CHAPTER

4

CHEMICAL KINETICS

Syllabus

- *Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions), concept of collision theory (elementary idea, non mathematical treatment). Activation energy, Arrhenius equation.*

Trend Analysis

List of Concept names	2018	2019		2020	
	D/OD	D	OD	D	OD
Rate of reaction, Rate law, Rate constant and Numericals	1 Q (2 marks)	1 Q (2 marks)	-	1 Q (1 mark)	-
Order of reaction, Integrated rate equation, Half Life and Numericals	-	-	1 Q (2 marks) 1 Q (3 marks)	2 Q (1 mark) 1 Q (5 marks)	3 Q (1 mark)
Collision theory, Arrhenius equation and Numericals	1 Q (3 marks)	-	-	1 Q (5 marks)	1 Q (1 mark) 1 Q (3 marks)

TOPIC-1

Rate of a Chemical Reaction and Factors Affecting Rate of Reactions

Revision Notes

- **Chemical Kinetics :** It is the branch of physical chemistry which deals with study of the rate of chemical reaction and the mechanism by which the reaction occurs.
- **Rate of Reaction :** The rate of reaction is the change of concentration of any reactant or product with time, for a reaction.

$$A + B \rightarrow C$$

$$\text{Rate of reaction, A} = \frac{\text{Decrease in concentration of A}}{\text{Time taken}} = \frac{-\Delta[A]}{\Delta t}$$

$$\text{Similarly,} \qquad B = \frac{-\Delta[B]}{\Delta t}$$

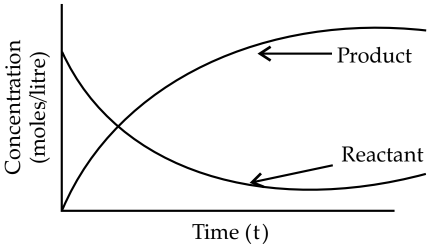
$$\text{and for product} \qquad C = \frac{\Delta[C]}{\Delta t}$$

where, [A], [B] and [C] are molar concentrations of the reactants and the product respectively.

- Unit of rate of reaction : mol L^{-1} s^{-1} or mol L^{-1} min^{-1} (in liquid), atm s^{-1} or atm min^{-1} (in gaseous form)
- **Instantaneous rate of reaction :** Instantaneous rate is defined as the rate of change in concentration of any one of the reactant or product at a particular time.

Instantaneous rate $= \frac{dx}{dt} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{+d[C]}{dt}$

- **Average rate of reaction :** The rate of reaction measured over a long time interval is called average rate of a reaction. Average rate $= \frac{\Delta x}{\Delta t}$, where, Δx = change in concentration in given time and Δt = time taken.
- **Factors affecting the rate of a chemical reaction :**
  - **(i) Concentration of reactants :** Rate of reaction is directly proportional to the concentration of the reactants. Thus, to increase the rate of a reaction the concentration of the reactants has to be increased.
  - **(ii) Temperature :** The rate of a reaction increases with the increase in temperature. Increase in temperature increases the kinetic energy of the molecules which results in the increase in rate of reaction.
  - **(iii) Pressure :** Pressure affects the rate of only gaseous reactions. Increase in pressure decreases volume and increases concentration. Increase in concentration increases the rate of reaction.
  - **(iv) Presence of catalyst :** The rate of many reactions is greatly affected by the presence of a catalyst. In the presence of a catalyst, the activation energy of a reaction decreases due to which the reaction proceeds at a faster rate.
  - **(v) Nature of the reactants :** In a chemical reaction, some bonds are broken while some new bonds are formed. Thus, if the molecules are simpler, then less bonds will rupture and the rate of reaction becomes fast while in complex molecules, more bonds will rupture and consequently the rate of reaction decreases.
  - **(vi) Surface area of the reactants :** In some heterogeneous reactions, the reaction takes place at the surface of the reactant. Thus in such reactions, the reaction rate is greatly affected by the surface area. Marble powder reacts faster than marble chips.
  - **(vii) Effect of radiations :** The reactions which are initiated by the radiations of particular wavelengths are termed as photochemical reactions. These reactions generally proceed at a faster rate than normal thermal reactions.



  - **(viii) Effect of physical state :** Rate of reaction depends upon physical state of the reactant, *e.g.*, $I_2(g)$ reacts faster than $I_2(s)$. $AgNO_3(aq)$ reacts with NaCl but $AgNO_3(s)$ does not react with NaCl.
- **Rate Law :** Rate law or rate equation is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant. The rate law states that the rate of reaction is directly proportional to the product of molar concentration of reactants and each concentration is raised to some power which may or may not be equal to stoichiometric coefficients of reacting species.

$$\text{Rate} = k[A]^m [B]^n$$

- **Rate Constant :** Rate constant is also called specific reaction rate. When concentration of both reactants are unity (one), then the rate of reaction is known as rate constant. It is denoted by '*k*'.
- **Molecularity :** Total number of atoms, ions or molecules of the reactants involved in the reaction is termed as molecularity. It is always a whole number. It is never more than three. It cannot be zero.

