{constant}$ (T constant)

MATCHING TYPE QUESTIONS

125. (a) **126. (b)** **127. (a)** **128. (c)** **129. (b)**
130. (a) **131. (d)**

CRITICAL THINKING TYPE QUESTIONS

132. (c) $-\frac{1}{5}\frac{d[Br^-]}{dt}=\frac{1}{3}\frac{d[Br_2]}{dt}$

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

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

134. (b) Rate of disappearance of reactants = Rate of appearance of products

$$-\frac{1}{2}\frac{d(N_2O_5)}{dt}=\frac{1}{4}\frac{d(NO_2)}{dt}=\frac{d(O_2)}{dt}$$

$$\frac{1}{2}k(N_2O_5)=\frac{1}{4}k'(N_2O_5)=k''(N_2O_5)$$

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

$$k'=2k,\quad k''=\frac{k}{2}$$

135. (b) Rate law has to be determined experimentally as Cl_2 is raised to power $\frac{1}{2}$ in rate law whereas its stichiometric coefficient in balanced chemical equation is 1.

136. (d) As the slowest step is the rate determining step thus the mechanism B will be more consistent with the given information also because it involve one molecule of H_2 and one molecule of ICl it can expressed as

$r=k[H_2][ICl]$

Which shows that the reaction is first order w.r.t. both H_2 & ICl.

137. (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 $=K\sqrt{k[A_2]}[B_2]$

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

138. (d) From 1st and 2nd sets of data - no change in rate is observed with the change in concentration of 'C'. So the order with respect to 'C' is zero.

From 1st and 4th sets of data

Dividing eq. (4) by eq. (1)

$$\frac{1.25\times10^{-3}}{5.0\times10^{-3}}=\left[\frac{0.005}{0.010}\right]^x$$

or $0.25=(0.5)^x$ or $(0.5)^2=(0.5)^x$

$\therefore x=2$

The order with respect to 'A' is 2 from the 1st and 3rd sets of data dividing eq. (1) by eq. (3)

$$\frac{5.0\times10^{-3}}{1.0\times10^{-2}}=\left[\frac{0.005}{0.010}\right]^y$$

or $(0.5)^1=(0.5)^y\Rightarrow y=1$

The order with respect to 'B' is 1

So the order with respective the reactants A, B and C is 2, 1 and 0.

139. (N) None of the given options is correct.

The given reaction is : $2X+Y\longrightarrow Z$

$$-\frac{d[X]}{2dt}=\frac{d[Z]}{dt}$$

$\therefore$ Rate of formation of Z is half of the rate of disappearance of X.

$$\frac{-d[X]}{2dt}=\frac{-d[Y]}{dt}$$

Rate of disappearrance of X is not equal to rate of disappearance of Y.

140. (a) Rewriting the given data for the reaction

$$CH_3COCH_3(aq)+Br_2(aq)\xrightarrow{H^+}$$
$$CH_3COCH_2Br(aq)+H^+(aq)+Br^-(aq)$$

S. No.	Initial concent -ration of CH_3COCH_3 in M	Initial concentr -ation of Br_2 in M	Initial concentr -ation of H^+ in M	Rate of disappearance of Br_2 in Ms^{-1} i.e. $-\frac{d}{dt}[Br_2]$ or $\frac{dx}{dt}$
1	0.30	0.05	0.05	5.7×10^{-5}
2	0.30	0.10	0.05	5.7×10^{-5}
3	0.30	0.10	0.10	1.2×10^{-4}
4	0.40	0.05	0.20	3.1×10^{-4}

Actually this reaction is autocatalyzed and involves complex calculation for concentration terms.

We can look at the above results in a simple way to find the dependence of reaction rate (i.e., rate of disappearance of Br_2).

From data (1) and (2) in which concentration of CH_3COCH_3 and H^+ remain unchanged and only the concentration of Br_2 is doubled, there is no change in rate of reaction. It means the rate of reaction is **independent of concentration of Br_2.**

Again from (2) and (3) in which ($CH_3CO\ CH_3$) and (Br_2) remain constant but H^+ increases from 0.05 M to 0.10 i.e. doubled, the rate of reaction changes from 5.7×10^{-5} to 1.2×10^{-4} (or 12×10^{-5}), thus it also becomes almost doubled. It shows that rate of reaction is directly proportional to $[H^+]$. From (3) and (4), the rate should have doubled due to increase in conc of $[H^+]$ from 0.10 M to 0.20 M but the rate has changed from 1.2×10^{-4} to 3.1×10^{-4}. This is due to change in concentration of CH_3COCH_3 from 0.30 M to 0.40 M. Thus the rate is directly proportional to $[CH_3\ COCH_3]$.

We now get

$$\text{rate} = k\,[CH_3COCH_3]^1[Br_2]^0[H^+]^1$$
$$= k\,[CH_3COCH_3][H^+].$$

141. (d) Overall order = sum of orders w.r.t each reactant.

Let the order be x and y for G and H respectively

Exp.No.	[G]mole litre^{-1}	[H]mole litre^{-1}	rate(mole litre^{-}time^{-1})
1	a	b	r
2	$2a$	$2b$	$8r$
3	$2a$	b	$2r$

$\because$ For (1) and (3), the rate is doubled when conc. of G is doubled keeping that of H constant i.e.,

rate $\propto [G]$ $\therefore x = 1$

From (2) and (3), $y = 2$

$\therefore$ Overall order is 3.

