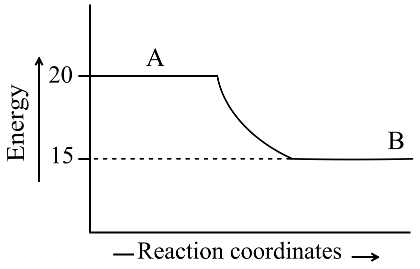
4.CHEMICAL KINETICS

Single Correct Answer Type

1. What can you say about the existence of A if the potential energy diagram for the reaction $A \rightarrow B$ looks like



a) A will exist
b) A will not exist
c) B will not exist
d) A and B are in equilibrium

2. A catalyst only

a) Decreases activation energy
b) Increases activation energy
c) Both of them
d) Comes to equilibrium

3. $A \rightarrow$ Product, $[A]_0 = 2M$. After 10 min reaction is 10% completed. If $\frac{d[A]}{dt} = k[A]$, then $t_{1/2}$ is approximately

a) 0.693 min
b) 69.3 min
c) 66.0 min
d) 0.0693 min

4. For an endothermic reaction, where ΔH represnts the enthalpy of reaction in kJ mol^{-1} , the minimum value for the energy of activation will be

a) Less than ΔH
b) Zero
c) More than ΔH
d) Equal to ΔH

5. In a first order reaction, the concentration of the reactant decreases from 0.8 M to 0.4 M in 15 min. The time taken for the concentration to change from 0.1 M to 0.025 M is

a) 60 min
b) 15 min
c) 7.5 min
d) 30 min

6. For a first order reaction $A \rightarrow P$, the temperature (T) dependent rate constant (k) was found to follow the equation.

$\log k = -(2000)/T + 6.0$

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}

7. In a second order reaction, 20% of a substance is dissociated in 40 min. The time taken by 80% of its dissociation is

a) 160 min
b) 640 min
c) 200 min
d) 320 min

8. For the chemical reaction $A + 2B \rightarrow C$, rate of the reaction is increased by 2.82 times when the concentration of A is doubled and increased by 9 times when the concentration of B was tripled. What is the order with respect to B, A, and the total order?

a) 3/2, 2;7/2
b) 2, 3/2; 7/2
c) 5/2, 2:9/2
d) 2, 5/2; 9/2

9. What specific name can be given to the following sequence of steps:

$Hg + h\nu \rightarrow Hg^*$

$Hg^* + H_2 \rightarrow H_2^* + Hg$

a) Fluorescence
b) Phosphorescence
c) Photosensitization
d) Chemiluminescence

10. For a second order reaction $dx/dt = k(a-x)^2$. Its half life period is

a) $\frac{1}{a \cdot k}$
b) $\frac{0.693}{k}$
c) $\frac{a}{k}$
d) $\frac{0.693}{ak}$

11. It is generalized that a 10°C increase in temperature causes the rate of reactions to double. Applied to a

reaction at 295 K, what is the value of E_a?

a) 120 kcal mol^{-1}

b) 1200 kcal mol^{-1}

c) 1.2 kcal mol^{-1}

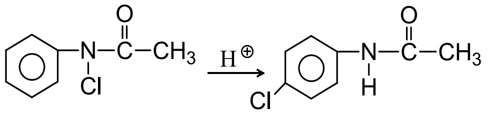
d) 12 kcal mol^{-1}

12. A Geigger Muller counter is used to study the radioactive process. In the absence of radioactive substance A, it counts 3 disintegration per second (dps). At the start in the presence of A, it records 23 dps; and after 10 min 13 dps

1. What does it count after 20 min?
2. What is the half life of A?

a) 8 dps, 10 min b) 5 dps, 10 min c) 5 dps, 20 min d) 5 dps, 5 min

13.



The reaction kinetics can be studied by

a) Measurement of pH b) Titration with hypo after adding KI

c) Both correct d) None is correct

14. Diazonium salt decomposes as

$C_6H_5N_2^{\oplus}Cl^{\ominus} \rightarrow C_6H_5Cl + N_2$

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

a) A first order reaction b) A second order reaction

c) Independent of the initial concentration of reactant d) A zero order reaction

15. In a reaction carried out at 500 K, 0.001% of the total number of collisions are effective. The energy of activation of the reaction is approximately

a) 15.8 kcal mol^{-1} b) 11.5 kcal mol^{-1} c) 12.8 kcal mol^{-1} d) Zero

16. If a reaction involves gaseous reactants and products, the units of its rate are

a) atm b) atm-s c) atm-s^{-1} d) $atm^2\ s^2$

17. For a reaction $pA + qB \rightarrow$Products, the rate law expression is $r = k[A][B]^m$. Then

a) $(p+q) = (1+m)$ b) $(p+q) > (1+m)$

c) $(p+q)$ may or may not be equal to $(1+m)$ d) $(p+q) = (1+m)$

18. 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 $T \rightarrow \infty$ is

a) $2.0 \times 10^{18}\ s^{-1}$ b) $6.0 \times 10^{14}\ s^{-1}$ c) Infinity d) $3.6 \times 10^{30} s^{-1}$

19. In an acidic medium, the rate of reaction between $(BrO_3^{\ominus})$ and $Br^{\ominus}$ ions is given by the expression

$$\frac{-d[BrO_3^{\ominus}]}{dt} = k\,[BrO_3^{\ominus}][Br^{\ominus}][H^{\oplus}]^2$$

It means

a) The rate constant of overall reaction is 4 s^{-1}

b) The rate of reaction is independent of the concentration of acid

c) The change in pH of the solution will not affect the rate

d) Doubling the concentration of $H^{\oplus}$ ions will increase the reaction rate by 4 times

20. The quantum yield of photosynthesis of

a) $HCl > HBr$ b) $HCl < HBr$ c) $HCl = HBr$ d) None

21. 90% of first order reaction was completed in 100 min. What is the half life of the reaction?

a) 63.3 min b) 53.3 min c) 43.3 min d) 30 min

22. The rate of certain hypothetical reaction

$A + B + C \rightarrow$ Products, is given by

$r = -\frac{dA}{dt} = k[A]^{1/2}[B]^{1/3}[C]^{1/4}$

The order of a reaction is given by

a) 1 b) 1/2 c) 2 d) 13/12

23. For the chemical reaction

$I^{\ominus} + OCl^{\ominus} \longrightarrow Cl^{\ominus} + OI^{\ominus}$

$$\text{Rate} = \frac{k[OCl^{\ominus}]\,[I^{\ominus}]}{[\overset{\ominus}{O}H]}$$

The order and molecularity of the reaction is

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

24. At a certain temperature, the first order rate constant k_1 is found to be smaller than the second order rate constant k_2. If $E_a(1)$ of the first order reaction is greater than $E_a(2)$ of the second order reaction, then as temperature is raised:

a) $k_2$will increase faster than k_1s

b) k_1 will increase faster than k_2 but will always remain less than k_2

c) k_1 will increase faster than k_2 and become equal to k_2

d) k_1 will increase faster than k_2 and become greater than k_2

25. 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 of the reaction,

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

26. A hypothetical reaction $A_2 + B_2 \rightarrow 2AB$ follows the mechanism as given below:

$A_2 \rightleftharpoons A + A$ (fast)

$A + B_2 \rightarrow AB + B$ (slow)

$A + B \rightarrow AB$ (fast)

The order of the overall reaction is

a) 2 b) 1 c) 1.5 d) 0

27. In the Wilhelmey equation of a first order reaction $c_t = c_0 e^{-kt}$. If the initial concentration c_0 is increased m times, then

a) The value of k will, increase m times b) The value of k will decrease m times

c) The value of k will remain unchanged d) None of these

28. Select the law that corresponds to data shown for the following reaction A + B → Products

Exp	**[A]**	**[B]**	**Initial rate**
1	0.012	0.035	0.1
2	0.024	0.070	0.8
3	0.024	0.035	0.1
4	0.012	0.070	0.8

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

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

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

30. For a single step reaction X + 2Y →Products, the molecularity is

a) Zero b) 2 c) 3 d) 1

31. In a first order reaction, the concentration of the reactants is reduced to 25% in one hour. The half-life period of the reactions is

a) 2 hr b) 4 hr c) 1/2 hr d) 1/4 hr

32. The rate constant for the reaction

$2N_2O_5 \rightarrow 4NO_2 + O_2$

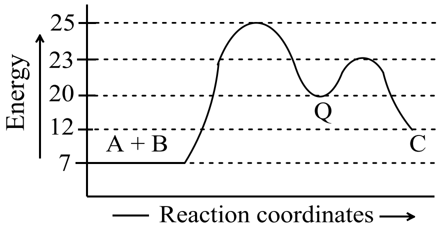
Is $3.0 \times 10^{-5}\text{s}^{-1}$. If the rate is $2.40 \times 10^{-5}\text{ mol L}^{-1}\text{s}^{-1}$, then the concentration of N_2O_5(in mol L^{-1}) is

a) 1.4 b) 1.2 c) 0.04 d) 0.8

33. If a reaction A + B → C is exothermic to the extent of 30 kJ mol^{-1} and the forward reaction has an activation energy. 70 kJ mol^{-1}, the activation energy for the reverse reaction is

a) 30 kJ mol^{-1} b) 40 kJ mol^{-1} c) 70 kJ mol^{-1} d) 100 kJ mol^{-1}

34. In a multistep reaction such as A + B → Q → C. The potential energy diagram is shown below. What is E_a for the reaction Q → C?



a) 3 kcal mol^{-1} b) 5 kcal mol^{-1} c) 8 kcal mol^{-1} d) 11 kcal mol^{-1}

35. For which of the following reactions, the units of rate constant and rate of reaction are same?

a) First order reaction b) Second order reaction

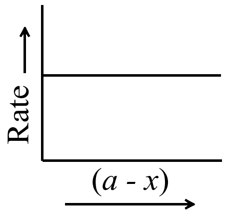
c) Third order reaction d) Zero order reaction

36. The temperature at which the average speed of perfect gas molecules is double than at 17°C is

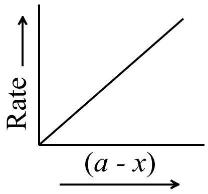
a) 34°C b) 68°C c) 162°C d) 887°C

37. Which of the following graphs is for a second order reaction?

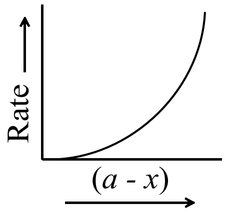
a)



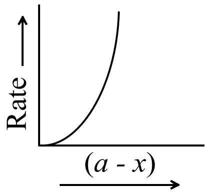
b)



c)



d)



38. For a chemical reaction A → Products, the rate of reaction doubles when the concentration of A is increased by 4 times. The order of reaction is

a) 4 b) 0 c) 1/2 d) 1

39. 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

40. In a first order reaction the concentration of reactant decreases from 800 mol/dm^6 to 50 mol/dm^6 in 2×10^4 s. The rate constant of reaction in s^{-1} is

a) 2×10^4 b) 3.45×10^{-5} c) 1.386×10^{-4} d) 2×10^{-4}

41. If a graph is plotted between $\log(a - x)$ and t, the slope of the straight line is equal to -0.03. The specific reaction rate will be

a) 6.9×10^{-2} b) 6.9 c) 0.69 d) 6.9×10^{-4}

42. The inversion of a sugar follows first order rate equation which can be followed by nothing the change in the rotation of the plane of polarization of light in the polarimeter. If r_∞, r_t and r_0 are the rotations at $t = \infty, t = t$, and $t = 0$, then the first order reaction can be written as

a) $k = \frac{1}{t}\log\frac{r_t - r_\infty}{r_0 - r_\infty}$

b) $k = \frac{1}{t}\ \mathrm{In}\frac{r_0 - r_\infty}{r_t - r_\infty}$

c) $k = \frac{1}{t}\mathrm{In}\frac{r_\infty - r_0}{r_\infty - r_t}$

d) $k = \frac{1}{t}\mathrm{In}\frac{r_\infty - r_t}{r_\infty - r_0}$

43. True statement is

a) Positive catalyst increases the rate of reaction

b) During the course of the reaction, specific reaction rate remains constant

c) Rate constant always increases with rise in temperature whether the reaction is endothermic or exothermic

d) All are correct

44. Given the following two mechanism, one with catalyst and the other without catalyst

1. $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$ (slow)
2. $\mathrm{C} + \mathrm{B} \rightarrow \mathrm{F} + \mathrm{A}$ (fast)
3. $\mathrm{B} + \mathrm{B} \rightarrow \mathrm{F}$ (slow)

Which mechanism uses the catalyst and what is it?

a) Step (i), A b) Step (ii), B c) (c)Step (iii), F d) Steps (i) and (ii), C

45. The inversion of cane sugar proceeds with half life of 500 min at pH 5 for any concentration of sugar. However, if pH=6, the half life changes to 50 min. The rate law expression for the sugar inversion can be written as

a) $r = k[\mathrm{sugar}]^2[\mathrm{H}]^6$ b) $r = k[\mathrm{sugar}]^1[\mathrm{H}]^0$ c) $r = k[\mathrm{sugar}]^0[\mathrm{H}\oplus]^6$ d) $r = k[\mathrm{sugar}]^0[\mathrm{H}\oplus]^1$

46. The rate of reaction between A and B increases by a factor of 100, when the concentration with respect to A is increased 10 folds, the order of reaction w.r.t A is

a) 10 b) 1 c) 4 d) 2

47. In the presence of acid, the initial concentration, of cane-sugar was reduced from 0.2 M to 0.1 in 5 hr and to 0.05 M in 10 hr. The reaction must be of

a) Zero order b) First order c) Second order d) Fractional order

48. The wrong statement is

a) All the collisions between reactant molecules do not lead to a chemical change

b) A zero order reaction proceeds at a constant rate independent of concentration or time

c) Fast reactions have low activation energies

d) In a first order reaction, the reaction ideally takes finite time to be complete

49. The composition of $\mathrm{N_2O_5}$ is a first order reaction represented by: $\mathrm{N_2O_5} \rightarrow \mathrm{N_2O_4} + 1/2\mathrm{O_2}$

After 20 min the volume of $\mathrm{O_2}$ produced is 10 mL and at the end of the reaction 40 mL. The rate constant is equal to

a) $\frac{1}{20}\ \ln\frac{30}{50}$ b) $\frac{1}{20}\ \ln\frac{50}{30}$ c) $\frac{1}{20}\ \ln\frac{50}{40}$ d) $\frac{1}{20}\ \ln\frac{40}{30}$

50. Two substance A and B are present such that $[\mathrm{A_0}] = 4[\mathrm{B_0}]$ and half life of A is 5 min and that of B is 15 min. If they start decaying at the same time following first order kinetics how much time later will take if the concentration of both of them would be same?

a) 15 min b) 10 min c) 5 min d) 12 min

51. The second order rate constant is usually expressed as

a) $\mathrm{Mol\ L\ s^{-1}}$ b) $\mathrm{Mol^{-1}\ L^{-1}s^{-1}}$ c) $\mathrm{Mol\ L^{-1}s^{-1}}$ d) $\mathrm{Mol^{-1}L\ s^{-1}}$

52. The rate equation for the reaction $2\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$ is found to be: rate $= k[\mathrm{A}][\mathrm{B}]$. The correct statement in

relation of this reaction is that

a) The value of k is independent of the initial concentration of A and B

b) $t_{1/2}$ is a constant

c) The rate of formation of C is twice the rate of disappearance of A

d) The unit of k must be s^{-1}

53. The half-time period of a second order reaction is

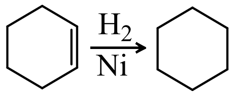
a) Proportional to the initial concentration of reactants

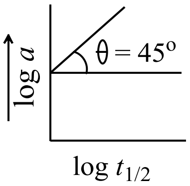
b) Independent of the initial concentration of reactants

c) Inversely proportional to the initial concentration of reactants

d) Inversely proportional to the square of initial concentration of reactants

54. Which of the following is correct graph for the reaction?



a)


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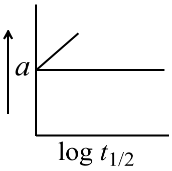
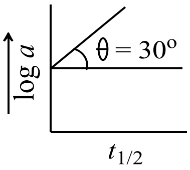
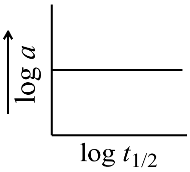


c)


d)


55. For the chemical reaction

$$I^{\ominus} + OCl^{\ominus} \longrightarrow Cl^{\ominus} + OI^{\ominus}$$

$$\text{Rate} = \frac{k[OCl^{\ominus}]\,[I^{\ominus}]}{[\overset{\ominus}{O}H]}$$

the molecularity and order with respect to $[\overset{\ominus}{OH}]$ is

a) 0, 1 b) 0, −1 c) 1, 0 d) −1, 0

56. For a chemical reaction A → F, it is found that the rate of reaction doubles when the concentration of A is increased four times. The order in A for this reaction is

a) 2 b) 1 c) 1/2 d) Zero

57. The rate constant of a reaction depends on

a) Temperature b) Mass c) Weight d) Time

58. The rate constant of a reaction depends on

a) Temperature b) Initial concentration of the reactions

c) Time of reaction d) Extent of reaction

59. The rate constant of a reaction is 1.5×10^{-3} at 25°C and 2.1×10^{-2} at 60°C. The activation energy is

a) $\frac{35}{333} R \log_e \frac{2.1 \times 10^{-2}}{1.5 \times 10^{-2}}$ b) $\frac{298 \times 333}{35} R \log_e \frac{21}{1.5}$ c) $\frac{298 \times 333}{35} R \log_e 2.1$ d) $\frac{298 \times 333}{35} R \log_e \frac{2.1}{1.5}$

60. For hypothetical chemical reaction A → I, it is found that the reaction is third order in A. What happens to the rate of reaction when the concentration of A is doubled?

a) Rate increases by a factor of 2 b) Rate decreases by a factor of 3

c) Rate increases by a factor of 8 d) Rate remains unaffected

61. The specific rate constant of a first order reaction depends on the

a) Concentration of the reactant

b) Concentration of the product

c) Time

d) Temperature

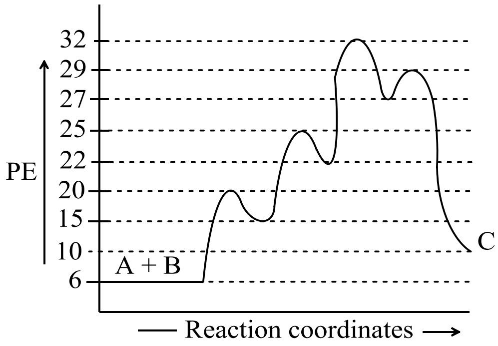
62. 90% of a first order reaction was completed in 100 min. How much time it will take for 80% completion of a reaction

a) 90 min b) 80 min c) 70 min d) 60 min

63. An example of autocatalytic raction is

a) Decomposition of nitroglycerine
b) Thermal decomposition of $KClO_3$ and MnO_2 mixture
c) Breakdown of $^{14}C_6$
d) Hydrogenation of vegetable oil using nickel catalysts

64. What is ΔH for the reaction $A + B \rightarrow C$ where the mechanism involves several kinetic steps



a) 11 kcal mol^{-1} b) 4 kcal mol^{-1} c) 5 kcal mol^{-1} d) 22 kcal mol^{-1}

65. The rate law for the reaction
$RCl + NaOH(aq) \rightarrow ROH + NaCl$ is given by
Rate=$k[RCl]$. The rate of the reaction will be
a) Doubled on doubling the concentration of sodium hydroxide
b) Halved on reducing the concentration of alkyl halide to one half
c) Decreased on increasing the temperature of the reaction
d) Unaffected by increasing the temperature of the reaction

66. The half-life period for catalyst decomposition of AB_3 at 50 mm is found to be 4 hr and at 100 mm it is 2.0 hr. The order of reaction is
a) 3 b) 1 c) 2 d) 0

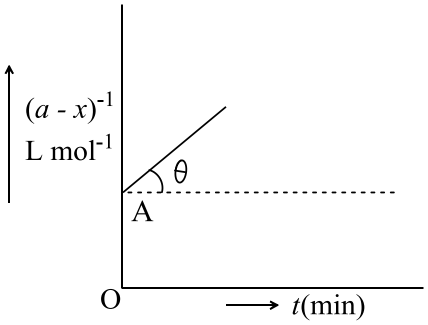
67. If I is the intensity of an absorbed light and c is the concentration of AB for the photochemical process. $AB + h\nu \rightarrow AB^*$, the rate of formation of AB^* is directly proportional to
a) c b) I c) I^2 d) $c \times I$

68. For the reaction $2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$, at 900 K following data are observed

Initial pressure of NO (atm)	Initial pressure of H_2 (atm)	Initial rate of pressure decrease (atm min^{-1})
0.150	0.40	0.020
0.075	0.40	0.005
0.150	0.20	0.010

Find out the order of reaction
a) 3 b) 2 c) 1 d) 0

69. Following is the graph between $(a-x)^{-1}$ and time t for second order reaction $\theta = \tan^{-1}(0.5)$ $OA = 2L\ mol^{-1}$



Hence, the are at the start of the reaction is
a) 1.25 mol $L^{-1}min^{-1}$ b) 0.5 mol $L^{-1}min^{-1}$ c) 0.125 mol $L^{-1}min^{-1}$ d) 12.5 mol $L^{-1}min^{-1}$

70. 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) $0.0693 \text{ mol min}^{-1}$ b) $0.0693 \times 2 \text{ mol min}^{-1}$

c) $0.0693 \times 5 \text{ mol min}^{-1}$ d) $0.0693 \times (5)^2 \text{ mol min}^{-1}$

71. When ethyl acetate was hydrolyzed in the presence of 0.1 M HCl, the constant was found to be $5.40 \times 10^{-5} \text{s}^{-1}$. But when 0.1 M H_2SO_4 was used for hydrolysis, the rate constant was found to be $6.20 \times 10^{-5} \text{s}^{-1}$. From these we can say that

a) H_2SO_4 is stronger than HCl

b) H_2SO_4 and HCl are both of the same strength

c) H_2SO_4 is weaker than HCl

d) The data is insufficient to compare the strength of HCl and H_2SO_4

72. The plot of $\log k$ vs $1/T$ helps to calculate

a) The energy of activation

b) The rate constant of the reaction

c) The order of the reaction

d) The energy of activations as well as the frequency factor

73. Which one of the following statement for order of reaction is not correct ?

a) Order can be determined experimentally

b) Order of reaction is equal to sum of the power of concentration terms in differential rate law

c) It is not affected with stoichiometric coefficients of the reactants

d) Order cannot be fractional

74. For gaseous reaction, the rate is often expressed in terms of dP/dt instead of dc/dt or dn/dt (where c is the concentration and n the number of mol). What is the relation among these three expressions?

a) $\frac{dc}{dt} = \frac{1}{V}\left(\frac{dn}{dt}\right) = \frac{1}{RT}\left(\frac{dP}{dt}\right)$ b) $\frac{dc}{dt} = \left(\frac{dn}{dt}\right) = \left(\frac{dP}{dt}\right)$

c) $\frac{dc}{dt} = \left(\frac{dn}{dt}\right) = \frac{V}{RT}\left(\frac{dP}{dt}\right)$ d) None of these

75. The hydrolysis of ester in alkaline medium is a

a) First order reaction with molecularity 1

b) Second order reaction with molecularity >2

c) First order reaction with molecularity 2

d) Second order reaction with molecularity 1

76. For a certain decomposition, the rate is 0.30 M s^{-1} when the concentration of the reactant is 0.20 M. If the reaction is second order, the rate (in M s^{-1}) when concentration is increased three times is

a) 0.30 b) 0.90 c) 0.60 d) 2.70

77. Collision theory is applicable to

a) First order reactions b) Zero order reactions

c) Biomolecular reactions d) Intermolecular reactions

78. How will the rate of reaction $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ change if the volume of the reaction vessel is halved?

a) It will be 1/6th of its initial value b) It will be 1/4th of its initial value

c) It will be 8 times of its initial value d) It will be 4 times of its initial value

79. In a certain gaseous reaction between A and B, $A + 3B \rightarrow AB_3$. The initial rates are reported as follows:

[A]	[B]	Rate
0.1 M	0.1 M	0.002 M s^{-1}
0.2 M	0.1 M	0.002 M s^{-1}
0.3 M	0.2 M	0.008 M s^{-1}
0.4 M	0.3 M	0.018 M s^{-1}

The rate law is

a) $r = k[A][B]^3$ b) $r = k[A]^0[B]^2$ c) $r = k[A][B]$ d) $r = k[A]^0[B]^3$

80. Which of the following expression can be used to describe the instantaneous rate of the reaction?

$2A + B \rightarrow A_2B$

a) $-\frac{dA}{2dt}$ b) $-\frac{dA}{dt}$ c) $\frac{d(A_2B)}{2dt}$ d) $-\frac{1}{2}\frac{dA}{dt}\frac{dB}{dt}$

81. The half life of decomposition of N_2O_5 is a first order reaction represented by
$N_2O_5 \rightarrow N_2O_4 + 1/2O_2$
After 15 min the volume of O_2 produced is 9 mL and at the end of the reaction 35 mL. The rate constant is equal to
a) $\frac{1}{15}\log_e\frac{35}{26}$
b) $\frac{1}{15}\log_e\frac{44}{26}$
c) $\frac{1}{15}\log_e\frac{35}{36}$
d) None of the foregoing

82. Which of the following theory is not related to the chemical kinetics?
a) Collision theory b) Absolute theory
c) Absolute reaction rate d) VSEPR theory

83. Which of the following explains the increase of the reaction rate by catalyst?
a) Catalyst decreases the rate of backward reaction so that the rate of forward reaction increases
b) Catalyst provides extra energy to reacting molecules so that they may produce effective collisions
c) Catalyst provides an alternative path of lower activation energy to the reactants
d) Catalyst increases the number of collisions between the reacting molecules

84. The mechanism of the reaction
$2NO + O_2 \rightarrow 2NO_2$ is

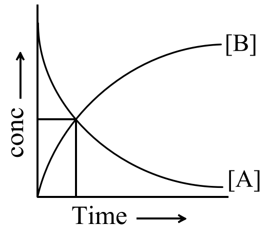
$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(\text{fast});$$

$$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2 \text{ (slow)}$$

The rate constant of the reaction is
a) k_2 b) $k_2k_1(k_{-1})$ c) k_2k_1 d) $k_2\left(\frac{k_1}{k_{-1}}\right)$

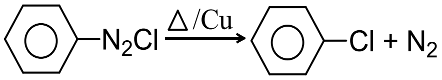
85. For which of the following represents the expression for three/forth life of reaction?
a) $\frac{k}{2.303}\log 4/3$ b) $\frac{2.303}{k}\log 3/4$ c) $\frac{2.303}{k}\log 4$ d) $\frac{2.303}{k}\log 3$

86. The accompanying figure depicts a change in concentration of species A and B for the reaction A → B, as a function of time. The point of inter section of the two curves represents



a) $t_{1/2}$ b) $t_{3/4}$
c) $t_{2/3}$ d) Data insufficient to predict

87. 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 $I^{\ominus}$ ion by $S_2O_8^{2-}$ ion

88.


(A)

Half life is independent of the concentration of A. After 10 min volume of N_2 gas is 10 L and after complete reaction is 50 L. Hence, the rate constant is

a) $\frac{2.303}{10}\log 5\ \text{min}^{-1}$ b) $\frac{2.303}{10}\log 1.25\ \text{min}^{-1}$ c) $\frac{2.303}{10}\log 2\ \text{min}^{-1}$ d) $\frac{2.303}{10}\log 4\ \text{min}^{-1}$

89. For the reaction:

$[Cr(H_2O)_6]^{3+} + [SCN^{\ominus}] \rightarrow [Cr(H_2O)_5NCS]^{2+}H_2O$

The rate law is: $r = k[Cr(H_2O)_6]^{3+}[SCN^{\ominus}]$

The value of k is 2.0×10^{-6} L mol^{-1}s^{-1} at 14°C and 2.2×10^{-5} L mol^{-1}s^{-1} at 30°C. What is the value of E_a?

a) 26 kcal mol^{-1} b) 2.6 kcal mol^{-1} c) 2600 kcal mol^{-1} d) 260 kcal mol^{-1}

90. If the concentration is measured in mol L^{-1} and time in minutes, the unit for the rate constant of a third order reaction is

a) mol L^{-1} min^{-1} b) L^2 mol^{-2} min^{-1} c) L mol^{-1} min^{-1} d) min^{-1}

91. The activation energy for most of the reaction is approximately 50 kJ mol^{-1}. The arte for temperature coefficient for such reaction will be

a) ≈ 2 b) ≈ 3 c) <1 d) >4

92. Which of the following expressions is correct for first order reactions (c_0 refers to initial concentration of reaction)

a) $t_{1/2} \propto c_0$ b) $t_{1/2} \propto c_0^{-1}$ c) $t_{1/2} \propto c_0^{-2}$ d) $t_{1/2} \propto c_0^0$

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

a) 1 mol of A and 1 mol of B in a 1-L vessel b) 2 mol of A and 2 mol of B in a 2-L vessel

c) 3 mol of A and 3 mol of B in a 3-L vessel d) All would react at the same rate

94. A first order reaction: A → Products and a second order reaction: 2R → Products both have half time of 20 min when they are carried out taking 4 mol L^{-1} of their respective reactants. The number of mole per liter of A and R remaining unreacted after 60 min from the start of the reaction, respectively, will be

a) 1 and 0.5 M b) 0.5 M and negligible c) 0.5 and 1 M d) 1 and 0.25 M

95. Under the same reaction condition, initial concentration of 1.386 $mol\ dm^{-3}$ of a substance become half in 40 s and 20 s through first order and zero order kinetics respectively. Ratio $\left(\frac{K_1}{K_0}\right)$ of the rate constants for first order (k_1) and zero order (k_0) of the reaction is

a) 0.5 $mol^{-1}dm^{-3}$ b) 1.0 $mol^{-1}dm^{-3}$ c) 1.5 $mol^{-1}dm^{-3}$ d) 2 $mol^{-1}dm^{-3}$

96. A catalysts is used

a) Only for increasing the velocity of a reaction

b) For altering the velocity of a reaction

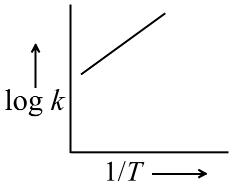
c) Only for decreasing the velocity of a reaction

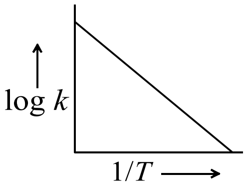
d) All (a), (b), and (c) are correct

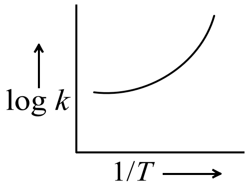
97. If a is the initial concentration of reaction, then the half life period of a reaction, of nth order is

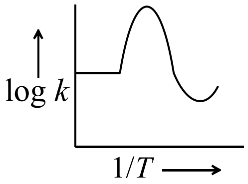
a) a^n b) a^{n-1} c) a^{1-n} d) a^{n+1}

98. A graph plotted between $\log k$ versus $1/T$ for calculating activation energy is shown by

a) 

b) 

c) 

d) 

99. 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

a) 2×10^{-4} mol$^{1/2}$ L$^{-1/2}$ s^{-1} b) 1×10^{-2} s^{-1}

c) 2×10^{-4} mol$^{-1/2}$ L$^{1/2}$ s^{-1} d) 25 mol^{-1} L min^{-1}

100. A catalyst lowers the activation energy 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

101.

