CLASS XII

NAME OF THE BOOK NCERT Part 1

NAME OF THE CHAPTER Chemical Kinetics

CHAPTER NO. 3

Q. No. Marks Type Level Question

1. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $k = Ae^{-Ea/RT}$. Activation energy (Ea) of the reaction can be calculated by plotting

(a) k vs T (b) k vs 1/ logT (c) log k vs 1/ T (d) log k vs 1/ log T

Ans. C

2. Which of the following will affect the rate at which a candle burns?

a)Shape of the candle.

b) Length of the wick.

c) The temperature of air.

d)Air pressure.

Ans. C

3 For a first order reaction with half-life of 150 s, the time taken for the concentration of the reactant to fall from M/10 to M/100 will be approximately

(a) 1500 s (b) 498 s (c) 900 s (d) 598 s

Ans. B

4 A catalyst

(1) increases the average kinetic energy of reacting molecules.

(2) increases the activation energy.

(3) alters the reaction mechanism.

(4) increases the frequency of collisions of reacting species.

Ans. C

5 For a hypothetical reaction $A + B \rightarrow C + D$, the rate = $k[A]^{1/2}[B]^{3/2}$. On doubling the concentration of A and B the rate will be

(a) 4 times. (b) 2 times. (c) 3 times. (d) 6 times

Ans. A

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

(a) positive slope and zero intercept.

(b) negative slope and zero intercept.

(c) positive slope and non-zero intercept.

(d) negative slope and non-zero intercept

Ans. D

7 The rate of the reaction $2NO + Cl_2 \rightarrow 2NOCl$ is given by the rate equation rate = $k[NO]^2 [Cl_2]$ the value of rate constant can be increased by

(a) increasing the concentration of NO.

(b) increasing the concentration of the Cl_2 .

(c) increasing the temperature.

(d) doing all of these.

Ans. C

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

$-d[N_2O_5]/dt = k[N_2O_5]$; $d[NO_2]/dt = k'[N_2O_5]$; $d[O_2]/dt = k''[N_2O_5]$

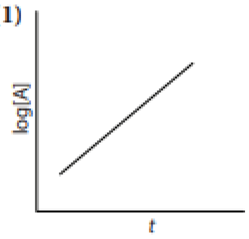
The relationships between k and k′ and between k and k″ are

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

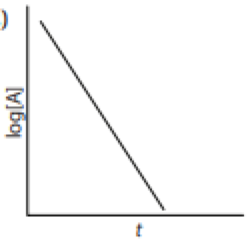
Ans. C

9 For the following first order reaction A → Products, which one of the following is correct plot of log[A] versus time?

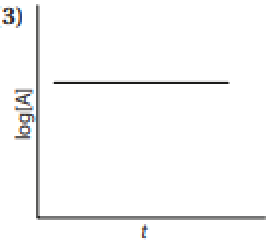
(1)



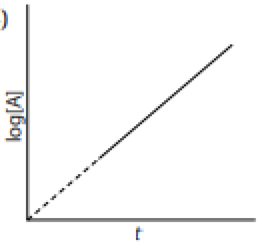
(2)



(3)



(4)



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

Ans. B

10 A reaction of first-order completed 90% in 90 min, hence, it is completed 50% in approximately

(a) 50 min. (b) 54 min. (c) 27 min. (d) 623 min.

Ans. C

11 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 reaction relative to the original rate would be

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

Ans. A

12 If 60% of a first order reaction was completed in 60 min, 50% of the same reaction would be completed in approximately

(a) 40 min (b) 50 min (c) 45 min (d) 60 min (log 4 = 0.60, log 5 = 0.69)

Ans. C

13 In a reaction 2A → Products; the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 min. The rate of the reaction during this interval is

(a) 0.05 M min^{-1} (b) 0.005 M min^{-1} (c) 0.5 M min^{-1} (d) 5 M min^{-1}

Ans. B

14 If concentration is measured in mol L^{-1} and time in minutes, the unit for the rate constant of n^{th} order reaction is

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

Ans. B

15 The reaction of high molecularity are rare because
(a) Many body collisions have a low probability.
(b) Many body collisions are not favoured energetically.
(c) Activation energy of many body collisions is very large
(d) Very high concentration is required for such reactions.

Ans. A

16. The half-life of a substance in a certain enzyme-catalyzed reaction is 138 s. The time required for the concentration of the substance to fall from 1.28 mg L^{-1} to 0.04 mg L^{-1}

(a) 276 s (b) 414 s (c) 552 s (d) 690 s

Ans. D

17 The decomposition of phosphine (PH_3) on tungsten at low pressure is a first order reaction. It is because the

(a) rate is inversely proportional to the surface coverage.

(b) rate is independent of the surface coverage.

(c) rate of decomposition is very slow.

(d) rate is proportional to the surface coverage.

Ans. D

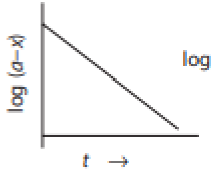
18 Half life period of a first order reaction is 10 min. What percentage of the reaction will be completed in 100 min?