142. (a) As doubling the initial conc. doubles the rate of reaction, order =1

143. (a)

144. (c) Rate law : $-\frac{d[A]}{dt} = k[A]^x[B]^y$

Doubling $[A]$, rate is doubled. Hence $2^x = 2$, $x = 1$

Similarly $y = 1$; $-\frac{d[A]}{dt} = k[A][B]$

$$k = \frac{\text{rate}}{[A][B]} = \frac{2.0\times10^{-4}}{1\times10^{-2}\times2\times10^{-2}} = 1$$

$$\frac{(\text{rate})_2}{(\text{rate})_1} = \frac{k(2[A])(2[b])}{k[A][B]} = 4$$

145. (d) For a zero order reaction,

$t_{1/2} \propto a_0$ (initial concentration or initial pressure)

$(t_{1/2})_1 \propto P_1$

$(t_{1/2})_2 \propto P_2$

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{P_2}{P_1},\ \frac{(t_{1/2})_2}{45} = \frac{16}{4}$$

$$(t_{1/2})_2 = \frac{16}{4}\times45 = 180 \text{ min}$$

146. (a) Given initial concentration $(a) = 2.00$ M; Time taken $(t) = 200$ min and final concentration $(a-x) = 0.15$ M. For a first order reaction rate constant,

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{200}\log\frac{2.00}{0.15}$$

$$= \frac{2.303}{200}\times(0.301+0.824) = 1.29\times10^{-2}\ \text{min}^{-1}.$$

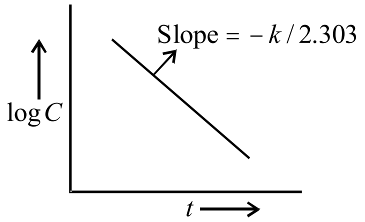
Further

$$(t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{1.29\times10^{-2}} = 53.72\ \text{min}.$$

147. (d) $t_{1/2} = 5$ years, $T = 15$ years hence total number of half life periods $= \frac{15}{5} = 3$.

$\therefore$ Amount left $= \frac{64}{(2)^3} = 8\text{g}$

148. (b)



149. (b) Let x torr of C_2H_4O decompose after 20 min. Then, $80 - x + 2x = 120$; $x = 40$ torr = 50% of initial pressure. Hence $t_{1/2} = 20$ min. For 75% reaction, fraction left

$$= \frac{25}{100} = \frac{1}{4} = \left(\frac{1}{2}\right)^2$$

No. of half lives = 2. Time needed for 75% reaction., $2\times20 = 40$ min

150. (d)

151. (d) The integrated rate equations are different for the reactions of different reaction orders. We shall determine these equations only for zero and first order chemical reactions.

152. (b) $\frac{r_{100°C}}{r_{10°C}} = 2^{\left(\frac{T_2-T_1}{10}\right)} = 2^{\left(\frac{100-10}{10}\right)} = 2^9 = 512$ (where 2 is temperature coefficient of reaction)

153. (d) $\log k = \log A - \frac{E_a}{2.303RT}$ ...(1)

Also given $\log k = 6.0 - (2000)\frac{1}{T}$ ...(2)

On comparing equations, (1) and (2)

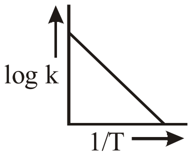
$\log A = 6.0 \Rightarrow A = 10^6\, s^{-1}$

and $\frac{E_a}{2.303\, R} = 2000$;

$\Rightarrow E_a = 2000 \times 2.303 \times 8.314 = 38.29\, kJ\, mol^{-1}$

154. (b) We know more will be activation energy lesser will be rate constant. Thus if $E_1 > E_2$ then $k_1 < k_2$. As temperature increases, it will effect both rates in similar way.

155. (b) A graph plotted between log k vs $\frac{1}{T}$ for calculating activation energy is shown as



from Arrhenius equation

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

156. (b) $T_2 = T$(say), $T_1 = 25°C = 298K$,

$E_a = 104.4\, kJ\, mol^{-1} = 104.4 \times 10^3\, J\, mol^{-1}$

$k_1 = 3 \times 10^{-4}$, $k_2 = ?$,

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

$$\log\frac{k_2}{3\times10^{-4}} = \frac{104.4\times10^3\ J\ mol^{-1}}{2.303\times(8.314\ J\ K^{-1} mol^{-1})}\left[\frac{1}{298} - \frac{1}{T}\right]$$

As $T \to \infty, \frac{1}{T} \to 0$

$$\therefore \log\frac{k_2}{3\times10^{-4}} = \frac{104.4\times10^3\ J\ mol^{-1}}{2.303\times8.314\times298}$$

$$\log\frac{k_2}{3\times10^{-4}} = 18.297, \frac{k_2}{3\times10^{-4}} = 1.98\times10^{18}$$

$$k_2 = (1.98\times10^{18})\times(3\times10^{-4}) = 6\times10^{14}\,s^{-1}$$

157. (d)

158. (b) For 10°C rise of temperature the rate is almost doubled.

159. (c) $k_1 = A_1 e^{-E_{a_1}/RT}$ ....(i)

$k_2 = A_2 e^{-E_{a_2}/RT}$ ....(ii)

On dividing eqn (i) from eqn. (ii)

$\frac{k_1}{k_2} = \frac{A_1}{A_2}(E_{a_2} - E_{a_1})/RT$ ....(iii)

Given $E_{a_2} = 2E_{a_1}$

On substituting this value in eqn. (iii)

$k_1 = k_2 A \times e^{E_{a_1}/RT}$

160. (a) **161. (b)** **162. (b)** **163. (b)** **164. (b)**