$A + B \rightarrow C$			
	[A]	[B]	[Rate]
1	1.0	1.0	0.25
2	2.0	1.0	0.50
3	1.0	2.0	0.25

Rate is expressed in mol $L^{-1}min^{-1}$

In the above reaction, the order is

a) Zero in A and one in B b) One in A and zero in B

c) One in both A and B d) Zero in both A and B

102. The concentration of R in the reaction R→P was measured as a function of time and the following data is obtained

[R](molar)	1.00	0.75	0.40	0.10
t (min)	0.00	0.05	0.12	0.18

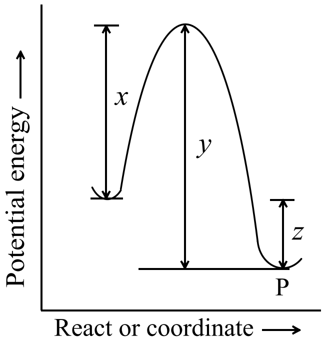
The order of the reaction is

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

103. For a reaction, $X(g) \rightarrow Y(g) + Z(g)$. The half-life period is 10 min. In what period of time would the concentration of X be reduced top 10% of the original concentration?

a) 20 min b) 33 min c) 15 min d) 25 min

104. The potential energy diagram for a reaction R → P is given below. $\Delta H^{\ominus}$ of the reaction corresponds to the energy



a) x b) y c) z d) $(x + y)$

105. A reaction $A_2 + B_2 \rightarrow 2AB$ occurs by the following mechanism:

$A \rightarrow A + A$ (slow)

$A + B_2 \rightarrow AB + B$ ... (fast)

$A + B \rightarrow AB$ ... (fast)

Its order would be

a) 3/2 b) 1 c) Zero d) 2

106. At 27°C it was observed in the hydrogenation of a reaction, the pressure of $H_2(g)$ decreases from 10 atm to 2 atm in 10 min. Calculate the rate of reaction in M min^{-1} (Given $R = 0.08$ L atm $K^{-1}mol^{-1}$)

a) 0.02 b) 0.03 c) 0.04 d) 0.05

107. For the reaction $X + 3Y \rightarrow Z$, which form of differential rate law is incorrect?

a) $dX/dt = dY/3dt$ b) $3dZ/dt = -dY/dt$ c) $dZ/dt = -dX/dt$ d) $-dX/dt = dZ/dt$

108. For a zero order reaction, the plot of concentration, vs time is linear with

a) +ve slope and zero intercept

b) −ve slope and zero intercept

c) +ve slope and non-zero intercept

d) −ve slope and non-zero intercept

109. A catalyst decreases E_a from 100 kJ mol^{-1} to 80 kJ mol^{-1}. At what temperature the rate of reaction in the absence of catalyst at 500 K will be equal to rate reaction in the presence of catalyst

a) 400 K b) 200 K c) 625 K d) None of these

110. Phosphorus undergoes slow combustion and glows in dark. The process is called

a) Photochemical change
b) Chemiluminescence
c) Fluorescence
d) Phosphorescence

111. The slope of the line for graph of log k versus $1/T$ for the reaction $N_2O_5 \rightarrow 2NO_2 + 1/2O_2$ is -5000. Calculate the energy of activation of the reaction (in kJ $K^{-1}mol^{-1}$)

a) 95.7
b) 9.57
c) 957
d) None

112. In a hypothetical reaction $2X + Y \rightarrow M + N$. If the concentration of Y is kept constant but that of X is tripled, the rate of reaction then will be

a) Increased by 3 times
b) Increased by 6 times
c) Increased by 9 times
d) Unpredictable

113. $t_{1/2} =$ constant confirms the first order of the reaction as one $a^2t_{1/2} =$ constant confirms that the reaction is of

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

114. The reaction $A(g) + 2B(g) \rightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A and B are $P_A = 0.60$ and $P_B = 0.80$ atm. When $P_C = 0.2$ atm, the rate of reaction relative to the initial rate is

a) 1/48
b) 1/24
c) 9/16
d) 1/6

115. The thermal decomposition of a compound is of first order. If 50% of a sample of the compound is decomposed in 120 min how long will it take for 90% of the compound to decompose?

a) 399 min
b) 410 min
c) 250 min
d) 120 min

116. A substance "A" decomposes in solution following the first order kinetics. Flask I contains 1 L of 1 M solution of A and flask II contains 100 mL of 0.6 M solution. After 8 hr, the concentration, of A in flask I becomes 0.25 M. What will be the time for concentrating of A in flask II to become 0.3 M?

a) 0.4 hr
b) 2.4 hr
c) 4.0 hr
d) Unpredictable as rate constant is not given

117. 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) $r = k[A][C]$

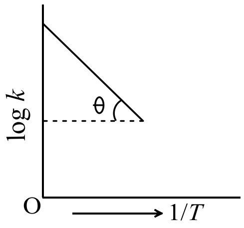
118. The term $-dx/dt$ in the rate expression refers to

a) The concentration of the reactants
b) Increase in the concentration of the reactants
c) The instantaneous rate of the reaction
d) The average rate of the reaction

119. The half life for the viral 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

120. Graph between $\log k$ and $1/T$ [k is rate constant (s^{-1}) and T and temperature (K)] is a straight line with $OX = 5, \theta = \tan^{-1}(1/2.303)$. Hence $-E_a$ will be



a) 2.303×2 cal
b) $2/2.303$ cal
c) 2 cal
d) None

121. The reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is first order w.r.t N_2O_5. Which of the following graphs would yield a straight line?

a) $\log p_{N_2O_5}$ vs time with –ve slope

b) $(p_{N_2O_5})^{-1}$ vs time

c) $p_{N_2O_5}$ vs time

d) $\log p_{N_2O_5}$ vs time with +ve slope

122. The activation energy of reactant molecules in a reaction depends upon

a) Temperature
b) Nature of the reactants
c) Collision per unit time
d) Concentration of reactants

123. The activation energy for a simple chemical reaction A → B is E_a in the forward reaction. The activation energy of the reverse reaction

a) Is negative of E_a
b) Is always less than E_a
c) Can be less than or more than E_a
d) Is always double of E_a

124. The rate of reaction increases by the increase of temperature because

a) Collision frequency is increased
b) Energy products decreases
c) Fraction of molecules processing energy $\geq E_T$ (threshold energy) increases
d) Mechanism of a reaction is changed

125. For the chemical reaction

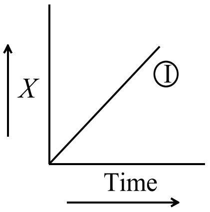
$5Br^{\ominus} + BrO_3^{\ominus} + 6H^{\oplus} \rightarrow 3Br_2 + 3H_2O$

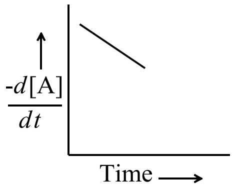
Rate $= k[Br^{\ominus}][BrO_3^{\ominus}][H^{\oplus}]^2$

The molecularity and order of reaction with respect to $[Br^{\ominus}]$ is

a) 5, 1
b) 1, 5
c) 1, 1
d) 6, 2

126. The graph between concentration (X) of the product and time of the reaction A → B is of the type I. Hence, graph between $-\frac{d[A]}{dt}$ and time will be the type:



a)


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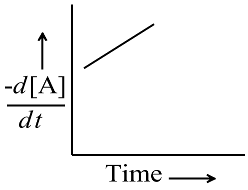
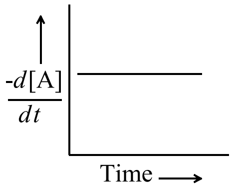
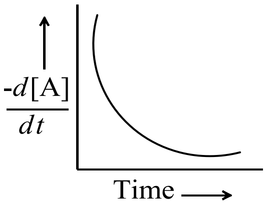


c)


d)


127. In the reaction A + B → C + D, the concentration of A and B are equal and the rate of the reaction is rate= $k[A][B]$. The integrated rate equation for this reaction is

a) $k = \frac{x}{t(a-x)}$
b) $k = \frac{xa}{(a-x)}$
c) $k = \frac{1}{t}\frac{x}{a(x-a)}$
d) $k = -\frac{1}{t}\frac{x}{a(x-a)}$

128. A chemical reaction occurs as a result of collisions between reacting molecules. Therefore, the reaction rate is given by

a) Total number of collisions occurring in a unit volume per second
b) Fraction of molecules which posses energy less than the threshold energy
c) Total number of effective collisions
d) None of the above

129. 80% of a first order reaction was completed in 70 min. How much it will take for 90% completion of reaction

a) 114 min
b) 140 min
c) 100 min
d) 200 min

130. The half life of a radioactive element is 20 min. The time interval between the stages of its 33% and 67% decay is

a) 40 min b) 20 min c) 30 min d) 25 min

131. For producing effective collisions, the colliding molecules must have

a) A certain minimum amount of energy b) Energy equal to or greater than threshold
c) Proper orientation d) Threshold energy and proper orientation both

132. The slowest step of a particular reaction is found to be $1/2X_2 + Y_2 \rightarrow XY_2$. The order of the reaction is

a) 2 b) 3 c) 3.5 d) 1.5

133. The free energy change due to a reaction is zero when

a) The reactants are initially mixed b) A catalyst is added
c) The system is at equilibrium d) The reactants are completely consumed

134. The rate of a chemical reaction generally increase rapidly even for small temperature increase because of a rapid increase in

a) Collision frequency
b) Fraction of molecules with energies in excess of the activation energy
c) Activation energy
d) Average kinetic energy of molecules

135. Which of the following expressions given the effect of temperature on the rate constant?

a) $\text{In } A = RT \ln E_a - \ln k$ b) $\text{In } k = \text{In } A - E_a/RT$
c) $k = AE_a/RT$ d) None of these

136. Rate constant $k = 1.2 \times 10^3 \text{ mol}^{-1}\text{L s}^{-1}$ and $E_a = 2.0 \times 10^2 \text{kJ mol}^{-1}$. When $T \rightarrow \infty$

a) $A = 2.0 \times 10^2 \text{kJ mol}^{-1}$ b) $A = 1.2 \times 10^3 \text{ mol}^{-1}\text{L s}^{-1}$
c) $A = 1.2 \times 10^3 \text{mol L}^{-1}\text{s}^{-1}$ d) $A = 2.4 \times 10^3 \text{kJ mol}^{-1}\text{s}^{-1}$

137. What is the order of reaction which has a rate expression rate $= k[\text{A}]^{3/2}[\text{B}]^{-1}$

a) 3/2 b) 1/2 c) Zero d) None of these

138. Mark the correct statement in a reversible reaction

a) A catalyst catalyzes the forward reaction
b) A catalyst catalyzes the backward reaction
c) A catalyst influence a direct and a reverse reaction to the same extent
d) A catalyst increases the rate of forward reaction and decreases the rate of backward reaction

139. A catalyst

a) Increases the free energy change in the reaction
b) Decreases the free energy change in the reaction
c) Does not increase or decrease the free energy change in the reaction
d) Can either increase or decrease the free energy change depending on what catalyst we use

140. For the reaction $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$, doubling the concentration of both the reactants increases the reaction rate by 8 times and doubling the initial concentration of only B simply doubles the reaction rate. The rate law for the reaction is

a) $r = k[\text{A}][\text{B}]^2$
b) $r = k[\text{A}][\text{B}]$
c) $r = k[\text{A}]^{1/2}[\text{B}]$
d) $r = k[\text{A}]^2[\text{B}]$

141. The specific rate constant of a first order reaction depends on the

a) Concentration of the reactant b) Concentration of the product
c) Time d) Temperature

142. The chemical reaction $2\text{O}_3 \rightarrow 3\text{O}_2$ proceeds as follows:

$\text{O}_3 \rightleftharpoons \text{O}_2 + \text{O}$ (fast)
$\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$ (slow)
The rate law expression should be

a) $r = k[\text{O}_3]^2$

b) $r = k[O_3]^2[O_2]^{-1}$
c) $r = k[O_3][O_2]$
d) Unpredictable

143. The activation energy for the forward reaction X → Y is 60 kJ mol^{-1} and ΔH is -20 kJ mol^{-1}. The activation energy for the reverse reaction is

a) 40 kJ mol^{-1} b) 60 kJ mol^{-1} c) 80 kJ mol^{-1} d) 20 kJ mol^{-1}

144. A sample of $_{53}I^{131}$, as $I^{\ominus}$ ion, was administrated to a patient in a carrier consisting 1.0 mg of stable $I^{\ominus}$ ion. After 4.0 days, 60% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable $I^{\ominus}$ ion had migrated to the thyroid gland? Given; $t_{1/2}$ of $I^{131} = 8$ days

a) 0.65 mg b) 0.75 mg c) 0.85 mg d) 0.95 mg

145. A reaction takes place in three steps. The rate constants are k_1, k_2, and k_3. The overall rate constant $k = \frac{k_1 k_3}{k_2}$. If E_1, E_2 and E_3(energy of activation) are 60, 30 and 10 kJ, respectively, the overall energy of activation is

a) 40 b) 30 c) 400 d) 60

146. When the rate is determined by the change in concentration of two different reactants, then the kinetic equation may be expressed as

a) $k_2 = \dfrac{2.303}{(a-b)t}\log\dfrac{(a-x)b}{(b-x)a}$
b) $k_2 = \dfrac{2.303}{(a-b)t}\log\dfrac{(a-x)}{(a+x)}$
c) $k_2 = \dfrac{2.303}{(a-b)}\log\dfrac{(a-x)}{(b-x)}$
d) $k_2 = \dfrac{1}{t}\times\dfrac{x}{(a-x)}$

147. The efficiency of an enzyme in catalyzing a reaction is due to its capacity

a) To form a strong enzyme-substrate complex
b) To decrease the bond energy of all substrate molecules
c) To change the shape of the substrate molecule
d) To lower the activation energy of the reaction

148. Which of the following statements regarding catalyst is **not true**?

a) A catalyst remains unchanged in composition and quantity at the end of the reaction
b) A catalyst can initiate a reaction
c) A catalyst does not alter the equilibrium in a reversible reaction
d) Catalyst are sometimes very specific in respect of reaction

149. The decomposition of H_2O_2 can be followed by titration with $KMnO_4$ and is found to be a first order reaction. The rate constant is 4.5×10^{-2}. In an experiment, the initial titre value was 25 mL. The titre value will be 5 mL after a lapse of

a) $4.5 \times 10^{-2} \times 5$ min
b) $\dfrac{\log_e 5}{4.5 \times 10^{-2}}$ min
c) $\dfrac{\log_e 5/4}{4.5 \times 10^{-2}}$ min
d) None of the above

150. Burning coal is represented as $C(s) + O_2(g) \rightarrow CO_2(g)$. The rate of this reaction is increased by

a) Decrease in the concentration of oxygen b) Powdering the lumps of coal
c) Decreasing the temperature of coal d) Providing inert atmosphere

151. In a certain reaction, 10% of the reactant decomposes in one hour, 20% in two hours, 30% in three hours, and so on. The dimension of the velocity constant (rate constant) are

a) Hr^{-1} b) Mol L^{-1}hr^{-1} c) L mol^{-1}s^{-1} d) Mol s^{-1}

152. The rate of chemical reaction

a) Increases as the reaction proceeds b) Decreases as the reaction proceeds
c) May increase or decrease during the reaction d) Remains constant as the reaction proceeds

153. In a multistep reaction such as $A + B \rightarrow Q \rightarrow C$, E_a for the reaction $Q \rightarrow C$ which statement is true?
a) Reaction $A + B \rightarrow Q$ is faster
b) Reaction $Q \rightarrow C$ is faster
c) Reaction in (a) and (b) are equal
d) Unpredictable

154. A follows first order reaction , A→ product Concentration of A, change from 0.1 M to 0.025 M in 40 min. find the rate of reaction of A when concentration of A is 0.01 M.
a) $3.47\times 10^{-4} M$ min^{-1}
b) $3.47\times 10^{-5} M$ min^{-1}
c) $1.73\times 10^{-4} M$ min^{-1}
d) $1.73\times 10^{-5} M$ min^{-1}

155. A gaseous reaction, $A_2(g) \rightleftharpoons B(g) + 1/2C(g)$ shows increase in the pressure from 100 mm to 120 mm in 5 min. The rate of disappears of A_2 is
a) 4 mm min^{-1}
b) 8 mm min^{-1}
c) 16 mm min^{-1}
d) 2 mm min^{-1}

156. For a chemical reaction $2X + Y \rightarrow Z$, the rate of appearance of Z is 0.05 mol $L^{-1}\text{min}^{-1}$. The rate of disappearance of X will be
a) 0.05 mol $L^{-1}\text{hr}^{-1}$ b) 0.05 mol $L^{-1}\text{min}^{-1}$ c) 0.1 mol $L^{-1}\text{min}^{-1}$ d) 0.25 mol $L^{-1}\text{min}^{-1}$

157. Which of the following statement is correct
a) For reaction $xX \rightarrow yY$
Rate $= \frac{1dx}{xdt} = \frac{dy}{dt}$
b) The parameter, rate constant, and specific reaction rate have different meaning
c) For any reaction the value of specific reaction rate is independent of the initial concentration of reactants
d) $E_a = E_R + E_{\text{Threshold}}$

158. The dissociation of nitrogen pentoxide is a first order reaction. In first 24 min, 75% of nitrogen pentaoxide is dissociated. What amount of nitrogen pentaoxide will be left behind after one hour of the start of reaction?
a) Approximately 1% b) Approximately 2% c) Approximately 3% d) None

159. $k_{34^\circ}; \ k_{35^\circ} < 1$, then
a) Rate increases with the rise in temperature
b) Rate decreases with rise in temperature
c) Rate does not change with the rise in temperature
d) None of the above

160. The rate of reaction A + B → Products is given by the equation $r = k[A][B]$. If B is taken in large excess, the order of the reaction would be
a) 2 b) 1 c) 0 d) Unpredictable

161. If the initial concentration of reactants in certain reaction is double, the half-life period of the reaction doubles, the order of a reaction is
a) Zero b) First c) Second d) Third

162. $2N_2O_5 \rightarrow 4NO_2 + O_2$
If $-\frac{d[N_2O_5]}{dt} = k_1[N_2O_5]$
$$\frac{d[NO_2]}{dt} = k_2[N_2O_5]$$
$$\frac{d[O_2]}{dt} = k_3[N_2O_5]$$

What is the relation between k_1, k_2 and k_3?

a) $k_1 = k_2 = k_3$ b) $2k_1 = k_2 = 4k_3$ c) $2k_1 = 4k_2 = k_3$ d) None

163. For the chemical reaction $A + B + C \rightarrow E$, the rate of the reaction is doubled when the concentration of B was doubled, and when the concentration, of both A and B was doubled rate become doubled and when the concentration of both B and C was doubled rate become quadrupled. What is the order with respect to A, B, and C and the total order?

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

164. The reaction $A \rightarrow B$ follows first order kinetics. The time taken for 0.8 mol of A to produce 0.6 mol of B is 1 hr. What is the time taken for the conversion of 0.9 mol of A to product 0.675 mol of B?

a) 1 hr b) 0.5 hr c) 0.25 hr d) 2 hr

165. The hydrolysis of an ester was carried out with 0.1 M H_2SO_4 and 0.1 M HCl separately. Which of the following expressions between the arte constants is expected? The rate expression being rate $= k[\text{H}^{\oplus}][\text{ester}]$

a) $k_{\text{HCl}} = k_{\text{H}_2\text{SO}_4}$ b) $k_{\text{HCl}} > k_{\text{H}_2\text{SO}_4}$ c) $k_{\text{HCl}} < k_{\text{H}_2\text{SO}_4}$ d) $k_{\text{H}_2\text{SO}_4} = 2k_{\text{HCl}}$

166. A second order reaction requires 70 min to change the concentration of reactants from 0.08 M to 0.01 M. How much time will it require to become 0.04 M?

a) 10 min b) 20 min c) 30 min d) 40 min

167. The rate of a certain reaction increases by 2.3 times when the temperature is raised from 300 K to 310 K. If k is the rate constant at 300 K, then the rate constant at 310 K will be equal to

a) $2k$ b) k c) 2.3 k d) $3k^2$

168. For a hypothetical reaction $A \rightarrow B$, the rate constant is 0.25 s^{-1}. If the concentration of A is reduced to half, then the value of rate constant is

a) 0.25 s^{-1} b) 0.30 s^{-1} c) 0.075 s^{-1} d) 2.25 s^{-1}

169. A catalyst is a substance which

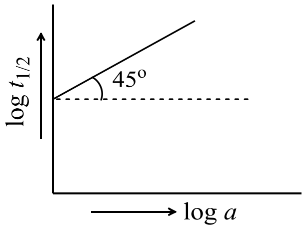
a) Increases the equilibrium concentration of the product

b) Changes the equilibrium constant of the reaction

c) Shortens the time to each equilibrium

d) Supplies energy to the reaction

170. Following is the graph between $\log T_{50}$ and $\log a$ (a =initial concentration) for a given reaction at 27°C. Hence order is



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

171. For a hypothetical reaction: A + B →Products, the rate law is $r = k[A][B]^0$. The order of reaction is

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

172. In the formation of sulphur trioxide by the contact process,

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

The rate of reaction is expressed as

$$-\frac{d(O_2)}{dt} = 2.5 \times 10^{-4} \text{mol L}^{-1}\text{s}^{-1}$$

The rate of disappearance so (SO_2) will be

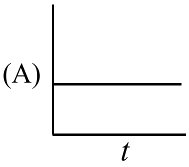
a) 5.0×10^{-4}mol $L^{-1}s^{-1}$ b) -2.25×10^{-4}mol $L^{-1}s^{-1}$

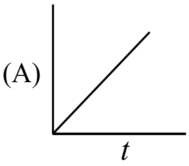
c) 3.75×10^{-4}mol $L^{-1}s^{-1}$ d) 50.0×10^{-4}mol $L^{-1}s^{-1}$

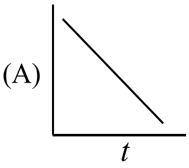
173. 60% of a first order reaction was completed in 60 min. The time taken for reactants to decompose to half of their original amount will be

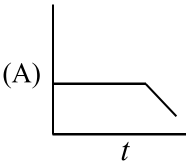
a) =30 min b) =45 min c) =20 min d) =40 min

174. Which curve represents zero order reaction?

a) 

b) 

c) 

d) 

175. The half-life period of the reaction in the above question is

a) 1.386 min b) 4 min c) 16 min d) 2 min

176. An exothermic reaction A → B has an activation energy of 17 kJ per mole of A. The heat of the reaction is 40 kJ. Calculate the activation energy for the reverse reaction

B → A

a) 60 kJ b) 57 kJ c) 75 kJ d) 90 kJ

177. The activation energy for a hypothetical reaction A → X is 12.49 kcal mol^{-1}. If temperature is raised to 305 from 295 K, the reaction rate increased by 0.002 kcal K^{-1}mol^{-1} is almost equal to

a) 60% b) 50% c) 100% d) Unpredictable

178. When $KClO_3$ is heated, it decomposes into KCl and O_2. If some MnO_2 is added, the reaction goes much faster because

a) MnO_2 decomposes to give O_2
b) MnO_2 provides heat by reacting
c) Better contact is provided by MnO_2
d) MnO_2 acts as a catalyst

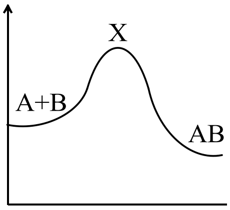
179. In a first order reaction, 75% of the reactants disappeared in 1.386 hr. What is the rate constant?

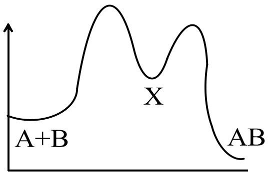
a) $3.6 \times 10^{-3} s^{-1}$ b) $2.7 \times 10^{-4} s^{-1}$ c) $72 \times 10^{-3} s^{-1}$ d) $1.8 \times 10^{-3} s^{-1}$

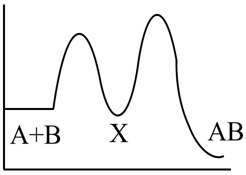
180. For an exothermic chemical process occurring in two steps as

1. A + B → X (slow)
2. X → AB (fast)

The progress of the reaction can be best described by

a) 

b) 

c) 

d) All are correct

181. In fire files the flashes are produced due to the slow combustion of a protein Iuciferin in air and moisture. The phenomenon is known as

a) Photochemical change
b) Photocombustion
c) Chemiluminescence
d) None of these

182. The mechanism for the overall reaction is

$A_2 + B \rightarrow C$

$A_2 \rightarrow 2A$ (slow)

$2A + B \rightarrow C$ (fast)

If catalyst D changes the mechanism to

$A_2 + D \rightarrow A_2D$ (slow)

$A_2D \rightarrow 2A + D$ (fast)

$2A + B \rightarrow C$ (fast)

Which is the rate expression for the reaction with and without a catalyst?

a) $r = k'[A_2][D], r = k[A_2]$ b) $r = k[A_2], r = k'[A_2][D]$

c) $r = k'[A_2D], r = k[A_2][B]$ d) $r = k[A_2][B], r = k'[A_2D]$

183. For a first order reaction, $t_{0.75}$ is 1386 s. Therefore, the specific rate constant is

a) 10^{-1}s^{-1} b) 10^{-3}s^{-1} c) 10^{-2}s^{-1} d) $10^{-4}\ \text{s}^{-1}$

184. Consider a gaseous reaction, the rate of which is given by $k[A][B]$. The volume of the reaction vessel containing these gases is suddenly reduced to 1/4th of the initial volume. The rate of the reaction as compared with original rate is

a) 1/16 times b) 16 times c) 1/8 times d) 8 times

185. When the concentration of a reactant in reaction A → B is increased by 8 times but rate increases only 2 times, the order of the reaction would be

a) 2 b) 1/3 c) 4 d) 1/2

186. For the reaction: $2HI \rightarrow H_2 + I_2$, the expression $-d(\text{HI})/2dt$ represents

a) The rate of formation of HI b) The rate of disappearance of HI

c) The instantaneous rate of the reaction d) The average rate of reaction

187. The rate constant of forward and backward reactions for certain hypothetical reactions are 1.1×10^{-2} and 1.5×10^{-3}, respectively. The equilibrium constant of the reaction is

a) 7.33 b) 0.733 c) 73.3 d) 733

188. 70% of a first order reaction was completed in 70 min. What is the half life of the reaction?

a) 4.2 min b) 42 min c) 4.2 hr d) 4.2 s

189. In a catalytic reaction involving the formation of ammonia by Haber's process $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of appearange of NH_3 was measured as 2.5×10^{-4} mol $\text{L}^{-1}\text{s}^{-1}$. The rate of disappearance or H_2 will be

a) 2.50×10^{-4} mol $\text{L}^{-1}\text{s}^{-1}$ b) 1.25×10^{-4} mol $\text{L}^{-1}\ \text{s}^{-1}$

c) 3.75×10^{-4} mol $\text{L}^{-1}\text{s}^{-1}$ d) 5.00×10^{-4}mol $\text{L}^{-1}\text{s}^{-1}$

190. The rate constant, the activation energy, and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4}\text{s}^{-1}$ 104.4 kJ mol^{-1}, and $6.0 \times 10^{14}\ \text{s}^{-1}$ respectively. The value of rate constant as $T \rightarrow \infty$ is

a) $2.0 \times 10^{18}\text{s}^{-1}$ b) $6.0 \times 10^{14}\text{s}^{-1}$ c) ∞ d) $3.6 \times 10^{30}\text{s}^{-1}$

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

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

192. A reaction rate constant is given by $k = 1.2 \times 10^{14} e^{\frac{-2500}{RT}} \text{s}^{-1}$. It means

a) $\log k$ versus $\log T$ will give a straight line with a slope as 25000

b) $\log k$ versus $\log T$ will give a straight line with a slope as -25000

c) $\log k$ versus T will give a straight line with a slope as -25000

d) $\log k$ versus $1/T$ will give a straight line

193. The oxidation of oxalic acid by acidified $KMnO_4$ is an example of autocatalysis. It is due to which of the following?

a) SO_4^{2-} b) MnO_4^{2-} c) Mn^{2+} d) $K^{\oplus}$

Multiple Correct Answers Type

194. The increase in the rate of a reaction for a rise in temperature is due to:

a) Increase in collision frequency

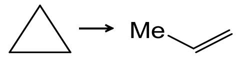
b) Shortening of mean free path

c) Increase in the number of activated molecules
d) None of the above

195. For a first order reaction:
a) The degree of dissociation is equal to $(1 - e^{-Kt})$
b) A plot of reciprocal concentration of the reactant vs time gives a straight line
c) The time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction
d) The pre-exponential factor in the Arrhenius equation has the dimension of time, (T^{-1})