(a) 25% (b) 50% (c) 99.9% (d) 75%

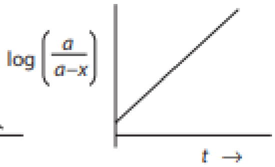
Ans. C

19 Which graph represents first-order reaction out of I, II and III?

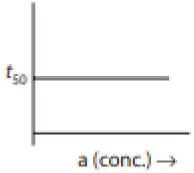
(I)



(II)



(III)

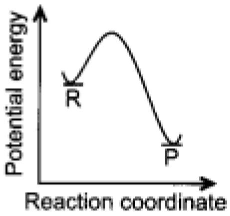


(a) I, II and III (b) I and II (c) II and III (d) I and III

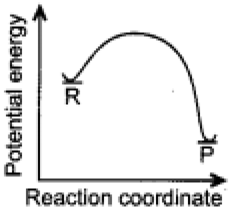
Ans. A

20 An endothermic reaction with high activation energy for the forward reaction is given by the diagram.

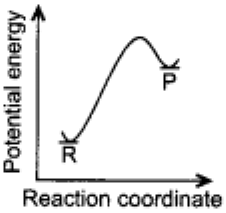
(*a*)



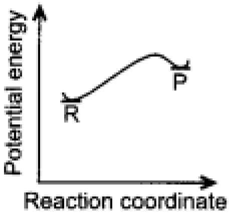
(*b*)



(*c*)



(*d*)



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

Ans. C

21 The reaction of hydrogen and iodine monochloride is given as

H_2 (g) + 2ICl(g)→HCl(g)+I_2 (g)

This reaction is of first order with respect to H_2(g) and ICl(g), the following mechanisms were proposed:

Mechanism A: H_2 (g)+2ICl (g) →HCl(g)+I_2 (g)

Mechanism B: H_2(g)+ ICl (g) → HCl(g)+HI(g); Slow

HI (g) + ICl (g) → HCl(g)+ I_2(g); Fast

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

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

Ans. B

22 For the reaction A + →B Products, it is observed that

(I) on doubling the initial concentration of A only, the rate of reaction is also doubled and (II) on doubling the initial concentration of both A and B, there is a change by a factor of 8 in the rate of the reaction

The rate of this reaction is given by

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

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

Ans. C

23 Half-lives of first order and zero order reaction are same. Ratio of rates at the start of reaction is

(a) 0.693 (b) 1/0.693 (c) 2 × 0.693 (d) 2/0.693

Ans. C

24 Mechanism of a hypothetical reaction X2 + Y2 → 2XY is given below:

(I) X2 → X + X (fast)

(II) X +Y2→ XY + Y (slow)

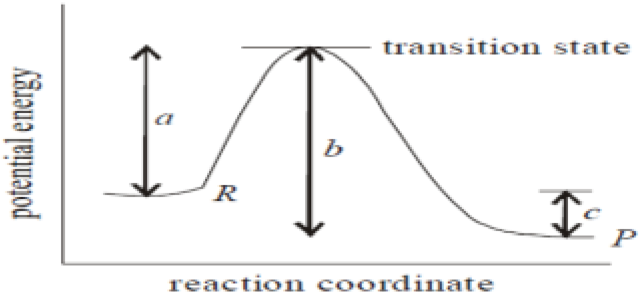
(III) X + Y → XY (fast)

The overall order of the reaction will be

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

Ans. C

25 The potential Energy diagram for a reaction , R → P is shown below



Enthalpy change of the reaction corresponds to ----

(a) a (b) c (c) a + b (d) b

Ans. B

26 In a first order reaction the a/ a− x was found to be 8 after 10 min. The rate constant is

a) (2 .303 3 log 2) /10 b) (2 .303 2 log 3) /10

c) 10 × 2.303 × 2 log 3 d) 10 × 2.303 × 3 log 2

Ans. A

27 For a reaction taking place in three steps,the overall rate constant is k = k1x k2/k3. If Ea_1, Ea_2 and Ea_3 are 40,50 and 60 kJ/mol the overall Ea is

(a) 30 kJ/mol (b) 40 kJ/mol (c) 60 kJ/mol (d) 50 kJ/mol

Ans. A

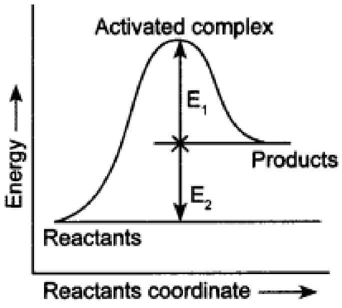
28 For the reaction, $N_2 + 3 H_2 \rightarrow 2NH_3$, if $d[NH_3]/dt = 4 \times 10^{-4}$ mol/ L/ s , the value of $-d[H_2]/dt$ would be

(a) 1×10^{-4} mol/L/s (b) 3×10^{-4} mol/L/s

(c) 4×10^{-4} mol/L/s (d)6×10^{-4} mol/L/s

Ans. D

29 Consider the Fig. and mark the correct option.



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

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

Ans. A

30 Which of the following statements are applicable to a balanced chemical equation of an elementary reaction?
(1) Order is same as molecularity.
(2) Order is less than the molecularity.
(3) Order is greater than the molecularity.
(4) Molecularity can never be zero.

a) 1 only b) 1 and 2 c) 1and 3 d) 1 and 4

Ans. D

Fill In The Blanks

31 Acid hydrolysis of an ester is an example of ………..

Ans. Pseudo first order reaction

32 The rate constant is equal to the rate of the reaction when concentration of reactants is ………..

Ans. unity

33 Molecularity of a chemical reaction will never be equal to ………..

Ans. Zero

34 When the concentration of reactant of first order reaction is oubled the rate becomes ………..times but for a …….. order reaction,the rate of reaction remains the same

Ans. 2 times,zero order

35 All radioactive disentegration reactions follow ……….. kinetics.

Ans. First order

36 The sum of powers of concentration terms involved in the experimentally determined rate law is called ……….. of a reaction

Ans. order

37 The total number of reactant species involved in an elementary step is called ………..

Ans. Molecularity

38. For a complex reaction order is given by the ………….. step of the reaction.

Ans. slowest

39 In the presence of a catalyst, the heat evolved or absorbed during the reaction………….

Ans. unchanged

40 In the graph showing Maxwell Boltzman distribution of energy, with increase in temperature curve broadens and shifts to the ……………side.

Ans. right hand/product

Assertion Reason

Note: In the following questions(41 to 50) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Both assertion and reason are correct and the reason is correct explanation of assertion.