196. Which of the following relations are correct if ΔH represents only magnitude?
a) Exothermic reactions : $E_{a(f)} + \Delta H = E_{a(b)}$
b) Endothermic reactions : $E_{a(f)} = E_{a(b)} + \Delta H$
c) Exothermic reactions : $\Delta H > E_a$
d) Endothermic reactions : $\Delta H < E_a$

197. The concept of $t_{1/2}$ is useful for the reactions of:
a) Zero order
b) First order
c) Second order
d) None of these

198. Which of the following is/are example of unimolecular reaction?
a) $O_3 \rightarrow O_2 + O$
b) 

c) $NO + O_3 \rightarrow NO_2 + O_2$
d) $O + NO + N_2 \rightarrow NO_2 + N_2$

199. In a hypothetical reaction X → Y, the activation energy for the forward and backward reactions is 15 and 9 kJ mol^{-1}, respectively. The potential energy of X is 10 kJ mol^{-1}. Then
Plot of $t_{1/2}$ vs. concentration
a) The heat of reaction is 6 kJ
b) The potential energy of Y is 16 kJ
c) The threshold energy of the reaction is 25 kJ
d) The reaction is endothermic

200. The reaction,
$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$ is:
a) Bimolecular reaction
b) II order reaction
c) III order reaction
d) None of these

201. Which of the following statements is/are correct?
a) The rate of the reaction involving the conversion of ortho-hydrogen to parahydrogen is $-\frac{d[H_2]}{dt} = k[H_2]^{3/2}$
b) The rate of reaction involving the thermal decomposition of acetaldehyde is $k[CH_3CHO]^{3/2}$
c) In the formation of phosgene gas from CO and Cl_2, the rate of the reaction is $k[CO][Cl_2]^{1/2}$
d) In the decomposition of H_2O_2, the rate of the reaction is $k[H_2O_2]$

202. Ion Arrhenius equation, $k = A \exp\left(-\frac{E_a}{RT}\right)$. A may be termed as the rate constant at
a) Very low constant at
b) Very high temperature
c) Zero activation energy
d) The boiling temperature of the reaction mixture

203. Which of the following statement is (are) correct?
a) Rate of reaction $\propto 1/E_a$
b) At lower temperature increase in temperature causes more change in the value of k
c) $k = Ae^{-E_a/RT}$
d) None is correct

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

205. Which of the following isomerization reactions is/are of the first order?
a) Cyclopropane → Propane
b) cis-But-2-ene → Trans-but-2-ene

c) Vinyl allyl ether → Pent-4-enal
d) $\mathrm{CH_3NC \rightarrow CH_3CN}$

206. If the rate of reaction between A and B is given by rate $= k[A][B]^2$, then the reaction (s) is/are:
a) First order in A
b) Second order in B
c) Third order overall
d) None of these

207. In acidic medium, the rate of reaction between $\mathrm{BrO_3^{\ominus}}$ and $\mathrm{Br^{\ominus}}$ is given by the expression

$$\frac{-d[\mathrm{BrO_3}^{\ominus}]}{dt} = k[\mathrm{BrO_3}^{\ominus}][\mathrm{Br}^{\ominus}][\mathrm{H}^{\oplus}]^2$$

a) The rate constant of the reaction depends upon the concentration of $\mathrm{H^{\oplus}}$ ions
b) The rate of reaction is independent of the concentration of the acid added
c) Doubling the concentration of $\mathrm{H^{\oplus}}$ ions will increase the reaction rate by 4 times
d) The change in pH of the solution will affect the rate of reaction

208. Taking the reaction, $\mathrm{A + 2B \rightarrow}$ Products, to be of second order, which of the following is/are the correct rate law expression(s)?
a) $\frac{dx}{dt} = k[\mathrm{A}]^2$
b) $\frac{dx}{dt} = k[\mathrm{A}][\mathrm{B}]^2$
c) $\frac{dx}{dt} = k[\mathrm{A}][\mathrm{B}]$
d) $\frac{dx}{dt} = k_1[\mathrm{A}] + k_2[\mathrm{B}]^2$

209. For a first order reaction,
a) The degree of dissociation is equal to $(1 - e^{-kt})$
b) A plot of reciprocal concentration of the reactant versus time given a straight line
c) The time taken for the completion of 75% of the reaction is thrice the time taken for 1/2 of the reaction
d) The pre-exponential factor in the Arrhenius equation has the dimension of time T^{-1}

210. Rate constant k varies with temperature by equation $\log k\ (\mathrm{min}^{-1}) = \log 5 - \frac{2000\ \mathrm{kcal}}{RT \times 2.303}$. We can conclude that
a) The pre exponential factor A is 10^5
b) E_a is 2000 kcal
c) E_a is 9.12 kcal
d) The pre-exponential factor A is 5

211. The rate of chemical reaction increases:
a) If the temperature is increased
b) If the concentration of the reactants is decreased
c) If the concentration of the reactants is increased
d) With time

212. The acid hydrolysis of ester is/are:
a) First order reaction
b) Bimolecular reaction
c) Pseudo unimolecular reaction
d) None of the above

213. The rate of chemical reaction(s) depend (s) upon:
a) Pressure
b) Temperature
c) Concentration
d) Catalyst

214. The rate expression for the reaction:
$\mathrm{NH_4CNO \rightleftharpoons NH_2CONH_2}$ can be derived from the mechanism:

i. $\mathrm{NH_4CNO} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{NH_4NCO}$ (Fast)

ii. $\mathrm{NH_4NCO} \xrightarrow{k_3} \mathrm{NH_3 + HNCO}$ (Fast)

iii. $\mathrm{NH_3 + HNCO} \xrightarrow{\mathrm{k_4}} \mathrm{NH_2CONH_2}$ (Slow)

Which of the following statement(s) is/are correct about the rate expression?
a) $\frac{d_{[\mathrm{urea}]}}{dt} = \frac{k_1k_3}{k_2}[\mathrm{NH_4NCO}]$
b) $\frac{d_{[\mathrm{urea}]}}{dt} = \frac{k_1k_3}{k_2k_4}[\mathrm{NH_4NCO}]$
c) $\frac{d_{[\mathrm{urea}]}}{dt} = k[\mathrm{NH_4NCO}]$
d) $\frac{d_{[\mathrm{urea}]}}{dt} = \frac{k_1 \times k_2}{k_3 \times k_4}[\mathrm{NH_4NCO}]$

215. A large increase in the rate of reaction for a rise in temperature is due to
a) Lowering of activation energy
b) Increase in the number of collisions
c) Shortening of means free path
d) Increase in the number of activated molecules

216. For the reaction, $3BrO^- \longrightarrow BrO_3^- + 2Br^-$ in an aqueous alkaline medium at 80°C, the value of the rate constant in the rate law in terms of $\frac{-d[BrO^-]}{dt}$ is $0.056\ L\ mol^{-1}s^{-1}$. What will be the rate constant when the rate law is stated in terms of $\frac{d[BrO_3^-]}{dt}$?

a) $18.7 \times 10^{-3}\ L\ mol^{-1}\ s^{-1}$
b) $37.4 \times 10^{-3}\ L\ mol^{-1}\ s^{-1}$
c) $0.0187\ L\ mol^{-1}\ s^{-1}$
d) $18.7 \times 10^{-2}\ L\ mol^{-1}\ s^{-1}$

217. Which of the following statements about the rate of a chemical reaction is/are not true?

a) The rate remains constant throughout the reaction in all order of reaction
b) The rate increases as the reaction proceeds
c) The rate decreases as the reaction proceeds
d) None of the above

218. The half-life period of any first order reaction:

a) Is independent of the initial concentration of the reactant
b) Is inversely proportional to the rate constant
c) Is always the same whatever the reaction
d) Is half the specific rate constant

219. For a I order reaction
$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$:

a) The concentration of the reactant decreases exponentially with time
b) The half-life of the reaction decreases with increasing temperature
c) The half-life of the reaction depends on the initial concentration of the reactant
d) The reaction proceeds to 99.6% completion in eight half-life duration

220. The velocity constant of a reaction is given by expression, Rate= $k[A]^2[B]$ the reaction is of

a) 1st order overall
b) 3rd order overall
c) 1st order with respect of B
d) 2nd order with respect to A

221. A reaction is catalysed by H^+ ions. The reaction has rate constant $3 \times 10^{-3} min^{-1}$ in pressure of acid HA and $2 \times 10^{-3}\ min^{-1}$ in presence of acid HB. If both HA and HB are strong acid, which is/are correct?

a) HA is stronger acid than HB
b) Relative strength for $HA : HB = 1.5$
c) The reaction, $NaB + HA \longrightarrow NaA + HB$ may be possible
d) HB is stronger acid than HA

222. Identify the true statement(s)

a) A catalyst is chemically unchanged at the end of a reaction
b) A catalyst may appear in the kinetic rate equation of the reaction
c) A catalyst will not affect the composition of an equilibrium mixture
d) A catalyst cannot cause a non-spontaneous ($\Delta G > 0$) reaction to proceed

223. Which of the following statement(s) is/are correct
The rate constant for the reaction

a) $2N_2O_5 \rightarrow 4NO_2 + O_2$, is $3.0 \times 10^{-5}\ s^{-1}$. If the rate is $2.40 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}$, then the concentration of $N_2O_5 = 0.8\ mol\ L^{-1}$
b) In the Arrhenius equation, $k = A \exp(-E/RT)$. A may be termed as the rate constant at very low temperature
c) If I is the intensity of absorbed light and c is the concentration of AB for the photochemical process $AB + h\nu \rightarrow AB^*$, the rate of formation of AB^* is directly proportional to I^2
d) 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 $T \rightarrow \infty$ is $6.0 \times 10^{14}s^{-1}$

224. The rate equation for the decomposition of N_2O_5 in CCl_4 is rate $= k[N_2O_5]$, when $k = 6.3 \times 10^{-4}\ s^{-1}$ at

320 K. What would be the initial rate of decomposition of N_2O_5 in a 0.10 M solution of N_2O_5?

a) 6.3×10^{-6} mol L^{-1} s^{-1}

b) 0.63×10^{-6} mol L^{-1} s^{-1}

c) 6.3×10^{-5} mol L^{-1} s^{-1}

d) 0.63×10^{-4} mol L^{-1} s^{-1}

225. Consider a chemical reaction, $2A + B \longrightarrow A_2B$. The reactant A will decrease at:

a) The same rate at which B will decrease

b) Twice the rate at which B will decrease

c) Half the rate at which B will decrease

d) Twice the rate at which A_2B will form

226. Which of the following is/are examples of pseudo unimoleclar reactions?

a) $CH_3CO_2C_2H_5 + H_2O \xrightarrow{H^{\oplus}} CH_3CO_2H + C_2H_5OH$

b) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^{\oplus}} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$

c) $CH_3COCl + H_2O \rightarrow CH_3CO_2H + HCl$

d) $CH_3CO_2C_2H_5 + H_2O \xrightarrow{\overset{\ominus}{O}H} CH_3CO_2H + C_2H_5OH$

227. Which of the following statements is/are true?

a) The order of a reaction can be zero

b) The order of an elementary reaction is equal to its molecularity

c) The order of the inversion of sucrose is 2

d) The order of a reaction may change if the experimental conditions are changed

228. According to the collision theory, most molecular collisions do not lead to reaction. Which of the following is/are necessary for collisions to successfully lead to reaction?

a) The total kinetic energy of the collision must be greater than some minimum value

b) A catalyst must be present at the collision

c) The colliding particles must be properly oriented in space when they collide

d) None of the above

229. A catalyst

a) Increases the average kinetic energy of the reacting molecules

b) Decreases the activation energy

c) Alters the reaction mechanism

d) Increases the frequency of the collisions of the reacting species

230. In a zero order reaction:

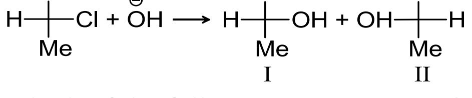
a) The rate is independent of the temperature of the reaction

b) The rate is independent of the concentration of the reactants

c) The half life depends on the concentration on the reactants

d) The rate constant has the unit mol L^{-1} s^{-1}

231.



Which of the following statement is/are correct?

a) It is unimolecular nucleophilc substitution reaction SN^1 if I or II is formed

b) It is bimolecular nucleophlic substitution reaction SN^2 if I or II is formed

c) It is SN^1 if I and is enantomer are formed so that the mixture is racemic

d) It is SN^2 if II is formed

232. The rate law for the reaction:

$RCl + NaOH \rightarrow ROH + NaCl$ is given by:

Rate $= k[RCl]$. The rate of this reaction is

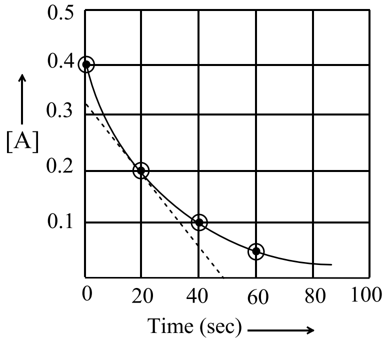
a) Doubled by doubling the concentration of NaOH

b) Halved by reducing the concentration of RCl by one half

c) Increased by increasing the temperature of the reaction

d) Unaffected by change of temperature

233. A certain reaction A → B follows the given concentration (Molarity)—time graph. Which of the following statements is/are true?



a) The reaction is second order with respect to A

b) The rate for this reaction at 20 s will be $7 \times 10^{-3}\text{Ms}^{-1}$

c) The rate for this reaction at 80 s will be $1.75 \times 10^{-3}\ \text{Ms}^{-1}$

d) The [B] will be 0.35 M at $t = 60$ s

234. Arrhenius equation may be written as:

a) $(d/dt)\log k = -(\Delta E/RT^2)$

b) $(d/dt)\log k = +(\Delta E/RT^2)$

c) $(d/dt)\log k = -(\Delta E/RT)$

d) $k = Ae^{-\Delta E/RT}$

235. Which of the following statements is/are correct?

a) A plot of $\log k_p$ versus $1/T$ is linear

b) A plot of log[X] versus time is linear for a first order reaction, $x \rightarrow p$

c) A plot of $\log p$ versus $1/T$ is linear at constant volume

d) A plot of p versus $1/V$ is linear at constant temperature

236. Which of the following reaction(s) is/are of the first order?

a) The decomposition of ammonium nitrate in an aqueous solution

b) The inversion of cane sugar in the presence of an acid

c) The acidic hydrolysis of ethyl acetate

d) All radioactive decays

237. In which of the following ways does an activated complex differ from an ordinary molecule?

a) It is quite unstable and has no independent existence

b) $\Delta_f H^{\ominus}$ is probably positive

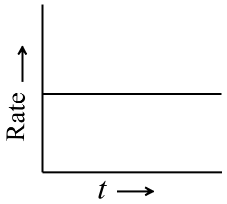
c) The system has a greater vibrational character

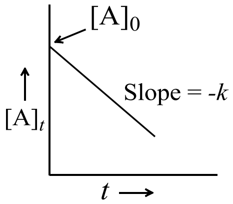
d) The system has no vibrational character

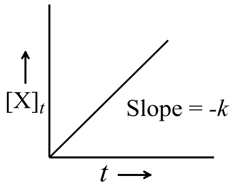
238. Which of the following graphs represents zero order if A → P

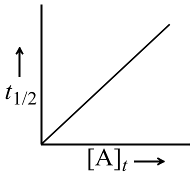
At $t = 0 \Rightarrow [A]_0$

At $t = t \Rightarrow [A]_t$

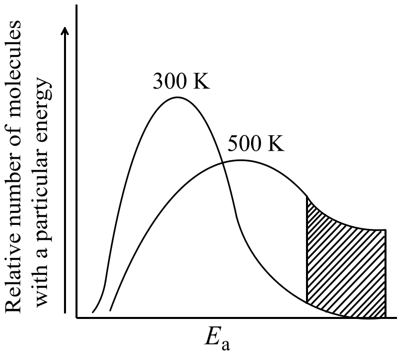
a)


b)


c) 

d) 

239. The distribution of molecular kinetic energy at two temperature is as shown in the following graph:



Which of the following conclusion is/are correct?

a) The number of molecular with energy E_a or grater is proportional to the shaded area for each temperature

b) The number of molecules with energy E_a or less is proportional to the shaded are for each temperature

c) The number of molecules with energy E_a is the mean of all temperature

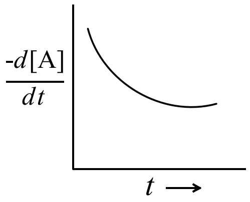
d) The graph follows the Maxwell-Boltzmann energy distribution law

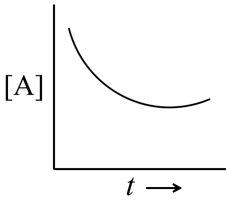
240. $$C_6H_6 + 3H_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C_6H_{12}$$

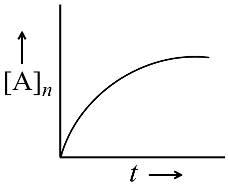
The rate of formation of for the forward reaction is first order with respect top C_6H_6 and H_2 each. Which one of the options is/are correct?

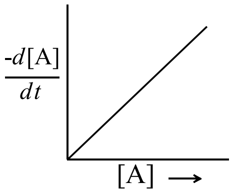
a) $k_{eq} = \frac{k_f}{k_b}$ b) $k_{eq} = \frac{[C_6H_{12}]}{[C_6H_6][H_2]^3}$ c) $r_f = k_f[C_6H_6][H_2]$ d) $r_b = k_b[C_6H_{12}][H_2]^{-2}$

241. Which of the following plots are correctly made for the reaction $nA \rightleftharpoons (A)_n$ if it obeys first order reaction?

a) 

b) 

c) 

d) 

242. The basic theory behind Arrhenius' equation is that

a) The number of effective collisions is proportional to the number of molecules above a certain threshold energy

b) As the temperature increases, so does the number of molecules with energies exceeding the threshold energy

c) The rate constant is function of temperature

d) The activation energy and pre-exponential factor are always temperature independent

243. Which of the following statements is/are true?

a) For endothermic reactions, energy of activation is always greater than heat of reaction

b) For exothermic reactions, energy of activation is always smaller than heat of reaction

c) Rate of reaction always increases with increase in temperature

d) Temperature coefficient of a reaction is given by $\frac{K_{t+10}}{K_t}$

244. Which of the following statements is/are correct?
   a) Law of mass action and rate law expressions are same for single step reactions
   b) Order for the slowest elementary reaction of a multi step reaction gives the order of the multi step reaction
   c) Both order and molecularity have normally a maximum value of 3
   d) Molecularity of a complex reaction, $A + 2B \longrightarrow C$ is 3

245. Which of the following statement (s) are not correct?
   a) A plot of $\log k_p$ versus $1/T$ is linear
   b) A plot of $\log k_p$ versus $1/T$ is nonlinear
   c) A plot of $\log P$ versus $1/T$ is linear at constant volume
   d) A plot of P versus $1/V$ is linear at constant temperature

246. The rate of a first order reaction is 3×10^{-5} mol L^{-1} s^{-1}, when the initial concentration is 0.2 mol L^{-1}. The rate constant k is:
   a) 15×10^{-5} b) 1.5×10^{-4} c) 0.6×10^{-5} d) 0.6×10^{-4}

247. Which one is correct according to the collision theory of the rate of reaction?
   a) The threshold energy level is a characteristics of reaction
   b) The energy of activation decreases with rise in temperature
   c) The energy of absorbed activated complex is lower than simple activated complex
   d) The energy of activated complex (both activated or adsorbed) is higher than reaction or product

248. The study of chemical kinetics becomes highly complicated if there occurs:
   a) Reversible reaction b) Side reaction c) Surface reaction d) None of these

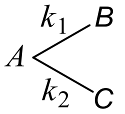
249. For a gaseous reaction: A(g) → B(g), the rate expression may be given as
   a) $-\dfrac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^n$ b) $-\dfrac{1}{V}\dfrac{dn_A}{dt} = k[\mathrm{A}]^n$ c) $-\dfrac{1}{RT}\dfrac{dP_\mathrm{A}}{dt} = k[\mathrm{A}]^n$ d) $-\dfrac{dP}{dt} = k[P_\mathrm{A}]^n$

250. Which of the following statement(s) is/are correct?
   a) Zero order reactions are complex reactions
   b) A reaction having first order may be either elementary or complex reaction
   c) A reaction having second order reaction must have molecularity =2
   d) A reaction with molecularity =2 must be a second order reaction

251. Which of the following statements is/are correct?
   a) It is possible to change the specific rate constant by changing the temperature.
   b) The specific rate constant is independent of the concentrations of the reacting species.
   c) In step-wise reactions the rate determining step is the slowest one.
   d) The rate of a catalysed reaction is always independent of the concentration of the catalyst.

252. For a reaction $2A + B \rightarrow C$ with the rate law $\frac{d[C]}{dt} = k[A][B]^{-1}$ and started with A and B in stoichiometric proportion which is/are true?
   a) $[C] = 2kt$
   b) $[C] = kt$
   c) Unit of k is mol L^{-1} s^{-1}
   d) $[A][B]$ and $[C]$ all will be linear functions of time

253. Consider the following case of completing 1st order reactions



   After the start of the reaction at $t = 0$ with only A, the $[B]$ is equal to the $[C]$ at all times. The time in which all three concentrations will be equal is given by
   a) $t = \dfrac{1}{3k_1}\ln 2$ b) $t = \dfrac{2}{2k_1}\ln 3$ c) $t = \dfrac{1}{3k_2}\ln 2$ d) $t = \dfrac{1}{2k_2}\ln 3$

254. $\mathrm{Zn} + 2\mathrm{H}^{\oplus} \rightarrow \mathrm{Zn}^{2+} + \mathrm{H}_2$
   The half-life period is independent of the concentration of zinc at constant pH. For the constant

concentration of Zn, the rate becomes 100 times when pH is decreased from 3 to 2. Hence,

a) $\frac{dx}{dt}=k[\mathrm{Zn}]^0[\mathrm{H}^{\oplus}]^2$

b) $\frac{dx}{dt}=k[\mathrm{Zn}][\mathrm{H}^{\oplus}]^2$

c) Rate is not affected if the concentration of zinc is made four times and that of $\mathrm{H}^{\oplus}$ion is halved

d) Rate becomes four times if the concentration of $\mathrm{H}^{\oplus}$ ion is doubled at constant Zn concentration

255. For a first order reaction

a) The degree of dissociation is equal to $(1-e^{-kt})$

b) A plot of reciprocal concentration of the reactant vs time gives a straight line

c) The time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of reaction

d) The pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}

256. For the reaction, $A+3B\longrightarrow C$, the differential form of the rate law is:

a) $\frac{d[C]}{dt}=-\frac{d[A]}{dt}$ b) $\frac{3d[C]}{dt}=\frac{-d[B]}{dt}$ c) $\frac{-3d[B]}{dt}=\frac{-d[C]}{dt}$ d) $\frac{d[A]}{dt}=\frac{d[C]}{dt}$

257. Which of the following statement is/are correct?

a) For the reaction $N_2(g)+3H_2(g)\rightarrow 2NH_3(g)$ under certain conditions of temperature and partial pressure of the reactant, the rate of formation of NH_3 is 0.001 kg h^{-1}. The rate of conversion of H_2 under the same conditions is 0.0015 kg hr^{-1}

b) The rate law for the reaction
$\mathrm{RCl}+\mathrm{NaOH(aq)}\rightarrow\mathrm{ROH}+\mathrm{NaCl}$
Is given by, rate $=k_1[\mathrm{RCl}]$. The rate of the reaction will be halved on reducing the concentration of alkyl halide to one half

c) The rate of the reaction in part (b) increased on decreasing the temperature of the reaction

d) The rate of chemical change is inversely proportional to the concentration at that instant

258. Which of the following statements is/are correct for the given reaction,
$4A+B=2C+2D$?

a) The rate of disappearance of B is one-fourth the rate of disappearance of A

b) The rate of appearance of C is half the rate of disappearance of B

c) The rate of formation of C and D are equal

d) The rate of formation of D is half the rate of disappearance of A

259. Rate constant for a reaction varies with temperature as, $\ln k(\sec^{-1})=14.34-\frac{1.25\times10^4}{T}$, which statement (s) is/are correct?

a) The graph plotted in between $\log_{10}k$ $vs\frac{1}{T}$ is straight line with $E_a=24.83$ kcal

b) Pre-exponential factor $=14.34$

c) The rate constant at 500 K is 2.35×10^{-5} $\sec^{-1}$

d) $E_a=30.63$ kcal

260. The specific rate constant of a first order reaction is independent of the:

a) Concentration of the reactants

b) Time

c) Temperature

d) Activation energy

261. The rate of reaction:

a) Decreases with time

b) Decreases with decrease in conc. of reactant

c) Increase with temperature

d) None of the above

262. Which of the following is (are) not correct for a first order reaction?

a) $t_{1/2}\propto a$ b) $t_{1/2}\propto 1/a$ c) $t_{1/2}\propto a^0$ d) $t_{1/2}\propto a^2$

263. Select the correct statement(s)

a) The order of reaction may be changed with change in the experimental conditions
b) The rate of reaction, either exothermic or endothermic, both decreases with decrease in the temperature
c) A reaction mixture thermodynamics stable should be kinetically unstable
d) A negative catalyst increase the energy of activation

264. For the reaction,
$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$ the rate law is, rate= $k[C_{12}H_{22}O_{11}]$

a) Order w.r.t. water is one	b) Order w.r t. sucrose is one
c) Reaction is pseudosecond order	d) Order of the reaction is one

265. In which of the following, E_a for backward reaction is greater than E_a for forward reaction?
a) $A \xrightarrow{E_a=50\text{ kcal}} B;\quad \Delta H = -10\text{ kcal}$
b) $A \xrightarrow{E_a=50\text{ kcal}} B;\ \ \Delta H = +10\text{ kcal}$
c) $A + 10\text{ kcal} \longrightarrow B; E_a = 50\text{ kcal}$
d) $A - 10\text{ kcal} \longrightarrow B; E_a = 50\text{ kcal}$

266. The rate of a chemical reaction (except zero order):
a) Decreases from moment to moment
b) Remains constant throughout
c) Depends upon the order of reaction
d) None of the above

267. The rate constant of a reaction is given by $k = 2.1 \times 10^{10}\ \exp(-2700/RT)$. It means that
a) $\log k$ versus $1/T$ will be a straight line with slope= $\frac{-2700}{2.303\ R}$
b) $\log k$ versus $1/T$ will be a straight line with intercept on $\log k$ axis = 2.1×10^{10}
c) The number of effective collisions are $2.1 \times 10^{10}\ \text{cm}^{-3}\text{s}^{-1}$
d) Half life of the reaction increases with increase of temperature

Assertion - Reasoning Type

This section contain(s) 0 questions numbered 268 to 267. Each question contains STATEMENT 1(Assertion) and STATEMENT 2(Reason). Each question has the 4 choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

a) Statement 1 is True, Statement 2 is True; Statement 2 **is** correct explanation for Statement 1

b) Statement 1 is True, Statement 2 is True; Statement 2 **is not** correct explanation for Statement 1

c) Statement 1 is True, Statement 2 is False

d) Statement 1 is False, Statement 2 is True

268

Statement 1: Formation of HI is a bimolecular reaction

Statement 2: Two molecules of reactants are involved in this reaction

269

Statement 1: The elementary reaction is single step reaction and does not possess mechanism.

Statement 2: An elementary reaction has order of reaction and molecularity same.

270

Statement 1: Threshold energy of a reaction is dependent of temperature.

Statement 2: The energy of activation decreases with increase in temperature.

271

Statement 1: For the reaction $2O_3 \longrightarrow 3O_2$, the rate $= K[O_3]^2[O_2]^{-1}$.

Statement 2: The reaction has −ve order for O_2.

272

Statement 1: Alcohols are dehydrated to hydrocarbons in presence of acidic zeolites.

Statement 2: Zeolites are porous catalyst.

273

Statement 1: Molecularity has no meaning for a complex reaction.

Statement 2: The overall Molecularity of a complex reaction is equal to the Molecularity of the slowest step.

274

Statement 1: The order of reaction may be negative.

Statement 2: In some cases, the rate of the reactions decreases as the concentration of the reactions increases.

275

Statement 1: According to transition state theory, for the formation of an activated complex, one of the vibrational degree of freedom is converted into translational degree of freedom.

Statement 2: Energy of the activated complex is higher than the energy of reactant molecules.

276

Statement 1: Every collision between molecules leads to a chemical reaction.

Statement 2: Only those molecules react during collisions which acquire threshold energy level.

277

Statement 1: The rate of reaction increase generally by 2 to 3 times for every 10°C rise in temperature

Statement 2: An increase in temperature increases the collision frequency

278

Statement 1: The rate constant of a zero order reaction has same units as the rate of reaction

Statement 2: Rate constant of a zero order reaction does not depend upon the units of concentration

279

Statement 1: The order of reaction can have fractional value.

Statement 2: The order of reaction can not be written from balanced equation of a reaction.

280

Statement 1: The molecularity of the reaction $H_2Br_2 \rightarrow 2HBr$ is 2

Statement 2: The order of the reaction is 3/2

281

Statement 1: For a first order, the concentration of a reactant decreases exponentially with time

Statement 2: The rate of reaction at any time depends upon the concentration of the reactant at that time

282

Statement 1: A catalyst does not affect the heat of reaction.

Statement 2: It increases the rate of reaction.

283

Statement 1: The order of a reaction can be fractional but molecularity is never fractional

Statement 2: The order of reaction does not depend upon the stoichiometric coefficient of a balanced equation

284

Statement 1: Both $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ and $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ have the same order of reaction

Statement 2: Both reactions proceed by the same mechanism

285

Statement 1: In the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of reaction is different in terms of N_2, H_2 and NH_3

Statement 2: The rate of reaction is equal to the rate of disappearance of a reactant or rate of formation of a product

286

Statement 1: Lower activation energy fasten is the reaction

Statement 2: If the activation energy of reaction is zero, temperature will have no effect on the rate constant

287

Statement 1: For each 1°C rise in temperature rate constant is nearly doubled.

Statement 2: Energy wise distribution of molecule in a gas is an exponential function of temperature.

288

Statement 1: The rate constant of a pseudo unimolecular reaction has the units of a second order reaction

Statement 2: A pseudo unimolecular reaction is a reaction of second order in which one of the reactant is present in large excess

289

Statement 1: $k = Ae^{-E_a/RT}$, the Arrhenius equation represents the dependance of rate constant with temperature

Statement 2: Plot of $\log k$ against $1/T$ is linear and the activation energy can be calculated with this plot

290

Statement 1: In the reaction $I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$, the two $S_2O_3^{2-}$ ions are used for every I_2.

Statement 2: The rate of disappearance of I_2 is one half the rate of disappearance of $S_2O_3^{2-}$

291

Statement 1: If the activation energy of a reaction is zero temperature will have no effect on the rate constant.

Statement 2: Lower the activation energy faster is the reaction.

292

Statement 1: The numerical value of specific rate constant is independent of the concentration of any species present in the reaction mixture

Statement 2: When a reaction is carried out in aqueous solution and some alcohol is added to the reaction mixture, the rate of reaction will not change

293

Statement 1: Hydrolysis of ethyl acetate in the presence of acid is a reaction of first order whereas in the presence of alkali, it is a reaction of second order

Statement 2: Acid acts as catalyst only whereas alkali act as one of the reactant

294

Statement 1: The rate expression of $2NO_2 + F_2 \longrightarrow 2NO_2F$ is $r = K[NO_2][F_2]$.

Statement 2: The reaction has the mechanism

$NO_2 + F_2 \xrightarrow{\text{slow}} NO_2F + F$

$NO_2 + F \xrightarrow{\text{Fast}} NO_2F$

295

Statement 1: According to the transition state theory, for the formation of an activated complex, one of the vibrational degree of freedom is converted into the transition degree of freedom

Statement 2: The energy of the activated complex is higher than the energy of the reactant molecules

296

Statement 1: Order of reaction can never be fractional for an elementary reaction.

Statement 2: An elementary reaction takes place by one step mechanism.

297

Statement 1: A catalyst always lower the energy of activation.

Statement 2: The catalyst-reactant interaction forms activated absorbed complex and adsorption is always exothermic.

298

Statement 1: The order of the reaction $CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$ is 2

Statement 2: The molecularity of this reaction is 2

299

Statement 1: Positive catalyst lowers the activation energy of the reaction whereas the heat of reaction remains same

Statement 2: The heat of reaction is equal to the difference between activation energies for forward and backward reactions

300

Statement 1: If the activation energy of a reaction is zero, temperature will have no effect on the rate constant

Statement 2: Lower the activation energy, faster is the reaction

301

Statement 1: For a first order reaction the plots of rate vs. concentration is straight line

Statement 2: For a first order reaction, Rate= $k[A]$

302

Statement 1: Positive catalysts increase the rate of reaction

Statement 2: Catalyst decrease the value of $\Delta G^{\ominus}$

303

Statement 1: An order with respect to any reactant or product can be zero, positive, negative, and fractional

Statement 2: Rate cannot decrease with increase in the concentration of a reactant or product

304

Statement 1: For: $aA + bB \rightarrow$Product. The order of reaction is equal to $(a + b)$

Statement 2: Rate of reaction $= k[\mathrm{A}]^a[\mathrm{B}]^b$

305

Statement 1: The emission of light during burning of P in O_2 is called chemiluminescence.

Statement 2: The chemical energy is converted into light energy.

306

Statement 1: The rate of a chemical reaction whether exothermic or endothermic increases with temperature

Statement 2: The rate of reaction$=k[\text{Reactant}]^n$ and k increases with temperature

307

Statement 1: Temperature coefficient is the ratio of two rate constants preferably at 35°C and 25°C.

Statement 2: It can also be given as $e^{-\frac{E_a}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]}$

308

Statement 1: Photosynthesis in plants involves reaction of CO_2 and H_2O in presence of light and chlorophyll.

Statement 2: It is chlorophyll which absorbs light and passes this energy to reactant molecules.

309

Statement 1: Rate constant K is equal to Arrhenius parameter if it involves free radical combination.

Statement 2: $E_a = 0$ for free radical combination.

310

Statement 1: For the reaction
$RCl + NaOH(aq) \rightarrow ROH + NaCl$, the rate of reaction is reduced to half on reducing the concentration of RCl to half

Statement 2: The rate of the reaction is represented by $k[RC]$, i.e., it is a first order reaction

311

Statement 1: As the temperature increases, rate of reaction increase

Statement 2: The rate of reaction increase due to, increase in collision frequency and shortening of mean free path

312

Statement 1: The rate of reaction sometimes does not depend on concentration

Statement 2: The order of reaction can be negative

313

Statement 1: The rate of reaction whether exothermic or endothermic, increases with temperature.

Statement 2: The rate of reaction $= K[\text{reactant}]^n$ and K increases with temperature.

314

Statement 1: $k \propto e^{-E_a/RT}$ the Arrhenius equation represents the dependence of rate constant with temperature

Statement 2: Plot of $\log k$ against $1/T$ is linear and the activation energy can be calculated with this plot

Matrix-Match Type

This section contain(s) 0 question(s). Each question contains Statements given in 2 columns which have to be matched. Statements (A, B, C, D) in **columns I** have to be matched with Statements (p, q, r, s) in **columns II**.

315.

Column-I	**Column- II**
(A) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^{\oplus}} C_6H_{12}O_6 + C_6H_{12}O_6$	(p) Pseudo first orde

(B) $CH_3COOC_2H_5 \xrightarrow[H^{\oplus} \text{ or } \overset{\ominus}{O}H]{HOH} CH_3COOH + C_2H_5OH$	(q) Zero order
(C) $H_2 + Cl_2 \xrightarrow{hv} 2HCl$	(r) Second order
(D) $CH_3Cl + \overset{\ominus}{O}H \longrightarrow CH_3OH + Cl^{\ominus}$	(s) First order

CODES :

	A	**B**	**C**	**D**
a)	b	c	a	c,d
b)	c	a	c,d	b
c)	a	c,d	b	c
d)	c,d	b	c	a

316. Where $a =$ initial concentration of the reactant and $b =$ initial pressure of the reactant

Column-I	**Column- II**
(A) $t_{1/2} =$constant	(p) First order
(B) $t_{1/2} \propto a$	(q) Pseudo first order
(C) $t_{1/2} \propto p^{-1}$	(r) Zero order
(D) $t_{1/2} \propto 1/a$	(s) Second order

CODES :

	A	**B**	**C**	**D**
a)	A,b	c	a,b	c,d
b)	c	a,b	c,d	a,b
c)	a,b	c,d	a,b	c
d)	c,d	a,b	c	a,b

317.

Column-I	**Column- II**
(A) $x = kt$	(p) $\text{L mol}^{-1}\text{s}^{-1}$
(B) $k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{(a)}\right]$	(q) s^{-1}
(C) $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$	(r) $\text{atm}^{-1}\text{s}^{-1}$
(D) $k = \frac{2.303}{t(a-b)} \log\left[\frac{b(a-x)}{a(b-x)}\right]$	(s) $\text{mol L}^{-1}\text{s}^{-1}$

CODES :

	A	B	C	D
a)	A,c	b	a,c	c
b)	c	a,c	b	a,c
c)	b	a,c	c	a,c
d)	a,c	c	a,c	b

318.

	Column-I		Column- II
(A)	Molecularity	(p)	0
(B)	Order	(q)	1/2
(C)	Temperature coefficient	(r)	Between 2 and 3
(D)	Activation energy for participation of all reactant molecules	(s)	2

CODES :

	A	B	C	D
a)	c	a	d	a,b,d
b)	a	d	a,b,d	c
c)	d	a,b,d	c	a
d)	a,b,d	c	a	d

319.

	Column-I		Column- II
(A)	$SO_2Cl_2 \rightarrow SO_2 + Cl_2$	(p)	s^{-1}
(B)	$CH_3COOC_2H_5 + NaOH$ $\rightarrow CH_3COONa$ $+ C_2H_5OH$	(q)	min^{-1}
(C)	$2H_2O_2 \rightarrow 2H_2O + O_2$	(r)	$L\ mol^{-1}min^{-1}$
(D)	$H_2O_2 + 2I^{\ominus} + 2H^{\oplus}$ $\rightarrow 2H_2O + I_2$	(s)	$L\ mol^{-1}s^{-1}$

CODES :

	A	B	C	D
a)	C,d	a,b	c,d	a,b
b)	a,c	b,d	b,d	a,c
c)	b,d	b,d	a,c	a,c

d)	a,b	c,d	a,b	c,d

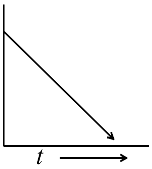
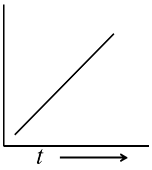
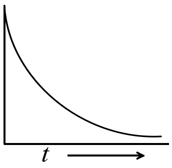
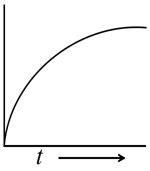
320.

	Column-I		**Column- II**
(A)	Sucrose in aqueous solution of dilute acid is hydrolyzed to glucose and fructose	(p)	Bimolecular
(B)	n-Propyl bromide in ethanolic solution given ethyl proply ether	(q)	Pseudo uni-molecular reaction
(C)	Benzyl bromide is converted into benzylthiol via carbocationic intermediate formation mechanism	(r)	Unimolecular
(D)	The reaction: $2O_3 \rightarrow 3O_2$ follows the mechanism 1. $O_3 \rightleftharpoons O_2 + O$ (Fast) 2. $O_3 + O \rightarrow 2O_2$ (Slow)	(s)	First order

CODES :

	A	**B**	**C**	**D**
a)	a	c,d	a,d	a,b,d
b)	a,b,d	a	c,d	a,d
c)	c,d	a,d	a,b,d	a
d)	a,d	a,b,d	a	c,d

321.

	Column-I		**Column- II**
(A)	[A] versus time	(p)	
(B)	$-\frac{d[A]}{dt}$ versus [A]	(q)	
(C)	$-\frac{d[A]}{dt}$ versus time	(r)	
(D)	log [A] versus time	(s)	

CODES :

	A	**B**	**C**	**D**

a)	a	b	c	d
b)	b	c	d	a
c)	b	c	a	c
d)	c	b	c	a

322.

	Column-I		**Column- II**
(A)	Elementary reactions	(1)	No energy of activation
(B)	Complex reactions	(2)	Low energy of activation
(C)	Free radical combinations	(3)	High energy of activation
(D)	Slow reactions	(4)	Several elementary steps
(E)	Fast reaction	(5)	Single step

CODES :

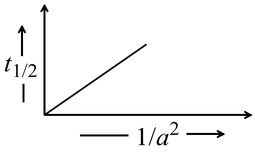
	A	**B**	**C**	**D**	**E**
a)	5	4	1	3	2
b)	2	5	4	3	2
c)	1	3	2	4	2
d)	4	1	3	2	2
e)	2	4	3	2	2

323.

Column-I **Column- II**

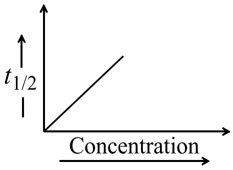
(A) Zero

(p)



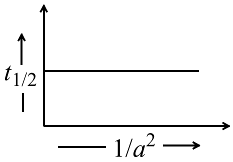
(B) First

(q)



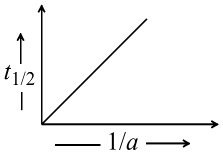
(C) Second

(r)



(D) Third

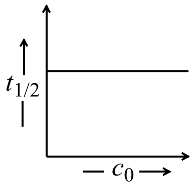
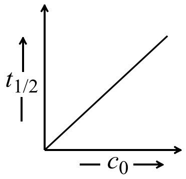
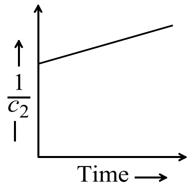
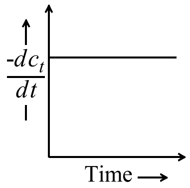
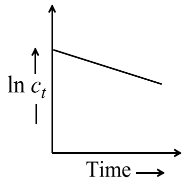
(s)



CODES :

	A	**B**	**C**	**D**
a)	c	d	a	b
b)	d	a	b	c
c)	a	b	c	d
d)	b	c	d	a

324.

	Column-I		**Column- II**
(A)		(p)	$t_\infty = 2 \times t_{1/2}$
(B)		(q)	$t_{3/4} = 2 \times t_{1/2}$
(C)		(r)	
(D)		(s)	$t_{1/2} \times c_0 =$ constant
		(t)	Zero order

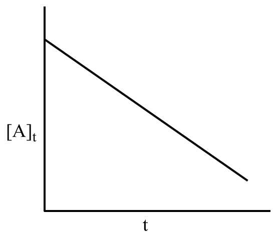
CODES :

	A	**B**	**C**	**D**
a)	b	a,d,e	d	a,c,e
b)	d	a,d	b	a,c
c)	a,d	d,e	a,c	d
d)	a,c	b	d	a,d

325.

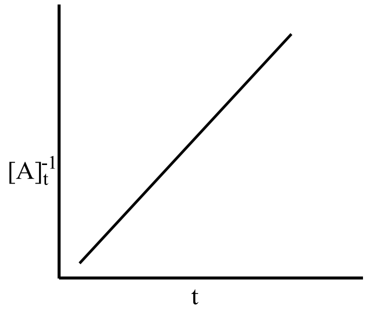
Column-I	**Column- II**

(A)



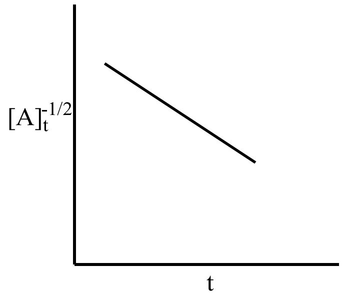
(1) $O.R \neq 1/2$

(B)



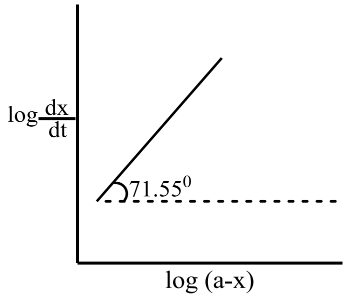
(2) $O.R. =$ zero

(C)



(3) $O.R. = 2$

(D)



(4) $O.R. = 3$

CODES :

	A	**B**	**C**	**D**
a)	2	3	1	4
b)	4	1	2	3
c)	3	2	4	1
d)	1	4	3	2

326.

	Column-I		**Column- II**
(A)	Rate $= k \times$Intensity of light	(p)	Second order
(B)	Rate $= k[A]^1[B]^1$	(q)	Zero order
(C)	Rate $= k[A]^{3/2}[B]^{1/2}$	(r)	First order when A is in excess
(D)	Rate $= k[A]^2[B]^1$	(s)	Second order when B is in excess

CODES :

	A	**B**	**C**	**D**
a)	b	a	a	c,d
b)	a,c	a	b	c
c)	a	a	c,d	b
d)	a	b	c	a,c

327.

Column-I	**Column- II**
(A) Collision theory	(p) Mol $L^{-1}s^{-1}$
(B) Zero order reaction	(q) Bimolecular reaction
(C) Photochemical reaction	(r) Fractional
(D) Intercept (in Arrhenius plot)	(s) In A
(E) Order of reaction	(t) Zero order reaction

CODES :

	A	**B**	**C**	**D**	**E**
a)	e	d	c	b	a
b)	d	c	b	a	a
c)	b	a	e	d	a
d)	a	e	d	c	a
e)	c	b	a	e	a

328.

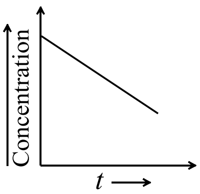
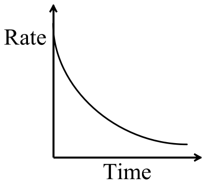
Column-I	**Column- II**
(A) Decomposition of H_2O_2	(p) $10t_{1/2}$
(B) k_{308}/k_{298}	(q) (2 to 3) (generally)
(C) $\frac{k}{A} = e^{-E_a/RT}$	(r) Fractions of collision which are effective
(D) $t_{99.9\%}$ (for first order)	(s) First order

CODES :

	A	**B**	**C**	**D**
a)	c	a	d	b
b)	a	d	b	c

c)	d	b	c	a
d)	b	c	a	d

329.

Column-I	**Column-II**
(A) Ester + NaOH → Alcohol + Salt	(p) $k = Ae^{-E_a/RT}$
(B) $2H_2O_2 \rightarrow 2H_2O + O_2$	(q) 
(C) $2NH_3 \xrightarrow[\text{zero order}]{\text{Au}} N_2 + 3H_2$	(r) 
(D) Sucrose $+ H_2O$ → Glucose + Fructose	(s) $t_{1/2} = x$ minutes at a constant temperature at any time of the reaction

CODES :

	A	**B**	**C**	**D**
a)	a	a,c,d	a,b	a,c,d
b)	a,c,d	a,b	a,c,d	a
c)	a,b	a,c,d	a	a,c,d
d)	a,c,d	a	a,c,d	a,b

330.

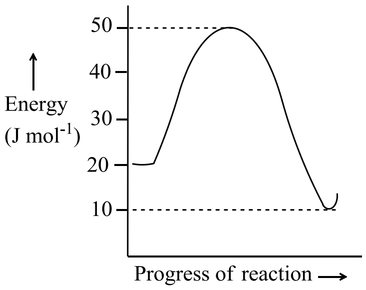
Column-I	**Column-II**
(A) $t_{1/2} = 0.693/k$	(p) Zero order
(B) $t_{1/2} = a/2k$	(q) First order
(C) $\lambda = 1/k$	(r) Average life
(D) $t_{3/4} = 2t_{1/2}$	(s) 75 % completion
	(t) 25% completion

CODES :

	A	**B**	**C**	**D**
a)	a	b,c	b,d	b
b)	b	a	b,c	b,d
c)	b,d	b	a,c	c,d

d)	b	a,c	c,d	b,d

331.



	Column-I		**Column- II**
(A)	E_a(f)	(p)	-10 kJ mol^{-1}
(B)	E_a(b)	(q)	40 kJ mol^{-1}
(C)	$\Delta_r H$	(r)	30 kJ mol^{-1}
(D)	$E_{\text{Threshold}}$	(s)	50 kJ mol^{-1}

CODES :

	A	**B**	**C**	**D**
a)	b	a	d	c
b)	c	b	a	d
c)	a	d	c	b
d)	d	c	b	a

332.

	Column-I		**Column- II**
(A)	Zero order reaction	(p)	$\frac{k_{t+10}}{k_t} = 2$ or 3
(B)	First order reaction	(q)	$2H_2O_2 \rightarrow 2H_2O + O_2$
(C)	Second order reaction	(r)	$-\frac{dx}{dt} = k[A]^2[B]$
(D)	Temperature coefficient	(s)	$H_2 + Cl_2 \xrightarrow{hv} 2HCl$
		(t)	$CH_3COOCH_3 + NaOH$ $\rightarrow CH_3COONa + CH_3OH$

CODES :

	A	**B**	**C**	**D**
a)	b	e	a	d
b)	a	b	d	c
c)	b	d	c	a
d)	d	b	e	a

Linked Comprehension Type

This section contain(s) 25 paragraph(s) and based upon each paragraph, multiple choice questions have to be answered. Each question has atleast 4 choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

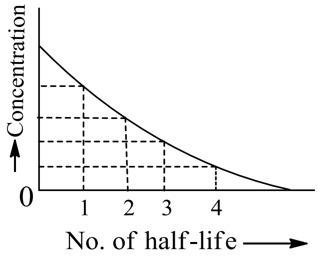
Paragraph for Question Nos. 333 to -333

Half-life $t_{1/2}$ of reaction is the time required for the concentration of reactant to derease by half, *ie*,

$[A]_t = \frac{1}{2}[A]$

$t_{1/2} = 0.693/K$

That is $t_{1/2}$ is independent of initial concentration. Figure shows that typical variation of concentration of reactant exhibiting first order kinetics. It may be noted that though the major portion of the first order kinetics may be over in a finite time, but the reaction will never cease as the concentration of reactant will be zero only at infinite time



333. 75% of a reaction of the first order was completed in 32 min. When was it half completed?
a) 8 min
b) 16 min
c) 64 min
d) 48 min

Paragraph for Question Nos. 334 to - 334

Note all chemical reactions proceed to a stage at which the concentrations of the reactants become vanishingly small. Here we consider the kinetics of such reactions. Let a reaction be represented in general terms by the scheme

$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$

Where k_1 and k_2 represent the rate constant for the forwards and reverse reactions respectively. The equilibrium constant for this reaction may be written as

$k = [B]_\infty/[A]_\infty = k_1/k_2$

The initial concentration of species A is $[A]_0$ and that of B is $[B]_0$. After a time t, let the concentration of species A be $[A]_t$ and that of B be $[B]_t$. The total rate of change of $[A]_t$ is given by

$d[A]_{t/dt} = -k_1[A]_t + k_2[B]_t$

$d[A]_{t/dt} = -k_1[A]_t + k_2([A]_0 - [A]_t)$

$d[A]_{t/dt} = -(k_1 + k_2)\left([A]_t - \frac{k_2}{k_1 + k_2}[A]_0\right)$

334. What is the k_c of the reaction $2C \rightleftharpoons 2A$?
a) 9/4
b) 2/3
c) 4/3
d) 5/2

Paragraph for Question Nos. 335 to - 335

The rate of reaction increases significantly with increase in temperature. Generally, rates of reactions are doubled for every 10° rise in temperature. Temperature coefficient gives us an idea about the change in the rate of a reaction for every 10° change in temperature

Temperature coefficient (μ) $= \frac{\text{Rate constant of } (T+10)\text{°C}}{\text{Rate constant at } T\text{°C}}$

Arrhenius gave an equation which describes arte constant k as a function of temperature

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

Where k is the rate constnat, A is the frequency factor or pre-exponetial factor, E_a is the activation energy, T is the temperature in Kelvin, and R is the universal gas constant.

Equation when expressed in logarithmic form becomes

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

335. For a reactio $E_a = 0$ and $k = 3.2 \times 10^8\ \text{s}^{-1}$ at 325 K. The value of k at 335 K would be

a) $3.2 \times 10^8 \text{s}^{-1}$ b) $6.4 \times 10^8 \text{s}^{-1}$ c) $12.8 \times 10^8 \text{s}^{-1}$ d) $25.6 \times 10^8\ \text{s}^{-1}$

Paragraph for Question Nos. 336 to - 336

The rate constant for the decomposition of a certain reaction is described by the equation:

$$\log k\ (\text{s}^{-1}) = 14 - \frac{1.25 \times 10^4\ \text{K}}{T}$$

336. Pre-exponential factor for this reaction is

a) $14\ \text{s}^{-1}$ b) $10^{14}\ \text{s}^{-1}$ c) $10^{-14}\ \text{s}^{-1}$ d) $1.25 \times 10^4\ \text{s}^{-1}$

Paragraph for Question Nos. 337 to - 337

The following data were observed for the following reaction at 25°C, $\text{CH}_3\text{OH} + (\text{C}_6\text{H}_5)_3\text{CCl} \rightarrow (\text{C}_6\text{H}_5)_3\text{C} \cdot \text{OCH}_3 + \text{HCl}$

Set	**Initial concentration (M)** $[\mathbf{A}]_0$	 $[\mathbf{B}]_0$	**Time (Δt) (min)**	**Final concentration (M)**
I	0.10	0.05	25	0.0033
II	0.10	0.10	15	0.0039
III	0.20	0.10	7.5	0.0077

337. Rates $\frac{d[\text{C}]}{dt}$ in sets I, II and III are, respectively, (in M min^{-1}):

I II III

a) 1.30×10^{-4} 2.6×10^{-4} 1.02×10^{-3} b) 0.033 0.0039 0.0077

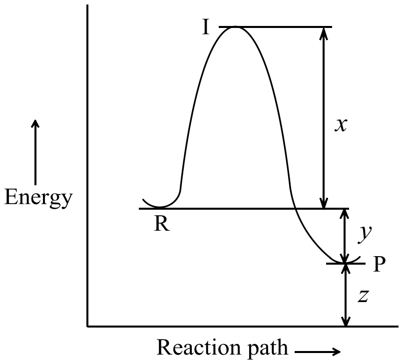
c) 0.02×10^{-4} 0.04×10^{-4} 0.017 d) None of above

Paragraph for Question Nos. 338 to - 339

The energy profile diagram for the reaction:

$\text{CO(g)} + \text{NO}_2\text{(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{NO(g)}$

In given below:



338. The activation energy of the forward reaction is

a) x b) y c) $x + y$ d) $x - y$

Paragraph for Question Nos. 339 to - 340

The reaction $S_2O_8^{2-} + 3I^{\ominus} \rightarrow 2SO_4^{2-} + I^{\ominus}_3$ is of first order both with respect to persulphate and iodide ions. Taking the initial concentration as a and b, respectively, and taking x as the concentration of the triodide at time t, a different rate equation can be written

Two suggested mechanisms for the reaction are:

I. $S_2O_8^{2-} + I^{\ominus} \rightleftharpoons SO_4I^{\ominus} + SO_4^{2-}$ (fast)

$I^{\ominus} + SO_4I^{\ominus} \xrightarrow{k_1} I_2 + SO_4^{2-}$ (show)

$I^{\ominus} + I_2 \xrightarrow{k_2} I_3^{\ominus}$(fast)

II. $S_2O_8^{2-} + I^{\ominus} \xrightarrow{k_1} S_2O_8\,I^{3-}$ (slow)

$S_2O_8I^{3-} \xrightarrow{k_2} 2SO_4^{2-} + I^{\oplus}$(fast)

$I^{\oplus} + I^{\ominus} \xrightarrow{k_3} I_2$ (fast)

$I_2 + I^{\ominus} \xrightarrow{k_4} I_3^{\ominus}$ (fast)

339. The general different equation for the above reaction is

a) $\frac{dx}{dt} = k[a - x][b - 3x]\ \ (k > 0)$

b) $\frac{dx}{dt} = -k[a - x][b - 3x]\ (k > 0)$

c) $\frac{dx}{dt} = k[a - x][b - x]\ \ (k > 0)$

d) $\frac{dx}{dt} = -k[a - x][b - x]\ \ (k > 0)$

Paragraph for Question Nos. 340 to - 341

Consider the reaction represented by the equation:

$CH_3Cl\ (g) + H_2O(g) \rightarrow CH_3OH(g) + HCl(g)$

Those kinetic data were obtained for the given reaction concentration:

Initial conc (M)		**Initial rate of disappearance**
[CH_3Cl]	**[H_2O]**	**of CH_3Cl($M\ s^{-1}$)**
0.2	0.2	1
0.4	0.2	2
0.4	0.4	8

340. The rate law for the reaction will be

a) $r = k[\mathrm{CH_3Cl}][\mathrm{H_2O}]$ b) $r = k[\mathrm{CH_3Cl}]^2[\mathrm{H_2O}]$ c) $r = k[\mathrm{CH_3Cl}][\mathrm{H_2O}]^2$ d) $r = k[\mathrm{CH_3Cl}]^2[\mathrm{H_2O}]^4$

Paragraph for Question Nos. 341 to - 342

For the reaction: $aA + bB \rightarrow cC + dD$

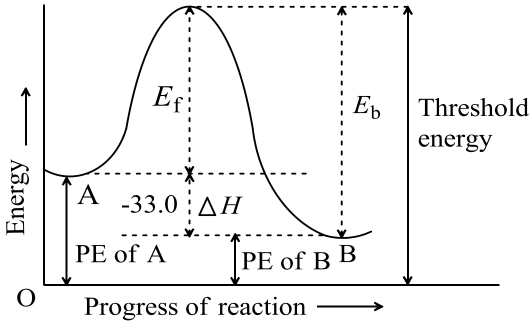
Rate $= \frac{dx}{dt} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$

341. For reaction $3\mathrm{BrO}^{\ominus} \rightarrow \mathrm{BrO_3}^{\ominus} + 2\mathrm{Br}^{\ominus}$, the value of rate constant at 80°C in the rate law for $-\frac{d[\mathrm{BrO}^{\ominus}]}{dt}$ was found to be $0.054\ \mathrm{L\ mol^{-1}s^{-1}}$. The rate constant (k) for the reaction in terms of $\frac{d[\mathrm{BrO_3}^{\ominus}]}{dt}$ is

a) $0.018\ \mathrm{L\ mol^{-1}s^{-1}}$ b) $0.162\ \mathrm{L\ mol^{-1}s^{-1}}$ c) $0.036\ \mathrm{L\ mol^{-1}s^{-1}}$ d) None

Paragraph for Question Nos. 342 to - 343

The energy change accompanying the equilibrium reaction $\mathrm{A} \rightleftharpoons \mathrm{B}$ is $-33.0\ \mathrm{kJ\ mol^{-1}}$



Assuming that pre-exponential factor is same for forward and backward reaction answer the following

342. The equilibrium constant k for the reaction at 300 K

a) 5.55×10^5 b) 5.67×10^3 c) 5.55×10^6 d) 5.67×10^2

Paragraph for Question Nos. 343 to - 344

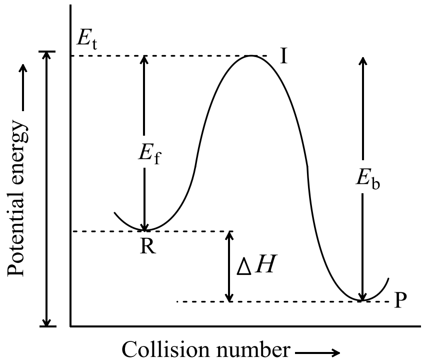
In the start of summer, a given sample of milk turns sour at room temperature (27°C) in 48 hours. In a refrigerator at 2°C, milk can be stored three times longer before it sours

343. The activation energy of the souring of milk is ($\mathrm{kJ\ mol^{-1}}$)

a) 30.210 b) 30.146 c) 30.0 d) 35.126

Paragraph for Question Nos. 344 to - 345

A collision between reactant molecules must occurs with a certain minimum energy before it is effective in yielding product molecules. This minimum energy is called activation energy E_a. Larger the value of activation energy, smaller the value of rate constant k. Larger is the value of activation energy, greater is the effect of temperature rise on rate constant k