(b) Both assertion and reason are correct but reason does not explain assertion.

(c) Assertion is correct but reason is incorrect.

(d) Assertion is incorrect but reason is correct

(e) Both assertion and reason are incorrect.

41 Assertion : Order of the reaction can be zero or fractional.

Reason : We cannot determine order from balanced chemical equation.

Ans. B

42 Assertion : All collision of reactant molecules lead to product formation.

Reason : Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

Ans. D

43 Assertion : Order and molecularity are same.

Reason : Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step.

Ans. D

44 Assertion : The enthalpy of reaction remains constant in the presence of a catalyst.

Reason : A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy but the difference in energy of reactant and product remains the same.

Ans. A

45 Assertion (A): The molecularity of the following reaction is 2. $H_2 + Br_2 \rightarrow 2HBr$
Reason (R): The order of reaction is 3/2.

Ans. C

46 Assertion : Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.

Reason : Reactant molecules undergo chemical change irrespective of their orientation during collision

Ans. C

47 Assertion : Rate constant of a zero order reaction has the same units as rate of reaction.

Reason : : Rate constant of a zero order reaction does not depend on the unit of concentration .

Ans. C

48 Assertion:Half life period is always independent of initial concentration.

Reason: Half life period is inversely proportional to rate constant.

Ans. D

49 Assertion:If the activation energy of the reaction is zero, temperature will have no effect on the rate constant.

Reason:Lower the activation energy faster is the reaction.

Ans. B

50 Assertion: The reaction X→ Y follows second order kinetics.If concentration of X is increased 3 times rate becomes 3 times.

Reason:The rate of reaction is directly proportional to concentration of reactants.

Ans. D

Short Answer Type I

51 **For first order reaction – A $\rightarrow$ B Write**
(1) Differential rate law.
(2) Integrated rate law.

Ans. For the reaction A $\rightarrow$ B, if the order =1

(i) Differential rate law is $\frac{-d[A]}{dt} = K[A]$

(ii) Integrated rate law is $t = \frac{2.303}{K}\log\frac{[R]}{[R]^2}$

52 **Define the terms – i) Order of a reaction**
ii) Molecularity of a reaction.

Ans. i) <u>Order of a reaction.</u>
The sum of powers of the concentration of the reactants in the rate law expression is called order of that reaction.
ii) <u>Molecularity of a reaction.</u>
The number of reacting species which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

53 **Differentiate between order and molecularity of a reaction?(2 points)**

Ans.

ORDER OF A REACTION	MOLECULARITY OF A REACTION
It is sum of the concentration terms on which the rate of reaction actually depends or it is the sum of the exponents of the concentrations in the rate law equation.	It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.

It need not be a whole number i.e. it can be fractional as well as zero.	It is always a whole number.
It can be determined experimentally only and cannot be calculated.	It can be calculated by simply adding the molecules of the slowest step.
It is for the overall reaction and no separate steps are written to obtain it.	The overall molecularity of a complex reaction has no significance. It is only slowest step whose molecularity has significance for the overall reaction.
Even the order of a simple reaction may not be equal to the number of molecules of the reactants as seen from the unbalance equation.	For simple reactions, the molecularity can usually be obtained from the Stoichiometry of the equation.

54 For a reaction: $H_2 + Cl_2 \longrightarrow 2HCl$

Rate = k

(i) Write the order and molecularity of this reaction.

(ii) Write the unit of k.

Ans. i) This reaction is zero order reaction and molecularity is two.

(ii) Unit of k = mol L^{-1} s^{-1}

55 How does a change in temperature affect the rate constant, of a reaction? How can this effect on the rate constant of a reaction be represented quantitatively?

Ans. The rate constant of a reaction increases with increase of temperature and becomes nearly double for every 10° rise in temperature.

The effect can be represented quantitatively by Arhenius equation $K = Ae^{-Ea/RT}$

Where [Ea = Activation energy of the reaction; A = Frequency factor]

56 For a reaction A + B → P, the rate is given by Rate = $k[A]\,[B]^2$

(i) How is the rate of reaction affected if the concentration of B is doubled?

(ii) What is the overall order of reaction if A is present in large excess?

Ans. For the reaction A + B → P rate is given

by Rate = $k[A]^1[B]^2$

(i) $r_1 = k[A]1\ [B]2$

$r_2 = k[\ A]^1[2B]^2 =$

$r_2 = k[A]^1\ [2B]^2 = 4k[A]^1\ [B]^2$

$r_1 = 4r_2$, rate will increase four times of actual rate.

(ii) When A is present in large amount, order w.r.t. A is zero.

Hence overall order = 0 + 2 = 2, second order reaction.

57 A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction.
(log 2 = 0.3010)

Ans. $t_{\frac{1}{2}} = 30$ minutes

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

$$\Rightarrow 30 \text{ minutes} = \frac{0.693}{k}$$

$$\Rightarrow k = \frac{0.693}{30}$$

$$\Rightarrow k = 0.0231 \text{ min}^{-1}$$

58 **For the chemical decomposition of** SO_2Cl_2**, its initial concentration is 0.8420 mol/L and final concentration is** 0.215 mol/L **in 2 hours. What is the average rate of this reaction?**

Ans. Rate of reaction = $\frac{\text{change in concentration}}{\text{time interval}}$

$= \frac{(0.8420 - 0.2105)mol/L}{2\text{Hr}}$

$= \frac{0.6315}{2}$

= 0.3158 mol/L/Hr.

59 **For the reaction** $2O_{3(g)} \rightleftarrows 3O_2, -\frac{\Delta[O_3]}{\Delta t}$ **was found to be 5.0 ×10^{-1} at m/s .**

Determine the value of $\frac{\Delta[O_3]}{\Delta t}$ **in atm /s during this period of time?**

Ans. From the equation

$$2O_{3(g)} \rightleftharpoons 3O_{2(g)}$$

$$-\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$$

$$\frac{\Delta[O_2]}{\Delta t} = \frac{-3}{2}\frac{\Delta[O_3]}{\Delta t}$$

$$= \frac{-3}{2}\times(-5.0)\times10^{-4}atms^{-1}$$

$$= 7.5\times10^{-4}atms^{-1}$$

60 For a first order reaction, show that time required for 99% completion is twice the time required for completion of 90% reaction.

Ans. For a first order reaction, the time required for 99% completion is

t_1 = 2.303/k Log 100/100-99
= 2.303/k Log 100
= 2x 2.303/k
For a first order reaction, the time required for 90% completion is

t_2 = 2.303/k Log 100/100-90
= 2.303/k Log 10
= 2.303/k
Therefore, $t_1 = 2t_2$
Hence, the time required for 99% completion of a first order reaction is twice the time required for the completion of 90% of the reaction.

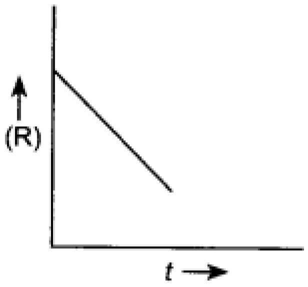
61 **Find the half-life of the first-order reaction which has a rate constant**

$k = 5.5 \times 10^{-14}\ s^{-1}$.

Ans. $t_{1/2} = 0.693/k = 0.693/5.5\times10^{-14}$

$= 1.26 \times 10^{13}$ s

62 **For a chemical reaction R → P, the variation in the concentration (R) vs t is as follows**



(i) Predict the order of the reaction.
(ii) What is the slope of the curve?

Ans. a)Zero order reaction
(b) slope = -k

63 a) Explain why H_2 and O_2 do not react at room temperature.
(b) Write the rate equation for the reaction $A_2 + 3B_2 \rightarrow 2C$, if the overall order of the reaction is zero.

Ans. i) H_2 and O_2 do not react at room temperature because they do not have enough activation energy to overcome the exceptionally high activation energy barrier.
(ii) $A_2 + 3B_2 \rightarrow 2C$
Rate = (dx/dt) = $K[A]^0 [B]^0$ = K (rate constant)

64 (i) What is the order of the reaction whose rate constant has same units as the rate of reaction?
(ii) For a reaction $A + H_2O \rightarrow B$; Rate $\propto [A]$,
What is the order of this reaction?

Ans. (i) The reaction whose rate constant has same units as the rate of reaction, will have zero order of reaction.
(ii) The order of this reaction will be pseudo first order reaction as the rate of reaction depends only on concentration of A only.

65 A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is reduced to half? What is the unit of rate constant for such a reaction?

Ans. Rate = $K [A]^2 = Ka^2$
If [A] = 1/2a Rate = $K (a/2)^2 = 1/4\ Ka^2$
∴ Rate = 1/4th (one fourth of original rate)
The unit of rate constant is $L\ mol^{-1}\ s^{-1}$

66 In general, it is observed that the rate of a chemical reaction doubles with every 10 degree rise in temperature. If the generalization holds good for the reaction in the temperature range of 295 K to 305 K, what would be the value of activation energy for this reaction ?
[$R = 8.314\ J\ mol^{-1}\ K^{-1}$] (Log 2=0.3010)

Ans.
$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R} = \left[\frac{T_2 - T_1}{T_1 . T_2}\right]$$

$$\log 2 = \frac{E_a}{2.303 \times 8.315} = \left[\frac{305 - 295}{305 \times 295}\right]$$

$$0.3010 = \frac{E_a}{2.303 \times 8.315} \times \frac{305 \times 295}{10}$$

Ea = 0.3010 x2.303 x 8.314 x 305 x 295/10

Ea =51855.19 J/mol

67 Derive an expression to calculate time required for completion of zero order reaction.

Ans.For a zero order reaction, R = [R]0 – kt

For completion of the reaction [R] =0 ∴ kt = [R]0

Or t = [R]0/ k

68 Derive an expression for half life period of first order reaction.

Ans. For a first order reaction, k = 2.303/ t log[R]0/ [R] When t = $t_{1/2}$, [R] = [R]0/2

Substituting these values in the above equation k = 2.303/ $t_{1/2}$ log [R]0/ [R]0/2

Or, $t_{1/2}$ = 2.303/k log 2 = 2.303/k x 0.3010 Or, $t_{1/2}$ = 0.693/ k

Thus for a first order reaction, half-life period is independent of initial concentration of the reacting species.

69 (a) Express the rate of the following reaction in terms of reactants and products: $2HI \rightarrow H_2 + I_2$

(b) If the rate expression for the above reaction is rate = $k[HI]^2$, what is the order and molecularity of the reaction?

Ans. a) $r_{av.} = -\frac{1}{2}\,\Delta[HI]/\Delta t = \Delta[H_2]/\Delta t = \Delta[I_2]/\Delta t$

b) Order =2, Molecularity = 2

70 Consider the pseudo order reaction, $CH3COOC_2H_5 + H_2O(H^+) \rightarrow CH_3COOH + C_2H_5OH$

(i) Identify the order and molecularity of the above reaction. (2) (ii) Give the rate law expression of the above reaction.

Ans. (i) Order = 1 and Molecularity = 2 (ii) r = k[$CH_3COOC_2H_5$]

Short Answer Type II

71 (i) Mention any two factors which influence the rate of a chemical reaction.

(ii) Define half life period of a reaction.

(iii) Write a relation which connects rate constant with temperature.

Ans. (i) Nature of reactants, Concentration of reactants, Temperature, Pressure, Effect of catalyst and influence of radiation [Any 2 factors are required].