E_f = Activation energy of forward reaction
E_b = Activation energy of backward reaction
$\Delta H = E_f - E_b$
E_f = Threshold energy

344. If a reaction A + B → C is exothermic to the extent of 30 kJ mol^{-1} and the forward reaction has an activation energy of 249 kJ mol^{-1} the activation energy for reverse reaction in kJ mol^{-1} is

a) 324 b) 279 c) 40 d) 100

Paragraph for Question Nos. 345 to - 346

The order of reaction is an experimentally determined quantity. It may be zero, positive, negative, or fractional. The kinetic equation of nth order reaction is

$k \times t = \frac{1}{(n-1)}\left[-\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$ ...(i)

Half life of nth order reaction depends on the initial concentration according to the following relation:

$t_{1/2} \propto \frac{1}{a^{n-1}}$ ...(ii)

The unit of the rate constant varies with the order but general relation for the unit of nth order reaction is

Unit of $k = \left[\frac{1}{\text{Conc}}\right]^{n-1} \times \text{Time}^{-1}$ ...(iii)

The different rate law for nth order reaction may be given as:

$\frac{dx}{dt} = k[A]^n$ ...(iv)

Where A denotes the reactant

345. The unit of rate and rate constant are same for

a) Zero order reaction b) First order reaction
c) Second order reaction d) Half order reaction

Paragraph for Question Nos. 346 to - 347

Consider the following elementary reaction,
2A + B + C → Products. All reactants are present in the gaseous state and reactant C is taken in excess

346. What is the rate expression of the reaction?

a) Rate = $k[A]^2[B][C]$ b) Rate = $k[A]^2[B]$ c) Rate= $k\frac{[A]^2[B]}{[C]}$ d) Rate = $k[C]^0$

Paragraph for Question Nos. 347 to - 348

For the reaction: $X(g) \rightarrow Y(g) + Z(g)$, the following data were obtained at 30°C:

Experiment	[X] (mol L^{-1})	Rate (mol $L^{-1}hr^{-1}$)
I	0.17	0.05
II	0.34	0.10
III	0.68	0.20

347. The rate constant of the above reaction is
    a) 0.588 hr^{-1} b) 0.294 hr^{-1} c) 0.123 hr^{-1} d) 0.210 hr^{-1}

Paragraph for Question Nos. 348 to - 349

The reaction $2AX(g) + 2B_2(g) \rightarrow A_2(g) + 2B_2X(g)$ has been studied kinetically and on the basis of the rate law following mechanism has been proposed

1. $2AX \rightleftharpoons A_2X_2$ (fast and reverse)
2. $A_2X_2 + B_2 \rightarrow A_2X + B_2X$ (slow)
3. $A_2X + B_2 \rightarrow A_2 + B_2X$ (fast)

Where all the reaction intermediates are gases under ordinary condition
From the above mechanism in which the steps (elementary) differ considerably in their rates, the rate law is derived using the principle that the slowest step is the rate-determining step (RDS) and the rate of any step varies as the product of the molar concentration of each reaching species raised to the power equal to their respective stoichiometric coefficients (law of mass action). If a reacting species is solid or pure liquid, its active mass, i.e., molar concentration is taken to be unity, the standard state. In order to find out the final rate law of the reaction, the concentration of any intermediate appearing in the rate law of the RDS is substituted in terms of the concentration of the reactant(s) by means of the law of mass action applied on equilibrium step

348. Let the equilibrium constant of Step I be 2×10^{-3} mol^{-1} L and the rate constants for the formation of A_2X and A_2 in Steps II and III are 3.0×10^{-2} $mol^{-1}L\ min^{-1}$ and 1×10^{3} $mol^{-1}L\ min^{-1}$ (all data at 25°C), then what is the overall rate constant ($mol^{-2}L^{2}min^{-1}$) of the consumption of B_2?
    a) 6×10^{-5} b) 1.2×10^{-4} c) 3×10^{-5} d) 1.5×10^{-5}

Paragraph for Question Nos. 349 to - 350

The rate law expression is given for a typical reaction. $n_1A + n_2B \rightarrow P$ as $r = k[A]^{n}[B]^{n_2}$. The reaction completes only in one step and A and B are present in the solution. If the reaction occurs in more than one step, then the rate law is expressed by considering the slowest step, i.e., for S_N1 reaction $r = k[RX]$
If the reaction occurs in more than one step and the rates of the steps involved are comparable, then steady state approximation is considered, i.e., the rate of formation of intermediate is always equal to the rate of decomposition of the intermediate
Consider the reaction:

$$\left[\begin{array}{l} I_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2I \text{ (rapid equilibrium)} \\ H_2 + 2I \xrightarrow{k_3} 2HI \text{ (slow)} \end{array}\right]$$

349. If we increase the concentration of I_2 two times, then the rate of formation of HI will

a) Increase four times b) Increase two times c) Remain same d) Cannot predict

Paragraph for Question Nos. 350 to - 351

A secondary alkyl halide (A) hydrolyzes with alkali (B) in aqueous medium simultaneously via $S_N 1$ and $S_N 2$ pathways with rate constants k_1 and k_2, respectively. From kinetic data, it was found that a plot of = $\frac{-1}{[A]}\frac{d[A]}{dt}$ vs[B] is straight line with a slope equal to 2.7×10^{-4} L mol^{-1}min^{-1} and intercept equal to 1.02×10^{-3}. Minimum initial concentration of [A]=0.2 M and [B], i.e., $\left[\overset{\ominus}{\mathrm{O}}\mathrm{H}\right] = 0.5$ M

350. The value of overall rate constant of the hydrolysis of A (in L mol^{-1}min^{-1}) is

a) 2.7×10^{-4} b) 1.02×10^{-3} c) 1.29×10^{-3} d) None of the above

Paragraph for Question Nos. 351 to - 352

If a unimolecular reaction, A(g) → Products, takes place according to the mechanism

I. $A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$

II. $A^* \xrightarrow[k_2]{} P$

Where k_1, k_{-1} and k_2 are the rate constants and P, A and A^* stand for product molecule, normal molecules of reactants and activated molecules of reactants respectively

351. Which of the following expressions are correct?

a) $\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*]$ b) $\frac{d[A^*]}{dt} = 0$

c) $[A^*] = \frac{k_1\,[A]^2}{k_{-1}[A] + k_2}$ d) All of the above

Paragraph for Question Nos. 352 to - 352

The thermal decomposition of N_2O_5 occurs as: $2N_2O_5 \longrightarrow 4NO_2 + O_2$

Experimental studies suggest that rate of decomposition of N_2O_5, rate of formation of NO_2 or rate of formation of O_2 all becomes double if concentration of N_2O_5 is doubled.

352. The correct mechanism for the decomposition of N_2O_5 is:

a) $N_2O_5 \xrightarrow{\text{Slow}} NO_2 + NO_3; N_2O_5 + NO_3 \xrightarrow{\text{Fast}} 3NO_2 + O_2$

b) $N_2O_5 \xrightarrow{\text{Fast}} NO_2 + NO_3; N_2O_5 + NO_3 \xrightarrow{\text{Slow}} 3NO_2 + O_2$

c) $N_2O_5 \xrightarrow{\text{Fast}} 2NO_2 + \frac{1}{2}O_2$

d) $N_2O_5 \xrightarrow{\text{Slow}} NO + NO_2 + 2O_2; N_2O_5 + NO_2 \xrightarrow{\text{Fast}} 3NO_2 + \frac{1}{2}O_2$

Integer Answer Type

353. Following are two first order reactions with their half times given at 25°C

$$\text{A} \xrightarrow{t_{1/2}=30\text{ min}} \text{Products}$$

$$\text{A} \xrightarrow{t_{1/2}=30\text{ min}} \text{Products}$$

The temperature coefficients of their reaction rates are 3 and 2, respectively, between 25°C and 35°C. If the above two reactions are carried out taking 0.4 M of each reactant but at different temperatures: 25°C for the first order reaction and 35°C for the second order reaction, find the ratio of the concentration of A and B after an hour

354. The unit of rate constant for a reaction is $\text{litre}^2\text{mol}^{-2}\text{t}^{-1}$. The order of reaction is…

355. The order of reaction for $H_2 + Br_2 \longrightarrow 2HBr$ if it is carried over water is:

356. An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? (take $\log_{10} 2 = 0.3$)

357. The initial concentration of both the reactants of a second order reaction are equal and 60% of the reaction gets completed in 30 s. How much time will be taken in 20% completion of the reaction?

358. A second order reaction requires 70 min to change the concentration of reactants from 0.08 M to 0.01 M. The time required to become 0.04 M$= 2x$ min. Find the value of x

359. If one starts with 1 Curie (Ci) of radioactive substance ($t_{1/2} = 15$ hr), the activity left after a period of two weeks will be about $0.02x$ μCi. Find the value of x

360. For the reaction : $2A + 3B \rightleftharpoons cC$ rate of formation of C is expressed as

$$\frac{d[C]}{dt} = -\frac{3[dA]}{dt}$$

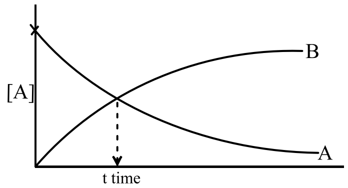
The value of c is:

361. If 80% of a radioactive element undergoing decay is left over after a certain period of time t from the start, how many such periods should elapse from the start for just over 50% of the element to be left over?

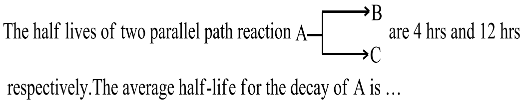
362. For the reaction $NO_2 + CO \rightarrow CO_2 + NO$, the experimental rate expression rate expression is $-dc/dt = k[NO_2]^2$. Find the number of molecules of CO involved in the slowest step

363. What is order of reaction for which rate becomes half if volume of the container having same amount of reactant is doubled? Assume gaseous phase reaction

364. For the I order reaction $3A \longrightarrow 2B$, the concentration of A and B at the intersection is given in figure.



If $[A]_0$=20 mol litre^{-1} then $[B]$at time t is equal to ……

365. 

The half lives of two parallel path reaction $A \to B$, $A \to C$ are 4 hrs and 12 hrs respectively.The average half-life for the decay of A is …

366. For the reaction:

$$H_2 + Cl_2 \xrightarrow[\text{Sunlight}]{} 2HCl$$

Taking place on water. Find the order of reaction

367. Two substance A($t_{1/2} = 5$ min) and B($t_{1/2} = 15$ min) follow first order kinetics and are taken in such a way that initially [A] = 4[B]. The time after which the concentration of both the substance will be equal is $5x$ min. Find the value of x

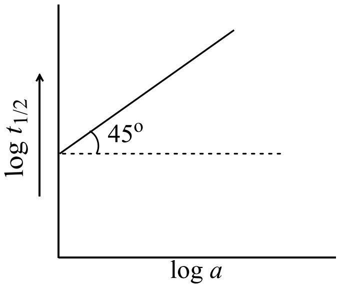
368. Energy of activation for a reversible reaction is 6 kcal (E_a forward) and heat of reaction is −3 kcal. The energy of activation for backward reaction in kcal is …

369. In the case of a first order reaction, the time required for 93.75% of reaction to take place is x times that required for half of the reaction. Find the value of x

370. Hydrolysis of an alkyl halide (RX) by dilute alkali [$\overset{\ominus}{\mathrm{OH}}$] takes place simultaneously by SN^2 and SN^1 pathway. A plot of $-\frac{1}{[\mathrm{RX}]}\frac{d[\mathrm{R-X}]}{dt}$ vs [$\overset{\ominus}{\mathrm{OH}}$] is a straight line of the slope equal to 2×10^3 mol^{-1} L h^{-1} and intercept equal to 1×10^2 h^{-1}. Calculate the initial rate (mole L^{-1}min^{-1}) of comsumption of RX when the reaction is carried out taking 1 mol L^{-1} of RX and 0.1 mol L^{-1} of [$\overset{\ominus}{\mathrm{OH}}$] ions

371. The half-life period of a reaction, becomes 16 times when reactant concentration is halved. The order of reaction is ...

372. Following is the graph between $\log t_{1/2}$ and $\log a$ (a initial concentration) for a given reaction at 27°C



Find the order of reaction

373. Consider the following statements for a second order reaction and score of each statement

$2\mathrm{A} \rightarrow \mathrm{P}$

		Score
a.	$[\mathrm{A}] = \frac{[\mathrm{A}_0]}{1 + kt}$	3
b.	A plot of $1/[\mathrm{A}]^2$ vs time will be straight line	2
c.	Half life is long when the concentration is low	1

Find the total score of the correct statements

374. The time required to complete 99.9% decay is ... times of the time required to complete 90% decay.

375. A reaction occurs in $'n'$ parallel paths. For each path having energy of activation as $E, 2E, 3E, \dots nE$ and rate constant $K, 2K, 3K, \dots nK$ respectively. if $E_{AV} = 3E$, then n is ...

376. For the reaction A →Products, it is found that the rate of reaction increases by a factor of 6.25 when concentration of A increases by a factor of 2.5. Calculate the order of reaction with respect to A

377. If $\frac{\mathrm{d[NH_3]}}{\mathrm{dt}} = 34$ g hr^{-1} for the reaction

$\mathrm{N_2 + 3H_2 \rightleftharpoons 2NH_3}$

then $\frac{\mathrm{d[H_2]}}{\mathrm{dt}}$ is ... g hr^{-1}.

378. The decomposition of $\mathrm{NH_3}$ on solid surface, $e.$g., Pt shows the order of reaction equal to:

379. The half-life period of a radioactive element is 40 days. If 32 g of this element is stored for 160 days, calculate the weight of the element that would remain in gram

: ANSWER KEY :

1)	b	2)	c	3)	c	4)	c	189)	c	190)	b	191)	b	192)	d
5)	d	6)	d	7)	b	8)	b	193)	c	1)	a, b, c	2)	a, d	3)	
9)	c	10)	a	11)	d	12)	a		a,b,d	4)	a, b, c				
13)	b	14)	a	15)	b	16)	c	5)	a,d	6)	a,b,c,d	7)	a, b	8)	
17)	c	18)	b	19)	d	20)	a		a,b,c,d						
21)	d	22)	d	23)	a	24)	a	9)	b,c	10)	a,b,c	11)	b,d	12)	
25)	d	26)	c	27)	c	28)	a		a,b,c,d						
29)	d	30)	c	31)	c	32)	d	13)	a, b, c	14)	c,d	15)	a,c	16)	
33)	d	34)	a	35)	d	36)	d		a,d						
37)	c	38)	c	39)	c	40)	c	17)	a,b	18)	a, c	19)	a, b, c	20)	
41)	a	42)	b	43)	d	44)	a		a, b, c, d						
45)	b	46)	d	47)	b	48)	d	21)	a,c	22)	c,d	23)	a, c	24)	
49)	d	50)	a	51)	d	52)	a		a, b						
53)	c	54)	a	55)	b	56)	c	25)	a, b	26)	a, b, d	27)	b,c,d	28)	
57)	a	58)	a	59)	b	60)	c		a, b, c						
61)	d	62)	c	63)	b	64)	b	29)	a,b,c,d	30)	a,d	31)	c, d	32)	
65)	b	66)	c	67)	b	68)	a		b, d						
69)	c	70)	c	71)	a	72)	d	33)	a,b,c	34)	a, b, d	35)	a,c	36)	
73)	d	74)	a	75)	b	76)	d		b,c						
77)	c	78)	c	79)	b	80)	a	37)	b, c, d	38)	c,d	39)	b,c	40)	
81)	a	82)	d	83)	c	84)	d		b,d						
85)	c	86)	a	87)	d	88)	b	41)	b, d	42)	a,b,d	43)	a,b,c,d	44)	
89)	a	90)	b	91)	a	92)	d		a,c						
93)	d	94)	c	95)	a	96)	b	45)	a,b,c,d	46)	a,d	47)	a,b,c,d	48)	
97)	c	98)	b	99)	a	100)	b		a,b,c,d						
101)	b	102)	a	103)	b	104)	c	49)	a,b,c,d	50)	a, c, d	51)	a, b, c	52)	
105)	b	106)	b	107)	d	108)	a		b,c						
109)	a	110)	d	111)	a	112)	d	53)	a, b	54)	a,b,c,d	55)	b, c	56)	
113)	d	114)	d	115)	a	116)	c		a,b,c,d						
117)	b	118)	c	119)	d	120)	c	57)	a,b	58)	a, b, c	59)	a,c,d	60)	
121)	a	122)	b	123)	c	124)	c		b,d						
125)	a	126)	c	127)	c	128)	c	61)	b,c,d	62)	a,d	63)	a, b	64)	b
129)	c	130)	b	131)	d	132)	d	65)	a, c, d	66)	a, b, c	67)	a, b	68)	
133)	c	134)	b	135)	b	136)	b		a, b, c						
137)	b	138)	c	139)	c	140)	d	69)	a,b,d	70)	a,b	71)	b,d	72)	
141)	d	142)	b	143)	c	144)	c		a, c						
145)	a	146)	a	147)	d	148)	b	73)	a, c	74)	a,b	1)	a	2)	c
149)	b	150)	b	151)	b	152)	b		3)	d	4)	d			
153)	b	154)	a	155)	b	156)	c	5)	a	6)	b	7)	a	8)	b
157)	c	158)	c	159)	a	160)	b	9)	b	10)	b	11)	c	12)	b
161)	a	162)	b	163)	b	164)	a	13)	b	14)	b	15)	d	16)	a
165)	b	166)	a	167)	c	168)	a	17)	e	18)	e	19)	b	20)	b
169)	c	170)	a	171)	b	172)	a	21)	a	22)	a	23)	b	24)	b
173)	b	174)	c	175)	b	176)	b	25)	c	26)	a	27)	c	28)	b
177)	c	178)	d	179)	b	180)	a	29)	c	30)	c	31)	d	32)	b
181)	c	182)	a	183)	b	184)	b	33)	b	34)	a	35)	c	36)	c
185)	b	186)	c	187)	a	188)	b	37)	b	38)	c	39)	b	40)	d

41)	c	42)	c	43)	c	44)	a
45)	b	46)	c	47)	a	1)	c
	2)	a	3)	b	4)	c	
5)	d	6)	b	7)	d	8)	a
9)	d	10)	a	11)	a	12)	a
13)	c	14)	c	15)	a	16)	b
17)	b	18)	d	1)	b	2)	a
	3)	a	4)	b			
5)	a	6)	a	7)	a	8)	c
9)	a	10)	a	11)	b	12)	b

13)	a	14)	b	15)	b	16)	b
17)	b	18)	b	19)	d	20)	a
1)	2	2)	3	3)	0	4)	9
5)	5	6)	5	7)	9	8)	6
9)	3	10)	0	11)	1	12)	8
13)	3	14)	0	15)	3	16)	9
17)	4	18)	5	19)	5	20)	0
21)	4	22)	3	23)	4	24)	2
25)	6	26)	0	27)	2			

: HINTS AND SOLUTIONS :

1 **(b)**

Factual statement

2 **(c)**

Factual statement

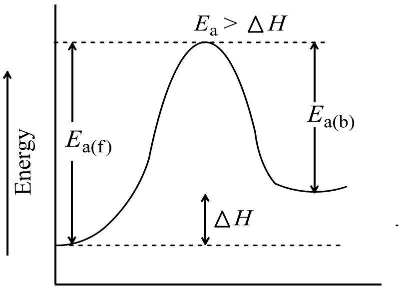
3 **(c)**

$$k = \frac{2.303}{10}\log\frac{100}{90} = 0.001054\ \text{min}^{-1}$$

$$t_{1/2} = \frac{2.303}{k} = \frac{2.303}{0.001054} \approx 66\ \text{min}$$

4 **(c)**

For endothermic reaction:



5 **(d)**

$$0.8\ \text{M} \xrightarrow{t_{1/2}=15\ \text{min}} 0.4\ \text{M}$$

$$\therefore 0.1\ \text{M} \xrightarrow[t_{1/2}=15\ \text{min}]{} 0.05\ \text{M} \xrightarrow[t_{1/2}=15\ \text{min}]{} 0.025\ \text{M}$$

Thus, total time $= (15 + 5) = 30$ min

6 **(d)**

Comparing the slope and intercept of the given equation with the following Arrhenius equation :

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

Hence, $\log A = 6$ *i.e.*, $A = 10^6 \text{s}^{-1}$

Comparing slope gives E_a =38.3 kJ/mol

7 **(b)**

For second order reaction,

When $x = 20\%, (a - x) = 80\%, a = 100\%$

$$k_2 = \frac{1}{t}.\frac{x}{a(a-x)}$$

$$= \frac{1}{40} \times \frac{20}{100 \times (100 - 20)}$$

$$= \frac{1}{2\times100\times80} \quad ...(i)$$

When $x = 80\%, (a - x) = 20\%$

$$k_2 = \frac{1}{t} \times \frac{80}{100\times20} = 1/25t \quad ...(ii)$$

From equations (i) and (ii),

$$t = \frac{2 \times 100 \times 80}{25} = 640\ \text{min}$$

8 **(b)**

$r_1 = k\ [\text{A}]^x[\text{B}]^y[\text{C}]^z$ ...(i)

$r_2 = 2r_1 = k[\text{A}]^x[2\text{B}]^y[\text{C}]^z$ ...(ii)

$r_3 = 2r_1 = k[2\text{A}]^x[2\text{B}]^y[\text{C}]^z$ ...(iii)

$r_4 = 4r_1 = k[\text{A}]^x[2\text{B}]^y[2\text{C}]^z$ ...(iv)

Sove for x, y, and $z, x = 0, y = 1, z = 1$

Order w.r.t. $[\text{A}] = 0, [\text{B}] = 1, [\text{C}] = 1$

Total order $= 0 + 1 + 1 = 2$

9 **(c)**

Factual statement

10 **(a)**

Second order reactions: Reaction rate depends upon the concentration of two reactants

$$\frac{dx}{dt} = k[\text{A}][\text{B}] = k[\text{A}]^2$$

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

[$(a - x)$and $(b - x)$ are the concentration of A and B after time interval t.]

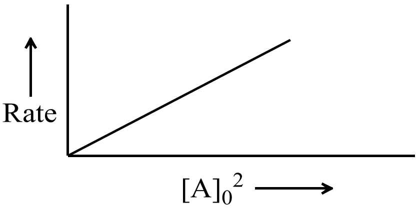
When concentrations of both the reactants are same,

$$k = \frac{1}{t}.\frac{x}{a(a-x)}$$

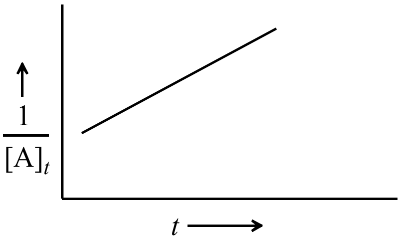
(x is the concentration changed in time interval t)

Half-life period, $t_{1/2} = 1/ka$, i.e., inversely proportional to initial concentration. The units of k are liter $\text{mol}^{-1}\text{time}^{-1}$.

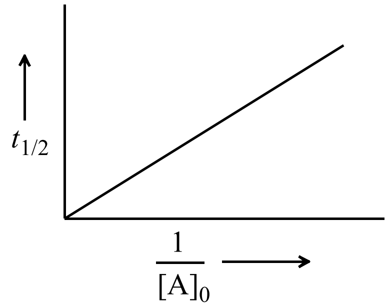
Plot of rate versus $[\text{A}]_0^2$



Plot of $\frac{1}{[\text{A}]_t}$ versus t



Plot of $t_{1/2}$ versus $\frac{1}{[\text{A}]_0}$



11 **(d)**

"Formula and Concepts"

Only reactions whose E_a falls in the range of $50-55\ \text{kJ mol}^{-1}$ or $12-13\ \text{kcal mol}^{-1}$ are found to double their rate for 10°C rise in temperature i.e., from 298 to 308 K

Alternatively

Use Arrhenius equation

$T_1 = 295\ \text{K}, T_2 = 305\ \text{K}$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.3 \times 2 \times 10^{-3}}\left(\frac{10}{295 \times 305}\right)$$

$$E_a = \frac{\log(2) \times 2.3 \times 2 \times 10^{-3} \times 295 \times 305}{10}$$

$$E_a = \frac{0.3 \times 4.6 \times 295 \times 305}{10^4}$$

$= 12.4\ \text{kcal mol}^{-1}$

$= 12\ \text{kcal mol}^{-1}$

12 **(a)**

In the absence of A,3 dps is zero error, hence

Initial count $= 23 - 3 = 20$ dps

After 10 min$= 13 - 3 = 10$ dps

After 20 min $= 5$ dps (recorded$= 5 + 3 = 8$ dps)

(50% fall in 10 min, $T_{50} = 10$ min)

13 **(b)**

Cl attached to N in reactant oxidizes KI to I_2 which can be determined by hypo ($Na_2S_2O_3$)

14 **(a)**

$r_1 = k[\text{salt}]^n$

$r_2 = 2r_1 = k[2\ \text{salf}]^n$

$\frac{2r_1}{r_1} = (2)^n$

$(2)^1 = (2)^n$

$n = 1$

15 **(b)**

The fraction of molecules having energy equal to or greater than E_a is:

$$x = \frac{n}{N} = e^{-E_a/RT}\left(x = \frac{n}{N} = 0.001\% = \frac{0.01}{100} = 10^{-5}\right)$$

$$\therefore \log x = \frac{-E_a}{2.3 \times RT}\ (R = 2\ \text{cal mol}^{-1}\text{K}^{-1}, \text{T} = 500\ \text{K})$$

$$\log 10^{-5} = \frac{E_a}{2.3 \times 2 \times 500}$$

$E_a = 11.5 \times 103\ \text{cal mol}^{-1} = 11.5\ \text{kcal mol}^{-1}$

16 **(c)**

Factual statement

17 **(c)**

Factual statement

18 **(b)**

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

As $T \to \infty, k = A = 6.04 \times 10^{14}\text{s}^{-1}$

19 **(d)**

Order w.r.t. $[H^{\oplus}] = 2$

Hence, doubling the concentration of $[H^{\oplus}]$ ions will increase the reaction rate by 4 times

20 **(a)**

Negative catalyst or inhibitors are those substance which decrease the rate of a reaction

21 **(d)**

Use direct formula as given below:

$$t_{90\%} = \log\frac{100}{100-90} = \log 10 = 1$$

$t_{1/2} = 0.3$

$$\frac{t_{1/2}}{t_{80\%}} = \frac{0.3}{1} \Rightarrow t_{1/2} = 100 \times 0.3 = 30\ \text{min}$$

22 **(d)**

$$\text{OR } = \frac{1}{2} + \frac{1}{3} + \frac{1}{4} = \frac{13}{12}$$

23 **(a)**

$$\text{a. Rate} = \frac{k[OCl^{\ominus}][I^{\ominus}]}{[\overset{\ominus}{OH}]}$$

Order of reaction $= 1 + 1 - 1 = 1$

Molecularity of reaction $= 1 + 1 = 2$

b. Molecularity w.r.t. $[\overset{\ominus}{OH}] = 0$

Order w.r.t. $[\overset{\ominus}{OH}] = -1$

24 **(a)**

Since $k_2 > k_1$

25 **(d)**

$aG + bH \to Products$

Suppose order of reaction =n

When concentration of both G and H doubled then rate increases by eight times.

$rate = k(reactants)^n$

$(8) = k(2)^n$

$(2)^3 = k(2)^n$

n=3

When concentration of G is doubled keeping the concentration of H fixed, the rate is doubled.

$Rate = [G]^1$

then,

$Rate = [G]^1[H]^2$

26 **(c)**

Since (A) is the intermediate reactive species whose concentration is determined from equilibrium step

Slow step is:

$A + B_2 \rightarrow AB + B$ (slow)

$r = k[A][B_2]$ ...(i)

From equilibrium step

$A_2 \rightleftharpoons A + A$ (fast)

$$k_{eq} = \frac{[A]^2}{[A_2]}$$

$$\therefore [A] = \left(k_{eq}[A_2]\right)^{1/2}$$

Substitute the value of [A] in equation (i),

$r = k \cdot k_{eq}\ ^{1/2}[A_2]^{1/2}[B_2]$

Thus, order of reaction $= \frac{1}{2} + 1 = 1\frac{1}{2}$

27 **(c)**

First order reaction is independent of c_0. Hence, k is constant

28 **(a)**

From experiments (3) and (2), [A] is constant and [B] is doubled and rates becomes 8 times, so order w.r.t [B]=3

From experiment (1) and (3), [B] is constant and [A] is doubled, but rate does not change, so order w.r.t. [A] = 0. Thus,

Rate $= k[B]^3$

29 **(d)**

$A \rightarrow B, \Delta H = -10$ kJ mol^{-1}

It is an exothermic reaction

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

$= 50 - (-10)$

$= 60$ kJ

30 **(c)**

Since three molecules are colliding simultaneously, so molecularity is 3. It is determined theoretically from the number of reactant molecules in a balanced chemical reaction

31 **(c)**

Use direct formula:

$$\frac{t_{1/2}}{t_{25\%(\text{left})}} = \frac{0.3}{\log\left(\frac{100}{25}\right)}$$

$$t_{1/2} = t_{25\%} \times \frac{0.3}{\log 4}$$

$$= 1 \text{ hr} \times \frac{0.3}{0.6} = \frac{1}{2}\text{hr}$$

Note: 25% *is the amount left*

32 **(d)**

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

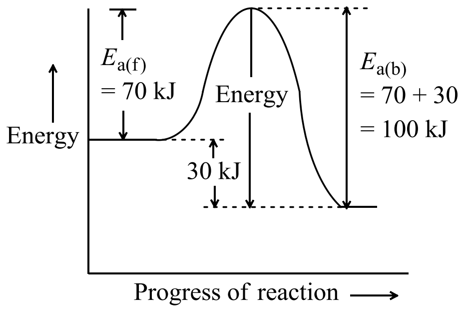
This reaction is a first order reaction

Rate $= k[N_2O_5]$

$2.40 \times 10^{-5} = 3.0 \times 10^{-5} \times [N_2O_5]$

or $[N_2O_5] = 0.8$ mol L^{-1}

33 **(d)**



By seeing the curve, activation energy for backward reaction =100 kJ

34 **(a)**

For Q → C

$E_a = 23 - 20 = 3$ kcal mol^{-1}

35 **(d)**

Unit of rate= mol L$^{-1}t^{-1}$

Unit of zero order = mol L$^{-1}t^{-1}$

36 **(d)**

Average speed ($V_{av} \propto (T)^{\frac{1}{2}}$

$$\therefore \frac{(V_{av})_2}{(V_{av})_1} = \sqrt{\frac{T_2}{T_1}} \quad \left(\text{Given } \frac{(V_{av})_2}{(V_{av})_1} = 2\right)$$

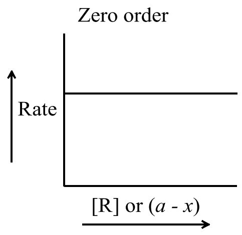
$$(2)^2 = \frac{T_2}{T_1} \Rightarrow T_2 = 4T_1$$

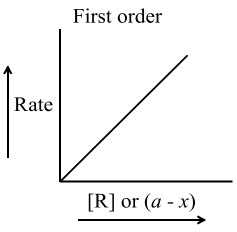
$T_1 = 273 + 17 = 290$ K

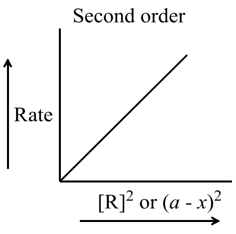
$\therefore T_2 = 4 \times 290 = 1160 \text{ K} = 1160 - 273 = 887°\text{C}$

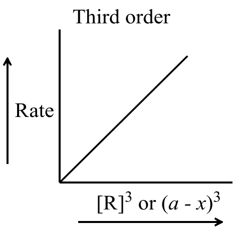
37 **(c)**

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









38 **(c)**

$r_1 = k[\mathrm{A}]^n$

$r_2 = 2r_1 = k[4\mathrm{A}]^n$

Divide equation (ii) by (i),

$(2)^1 = (4)^n = (2)^{2n}$

$\therefore 2n = 1$

$n = \frac{1}{2}$

39 **(c)**

$k = Ae^{-E_\mathrm{a}/RT}$

$\therefore \frac{-E_\mathrm{a}}{R} = -40000$

$\therefore E_\mathrm{a} = 40000 \times 2 = 80000$ cal

40 **(c)**

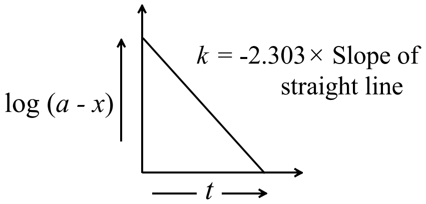
$k = \frac{2.303}{t} log \frac{A_0}{A_t}$

$= \frac{2.303}{2 \times 10^4} log \frac{800}{50}$

$= 1.386 \times 10^4 s^{-1}$

41 **(a)**

Graph of $\log(a - x)$ vs t is a straight line, which shows first order reaction



$k = (-2.303) \times (-0.03)$

$= 0.069 = 6.9 \times 10^{-2}$

42 **(b)**

$$\mathrm{C_{12}H_{22}O_{11} + H_2O + H^{\oplus} \longrightarrow \underset{(Glucose)}{C_6H_{12}O_6} + \underset{(Fructose)}{C_6H_{12}O_6}}$$

The rate is measured by measuring the change in the angle of rotation (optical activity) by a polarimeter. Sucrose is $dextro - rotatory$, glucose is $dextro - rotatory$, and fructose is $leavo - rotatory$. The change produced in rotatory power in time t gives a measure of x, the quantity of sucrose decomposed in that time.

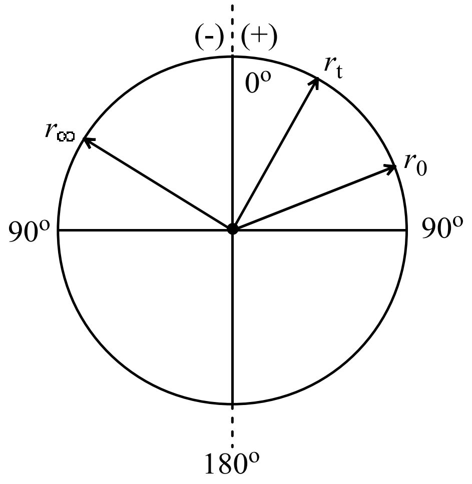
The total change in the rotatory power produced at the end of reaction gives the measure of c_0, the initial concentration of sucrose.

If r_0, r_t, and r_∞ represent rotations at the start of reaction, after time t, and at the end of reaction, respectively, then

$\Rightarrow c_0 \propto r_0 - r_\infty$ and $x \propto r_0 - r_t$

$\Rightarrow c_0 - x \propto r_t - t_\infty$

$\Rightarrow k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$



43 **(d)**

All factual statements

44 **(a)**

Since (A) is recovered back in the reaction, so it is catalyst in the step (i)

45 **(b)**

Since $t_{1/2}$ does not depends upon the sugar concentration means it is first order w.r.t. [sugar]

$\therefore t_{1/2} \propto [\mathrm{Sugar}]^1$

$t_{1/2} \times a^{n-1} = k$

$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{[\mathrm{H}^\oplus]_1^{1-n}}{[\mathrm{H}^\oplus]_2^{1-n}}$

$= \frac{500}{50} = \left(\frac{10^{-5}}{10^{-6}}\right)^{1-n}$

$10 = (10)^{1-m} \Rightarrow n = 0$

46 **(d)**

$r_1 = k[\mathrm{A}]^n$

$r_2 = 100r_1 = k[10\ \mathrm{A}]^n$

$\frac{100r_1}{r_1} = (10)^n$

$(10)^2 = (10)^n$

$n = 2$

47 **(b)**

$0.2\ \mathrm{M} \xrightarrow[t_{1/2}=5\ \mathrm{hr}]{} 0.1\ \mathrm{M} \xrightarrow[t_{1/2}=5\ \mathrm{hr}]{} 0.05\ \mathrm{M}$

From $0.2\ \mathrm{M} \xrightarrow[t=10\ \mathrm{hr}]{} 0.05\ \mathrm{M}$

So $t_{1/2}$ is constant which is characteristic of first order reaction

Hence, $t_{1/2} \propto (a)^0$

48 **(d)**

Factual statement

49 **(d)**

Consider a condition when one of the product is estimated directly or indirectly, i.e., $when\ V_0$ is not given

For example, in the decomposition of NH_4NO_2, the volume of N_2 is directly measured at different intervals of time. Then, the formula used is

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

An example is the decomposition of ammonium (NH_4NO_2) and benzene diazonium chloride ($C_6H_5N = NCl$)

$$NH_4NO_2(s) \longrightarrow 2H_2O(l) + N_2(g)$$

$$C_6H_5 - N = N - Cl(l) \longrightarrow C_6H_5 - Cl(l) + N_2(g)$$

The rate of both the reactions is studied (measured) in similar manner. The volume of nitrogen (N_2) is collected after a regular interval of times as follows:

Time instants	$t = 0$	t_1	t_2	t_3	t_4	t_∞
Vol of N_2	0	V_1	V_2	V_3	V_4	V_∞

At $t = 0$, clearly the volume of $N_2 = 0$

Time instant $t = \infty$ means the end of a reaction, i.e., when whole of NH_4NO_2 or $C_6H_5 - N = N - Cl$ is decomposed

$\Rightarrow$ At $t = \infty, V_\infty$ corresponds to the initial volume of NH_4NO_2 or $C_6H_5 - N = N - Cl$

(Note that the ratio of stoichiometric coefficient for both $N_2 : NH_4NO_2$ or $N_2 : C_6H_5N = NCl$ is 1 : 1)

$\Rightarrow c_0 \propto V_t$

At $t = t_1, t_2, t_3, \ldots$ the volume of N_2 corresponds to the concentration of product formed, i.e., equal to x

$\Rightarrow x \propto V_t$

$\Rightarrow c_0 - x \propto V_\infty - V_t$

Hence, from first order kinetic

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

or $k = \frac{1}{t} \text{In} \frac{V_\infty}{V_\infty - V_t}$

$$k = \frac{1}{20} \text{In} \frac{40}{(40 - 10)}$$

$$= \frac{1}{20} \text{In} \frac{40}{30}$$

50 **(a)**

Amount of A left in n_1 halves $= \left(\frac{1}{2}\right)^{n_1} [A_0]$

Amount of B left in n_2 halves $= \left(\frac{1}{2}\right)^{n_2} [B_0]$

At the end, according to the question

$$\frac{[A_0]}{2^{n_1}} = \frac{[B_0]}{2^{n_2}} \Rightarrow \frac{4}{2^{n_1}} = \frac{1}{2^{n_2}}, \qquad ([A_0] = 4[B_0])$$

$$\frac{2^{n_1}}{2^{n_2}} = 4 \Rightarrow 2^n 1^{-n_2} = (2)^2 \Rightarrow n_1 = n_2 = 2$$

$\therefore n_2 = (n_1 - 2) \quad \ldots$(i)

Also $t = n_1 t_{1/2}(A); t = n_2 t_{1/2}(B)$

(Let concentration of both becomes equal after time t)

$$\therefore \frac{n_1 \times t_{1/2}(A)}{n_2 \times t_{1/2}(B)} = 1 \Rightarrow \frac{n_1 \times 5}{n_2 \times 15} = 1 \Rightarrow \frac{n_1}{n_2} = 3 \quad \ldots\text{(ii)}$$

From equations (i) and (ii), we get

$n_1 = 3, n_2 = 1$

$t = 3 \times 5 = 15$ min

51 **(d)**

Factual statement

52 **(a)**

For second order reaction

1. Correct statement
2. $t_{1/2} \propto (a)^{-1}$
3. $\frac{d[C]}{dt} = \frac{-d[A]}{2dt}$
4. For second order, units of k is $mol^{-1}s^{-1}$

53 **(c)**

Factual statement

54 **(a)**

As the reaction occurs in the presence of a catalyst and $H_2(g)$ absorbs on the surface of Ni, therefore it is a zero order reaction. Hence, answer is (a)

55 **(b)**

a. Rate $= \dfrac{k[OCl^\ominus][I^\ominus]}{[\overset{\ominus}{OH}]}$

Order of reaction $= 1 + 1 - 1 = 1$

Molecularity of reaction $= 1 + 1 = 2$

b. Molecularity w.r.t. $[\overset{\ominus}{OH}] = 0$

Order w.r.t. $[\overset{\ominus}{OH}] = -1$

56 **(c)**

$r_1 = k[A]^n$

$r_2 = 2r_1 = k[4A]^n$

$$\frac{2r_1}{r_1} = (4)^n$$

$(2)^1 = (2)^{2n}$

$$n = \frac{1}{2}$$

57 **(a)**

Factual statement

58 **(a)**

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

The rate constant of a reaction does not change with change in concentrations, time, or extent of the reaction. It increases with increase in temperature

59 **(b)**

$T_1 = 273 + 25 = 298$ K

$T_2 = 273 + 60 = 333\text{ K}$

$\log\frac{k_2}{k_1} = \frac{E_a}{2.3\,R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$

or $\log_e\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{T_2-T_1}{T_1T_2}\right)$

$\log_e\frac{2.1\times10^{-2}}{1.5\times10^{-3}} = \frac{E_a}{R}\times\left(\frac{35}{333\times298}\right)$

$\therefore E_a = \frac{298\times333}{35}\times R\times\log_e\frac{21}{1.5}$

60 **(c)**

$r_1 = k[\text{A}]^3$ ...(i)

$r_2 = k[2\text{A}]^3$ ...(ii)

Dividing equation (ii) by (i),

$r_2 = 8r_1$

61 **(d)**

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

The rate constant of a reaction does not change with change in concentrations, time, or extent of the reaction. It increases with increase in temperature

62 **(c)**

$t_{90\%} = \log\frac{100}{100-90} = \log 10 = 1$

$t_{80\%} = \log\frac{100}{100-80} = \log 5 = 0.7$

$\frac{t_{80\%}}{t_{90\%}} = \frac{0.7}{1}$

$\therefore\ t_{80\%} = 100\times0.7 = 70\text{ min}$

63 **(b)**

Factual statement

64 **(b)**

$\Delta H = 10 - 6 = 4\text{ kcal mol}^{-1}$

65 **(b)**

Factual statement

66 **(c)**

When initial pressure of $AB_3 = 50$ mm

$t_{1/2} = 4$ hr

When initial pressure of $AB_3 = 100$ mm

$t_{1/2} = 2$ hr

It means when concentration is doubled, half life is halved. So, it is a second order reaction

For second order reaction : $t_{1/2} \propto (a)^{-1}$

67 **(b)**

For photochemical reactions, the rate of reaction is directly proportional to the intensity of light

68 **(a)**

From experiment I and II, $[H_2]$ is constant and [NO] is doubled. Then rate becomes 4 times

So order of reaction w.r.t. (NO) = 2

From experiment I and III, [NO] is constant, and $[H_2]$ is doubled then rate becomes 2 times. So order of reaction w.r.t. $(H_2) = 1$

Total order = 3

Hence answer (a) is correct

69 **(c)**

$kt = \left(\frac{1}{a-x} - \frac{1}{a}\right)$

$\frac{1}{a-x} = kt + \frac{1}{a}$

Graph between $(a-x)^{-1}$ and time t is a straight line, hence, $k = \tan\theta = 0.5$

$\text{OA} = \frac{1}{a} = 2$

$\therefore a = \frac{1}{2} = 0.5$

$\therefore R = k[\text{A}]^2$

$= 0.5\times(0.5)^2$

$= 0.125\text{ L mol}^{-1}\text{min}^{-1}$

70 **(c)**

$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0693} = 10\text{ min}$

Reactant after 10 min=5 mol

Rate $\left(\frac{dx}{dt}\right) = k[\text{A}] = 0.0693\times5\text{ mol min}^{-1}$

71 **(a)**

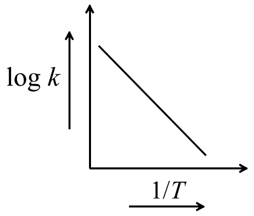
Since $k_{H_2SO_4} > k_{HCl}$, hence H_2SO_4 is stronger acid than HCl

72 **(d)**

According to Arrhenius equation

$\log k = \log A - \frac{E_a}{2.303}\cdot\frac{1}{T}$

Plot of $\log k$ vs $\frac{1}{T}$ is a straight line



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

Intercept = $\log A$

74 **(a)**

$c = \frac{n}{V} = \frac{P}{RT}$

$\therefore \frac{dc}{dt} = \frac{1}{V}\frac{dn}{dt} = \frac{1}{RT}\frac{dP}{dt}$

75 **(b)**

Factual statement

76 **(d)**

$r_1 = k[\text{A}]^2$

$0.30\text{ M s}^{-1} = k(0.2)^2$ ...(i)

$r_2 = k(0.2\times3)^2$

From equations (i) and (ii),

$r_2 = r_1\times9 = 0.3\times9 = 2.7\text{ M s}^{-1}$

77 **(c)**

Factual statement

78 **(c)**

$V = \frac{1}{2}$, then concentration $= 2$ times

Assuming the rate law as:

$r_1 = k[SO_2]^2[O_2]$

$r_2 = k[2SO_2]^2[2O_2]$

$r_2 = 8r_1$

79 **(b)**

In experiment I and II, [B] is constant and [A] is doubled. The rate does not change. So order w.r.t. [A]=zero

Let rate $= k[A]^0[B]^x$

$r_2 = 0.002 \text{ M s}^{-1} = k[0.1]^x$

$r_3 = 0.008 \text{ M s}^{-1} = k[0.2]^x$

$\frac{r_3}{r_2} = 4 = (2)^x$

$\therefore \ (2)^2 = (2)^x$

$x = 2$

So order w.r.t. [B]=2

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

80 **(a)**

Factual statement

81 **(a)**

$$k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$$

$$= \frac{1}{t}\log_e\frac{V_\infty}{V_\infty - V_t}$$

$$= \frac{1}{15}\log_e\frac{35 \text{ mL}}{(35-9)\text{mL}} = \frac{1}{15}\log_e\frac{35}{26}$$

82 **(d)**

Factual statement

83 **(c)**

Factual statement

84 **(d)**

Slow step is the rate determining step (RDS) and (N_2O_2) is the reactive intermediate

$\therefore \ r = k_2[N_2O_2][O_2]$ ...(i)

From reversible reaction, $[N_2O_2]$ is:

$\frac{k_1}{k_{-1}} = \frac{[N_2O_2]}{[NO]^2}$ ...(ii)

Substitute $[N_2O_2]$ in equation (i),

$$r = k_2\left(\frac{k_1}{k_{-1}}\right)[NO]^2[O_2]$$

Hence, rate constant $= k_2\left(\frac{k_1}{k_{-1}}\right)$

85 **(c)**

$$t_{3/4} = \frac{2.303}{k}\log\frac{1}{\left(1-\frac{3}{4}\right)} = \frac{2.303}{k}\log 4$$

86 **(a)**

The intersection point indicates that half life of the reactant A is converted to B

87 **(d)**

It is second order reaction, first order both w.r.t. $S_2O_8^{2-}$ and $I^\ominus$

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

All order options are of first order reaction

The reaction $S_2O_8^{2-} + 3I^\ominus \rightarrow 2SO_4^{2-} + I^\ominus_3$ is of first order both with respect to persulphate and iodide ions. Taking the initial concentration as a and b, respectively, and taking x as the concentration of the triodide at time t, a different rate equation can be written

Two suggested mechanisms for the reaction are:

I. $S_2O_8^{2-} + I^\ominus \rightleftharpoons SO_4I^\ominus + SO_4^{2-}$ (fast)

$I^\ominus + SO_4I^\ominus \xrightarrow{k_1} I_2 + SO_4^{2-}$ (show)

$I^\ominus + I_2 \xrightarrow{k_2} I_3^\ominus$(fast)

II. $S_2O_8^{2-} + I^\ominus \xrightarrow{k_1} S_2O_8\, I^{3-}$ (slow)

$S_2O_8I^{3-} \xrightarrow{k_2} 2SO_4^{2-} + I^\oplus$(fast)

$I^\oplus + I^\ominus \xrightarrow{k_3} I_2$ (fast)

$I_2 + I^\ominus \xrightarrow{k_4} I_3^\ominus$ (fast)

88 **(b)**

It follows first order kinetics since T_{50} is independent of concentration

	$A \rightarrow PhCl + N_2$		
$t = 0$	a	0	0
$t = 10$ min	$(a - x)$	x	x
Complete	0	a	a

Hence, $x = 10$ L, $a = 50$ L

$$\therefore k = \frac{2.303}{10}\log\frac{50}{40} = \frac{2.303}{10}\log 1.25 \ \text{min}^{-1}$$

89 **(a)**

Use Arrhenius equation

$T_1 = 273 + 14 = 287 \text{ K}, T_2 = 273 + 30 = 303 \text{ K}$

$$\log\frac{k_2}{K_1} = \frac{E_a}{2.303\, R}\left[\frac{T_2 - T_1}{T_1 \times T_2}\right]$$

$$\log\frac{2.2 \times 10^{-5}}{2.0 \times 10^{-6}} = \frac{E_a}{2.303 \times 2 \times 10^{-3}}\left(\frac{16}{287 \times 303}\right)$$

$$E_a = \frac{\log(11) \times 2.303 \times 2 \times 10^{-3} \times 287 \times 303}{16}$$

$$= \frac{1.0414 \times 2.303 \times 2 \times 287 \times 303}{16000}$$

$= 26 \text{ kcal mol}^{-1}$

90 **(b)**

$k = [\text{conc}]^{1-n}\text{min}^{-1}$

For third order reaction $= [\text{mol L}^{-1}]^{1-3}\text{min}^{-1}$

$= \text{L}^2\text{mol}^{-2}\text{min}^{-2}$

91 **(a)**

Only reactions whose E_a falls in the range of $50 - 55$ kJ mol^{-1} or $12 - 13$ kcal mol^{-1} are found to double their rate for this range (i.e., from 298 to 308 K) of temperature

92 **(d)**

Factual statement

93 **(d)**

Since all have same concentration of reactants, all would react at same time

94 **(c)**

In the case of first order reaction $t_{1/2}$ will remain constant independent of initial concentration. So,

$$4 \text{ mol L}^{-1} \xrightarrow{20 \text{ min}} 2 \text{ mol L}^{-1} \xrightarrow{20 \text{ min}} 1 \text{ mol L}^{-1} \xrightarrow{20 \text{ min}} 0.5 \text{ mol L}^{-1}$$

That is, after 60 min 0.5 mol L^{-1} of A will be left unreacted

In the case of second order reaction, $t_{1/2}$ is inversely proportional to the initial concentration of reactant, i.e., $t_{1/2}$ will go on doubling as the concentration of reactant will go on getting half, i.e., $t_{1/2}a$ will be constant. So,

$$4 \text{ mol L}^{-1} \xrightarrow{20 \text{ min}} 2 \text{ mol L}^{-1} \xrightarrow{20 \text{ min}} 1 \text{ mol L}^{-1} \xrightarrow{20 \text{ min}} 0.5 \text{ mol L}^{-1}$$

That is, after 60 min, the concentration of A remaining unreached will be 1 mol L^{-1}

Note: $t_{\frac{1}{2}}a = 20\,min \times 4M = 40\,min \times 2\,M = 80\,mol\,L^{-1}min^{-1}, a\ constant$

95 **(a)**

First order kinetics, $k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{40} s^{-1}$

Zero order kinetics, $k_0 = \frac{C_0}{2t_{1/2}} = \frac{1.386}{2 \times 20}$

Hence, $\frac{k_1}{k_0} = \frac{0.693}{1.386} = 0.5$

96 **(b)**

Factual statement

97 **(c)**

Factual statement

98 **(b)**

According to Arrhenius equation,

$k \propto T$ and $k = Ae^{-E_\mathrm{a}/RT}$

$$\log k = \log A - \frac{E_\mathrm{a}}{2.303 \times R} \times \frac{1}{T}$$

($y = c + mx$, equation of straight line)

The value of $\log x$ should increase uniformily with T or decrease with $1/T$. Hence, the answer is (b)

99 **(a)**

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

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

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

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

100 **(b)**

$$\frac{E'_a}{T_1} = \frac{E_a}{T_2} = \frac{10}{300} = \frac{20}{T_2}$$

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

101 **(b)**

In experiment (1) and (3), [A] is constant and [B] becomes double, but rate does not change, so order w.r.t. B = 0

In experiment (1) and (2), [B] is constant and [A] is doubled and the rate also is doubled. So order w.r..t [A] = 1

102 **(a)**

$$k_I = \frac{\Delta[R]}{\Delta t} = \frac{0.25}{0.05} = 5$$

$$k_{II} = \frac{\Delta[R]}{\Delta t} = \frac{0.60}{0.12} = 5$$

So reaction must be zero order

103 **(b)**

Use the formula : $\frac{t_{10\%(\text{left})}}{t_{1/2}} = \frac{\log\left(\frac{100}{10}\right)}{0.3}$

$$t_{10\%}(\text{left}) = \frac{t_{1/2} \times 1}{0.3}$$

$$= \frac{10 \text{ min}}{0.3} = 33 \text{ min}$$

104 **(c)**

For exothermic reaction,

$\Delta H^{\ominus}$ =(PE of product)$-$ (PE of reactant)= z

105 **(b)**

Slowest step is

$\mathrm{A_2 \rightarrow A + A}$ (slow)

Hence, $r = k[\mathrm{A_2}]$

Therefore, OR = 1

106 **(b)**

Rate $= \frac{(10-2)\text{atm}}{10 \text{ min}} = 0.8$ atm min^{-1}

Rate in M min^{-1} is given by:

Rate $= \frac{\Delta\,(n/v)}{\Delta t}$ M min^{-1} $= \frac{\Delta P}{\Delta t} \times \frac{1}{RT}$

$$= \frac{0.8}{0.08 \times 300}$$

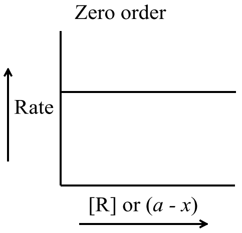
$= 0.03$ M min^{-1}

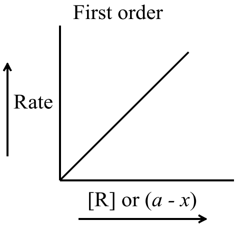
107 **(d)**

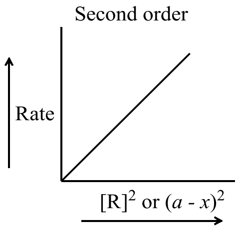
$\mathrm{X + 3Y \rightarrow Z}$

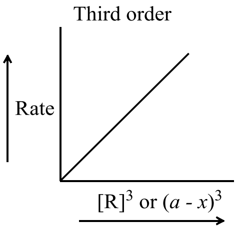
$$\text{Rate} = \frac{-d[\text{X}]}{dt} = \frac{-d[\text{Y}]}{3dt} = \frac{d[\text{Z}]}{dt}$$

108 **(a)**

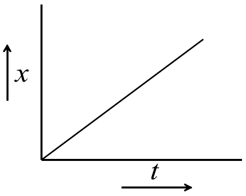








For zero order:



$\therefore$ Slope=+ve

Intercept = Zero

109 **(a)**

$$\frac{-E_a}{RT_1}=\frac{-E'_a}{RT_2}\Rightarrow\frac{100}{500}=\frac{80}{T}$$

$\therefore\ T' = 400$ K

110 **(d)**

Factual statement

111 **(a)**

Arrhenius equation:

$$\log k=\log A-\frac{2.303E_a}{R}\times\frac{1}{T}$$

$$\text{Slope}=\frac{-E_a}{2.303\times R}=-5000$$

$$\therefore\ \frac{-E_a}{2.303\times 8.314\times 10^{-3}\text{ kJ mol}^{-1}\text{K}^{-1}}=-5000$$

$\therefore E_a = 95.7\text{kJ K}^{-1}\text{mol}^{-1}$

112 **(d)**

It requires more data, e.g., different rate values are not given for different experiments

113 **(d)**

For nth order, $t_{1/2}\propto(a)^{1-n}$

$\Rightarrow \frac{t_{1/2}}{(a)^{1-n}}$ or $t_{1/2}\times(a)^{n-1}=$ Constant

$\therefore$ Given $t_{1/2}\times(a)^{n-1}=t_{1/2}(a)^2$

$\Rightarrow (a)^{n-1}=(a)^2$

$\therefore\ n-1=2\Rightarrow n=3$

Hence, third order reaction

114 **(d)**

$r_1=k[A][B]^2=k[0.6][0.80]^2$

After reaction

$$\begin{array}{cccc} A & +\ 2B\rightarrow & C & +\ D \\ 0.6-0.2 & 0.8-0.4 & 0.2 & 0.2 \\ 0.4 & 0.4 & 0.2 & 0.2 \end{array}$$

$$\frac{r_2}{r_1}=\frac{k(0.4)(0.4)^2}{(0.6)(0.8)^2}=\frac{1}{6}$$

115 **(a)**

$k=\frac{0.6932}{120}$ ...(i)

$$k=\frac{2.303}{t}\log\frac{a}{0.10a}$$

$=\frac{2.303}{t}\log 10$ ....(ii)

Equating (i) and (ii),

$$\frac{0.6932}{120}=\frac{2.303}{t}$$

$t=399$ min

116 **(c)**

Flask I:

$$\underbrace{1\text{ M}\xrightarrow[t_{1/2}=4\text{ hr}]{}0.5\text{ M}\xrightarrow[t_{1/2}=4\text{ hr}]{}0.25\text{ M}}_{t=8\text{ hr}}$$

$\therefore t_{1/2}=4$ hr

Flask II:

$$0.6\text{ M}\xrightarrow[t_{1/2}=4\text{ hr}]{}0.3\text{ M}$$

A first order reaction is independent of the initial concentration of the reactant

Hence, answer is (c)

117 **(b)**

Slow step is

A + B → C + D (slow)

Hence, $r=k[\text{A}][\text{B}]$

118 **(c)**

Factual statement

119 **(d)**

For the first order reaction for small finite change

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

$=0.015\text{ min}^{-1}$

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

120 **(c)**

$$\log k=\log A-\frac{E_a}{2.303RT}\ (y=c+mx)$$

$$\text{Slope}=\frac{-E_a}{2.303\ R}=\frac{1}{2.303}\text{ (given)}\left(\tan\theta=\frac{1}{2.303}\right)$$

$-E_a=2.303R\times$Slope

$$=2.303\times\frac{R}{2.303}=R=2\text{ cal}$$

122 **(b)**

Factual statement

123 **(c)**

For exothermic reaction, $(E_a)_f<(E_a)_b$

For endothermic reaction, $(E_{\mathrm{a}})_{\mathrm{f}} > (E_{\mathrm{a}})_{\mathrm{b}}$

124 **(c)**

Factual statement

126 **(c)**

Since [X] with time is increasing uniformly so change in concentration of A or B, i.e., $\frac{-d[\mathrm{A}]}{dt}$ or $\frac{d[\mathrm{B}]}{dt}$ is constant

127 **(c)**

It is a second ordered reaction

128 **(c)**

Factual statement

129 **(c)**

$$t_{80\%} = \log\frac{100}{100-80} = \log\frac{10}{2}$$

$$= \log 5 = 0.69 \approx 0.7$$

$$t_{90\%} = \log\frac{100}{100-90} = \log 10 = 1$$

$$\frac{t_{80\%}}{t_{90\%}} = \frac{0.7}{1} \Rightarrow \frac{70}{t_{90\%}} = \frac{0.7}{1}$$

$$\therefore t_{90\%} = \frac{70}{0.7} = \frac{700}{7} = 100 \text{ min}$$

130 **(b)**

Change in 67% to 33% is almost half the concentration change

$$67\% \xrightarrow[\text{change}]{\text{Half}} 33.5(\approx 33\%)$$

So time interval between the stages of its 33% and 67% decay is same as $t_{1/2} = 20$ min