(ii) It is the time taken to reduce the concentration of reactants to half of its initial concentration.

(iii) $k = A.e^{-Ea/RT}$ (The equation is known as Arrhenius equation)

72 (a) Define molecularity. (b) Give an example of pseudo first order reaction.

(c) Define activation energy (Ea)

Ans. (a) Molecularity of a reaction is the total number of reacting species which collide simultaneously in a chemical reaction.

(b) Hydrolysis of ester or inversion of cane sugar.

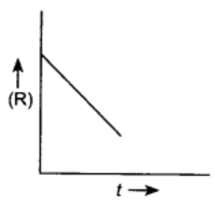
(c) It is the minimum amount of kinetic energy required for effective collision during a reaction.

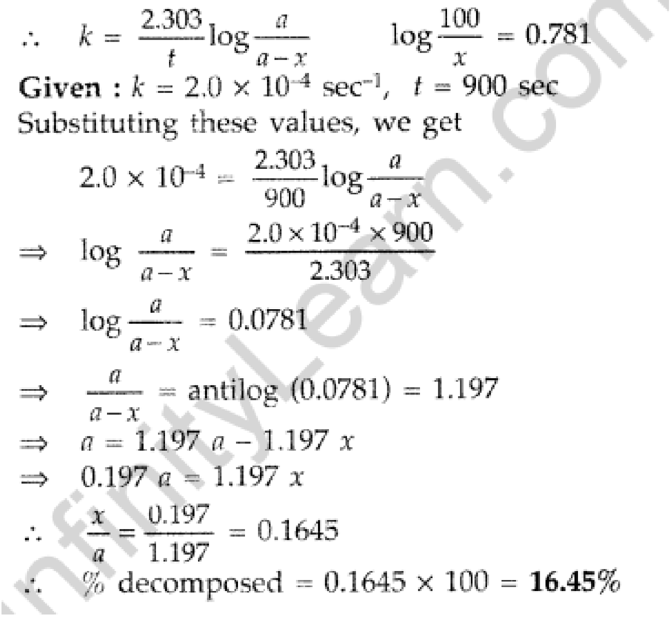
73 (a) Plot a graph showing variation in the concentration of reactants against time for a zero order reaction.

(b)Identify the order of reaction if the unit of rate constant is mol/ L/s .

(c) Write the unit of rate constant of a 2nd order reaction if concentration is in mol/ L and time in s.

Ans. a)





$\therefore \quad k = \frac{2.303}{t}\log\frac{a}{a-x} \qquad \log\frac{100}{x} = 0.781$

Given : $k = 2.0 \times 10^{-4}\ \text{sec}^{-1}$, $t = 900$ sec

Substituting these values, we get

$$2.0 \times 10^{-4} = \frac{2.303}{900}\log\frac{a}{a-x}$$

$$\Rightarrow \log\frac{a}{a-x} = \frac{2.0 \times 10^{-4} \times 900}{2.303}$$

$$\Rightarrow \log\frac{a}{a-x} = 0.0781$$

$$\Rightarrow \frac{a}{a-x} = \text{antilog}\ (0.0781) = 1.197$$

$$\Rightarrow a = 1.197\,a - 1.197\,x$$

$$\Rightarrow 0.197\,a = 1.197\,x$$

$$\therefore \frac{x}{a} = \frac{0.197}{1.197} = 0.1645$$

$\therefore$ % decomposed = 0.1645 × 100 = **16.45%**

b) Zero order

c) L/mol/s

74 a) Differentiate between average and instantaneous rate of reaction.

b)What is meant by Rate Constant of a reaction?

Ans. a) The average rate is the change in concentration of reactants or products over a selected/particular period of time. The instantaneous rate is the rate at a particular instant of time.

b)Rate constant: The rate of reaction when the molar concentration of each reactant is taken as unity.

75 a) Define rate law

b)Consider the decomposition reaction :2 H_2O_2 (OH^-/I^-)→$2H_2O + I^-$

This reaction takes place in two steps as given below :

Step 1. $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow) Step 2. $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$ (fast)

(1) Determine rate law expression. (2) Determine the order of reaction. (2)

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

b) . (1) Rate = $K[H_2O_2][I^-]$ (2) Order = 1 + 1 = 2

76 A first order gas phase reaction : $A_2B_2(g) \rightarrow 2A(g) + 2B(g)$ at the temperature 400°C has the rate constant $k = 2.0 \times 10^{-4}\ \text{sec}^{-1}$. What percentage of A_2B_2 is decomposed on heating for 900 seconds? (Antilog 0.0781 = 1.197)

Ans. Since the reaction is of the first order

77 The rate constant of a reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} respectively. Calculate the value of activation energy, E_n (R = 8.314 J K^{-1} mol^{-1}) (log 3.5= 0.544)

Ans. Given : k_2 = 0.07 s^{-1}, k_1, = 0.02 s^{-1}, T_1 = 500 K, T_2 = 700 K, E_a = ?

Using formula, $\log\frac{K_2}{K_1}=\frac{E_a}{2.303R}=\left[\frac{T_2-T_1}{T_1.T_2}\right]$

$$\log\frac{0.07}{0.02}=\frac{E_a}{2.303\times 8.314JK^{-1}mol^{-1}}=\left[\frac{700K-500K}{700K.500K}\right]$$

$$\log 3.5=\frac{E_a}{19.5}\times\left[\frac{200K}{350000K}\right]$$

$$\log 3.5=\frac{200E_a}{6702500}$$

$$0.544=\frac{2\times E_a}{67025}$$

$$E_a=18230.8J$$

78 For the first order thermal decomposition reaction, the following data were obtained:
$C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$

Time/sec	Total pressure/atm
0	0.30
300	0.50

Calculate the rate constant (Given: log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)

Ans. k =2.303/t log $p_0/2p_0 - p_t$

= 2.303/300 log 0.30/2x0.30 – 0.50

= 2.303/300 log 3 =2.303/300 x 0.4771

=1.099/300= 3.66 x 10^{-3}/s

79 For hydrolysis of methyl acetate in aqueous solution, the following results were observed

. t/s	0	30	60

CH_3COOH C/mol L-1	0.60	0.30	0.15

Show that it follows pseudo first order reaction as the concentration of water remains constant.