131 **(d)**

Factual statement

132 **(d)**

Slow step is:

$$\frac{1}{2}\mathrm{X}_2 + \mathrm{Y}_2 \rightarrow \mathrm{XY}_2$$

Hence,

$$r = k[\mathrm{X}_2]^{1/2}[\mathrm{Y}_2]$$

$\mathrm{OR} = \frac{1}{2} + 1 = 1\frac{1}{2}$

133 **(c)**

Factual statement

134 **(b)**

Factual statement

135 **(b)**

It is given by Arrhenius equation

$k = Ae^{-E_{\mathrm{a}}/RT}$

or In k = In $A - E_{\mathrm{a}}/RT$

136 **(b)**

$k = Ae^{-E_{\mathrm{a}}/RT}$

If $T \rightarrow \infty, k = \mathrm{A}$

137 **(b)**

$\mathrm{OR} = \frac{3}{2} - 1 = \frac{1}{2}$

138 **(c)**

Factual statement

139 **(c)**

Factual statement

140 **(d)**

For the reaction $\mathrm{A + B \longrightarrow C + D}$

Rate of reaction:

$r_1 = k[\mathrm{A}]^x[\mathrm{B}]^y$ ...(i)

$r_2 = 8r_1 = k[2\mathrm{A}]^x[2\mathrm{B}]^y$ ...(ii)

$r_3 = 2r_1 = k[\mathrm{A}]^x[2\mathrm{B}]^y$ ...(iii)

Dividing equation (iii) by (i),

$$\frac{2r_1}{r_1} = \frac{k[\mathrm{A}]^x[2\mathrm{B}]^y}{k[\mathrm{A}]^x[\mathrm{B}]^y}$$

$(2)^1 = (2)^y$

$y = 1$

Dividing equation (ii) by (i),

$$\frac{8r_1}{r_2} = \frac{k[2\mathrm{A}]^x[2\mathrm{B}]^y}{k[\mathrm{A}]^x[\mathrm{B}]^y}$$

$8 = (2x)^x(2)^y$

$8 = (2)^x(2)^1$

$4 = (2)^x$

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

$x = 2$

$\therefore r = k[\mathrm{A}]^2[\mathrm{B}]$

141 **(d)**

Factual statement

142 **(b)**

At temperature T K, rate constants are equal, hence

$$10^{13} \exp\left(\frac{-152300 \text{ J mol}^{-1}}{RT}\right) = 10^{14}\left(\frac{-157700 \text{ J mol}^{-1}}{RT}\right)$$

$$\exp\left(\frac{157700 - 152300}{RT}\right) = 10$$

$$\text{or } \log_{\mathrm{e}} \exp\left(\frac{157700-152300}{RT}\right) = \log_e 10$$

$$= 2.303 \log_{10} 10$$

$$\text{or } \frac{157700-152300}{8.314T} = 2.303$$

thus, $T = 282$ K

143 **(c)**

$E_{\mathrm{a}} = E_{\mathrm{a(f)}} + \Delta H$

$= 60 + 20 = 80 \text{ kJ mol}^{-1}$

Note : $\Delta H = -ve$ *means exothermic reaction, so only magnitude value is taken*

144 **(c)**

$$k = \frac{2.303}{t}\log\left[\frac{N_0}{N}\right]$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{4\text{ days}}\log\left(\frac{N_0}{N}\right)$$
$$\frac{0.693}{8\text{ days}} = \frac{2.303}{4\text{ days}}\log\left(\frac{N_0}{N}\right)$$
$\therefore\ \frac{N}{N_0} = 0.7\ \Rightarrow$ 70% of the initial activity is present. Given that 60% activity is migrated to thyroid gland is:

$\frac{60}{70} \times 100 \approx 85.7\ \%$

i.e., $1.0\text{ mg} \times \frac{85.7}{100} = 0.857\text{ mg}$

145 **(a)**

$k_1 = Ae^{-E_{a_1}/RT}$

$k_2 = Ae^{-E_{a_2}/RT}$

$k_3 = Ae^{-E_{a_3}/RT}$

Overall rate:

$$k = \frac{k_1 k_3}{k_2}$$

$\therefore$ Overall $E_a = E_{a_1} + E_{a_3} + E_{a_2}$

$= 60 + 10 - 30$

$= 40\text{ kJ}$

146 **(a)**

Two different reactants means second order reaction

A reaction is said to be of second order if its reaction rate is determined by the variation of two concentration terms

The kinetics of second order reactions are given as follows:

a. When concentrations of both reactants are equal or two molecules of the same reactant are involved in the change, i.e.,

$\mathrm{A + B \longrightarrow Products}$

or $\mathrm{2A \longrightarrow Products}$

Case I: When either one reactant or two reactants with same concentration

$\mathrm{2A \longrightarrow Products}$ or $\mathrm{A + B \longrightarrow Products}$

At $t = 0$ $\quad a \quad 0 \qquad a \quad a \quad 0$

At $t = t$ $\quad (a-x) \quad x \qquad (a-x)(b-x) \quad x$

$$\frac{dx}{dt} = k\,(a-x)^2$$

On integrating

$$\int \frac{dx}{(a-x)^2} = k\int dt$$

$$\therefore \frac{1}{(a-x)} = kt + c \qquad \dots\text{(i)}$$

Where c is the integrating constant

When $t = 0, x = 0, \quad \therefore c = \frac{1}{a}$

Substituting the value of c in equation (i),

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

or $kt = \frac{1}{(a-x)} - \frac{1}{a}$

or $t = \frac{1}{k}\cdot\frac{x}{a(a-x)} \qquad \dots\text{(ii)}$

Case II: When the two reactants have different concentrations

$\qquad A \ + \ B \longrightarrow \text{ Products}$

At $t = 0$ $\quad a \quad b \quad 0$

At $t = t$ $\quad (a-x)\ (b-x) \quad x$

$$\therefore \frac{dx}{dt} = k(a-x)(b-x)$$

This equation on integration gives:

$$t = \frac{1}{k}\cdot\frac{2.303}{(a-b)}\log\frac{b(a-x)}{a(b-x)} \qquad \dots\text{(iii)}$$

147 **(d)**

Factual statement

148 **(b)**

Factual statement

149 **(b)**

Use the formula:

$$t = \frac{2.303}{k}\log\frac{V_0}{V_t}$$
$$= \frac{1}{k}\text{In}\frac{V_0}{V_t}$$
$$= \frac{1}{4.5\times10^{-2}\text{ min}^{-1}}\text{In }\frac{25\text{ mL}}{5\text{ mL}}$$
$$= \frac{\log_e 5}{4.5\times10^{-2}}\text{ min}$$

150 **(b)**

Surface are increases

151 **(b)**

From the question, it is clear $t_{1/2} \propto a$. Hence, zero order reaction. So, dimension of $k = \text{mol L}^{-1}\text{hr}^{-1}$

For zero order: $t = \frac{x}{k}$ or $k = \frac{x}{t}$

If $t = t_{10\%} = 10$ min, $x = 10$,

Then, $k = \frac{10}{10} = 1\text{ mol L}^{-1}t^{-1}$,

Then, $k = \frac{20}{20} = 1\text{ mol L}^{-1}t^{-1}$

Similarly, for 30% and so on

Thus, reaction is of zero order

152 **(b)**

Factual statement

153 **(b)**

Since E_a for the reaction $\mathrm{A + B \rightarrow Q}$ $(25 - 7 = 18\text{ kcal mol}^{-1})$ is greater than E_a for the reaction $Q \rightarrow C$ (3 kcal mol^{-1}). Therefore, reaction $\mathrm{Q \rightarrow C}$ is faster

154 **(a)**

A→ $product$ (first order reaction)

For first order reaction ,

Rate constant (k)=$\frac{2.303}{t}log_{10}\frac{[A]_0}{[A]_t}$

At t= 40min,

$$=\frac{2.303}{40}log_{10}\frac{0.1}{0.025}=\frac{2.303}{40}log_{10}4$$

$$\frac{2.303}{40}\times 2log_{10}2=\frac{2.303}{40}\times 2\times 0.3010$$

=0.0347 min^{-1}

At concentration of $A=0.01\ M=[A]$

Rate $\frac{dx}{dt}k[A]$

$$\frac{dx}{dt}=0.0347\times 0.01$$

$$=3.47\times 10^{-4}mol\ L^{-1}\,min^{-1}$$

155 **(b)**

$$A_2(g)\ \longrightarrow\ B(g)\ +\ \frac{1}{2}C(g)$$

Initial P $\quad 0 \quad 0$

At eq $P-x$ $\quad x \quad \frac{x}{2}$

Total pressure $=P-x+x+\frac{x}{2}=P+\frac{x}{2}$

Initial pressure $(P)=100$ mm

Final pressure = Total pressure = 120 mm

$$\therefore P+\frac{x}{2}=120$$

$$100+\frac{x}{2}=120$$

$x=40$ mm

$$\therefore\frac{-d[A_2]}{dt}=\frac{40}{5}=8\ \text{mm min}^{-1}$$

156 **(c)**

$2X+Y\rightarrow Z$

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

$$\therefore\frac{-d[X]}{dt}=2\times\frac{-d[Z]}{dt}=2\times 0.05$$

$=0.1\ \text{mol L}^{-1}\ \text{min}^{-1}$

157 **(c)**

1. Wrong. $R=\frac{dx}{x\,dt}=\frac{dy}{y\,dt}$
2. Wrong. They have same meaning
3. Correct
4. $E_a=E_{\text{threshold}}-E_R$

158 **(c)**

$t_{75\%}=2t_{1/2}$

$$\therefore t_{1/2}=\frac{24\text{ min}}{2}=12\text{ min}$$

n =Number of half lives in 1 hr (60 min)= $\frac{60}{12}=5$

Amount of substance left after 5 half lives

$$=\left(\frac{1}{2}\right)^5=\frac{1}{32}$$

$\therefore$ % of amount left $=\frac{100}{32}=3.125\%=3\%$

159 **(a)**

$$\frac{k_{34°}}{k_{35°}}<1$$

or $\frac{k_{35°}}{k_{34°}}>1$

also, $k\propto T$

Hence, rate increase with rise of temperature

160 **(b)**

$r=k[A][B]^0$

Since [B] is in large excess, so its concentration does not change

$\therefore$ OR = 1

161 **(a)**

For zero order reaction

$t_{1/2}\propto(a)^1$

162 **(b)**

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

163 **(b)**

Let the rate of the reaction is

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

$r_1=3.0\times 10^{-3}=k[0.25]^x[0.25]^y$ ...(i)

$r_2=6.0\times 10^{-3}=k[0.5]^x[0.25]^y$ ...(ii)

$r_3=1.20\times 10^{-2}=k[0.5]^x[0.5]^y$ ...(iii)

Divide equation (ii) by (i)

$$\frac{6.0\times 10^{-3}}{3.0\times 10^{-3}}=\frac{k[0.5]^x[0.25]^y}{k[0.25]^x[0.25]^y}$$

$(2)^1=(2)^x\Rightarrow x=1$

Divide equation (iii) by (ii)

$$\frac{1.20\times 10^{-2}}{6.0\times 10^{-3}}=\frac{k[0.5]^x[0.5]^y}{k[0.5]^x[0.25]^y}$$

$\therefore(2)^1=(2)^y\Rightarrow y=1$

$\therefore r=k[A]^1[B]^1$

Total order = 1 + 1 = 2

164 **(a)**

Time for the conversion of 0.8 mol of A to 0.6 mol of

$$B=\frac{0.6}{0.8}=0.75=t_{75\%}$$

Similarly, time for the conversion of 0.9 mol of A to 0.675 mol of B $=\frac{0.675}{0.9}=0.75=t_{75\%}$

Hence, $t_{75\%}$ in both case= 1 hr

165 **(b)**

$[H_2SO_4]=0.1\text{ M}=0.1\times 2=0.2\text{ N}$

$[HCl]=0.1\text{ N}$

In case of H_2SO_4

$r_1=k[H^{\oplus}][\text{Ester}]$

$k_{H_2SO_4} = \frac{r_1}{2N \times [\text{Ester}]}$

In case of HCl,

$r_2 = k[H^{\oplus}][\text{Ester}]$

$k_{HCl} = \frac{r_2}{1N \times [\text{Ester}]}$

Hence $K_{HCl} > K_{H_2SO_4}$

166 **(a)**

For second order, when $(a-x) = 0.01$ M

$k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)}$

$k_2 = \frac{1}{70} \cdot \frac{0.07}{0.08 \times 0.01}$ …(i)

When $(a-x) = 0.04$ M

$k_2 = \frac{1}{t} \cdot \frac{0.04}{0.08 \times 0.04}$ …(ii)

From equations (i) and (ii),

$$\frac{0.07}{70 \times 0.08 \times 0.01} = \frac{0.04}{t \times 0.08 \times 0.04}$$

$\Rightarrow t = 10$ min

167 **(c)**

Since $k \propto T$

Hence, $k_{310\text{ K}} = 2.3\, k_{300\text{ K}}$

168 **(a)**

Rate constant for first order reaction is independent of initial concentration. Thus, $k = 0.25\text{ s}^{-1}$

169 **(c)**

A catalyst does not affect the chemical equilibrium. It alters the rate of a reaction. A positive catalyst helps to achieve the chemical equilibrium earlier

170 **(a)**

$t_{1/2} \propto \left(\frac{1}{a}\right)^{n-1}$ or $t_{1/2} = k(a)^{1-n}$

$\log t_{1/2} = \log k + (1-n)\log a\ (y = c + mx)$

Slope $= (1-n) = \tan 45 = 1$

$\therefore (1-n) = 1 \Rightarrow n = 0$

171 **(b)**

$r = [A][B]^0$

OR $= 1 + 0 = 1$

172 **(a)**

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Rate $= \frac{-d[SO_2]}{2dt} = \frac{-d[O_2]}{dt}$

$\therefore \frac{-d[SO_2]}{2dt} = 2 \times \frac{-d[O_2]}{2dt}$

$= 2 \times 2.5 \times 10^{-4}$

$= 5.0 \times 10^{-4}\text{ mol}^{-1}\text{L}^{-1}\text{s}^{-1}$

173 **(b)**

$t_{1/2} = \frac{0.69}{k} = \frac{0.3 \times 2.3}{k}$

$t_{60\%} = \frac{2.3}{k}\log\frac{100}{100-60} = \frac{2.3}{k}\log\frac{10}{4}$

$k = \frac{2.3}{60}\log\frac{10}{4}$

$\frac{0.3 \times 2.3}{t_{1/2}} = \frac{2.3}{60}\log\frac{10}{4}$

$= \frac{1}{60}[1 - 2\log 2] = \frac{1}{60}[1 - 0.6]$

$\frac{0.3}{t_{1/2}} = \frac{0.4}{60}$

$\therefore t_{1/2} = \frac{60 \times 0.3}{0.4} = 45$ min

Use direct relation

$t_{1/2} = 0.3, t_{x\%} = \left(\log\frac{100}{100-x}\right)$

$t_{60\%} = \log\frac{10}{4} = (0.4)$

$\frac{t_{1/2}}{t_{60\%}} = \frac{0.3}{0.4}$

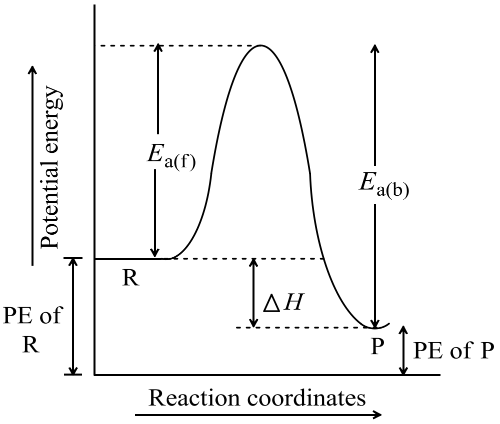
$\therefore t_{1/2} = t_{60\%} \times \frac{0.3}{0.4} = \frac{60 \times 3}{4} = 45$ min

175 **(b)**

$t_{1/2} = \frac{1}{ka} = \frac{1}{0.5 \times 0.5} = 4$ min

176 **(b)**

Exothermic reaction



According to graph,

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

$= 17 + 40 = 57\text{ kJ mol}^{-1}$

177 **(c)**

The rate of reaction becomes doubled for 10° rise in temperature. Hence, 100% increase in reaction rate

178 **(d)**

Factual statement

179 **(b)**

$t_{75\%} = 2t_{1/2}$

$\therefore\ t_{1/2} = \frac{1.386\text{ hr}}{2} = 0.693$ hr

$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{0.693} = 1\text{ hr}^{-1} = \frac{1}{3600\text{ s}}$

$= 2.7 \times 10^{-4}\text{ s}^{-1}$

180 **(a)**

Factual statement

181 **(c)**

Factual statement

182 **(a)**

i. Slow step in the reaction with catalyst is

$A_2 + D \rightarrow A_2D$ (Slow)

Hence, $r = k'[A_2][D]$

Ii. Slow step in the reaction without catalyst is:

$A_2 \rightarrow 2A$ (slow)

Hence, $r = k[A_2]$

183 **(b)**

$t_{0.75} = 2t_{1/2}$

$\therefore\ t_{1/2} = \frac{1386}{2} = 693\text{ s}$

$k = \frac{0.693}{693\text{ s}} = 10^{-3}\text{ s}^{-1}$

184 **(b)**

$r_1 k[A][B]$

$\left(V = \frac{1}{4}, \text{so concentration} = 4\text{ times}\right)$

$\therefore\ r_2 = k[4A][4B]$

$r_2 = 16\,r_1$

185 **(b)**

$r_1 = k[A]^n$

$r_2 = 2r_1 = k[8A]^n$

$\therefore\ \frac{2r_1}{r_1} = (8)^n$

$(2)^1 = (2)^{3n}$

$\therefore 3n = 1$

$n = \frac{1}{3}$

186 **(c)**

Factual statement

187 **(a)**

$k_{eq} = \frac{k_f}{k_b} = \frac{1.1 \times 10^{-2}}{1.5 \times 10^{-3}} = 7.33$

188 **(b)**

Use direct formula:

$t_{1/2} = 0.3, t_{70\%} = \log\frac{100}{100 - 70}$

$= \log\frac{10}{3} = [1 - 0.48] = 0.52 \approx 0.5$

$\frac{t_{1/2}}{t_{70\%}} = \frac{0.3}{0.5}$

$t_{1/2} = \frac{0.3 \times 70}{0.5} = 42\text{ min}$

189 **(c)**

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

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

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

$= \frac{3}{2} \times 2.5 \times 10^{-4}\text{mol L}^{-1}\text{s}^{-1}$

$= 3.75 \times 10^{-4}\text{mol L}^{-1}\text{s}^{-1}$

190 **(b)**

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

When $t \rightarrow \infty$

$k \rightarrow A$

$A = 6 \times 10^{14}\text{ s}^{-1}$

191 **(b)**

$t_{1/2} = \frac{0.693}{k} = 2100\text{ s} = 35\text{ min}$

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

192 **(d)**

Factual statement

193 **(c)**

Factual statement

196 **(a,b,d)**

For any reaction, $\Delta H = E_{a(f)} - E_{a(b)}$

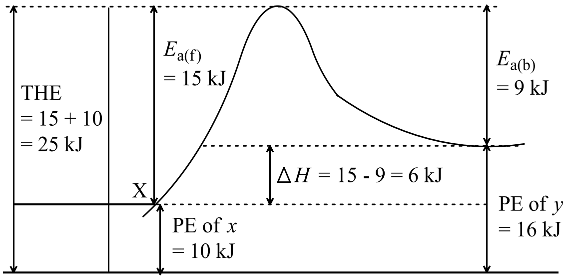
Also, for exothermic reaction $\Delta H \geq E_a$

198 **(a,d)**

In (a) and (b), number of reacting molecules are only one

199 **(a,b,c,d)**

For reaction X → Y



$E_{a(f)} = 15\text{ kJ mol}^{-1}, E_{a(b)} = 9\text{ kJ mol}^{-1}$

Heat of reaction $E_{a(f)} - E_{a(b)} = 15 - 9 = 6\text{ kJ mol}^{-1}$

Potential energy of Y is = 10 + 6 = 16 kJ

Threshold energy of the reaction =PE of X + $E_{a(f)}$

=10 kJ+15 kJ

=25 kJ

The reaction is endothermic because $E_{a(f)} > E_{a(b)}$

201 **(a,b,c,d)**

All factual statements

202 **(b,c)**

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

$k = A$; when $T \rightarrow \infty$ or $E_a = 0$ or both

203 **(a,b,c)**

Lower the activation energy, higher the rate of reaction. Rate constant depends upon the temperature

204 **(b,d)**

On integrating within limits K_1 to K_2 and T_1 to T_2

$$\int_{k_1}^{k_2} \ln K = -\frac{E_a}{R}\int_{T_1}^{T_2} \frac{1}{T}$$

$$\ln\frac{K_2}{K_1} = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

or $\ln\frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

205 **(a,b,c,d)**

All options self explanatory

207 **(c,d)**

Rate $\propto [\mathrm{H}^{\oplus}]^2$. Hence, doubling the concentration of $\mathrm{H}^{\oplus}$ ions will increase the reaction rate by 4 times. Also, the change in pH will change the concentration of $\mathrm{H}^{\oplus}$ and therefore, the rate will change

208 **(a,c)**

For second order reaction, order is 2

209 **(a,d)**

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

or $kt = \text{In}\frac{A_0}{A} = \text{In}\frac{1}{1-a}$

If a is the degree of dissociation

$$e^{kt} = \frac{1}{1-a}$$

or $1 - a = e^{-kt}$

or $a = 1 - e^{-kt}$

$\therefore k = Ae^{-E_\mathrm{a}/RT}$ (Arrhenius equation)

Pre-exponential factor has the same dimensions as the rate constant, and for a first order reaction that is (t^{-1})

210 **(a,b)**

Compare Arrhenius equation with the given equation

$$\log k = \log A - \frac{E_\mathrm{a}}{2.3R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Given equation:

$$\log k = \log 5 - \frac{2000}{2.3RT}$$

$\therefore \log A = \log 5 \Rightarrow A = 10^5$

$E_\mathrm{a} = 2000$ kcal

214 **(a,c)**

$\frac{d}{dt}[\mathrm{NH_2CONH_2}] = k_4[\mathrm{NH_3}][\mathrm{HNCO}]$ from (iii)

Applying steady state approximately to HNCO or $\mathrm{NH_3}$

$$\frac{d[\mathrm{HNCO}]}{dt} = 0 = k_3[\mathrm{NH_4NCO}] - k_4[\mathrm{NH_3}][\mathrm{HNCO}]$$

$$\therefore \frac{k_3}{k_4} = \frac{[\mathrm{NH_3}][\mathrm{HNCO}]}{[\mathrm{NH_4CNO}]}$$

$$\frac{d_{[\text{urea}]}}{dt} = k_4 \times [\mathrm{NH_3}][\mathrm{HNCO}]$$

$$= k_4 \times \frac{k_3}{k_4}[\mathrm{NH_4NCO}]$$

Also, $[\mathrm{NH_4NCO}] = \frac{k_1}{k_2} \times [\mathrm{NH_4CNO}]$

$$\therefore \frac{d_{[\text{urea}]}}{dt} = k_3 \times \frac{k_1}{k_2} \times [\mathrm{NH_4CNO}]$$

$$= k[\mathrm{NH_4CNO}]$$

215 **(c,d)**

As a result of increase in temperature the collision frequency increases. As a result, there is an increase in the number of effective collisions and thus rate of reaction increases

220 **(b,c,d)**

The rate of reaction is proportional to square of conc. Of A and to the concentration of B. Hence, it is of second order w.r.t. A and first order w.r.t. B overall order is $2 + 1 = 3$

222 **(a,b,c,d)**

Self explanatory

223 **(a,d)**

1. $r = k[\mathrm{N_2O_5}]$

$2.40 \times 10^{-5}\,\mathrm{M\,s^{-1}} = (3.0 \times 10^{-5}\mathrm{s^{-1}})[\mathrm{N_2O_5}]$

$\therefore [\mathrm{N_2O_5}] = 0.80$ M

2. At very high temperature or zero energy of activation

3. Directly proportional to I

4. According to Arrhenius equation

$k = Ae^{-E_\mathrm{a}/RT}$

As $T \to \infty, \therefore K = A$

Hence, $A = 6.0 \times 10^{14}\mathrm{s^{-1}}$

226 **(a,b,c)**

All statements are self explanatory

228 **(a,c)**

For an effective collision, molecules must possess sufficient energy and proper orientation

229 **(b,c)**

A catalyst provides an alternative path for the reaction occurring via a different activation state

A positive catalyst decreases the activation energy of a reaction, so that more number of molecules are able to cross the activation energy barrier and so the rate of the reaction is increased

A negative catalyst increases the activation energy of a reaction so that lesser number of molecules are able to cross the activation energy barrier and so the rate of the reaction is decreased

231 **(c,d)**

All options self explanatory

232 **(b,c)**

1. Rate is independent of [NaOH], hence wrong
2. Correct rate $\propto$ [RCl]
3. Correct rate $\propto T$
4. Wrong

233 **(b,d)**

Use initial rate law method, let the reaction be first order,

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

b. At $t = 20$ s, $k_1 = \frac{2.303}{20}\log\left(\frac{0.4}{0.2}\right)$

and at $t = 40$ s, $k_2 = \frac{2.303}{40}\log\left(\frac{0.4}{0.1}\right) = k_1$

$\Rightarrow$ Assumption is correct ($\because k_1 = k_2$)

Rate at 20 s $= k[\mathrm{A}] = \frac{0.693}{20} \times 0.2$

$= 0.0063 \approx 7 \times 10^{-3}\,\mathrm{M\,s^{-1}}$

Clearly, half life $t_{1/2} = 20$ s

d. In 60 s, number of life $= \frac{60}{20} = 3$

$\Rightarrow$ [B] at 60 s

$= 0.4 - 0.4\left(\frac{1}{2}\right)^3 = 0.35$ M

235 **(a,b,d)**

In $k_p =$ In $A - \frac{E_a}{R} \times \frac{1}{T}$ $(y = c + mx)$

Therefore, plotting a graph between $\log K_p$ versus $1/T$ is a straight line

For a first order reaction

$$\log A_t = \log A_0 - \frac{k}{2.3}t(y = c + mx)$$

The graph between $\log A_t$ and time is a straight line

At constant temperature, $PV =$constant for the given mass of a gas (Boyle's law). So, the graph between P and $1/V$ is a straight line

236 **(a,b,c,d)**

Factual statement

237 **(a,c)**

Self explanatory

238 **(a,b,c,d)**

$t_{1/2} \propto (a)^{1-n}$; $[\mathrm{A}]_t = [\mathrm{A}]_0 - kt$

and X $= kt$ are integrated form of zero order

239 **(a,d)**

Self explanatory

240 **(a,b,c,d)**

$$k_{\mathrm{eq}} = \frac{k_{\mathrm{f}}}{k_{\mathrm{b}}} = \frac{[\mathrm{C_6H_{12}}]}{[\mathrm{C_6H_6}][\mathrm{H_2}]^3} = \frac{[\mathrm{C_6H_{12}}]}{[\mathrm{C_6H_6}][\mathrm{H_2}][\mathrm{H_2}]^2}$$

$r_{\mathrm{f}} = k_{\mathrm{f}} \times [\mathrm{C_6H_6}][\mathrm{H_2}]$

$r_{\mathrm{b}} = k_{\mathrm{b}} \times$Unknown

At equilibrium, $r_{\mathrm{f}} = k_{\mathrm{b}}$

$\therefore\ r_{\mathrm{f}}[\mathrm{C_6H_6}][\mathrm{H_2}] = k_{\mathrm{b}} \times$Unknown

$r_{\mathrm{b}} = k_{\mathrm{b}} \times \frac{k_{\mathrm{f}}}{k_{\mathrm{b}}} \times [\mathrm{C_6H_6}][\mathrm{H_2}]$

$= k_{\mathrm{f}}[\mathrm{C_6H_6}][\mathrm{H_2}]$

$= k_{\mathrm{b}}[\mathrm{C_6H_{12}}][\mathrm{H_2}]^{-2}$

241 **(a,b,c,d)**

Self explanatory

242 **(a,b,c,d)**

Factual statement

245 **(b,c)**

Self explanatory

247 **(a,b,c,d)**

Self explanatory

249 **(a,b,c,d)**

Rate of reaction $= \frac{-d[\mathrm{A}]}{dt} = k[\mathrm{A}]^n$ or $\frac{-dP_{\mathrm{A}}}{dt} = k(P_{\mathrm{A}})^n$

$= \frac{1}{V}\frac{-dn_{\mathrm{A}}}{dt} = k[\mathrm{A}]^n \left[\because\ [\mathrm{A}]\frac{n_{\mathrm{A}}}{V}\right]$

$= -\frac{1}{RT}\frac{-dP_{\mathrm{A}}}{dt} = k[\mathrm{A}]^n \left[\because\ [\mathrm{A}]\frac{P_{\mathrm{A}}}{RT}\right]$

250 **(a,b)**

Only elementary bimolecular reactions have second order reaction

252 **(a,c,d)**

Reaction is zero order so rate of formation of product or rate of decomposition of reactant is constant so concentration will be linear function

For zero order reaction, $k = \frac{a}{2t_{1/2}}$

So unit of k is mol $\mathrm{L^{-1}\,s^{-1}}$

$\frac{dx}{dt} = k(2a - 2x) \times (a - x)^{-1} = 2\mathrm{K}$

$x = [C] = 2kt$

253 **(b,d)**

$k_1 = k_2 = \frac{2}{3}$rd of A has reacted for $[A] = [B] = [C]$

$\therefore k_1 + k_2 = \frac{1}{t}\ln\frac{[A]_0}{\frac{1}{3}[A]_0}$

Or $t = \frac{1}{k_1 + k_2}\ln 3 = \frac{1}{2k_1}\ln 3 = \frac{1}{2k_2}\ln 3$

254 **(b,c,d)**

1. Since $t_{1/2}$ is independent of concentration of Zn at constant pH means that the order w.r.t. [Zn]=1

2. Let $r_1 \propto \left[\mathrm{H}^{\oplus}\right]^x \Rightarrow r_1 \propto [10^{-3}]^x$ [when pH=3]

$r_2 = 100r_1 \propto [10^{-2}]^x$ [when pH = 2]

Thus, $\frac{r_2}{r_1} = \left[\frac{10^{-2}}{10^{-3}}\right]^x$

$100 = (10)^2 = [10]^x \Rightarrow x = 2$

Hence, order w.r.t. $\left[\mathrm{H}^{\oplus}\right] = 2$

b. Hence, the rate = $\left(\frac{dx}{dt}\right) = k[\mathrm{Zn}]\left[\mathrm{H}^{\oplus}\right]^2$

So (b) is the correct answer

c. $\left(\frac{dx}{dt}\right) = r_1 = k[\mathrm{Zn}]\left[\mathrm{H}^{\oplus}\right]^2$

$r_2 = k[\mathrm{Zn}]\left[\frac{\mathrm{H}^{\oplus}}{2}\right]^2$

Thus, $r_2 = r_1$

d. $r_1 = k[\mathrm{Zn}]\left[\mathrm{H}^{\oplus}\right]^2$ ...(i)

$r_2 = k[\mathrm{Zn}]\left[2\mathrm{H}^{\oplus}\right]^2$ ...(ii)

Divide (ii) by (i),

$r_2 = 4r_1$

255 **(a,d)**

For a first order reaction, A →Products, we have

In $\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = -kt$ or $[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-kt}$

In terms of degree of dissociation,

$[\mathrm{A}]_t = [\mathrm{A}]_0\ (1-\alpha)$

Hence, $[\mathrm{A}]_0(1-\alpha) = [\mathrm{A}]_0 e^{-kt}$

or $\alpha = 1 - e^{kt}$

The Arrehnius equation is $k = Ae^{-E_\mathrm{a}/RT}$

The dimension of pre-exponential factor A in the above expression is the same as that of rate constant k. For a first order reaction, the dimension of k is t^{-1}

257 **(b)**

1. $\frac{-d[\mathrm{H}_2]}{dt} = \frac{3}{2}\frac{d[\mathrm{NH}_3]}{dt} \times \frac{Mw \text{ of } \mathrm{H}_2}{Mw \text{ of } \mathrm{NH}_3}$

$= \frac{3}{2} \times 0.001 \times \frac{2}{17}$

$= 1.765 \times 10^{-4}\mathrm{kg\ hr}^{-1}$ (Hence, wrong)

2. Correct statement

3. Directly proportional (Wrong statement)

4. Increasing the temperature (Wrong statement)

262 **(a,b,d)**

For first order reaction, $t_{1/2} = \frac{0.693}{k}$, i.e., $t_{1/2}$ is independent of concentration

263 **(a,b)**

Kinetic stability and thermodynamic stability has no relation. Also, the function of negative catalyst to slow down the speed of reaction is not all related with energy of activation

264 **(b,d)**

The rate of the reaction is independent of the concentration of water because it is taken in excess and its conc does not change with time

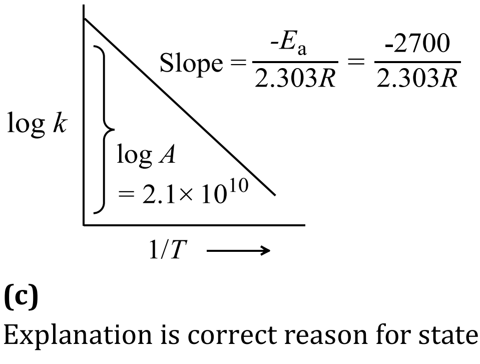
267 **(a,b)**

For Arrhenius equation $k = Ae^{-E_\mathrm{a}/RT}$

$= 2.1 \times 10^{10} \times e^{-2700/RT}$

or $\log k = \log A - \frac{E_\mathrm{a}}{2.303\ RT} = \log 2.1 \times 10^{10} - \frac{2700}{2.303\ RT}$

Plot of $\log k$ vs $1/T$



269 **(c)**

Explanation is correct reason for statement.