Ans. Here the concentration of water remains constant. So for being pseudo first order, the reaction should be first order with respect to the concentration of ester (i.e. methyl acetate).

The rate constant for pseudo first order reaction is: k= 2.303/ t log [R]0/ [R] where k = k'[H2O] Here [R]0 = 0.6 mol/L. When t = 30 s, [R] = 0.3 mol/L

So, k_1 = 2.303/30 log (0.6/0.3) = 0.0231/ s

When t = 60 s, [R] = 0.15 mol/L

So, k_2 = 2.303/60 log(0.6/0.15) = 0.0231/ s Since $k_1 = k_2$, it is a pseudo first order reaction.

80 The rate constant for the first order decomposition of H_2O_2 is given by the following equation:
log k = 14.2 – 1.0×10^4/T K
Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes.
(Given: R = 8.314 J K^{-1} mol^{-1})

Ans. Given: $t_{1/2}$ = 200 min E_a = ?, T = ?
Using Arrhenius equation

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

On comparing above equation with the given equation

$$\log k = 14.2 - \frac{1.0\times10^4}{T}K$$

$$\frac{E_a}{2.303RT} = \frac{1.0\times10^4}{T}K$$

$$E_a = 1.0\times10^4\times2.303\times8.314\left(Jmol^{-1}\right)$$

$$191471.42Jmol^{-1} = 191.471KJmol^{-1}$$

For First Order reaction

$$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{200\,\text{min}} = 0.0034\,\text{min}^{-1}$$

81 a) A reaction is first order in A and second order in B. Write the differential rate equation

b)The half-life for radioactive decay of $_{14}C$ is 5730 years. An archaeological artifact containing wood had only 80% of the $_{14}C$ found in a living tree. Estimate the age of the sample.(log 5=0.6989,log 4=0.6020)

Ans. a) The differential rate equation will be r = − d[R]/ dt = k[A][B]^2

b) We know radioactive decay reaction is the first order

Here, k = 0.693/ $t_{1/2}$ = 0.693/ 5730 years $^{-1}$

It is known that, t = 2.303/ k log [R]0/ [R] = 2.303/ 0.693/ 5730 log 100/ 80 = 1845 years

82 The decomposition of A into products has a value of K as 4.5 × 10^3/ s at 10°C and energy of activation 60 kJ/ mol. At what temperature would K be 1.5 × 10^4/ s ?

Ans. Using formula :

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{T_2-283}{283T_2}\right]$$

$$\log\frac{1.5\times10^4}{4.5\times10^3} = \frac{60000Jmol^{-1}}{2.303\times8.314JK^{-1}mol^{-1}}\left[\frac{T_2-283}{283T_2}\right]$$

$$\log 3.333 = 3133.63\left[\frac{T_2-283}{283T_2}\right]$$

$$\frac{0.5228}{3133.63} = \left[\frac{T_2-283}{283T_2}\right]$$

$$0.0472T_2 = T_2 - 283$$

$$0.9528T_2 = 283$$

$$T_2 = \frac{283}{0.9528} = 297K$$

$\therefore$ Temperature, T_2 will be = 297K – 273K = 24° C

83 What are the chief requirements that must be met by a plausible reaction mechanism? Why do we say "plausible" mechanism rather than "correct" mechanism?

Ans. A reaction mechanism must meet two criteria. 1) The sum of all of the steps in the mechanism must match the observed reaction, i.e., the stoichiometry of the reaction must be satisfied. 2) The reaction mechanism must account for the experimentally observed rate law.

Reaction mechanisms are considered "plausible" rather than "correct" because different sequences of elementary reactions may meet the two requirements.

84 A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed.
(Given: log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021)

Ans. $k = \frac{2.303}{t} \log \frac{A_0}{A}$

$= \frac{2.303}{20} \log \frac{100}{75}$

$= \frac{2.303}{20} \log 1.33$

$= \frac{2.303}{20} \times 0.1248$

$= 0.0143 \min^{-1}$

So for 75% completion of reaction

$k = \frac{2.302}{t} \log \frac{A_0}{A}$

$k = \frac{2.302}{t} \log \frac{100}{25}$

$k = \frac{2.302}{t} \log 4$

$$t = \frac{2.302}{0.0413} \times 0.6021 = 96.96 \text{ min}$$

85 Draw energy profile diagram between potential energy and reaction coordinate and show

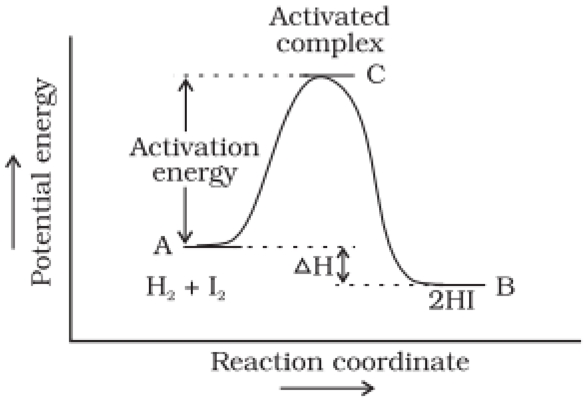
(i) Activated complex

(ii) Energy of activation for forward reaction

(iii) Energy of activation for backward reaction

(iv) Heat of reaction.

Ans.



Case Based

86 Read the passage given below and answer the following questions:

The rate of a reaction, which may also be called its velocity or speed, can be defined with relation to t.Draw the concentration of any of the reacting substances, or to that of any product of the reaction. If the species chosen is a reactant which has a concentration cat time t the rate is -dc/dt, while the rate with reference to a product having a concentration x at time t is dx/dt. Any concentration units may be used for expressing the rate; thus, if moles per litre are employed for concentration and seconds for the time, the units for the rate are moles litre-1sec-1. For gas reactions pressure units are sometimes used in place of concentrations, so that legitimate units for the rate would be(mm. Hg) sec-1 and atm.sec-1 The order of a reaction concerns the dependence of the rate upon the concentrations of reacting substances; thus, if the rate is found experimentally to be proportional to the αth power of the concentration of one of the reactants A, to the βth power of the concentration of a second reactant B, and so forth, via., rate = k $[A]^{\alpha}[B]^{\beta}$ (1)the over-all order of the reaction is = α + β (2) Such a reaction is said to be of the αth order with respect to the substance A, the β th order with respect to B and so on...

a)Define rate of a reaction.

b) For a reaction R → P, half-life (t1/2) is observed to be independent of the initial concentration of reactants. What is the order of reaction?

c) The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if k = 2.5 × 10−4mol $^{/}$L/s ?

Ans. a) The change in the concentration of any one of the reactants or products per unit time is called rate of a reaction.

b) The $t_{1/2}$ of a first order reaction is independent of initial concentration of reactants.

c) Rate of reaction = − 1/ 2 d[NH_3]/ dt = d[N_2]/ dt = 1/ 3 d[H_2] /dt = k = 2.5 × 10^{-4}mol/ L/ s Therefore, the rate of production of N2 is d[N2]/ dt = 2.5 × 10^{-4}mol/ L/s

And, the rate of production of H2 is d[H2]/dt = 3 d[N2]/ dt = 3 × 2.5 × 10^{-4}mol/ L/s = 7.5 × 10^{-4}mol/ L/s

OR

A reaction is of second order with respect to a reactant. How is its rate affected if the concentration of the reactant is (i) doubled (ii) reduced to half?

Ans: As Formula, $r = K[R|^2$ ...(Given)

(i) $R' = 2R \Rightarrow r = K[2R]^2 = 4KR^2$

∴ Rate becomes 4 times than original rate

$R'' = 1/2R \Rightarrow r = K[R/2]^2 = 1/\ 4KR^2$

∴ Rate becomes1/ 4 times than original rate

87 Read the passage given below and answer the following questions:

The Arrhenius equation is a formula for the temperature dependence of reaction rates. This equation has a vast and important application in determining the rate of chemical reactions and for calculation of energy of activation. Arrhenius provided a physical justification and interpretation for the formula. Arrhenius argued that for reactants to transform into products, they must first acquire a minimum amount of energy, called the activation energy Ea. At an absolute temperature T, the fraction of molecules that have a kinetic energy greater than Ea can be calculated from statistical mechanics. The concept of activation energy explains the exponential nature of the relationship, and in one way or another, it is present in all kinetic theories. The collision angle, the relative translational energy, the internal (particularly vibrational) energy will all determine the chance that the collision will produce a product molecule AB

a) Give Arrhenius equation for temperature dependence of reaction rates.

b) For a certain reaction large fraction of molecules has energy more than the threshold energy, yet the rate of reaction is very slow. Why?

c) What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20°C to 35°C? (R = 8.314 J mol^{-1} K^{-1}) (log 2 = 0.3010)

Ans. a) $k = A e^{-Ea/RT}$ where A is the Arrhenius factor or the frequency factor. R is gas constant and Ea is activation energy

b) Apart from the energy considerations, the colliding molecules should also have proper orientation for effective collision. This condition might not be getting fulfilled in the reaction.

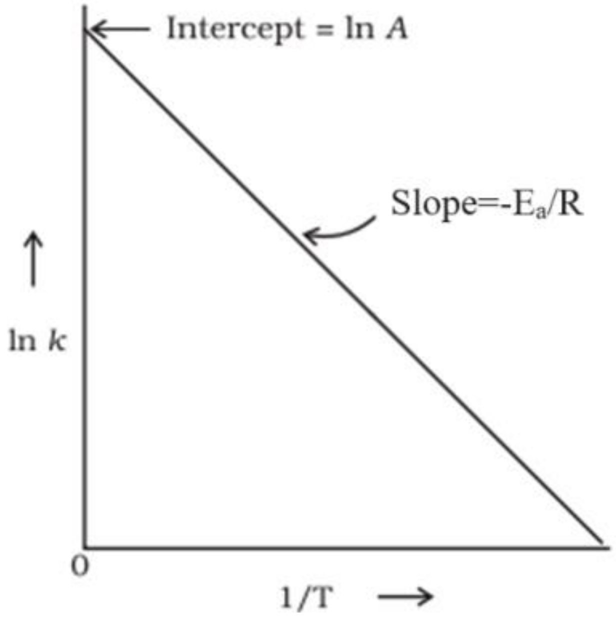
c) $\log k2/k1 = Ea/2.303T[T_2-T_1/T_1T_2]$

$\log 2 = Ea/2.303 \times 8.314[308-293/293 \times 308]$

Ea = 34.67 kJ/mol

OR

c) Draw a plot between ln k and 1/T.What would be the value of the slope and intercept?



Long Answer Type

88 a)Explain the following terms :
(i) Order of a reaction
(ii) Molecularity of a reaction
(b) A first order reaction is 15% completed in 20 minutes. How long will it take to complete 60% of the reaction ?