270 **(d)**

Both statement and explanation are correct.

271 **(d)**

Both statement and explanation are correct.

272 **(a)**

It is true that alcohol are dehydrated to alkenes in the presence of zeolites. This is because zeolites are shape-selective, porous solid catalyst and not first porous catalyst.

273 **(b)**
Molecularity of a reaction can be defined only for an elementary reaction because complex reaction does not take place in one single step an it is almost impossible for all the total molecules of the reactants to be in a state of encounter simultaneously.

274 **(a)**
The negative order with respect to a substance indicates that rate of reaction decreases as the concentration of that substance increases.

275 **(b)**
The formation of an activated complex takes place when vibrational degree of freedom convert into a translational degree of freedom. This statement is given by transition state theory. Also the energy of activated complex, is higher than the energy of reactant molecule, it is true but it is not the correct explanation of the assertion.

276 **(b)**
Explanation is correct and suggests that statement is wrong.

277 **(b)**
Correct reason: With increase of temperature by 10°, the fraction of molecules having effective collisions becomes 2 or 3 times

278 **(c)**
Correct (R), $k = \frac{\text{Concentration}}{\text{Time}} = \text{mol L}^{-1}\text{s}^{-1}$

i.e., it depends upon units of concentration

279 **(b)**
It is an experimentally determined value and depends upon the concentration change of reactant. It changes with pressure, temperature and concentration and it can have the fractional value.

280 **(b)**
Molecularity is 2 because two molecules of the reactants are involved in the given elementary reactions

281 **(b)**
Self explanatory

282 **(d)**
Both statement and explanation are correct.

283 **(a)**
Self explanatory

284 **(e)**
Correct (A) $H_2 + Cl_2 \rightarrow 2HCl$ is zero order while $H_2 + Br_2 \rightarrow$ is of order 1.5

Correct (R) The two reactions proceed by different mechanism

285 **(e)**
Correct (A) The rate of reaction is same in terms of different reactants and products

Correct (R) The rate of reaction is equal to the rate of disappearance or formation divided further by the stiochiometric coefficient

286 **(b)**
According to Arrhenius equation

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

When $E_a = 0, k = A$

287 **(b)**
Rate constant is nearly doubled for each 10°C rise in temperature. Also $K = e^{-E_a/RT}$.

288 **(a)**
Self explanatory

289 **(a)**
Self explanatory

290 **(b)**
The change in the concentrations of all the reactants and products can be expressed as

$$\frac{-d[I_2]}{dt} = -\frac{1}{2}\frac{d[S_2O_3^{2-}]}{dt} = \frac{d[S_4O_6^{2-}]}{dt} = \frac{1}{2}\frac{d[I^-]}{dt}$$

292 **(c)**
For reactions carried out in solution, changing the solvent will generally change the rate of a reaction. The rate of reaction will change, when some alcohol is added

293 **(a)**
Hydrolysis of ester in the presence of acid is

pseudo first order reaction

294 **(c)**
Explanation is correct reason for statement.

295 **(b)**
$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{X}^* \rightarrow$ Products

The activated complex X^* ahs higher energy than reactants. It is a special molecule which decomposes such that one vibrational degree of freedom is converted into a translational degree of freedom along the reaction coordinate

296 **(c)**
An elementary reaction is one step reaction and in such reactions order of reaction and molecularity are same. Note that molecularity can never be fractional.

297 **(c)**
Explanation is correct reason for statement.

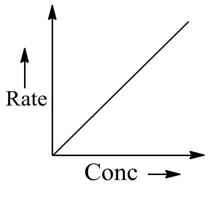
298 **(d)**
Hydrolysis of ester is pseudo first order reaction

300 **(b)**
Self explanatory

301 **(a)**
For first order reaction, $A \rightarrow$ products

Rate law equation is Rate $= k[A]$

The plot of rate *vs* concentration for first order reaction is given as



302 **(c)**
Catalyst does not alter the value of ΔG

303 **(c)**
The rate of reaction depends upon the concentration of reactants

304 **(b)**
Rate of reaction $= k[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}$

$\therefore$ Order of reaction $= a + b$

305 **(c)**
Chemiluminesence refers for emission of light as a result of chemical change.

306 **(b)**
Self explanatory

307 **(d)**
Both statement and explanation are correct.

308 **(c)**
Chlorophyll acts as photosensitizer. Neither $\mathrm{CO_2}$ nor $\mathrm{H_2O}$ absorbs light.

309 **(c)**
$K = Ae^{-Ea/RT}$ if $E_a = 0$ then $K = A$

310 **(c)**
The rate reaction is represented by $k[\mathrm{RCl}][\mathrm{NaOH}]$, i.e., it is a second order reaction

311 **(a)**
Increase in collision frequency also causes a decrease in mean free path and an increase in number of effective collisions. The collision frequency increases as the temperature is increased

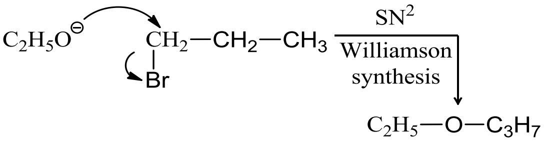
312 **(b)**
For zero order reaction, the rate of reaction does not depend upon the concentration

313 **(c)**
Explanation is correct reason for statement.

314 **(a)**
Self explanatory

315 **(c)**
(**a**→**a**)Inversion of cane sugar is pseudo first order reaction
(**b**→**c,d**)Hydrolysis of ester in the presence of acid is first order while in the pressure of base is second order reaction
(**c**→**b**) Photochemical reactions are of zero order
(**d**→**c**) SN^2 reactions are of second order

320 **(b)**
(a)is pseudo-unimolecular reaction, i.e., first order and biomolecular, and hence answer is (a, b, d)
(**b** → **a**)



It is SN^2 reaction, hence biomolecular and second order

Hence, answer is (p)

(**c** → **c**, **d**)

It proceeds via carbocation intermediate formation, hence proceeds via SN^1 reaction, so unimolecular and first order. Thus, answer is (c, d)

(**b** → **a**, **d**) Since slow step (RDS) involves two molecules, therefore, biomolecules. Rate $= k[O_3]^2[O_2]^{-1}$. Thus, order of reaction =1 and answer is (a, d)

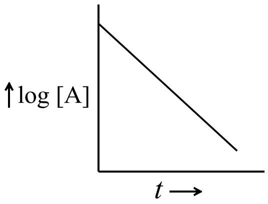
321 **(d)**

For first order reaction $= \frac{d[A]}{dt}$

$= -k[A]$

or $[A] = [A]_0 e^{-kt}$

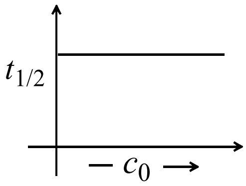
or In $[A] =$ In $[A]_0 - kt$



324 **(a)**

(**a**→**b**) First order reaction

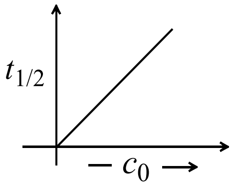
$t_{3/4} = 2t_{1/2}$



(**b**→**a, d, e**)

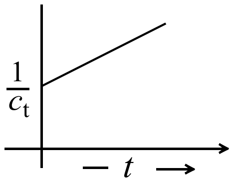
$t_{1/2} \propto c_0 \Rightarrow$ Zero order reaction

$\Rightarrow t_\infty = 2t_{1/2}$, rate is constant with time



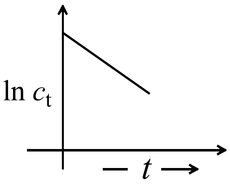
(**c**→**d**) Second order reaction

$t_{1/2} \propto c_0^{-1}$



(**d**→**a, c, e**)

First order reaction



326 **(a)**

(**a** →**q**) Zero order reaction does not depend upon the concentration of reactants

(**b**→**a**) Rate $= k[A]^1[B]^1$, i.e., order $= 1 + 1 = 2$

(**c**→**a**) Rate $= k[A]^{3/2}[B]^{1/2}$, i.e., order $= \frac{3}{2} + \frac{1}{2} = \frac{4}{2} = 2$

(**d**→**c,d**) When [A] is in excess, $[A] = 0$, OR $= 1$

When [B] is in excess, $[B] = 0$, OR $= 2$

327 **(c)**

All factual statement

328 **(c)**

(**a**→**d**)Decomposition of H_2O_2 is a first order reaction

(**b**→**b**)Temperature coefficient is generally 2~3

(**c**→**c**) $\frac{k}{A}$ =fraction of collisions which are effective

(**d**→**a**) $t_{99.9\%} = 10\ t_{1/2}$

329 **(a)**

(**a** → **a**)

(a)is a second order reaction

(p)is Arrhenius equation valid for all order reactions

(**b** → **a**, **c**, **d**)

(b)is a first order reaction

(p)is Arrhenius equation valid for first order also

(r) Graph (r) is exponentially decrease of rate with time. So, it is of first order

(s)$t_{1/2} = x$ min, i.e., $t_{1/2}$ for first order is constant at any time and at any temperature because $t_{1/2}$ is independent of a (initial concentration of reactant)

(**c** → **a**, **b**)

(c) is a zero order reaction

(p)Arrhenius equation is valid for zero order also

(q)Graph (q) is a graph for zero order reaction

(**d** → **a**, **c**, **d**)

(d)is a first order reaction

(p)Arrhenius equation is valid for first order also

(r)Graph (r) is of first order

(s)Statement is of first order

331 **(b)**

(**a** →**c**)Activation energy for forward reaction $= 50 - 20 = 30$ kJ mol^{-1}

(**b**→**b**)Activation energy for backward reaction

$= 50 - 10 = 40 \text{ kJ mol}^{-1}$

(**c**→**a**) $\Delta_t H = \Delta_P H - \Delta_R H = 10 - 20 = -10 \text{ kJ mol}^{-1}$

(**d**→**d**) $E_{\text{threshold}} = 50 \text{ kJ mol}^{-1}$

333 **(b)**

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

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\frac{100}{100-75}$$

$\therefore t_{1/2} = 16$ min

334 **(a)**

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C$$

$$k_c = \frac{k_f}{k_b} = \frac{[C]}{[A]} = \frac{0.4}{0.6}$$

For $2C \rightleftharpoons 2A$

$$k_c = \left(\frac{1}{k_c}\right)^2 = \left(\frac{1}{2/3}\right)^2 = \frac{9}{4}$$

335 **(a)**

$$\frac{k_{325}}{k_{335}} = \frac{Ae^{-E_a/R\times 325}}{Ae^{E_a/R\times 335}}$$

or $\frac{3.2\times10^{8}\text{ s}^{-1}}{k_{335}} = \frac{e^{-0/R\times325}}{e^{-0/R\times335}}$ or $e^0 = 1$

$\therefore\ k_{335} = 3.2 \times 10^{-8}\text{s}^{-1}$

336 **(b)**

$\log k = \log A - E_a/2.303\ RT$

$\therefore \log A = 14\ \Rightarrow A = 10^{14}\text{s}^{-1}$

337 **(a)**

Concentration of the product has been given:

$$\left(\frac{d[\text{C}]}{dt}\right)_{\text{I}} = \frac{0.0033}{25} = 1.32 \times 10^{4}\text{ M min}^{-1}$$

$$\left(\frac{d[\text{C}]}{dt}\right)_{\text{II}} = 2.6 \times 10^{-4}\text{ M min}^{-1}$$

$$\left(\frac{d[\text{C}]}{dt}\right)_{\text{III}} = 1.02 \times 10^{-3}\text{ M min}^{-1}$$

338 **(a)**

All factual statements

340 **(c)**

Comparing the rate law, the order w.r.t. $CH_3Cl = 1$ and w.r.t. $H_2O = 2$

$\therefore\ r = [CH_3Cl][H_2O]^2$

341 **(a)**

For the given reaction:

$$\frac{1}{3}\frac{-d[\text{BrO}^{\ominus}]}{dt} = \frac{d[\text{BrO}_3{}^{\ominus}]}{dt} = \frac{1}{2}\frac{d[\text{Br}]}{dt}$$

Since rate ∝ rate constant

$$\therefore\ \frac{d[\text{BrO}_3{}^{\ominus}]}{dt} = \frac{1}{3}\times 0.054 = 0.018\text{ L mol}^{-1}\text{s}^{-1}$$

342 **(a)**

$k_1 = Ae^{-E_f/RT};\ k_b = Ae^{-E_b/RT}$

$$\therefore k = \frac{k_f}{k_b} = \frac{Ae^{-E_f/RT}}{Ae^{-E_b/RT}} = e^{(E_b - E_f)RT}$$

or $\log k = \frac{E_b - E_f}{2.303\ RT}$

$$= \frac{33000\text{ J mol}^{-1}}{2.303 \times 8.314\text{ J K}^{-1}\text{mol}^{-1} \times 300\text{ K}} = 5.745$$

$\therefore k = \text{Antilog}\ (5.745) = 5.55 \times 10^5$

343 **(b)**

At 2°C (275 K), the reaction is three times slower than at 27°C (300 K). This implies that for souring of milk

$\frac{k_{300}}{k_{275}} = 3, T_1 = 275\text{ K}, T_2 = 300\text{ K}$

Applying Arrhenius equation

$$\log\frac{k_{300}}{k_{275}} = \frac{E_a}{2.303\ R}\left(\frac{T_2 - T_1}{T_2 T_1}\right)$$

$$\log 3 = \frac{E_a}{2.303 \times 8.314}\left(\frac{300 - 275}{275 \times 300}\right)$$

Or $E_a = 30.146\text{ kJ mol}^{-1}$

344 **(b)**

$\Delta H = E_f - E_b$

$= -30 = 249 + E_b$

$\therefore\ \Delta H = E_f - E_b$

$\therefore\ E_b = 249 + 30 = 279\text{ kJ mol}^{-1}$

345 **(a)**

For zero order reaction

$$\frac{dx}{dt} = k[\text{A}]^0 = k$$

∴ Unit of rate = mol $\text{L}^{-1}\text{time}^{-1}$

Unit of rate constant = mol $\text{L}^{-1}\text{time}^{-1}$

346 **(b)**

Since C is taken in excess, so its concentration does not change. So it is not taken in rate expression of the reaction

347 **(b)**

In experiment I and II, [X] becomes double and rate is also doubled. Thus, it is first order reaction

$r = k_f[\text{X}]$

$0.05\text{ mol L}^{-1}\text{hr}^{-1} = k_f \times 0.17\text{ mol L}^{-1}$

$\therefore k_f = 0.294\text{ hr}^{-1}$

348 **(b)**

Rate of overall reaction = Rate of step II

$$\left(+\frac{d[N_2O]}{dt}\right) = k_{\text{II}}[A_2X_2][B_2]$$

From equilibrium step, i.e., step I:

$k_c = \frac{[A_2X_2]}{[AX]^2}$, k_c = equilibrium constant of step I

$[A_2X_2] = k_c[AX]^2$

Thus, rate of overall reaction

$= k_{II}k_c[AX]^2[B_2]$

(k_{II} = rate constant of formation of A_2X)

$= k[AX]^2[B_2]$

k = Rate constant of overall reaction

Since for rate of A_2X consumed, 2 mol of B_2 are formed so rate constant for the consumption of B_2 will twice that of overall rate constant, i.e., $2k_{II}k_c$

$= 2 \times 3 \times 10^{-2} \times 2 \times 10^{-3}$

$= 1.2 \times 10^{-4}\ \text{mol}^{-2}\ \text{L}^2\text{min}^{-1}$

349 **(b)**

Factual statement for order reaction

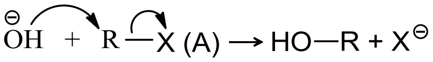
350 **(b)**

SN^1 reaction

$$\text{RX(A)} \longrightarrow \text{R}^{\oplus} + \text{X}^{\ominus} \xrightarrow{\overset{\ominus}{\text{OH}}} \text{R—OH}$$

Rate$= \frac{-d[A]}{dt} = k_1[RX]$ ...(i)

SN^2 reaction



$$\text{Rate} = \frac{-d[A]}{dt} = k_2[RX]\,[\overset{\ominus}{OH}] \qquad ...(ii)$$

Rate $= \frac{-d[A]}{dt} = k_2[RX][\overset{\ominus}{OH}]$ ...(ii)

Combining equations (i) and (ii),

Rate $= \frac{-d[A]}{dt} = k_1[RX] + k_2[RX][\overset{\ominus}{OH}]$

Or

$$\frac{-d[A]}{dt} = k_1[A] + k_2[A][B]$$

$\frac{-d[A]}{dt} = [A][k_1 + k_2[B]]$ ...(iii)

$\frac{1}{A} \times \frac{-d[A]}{dt} = k_1 + k_2[B]$ ...(iv)

$\begin{bmatrix} y = c + mx \\ \text{equation of stright line} \end{bmatrix}$

$\therefore$ Slope$(m) = k_2 = 2.7 \times 10^{-4}\ \text{L mol}^{-1}\text{min}^{-1}$

$= 0.27 \times 10^{-3}\ \text{L mol}^{-1}\text{min}^{-1}$

Intercept $(c) = k_1 = 1.02 \times 10^{-3}\ \text{L mol}^{-1}\text{min}^{-1}$

Overall rate constant $= k_1 + k_2$

$= (0.27 + 1.02) \times 10^{-3}$

$= 1.29 \times 10^{-3}\ \text{L mol}^{-1}\text{min}^{-1}$

351 **(d)**

$k_{eq} = \frac{k_1\,[A^*][A]}{[A]^2}$ ...(i)

$\frac{-d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*]$ ...(ii)

Since A^* is activated molecules of reactant, applying steady state approximately for $[A^*]$ i.e., $\frac{-d[A]}{dt} = 0$ in equation (ii), we get

$k_1[A]^2k_{-1} - k_{-1}[A^*][A] - k_2[A^*] = 0$

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

352 **(a)**

The rate of reaction is decided by the slowest step (I order) of reaction.

353 **(2)**

0.4 M of A $\xrightarrow{30\text{ min}}$ 0.2 M $\xrightarrow{30\text{ min}}$ 0.1 M (for A)

0.4 M of B $\xrightarrow{20\text{ min}}$ 0.2 M $\xrightarrow{20\text{ min}}$ 0.1 M $\xrightarrow{20\text{ min}}$ 0.05 (for B)

$\left(\frac{-d[B]}{dt}\text{ will be doubled and hence } t_{1/2} \text{ will be halved}\right)$

$\therefore \frac{[A]}{[B]} = 2$

357 **(5)**

For second order:

$k_2 = \frac{1}{t}\cdot\frac{x}{a(a-x)}$ [Let $a = 1$]

$= \frac{1}{30\text{ s}} \times \frac{0.6}{1(1-0.6)} = \frac{1}{30} \times \frac{0.6}{0.4}$

Now for 20% completion

$k_2 = \frac{1}{t}\cdot\frac{x}{a(1-x)}$

(Since k_2 is constant)

$\frac{1}{30} \times \frac{0.6}{0.4} = \frac{1}{t} \times \frac{1}{4}$

$t = \frac{30}{0.6} \times \frac{0.4}{4} = 5\text{s}$

358 **(5)**

For second order reaction:

$[R]_{\text{initial}} = 0.08$ M; $[R]_{\text{final}} = 0.01$ M

$x = 0.08 - 0.01 = 0.07$ M

$\therefore (a - x) = 0.08 - 0.07 = 0.01$ M

$k_2 = \frac{1}{t}.\frac{x}{a(a-x)}$

$= \frac{1}{70\text{ min}} \times \frac{0.07\text{ M}}{0.08\text{ M} \times 0.01\text{ M}}$ ...(i)

Now, time required to become concentration $=0.04$ M

i.e., $x = 0.04$ M

$k_2 = \frac{1}{t} \times \frac{0.04\text{ M}}{0.08\text{ M}\times(0.08-0.04)\text{M}}$ ...(ii)

From equations (i) and (ii)

$$\frac{0.07}{70 \times 0.08 \times 0.01} = \frac{0.04}{t \times 0.08 \times 0.04}$$

$t = 10$ min $= 2x$ min

$\therefore x = 5$ min

359 **(9)**

$$k=\frac{0.693}{15\text{ hr}}=0.0462\text{ hr}^{-1}$$

$$k=\frac{2.3}{14\times 24\text{ hr}}\log\frac{c_0}{c_t}$$

$$0.0462\text{ hr}^{-1}=\frac{2.3}{14\times 24\text{ hr}}\log\frac{1\text{ Ci}}{c_t}$$

Solve for c_t:

$\therefore c_t=1.82\times10^{-7}\text{ Ci}\approx0.18\ \mu\text{Ci}=0.02x\ \mu\text{Ci}$

$\therefore x=9$

361 **(3)**

Let $a=100, (a-x)=80$ (Amount left)

$\therefore$ Amount left $=\frac{a}{(2)^n}$ [$n=$number of half lives]

$$80=\frac{100}{(2)^n}\Rightarrow(2)^n=\frac{10}{8}$$

$\therefore\ n\log2=\log10-3\log2=1-3\times0.3=0.1$

$$n=\frac{0.1}{\log2}=\frac{0.1}{0.3}=\frac{1}{3}$$

$$n=\frac{1}{3}=\frac{t\begin{pmatrix}\text{Time for 80\% amount}\\\text{left or 20\% decomposed}\end{pmatrix}}{\begin{pmatrix}\text{Time for 50\% amount}\\\text{left or decomposed}\end{pmatrix}}\Rightarrow t_{1/2}=3t$$

Alternatively

$$\frac{t_{30\%(\text{left})}}{t_{1/2(\text{left})}}=\frac{\log\left(\frac{100}{80}\right)}{0.3}=\frac{1}{3}$$

$t_{1/2}=3t_{80\%(\text{left})}=3t$

362 **(0)**

Reaction between NO_2 and CO

$NO_2(g)+CO(g)\longrightarrow NO(g)+CO_2(g)$

The experimental observations reveal that the rate of reaction is proportional to the square of the concentration of nitrogen peroxide. This indicates that the rate-determining step in the mechanism of this reaction must be independent of the concentration of CO. keeping this in mind, a mechanism of the reaction may be suggested as:

$$\begin{array}{lll}\text{Step 1} & NO_2+NO_2\longrightarrow NO+NO_3 & \text{(Slow)}\\ \text{Step 2} & NO_3+CO\longrightarrow CO_2+NO_2 & \text{(Fast)}\\ \hline & NO_2+CO\longrightarrow CO_2+NO & \text{(Net reaction)}\end{array}$$

Although the above reaction proceeds through two steps but the rate of overall reaction is determined by the first step which is the slower of the two steps. Accordingly, the experimentally observed rate of the reaction is given by the expression:

Rate $=k[NO_2]^2$

363 **(1)**

Rate$=k[a]^n$

Case I: $r_1=k\left[\frac{a}{V}\right]^n$ ...(i)

Case II: $\frac{r_1}{2}=k\left[\frac{a}{2V}\right]^n$ ...(ii)

By equations (i) and (ii),

$(2)^1=(2)^n$

$\therefore\ n=1$

366 **(0)**

All photochemical reactions have zero order of reaction

367 **(3)**

[A]	[B]	Time (min)
$4a$	a	0
$2a$	–	5 min
a	–	10 min
$a/2$	$a/2$	15 min

$\therefore 5x=15$ min

$x=3$ min

369 **(4)**

$$t_{1/2}=\frac{0.0693}{k_1}$$

Also, $t_{93.75}=\frac{2.303}{k_1}\log\frac{100}{100-93.75}$

$$=\frac{2.303}{k_1}\log\frac{100}{6.25}$$

$$=\frac{2.303}{k_1}\log2^4$$

$$=\frac{4\times2.303\times\log2}{k_1}=\frac{4\times0.693}{k_1}=4t_{1/2}$$

370 **(5)**

$\frac{-d[RX]}{dt}=k_2[RX][\overset{\ominus}{OH}]$ (by SN^2 path way)

$k_2=$ rate constant of SN^2 reaction

$\frac{-d[RX]}{dt}=k_1[RX]$ (by SN^1 path way)

$k_1=$ rate constant of SN^1 reaction

$$\frac{-d[RX]}{dt}=k_2[RX][\overset{\ominus}{OH}]+k_1[RX]$$

$$-\frac{1}{[RX]}\frac{d[RX]}{dt}=k_2[\overset{\ominus}{OH}]+k_1$$

This is the equation of a straight line for $-\frac{1}{[RX]}\frac{d[RX]}{dt}$ vs $[\overset{\ominus}{OH}]$ plot with slope equal to k_2 and intercept equal to k_1

from question:

$k_2=2\times10^3\text{ mol}^{-1}\text{L hr}^{-1}, k_1=1\times10^2\text{hr}^{-1}$

$[RX]=1.0$ M and $[\overset{\ominus}{OH}]=0.1$ M

Hence,

$$\frac{-d[RX]}{dt}=2\times10^3\times1\times0.1+1\times10^2\times1$$

$=300\text{ mol L}^{-1}\text{hr}^{-1}$

$=5\text{ mol L}^{-1}\text{min}^{-1}$

372 **(0)**

$$t_{1/2} \propto \frac{1}{a_0^{n-1}}$$

$$t_{1/2} = k.\frac{1}{a_0^{n-1}}$$

$\log t_{1/2} = \log k - (n-1)\log a_0$ $[y = c + mx]$

$\tan 45° = -(n-1) = -(0-1)$

$\tan 45° = 1$

$\therefore n = 0$

373 **(4)**

Statement (a) and (c) are correct. So total score is $3 + 1 = 4$

376 **(2)**

Rate $(r) = k[\mathrm{A}]^n = k(\mathrm{X})^n$ ...(i)

$6.25 \times r = k(2.5\mathrm{X})^n$ ...(ii)

Or $6.25 \times k \times (\mathrm{X})^n = k(2.5 \times \mathrm{X})^n$

$$\Rightarrow \left(\frac{2.5\,X}{X}\right)^n = 6.25 \Rightarrow (2.5)^n = (2.5)^2$$

$\therefore n = 2$

379 **(2)**

Amount remaining after n half lives is

$= \frac{N_0}{2^n}$ (N_0 =initial amount)

$$= \frac{32}{(2)^4} = 2\text{g}$$

$$\left[n = \text{number of half lives} = \frac{160}{40} = 4\right]$$