Ans. a)Order: the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

Molecularity: The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction

b) For the first order reaction

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

1st case : a = 100, x = 15 time, t = 20 minutes

(a – x) = 100 – 15 = 85

$$t_{15\%} = \frac{2.303}{K}\log\frac{100}{85}$$

$$20 = \frac{2.303}{K}\log\frac{100}{85} \qquad \ldots\ldots\ldots\text{(i)}$$

2nd case : a = 100, x = 60 time, $t_{60\%}$= ?

$$t_{60\%} = \frac{2.303}{K}\log\frac{100}{40} \qquad \ldots\ldots\ldots\text{(ii)}$$

Dividing equation (ii) by (i) , we get

$$\frac{t_{60\%}}{20} = \log\frac{\frac{100}{40}}{\frac{100}{85}}$$

$$= \frac{\log 100 - \log 40}{\log 100 - \log 85}$$

$$= \frac{2.000 - 1.6021}{2.000 - 1.9294}$$

$$= \frac{t_{60\%}}{20} = \frac{0.399}{0.0706} = 5.64$$

$$t_{60\%} = 20 \times 5.64 = 112.8 \text{ minutes}$$

89 a)What are the factors that affect the rate of a reaction?

b) A first order reaction has a rate constant of 0.0051 min^{-1}. If we begin with 0.10 M concentration of the reactant, what concentration of reactant will remain in solution after 3 hours?(Antilog 0.3986 =2.503)

Ans. a) Nature of reactants, Concentration of reactants, Temperature, Pressure, Effect of catalyst and influence of radiation [Any 2 factors are required].

b) $[R]_0 = 0.10$ M, t = 3 hrs = 180 min
K = 0.0051 min^{-1} [R] = ?

Using formula $K = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$

$$0.0051 = \frac{2.303}{180}\log\frac{0.10}{[R]}$$

$$\log\frac{0.10}{[R]} = \frac{0.0051\times180}{2.303}$$

$$\log\frac{0.10}{[R]} = \frac{0.918}{2.303}$$

= 0.9386

$$\frac{0.10}{[R]} = anti\log(0.3986)$$

$$\frac{0.10}{[R]} = 2.503$$

$$[R] = \frac{0.10}{2.503} = 0.0399$$

∴ Concentration of reactant remains 0.040 M

90 a)Define i) Average rate of a reaction ii) Rate Constant

b) Half-life for a first order reaction 693 s. Calculate the time required for 90% completion of this reaction.

Ans. a)i) The change in concentration of a reactant or product of a chemical reaction in a given interval of time.

ii) *The rate of reaction when concentration of reactant is unity.*

Using formula

$$t_{\frac{1}{2}} = \frac{0.693}{K}$$

$$\Rightarrow 693s = \frac{0.693}{K}$$

$$K = \frac{0.693}{693}$$ = 0.001 s_{-1}

Using formula

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

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

$$t = \frac{2.303}{0.001}\log\frac{a}{a-0.9a}$$

$$t = \frac{2.303}{0.001}\log\frac{1}{0.1}$$

$$t = 2303\log 10$$

$$t = 2303\times 1$$

t = 2303 s

91 a) Differentiate between average rate and instantaneous rate.

b) During nuclear explosion, one of the products is 90Sr with half-life of 28.1 years. If 1μg of 90Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

Ans. **a)** The average rate is the change in concentration of reactants or products over a selected/particular period of time. The instantaneous rate is the rate at a particular instant of time.

b) $k=t_{1/2}/0.693$

K= 0.0247/year

After 10 years, let xμ be the concentration of $_{90}$Sr.

k=2.303/t log$[A]_0$/[A]
0.0247 = 2.303/10 years log 1/x

x = 0.782 μg

(ii) After 60 years, let yμ be the concentration of $_{90}$Sr.

$k=2.303/t \log[A]_0/[A]$

$0.0247 = 2.303/60$ years $\log 1/y$

$y = 0.228$ µg

92 a)Differentiate between order and molecularity of a reaction.(2 points)

b) A first order gas phase reaction : $A_2B_2(g) \rightarrow 2A(g) + 2B(g)$ at the temperature 400°C has the rate constant $k = 2.0 \times 10^{-4}$ sec^{-1}. What percentage of A_2B_2 is decomposed on heating for 900 seconds? (Antilog 0.0781 = 1.197)

Ans. a)

ORDER OF A REACTION	**MOLECULARITY OF A REACTION**
It is sum of the concentration terms on which the rate of reaction actually depends or it is the sum of the exponents of the concentrations in the rate law equation.	It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.
It need not be a whole number i.e. it can be fractional as well as zero.	It is always a whole number.
It can be determined experimentally only and cannot be calculated.	It can be calculated by simply adding the molecules of the slowest step.
It is for the overall reaction and no separate steps are written to obtain it.	The overall molecularity of a complex reaction has no significance. It is only slowest step whose molecularity has significance for the overall reaction.
Even the order of a simple reaction may not be equal to the number of molecules of the reactants as seen from the unbalance equation.	For simple reactions, the molecularity can usually be obtained from the Stoichiometry of the equation.

b) Since the reaction is of the first order

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

$$\log \frac{100}{x} = 0.781$$

Given $k = 2.0 \times 10^{-4} \sec^{-1}$ t = 900 sec

Substituting these values, we get

$$2.0 \times 10^{-4} = \frac{2.303}{900} \log \frac{a}{a-x}$$

$$\log \frac{a}{a-x} = \frac{2.0 \times 10^{-4} \times 900}{2.303}$$

$$\log \frac{a}{a-x} = 0.0781$$

$$\frac{a}{a-x} = anti \log \left(0.0781 \right)$$

a = 1.197, a – 1.19 x

0.197 a = 1.197 x

$$\frac{x}{a} = \frac{0.197}{1.197} = 0.1645$$

% decomposition = 0.1645 × 100 = 16.45%