  Example :

$$NH_4NO_2 \rightarrow N_2 + 2H_2O \text{ (Unimolecular reaction)}$$

$$2HI \rightarrow H_2 + I_2 \text{ (Bimolecular reaction)}$$

$$2NO + O_2 \rightarrow 2NO_2 \text{ (Trimolecular reaction)}$$

- **Elementary Reaction :** An elementary reaction is a chemical reaction in which one or more of the chemical species react directly to form products in a single reaction step and with a single transition state.
- For a complex reaction generally, molecularity of the slowest step is same as the order of the overall reaction.
- **Initial rate of reaction :** The rate at the beginning of the reaction when the concentrations have not changed appreciably is called initial rate of reaction**.**
- **Rate Determining Step :** The slowest step in the reaction mechanism is called rate determining step.

Objective Type Questions (1 mark each)

[A] MULTIPLE CHOICE QUESTIONS :

Q. 1. The unit of rate constant depends upon the

(a) molecularity of the reaction

(b) activation energy of the reaction

(c) order of the reaction

(d) temperature of the reaction

U [CBSE, Delhi Set-3, 2020]

Ans. Correct option : (c)

Explanation : For the reaction,

$$xA + yB \rightarrow \text{Product}$$

$$r = k[A]^x[B]^y$$

$$\frac{dx}{dt} = k[A]^x[B]^y$$

$$\text{mol L}^{-1}\text{s}^{-1} = k(\text{mol L}^{-1})^x(\text{mol L}^{-1})^y$$

$$k = \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^x(\text{mol L}^{-1})^y}$$

$$= (\text{mol L}^{-1})^{1-(x+y)}\text{s}^{-1}$$

Where $(x + y)$ = order of the reaction

Q. 2. Compounds 'A' and 'B' react according to the following chemical equation :

$$A_{(g)} + 2B_{(g)} \rightarrow 2C_{(g)}$$

Concentration of either 'A' or 'B' were changed keeping the concentration of one of the reactants constant and rates were measured as function of initial concentration. Following results were obtained. Choose the Correct option for this reaction. A&E

Experi-ment	Initial concentration of [A]/mol L^{-1}	Initial concentration of [B]/mol L^{-1}	Initial concentration of [C]/mol L^{-1}
1.	**0.30**	**0.30**	**0.10**
2.	**0.30**	**0.60**	**0.40**
3.	**0.60**	**0.30**	**0.20**

(a) Rate = $k\,[A]^2[B]$

(b) Rate = $k\,[A][B]^2$

(c) Rate = $k\,[A][B]$

(d) Rate = $k\,[A]^2[B]^0$

Ans. Correct option : (b)

Explanation : Suppose order with respect to A and B are x and y respectively.

Rate = $k[A]^x[B]^y$

For experiment 1,

$0.1 = k(0.3)^x(0.3)^y$ …(i)

For experiment 2,

$0.4 = k(0.3)^x(0.6)^y$ …(ii)

For experiment 3,

$0.2 = k(0.6)^x(0.3)^y$ …(iii)

Dividing equation (ii) by (i)

$$\frac{0.4}{0.1} = \frac{(0.6)^y}{(0.3)^y}$$

$$\therefore \quad y = 2$$

Dividing equation (iii) by (i)

$$\frac{0.2}{0.1} = \frac{(0.6)^y}{(0.3)^y}$$

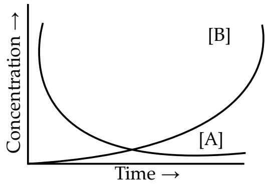
$$\therefore \quad x = 1$$

Rate law

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

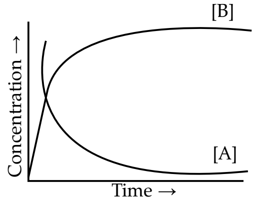
Q. 3. Consider the reaction A $\rightleftharpoons$ B. The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?

(a)

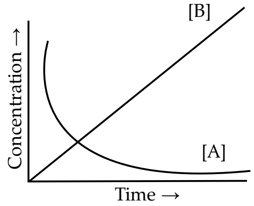


A&E

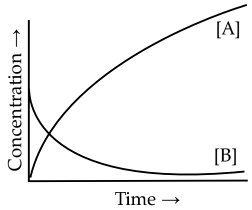
(b)



(c)



(d)



Ans. Correct option : (b)

Explanation : As the reactant A's concentration decreases with time, so the product B's concentration increases. Also since the reaction is reversible, the increase and decrease in concentration with respect to time is similar.

[B] ASSERTION AND REASON TYPE QUESTIONS :

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

Q. 1. Assertion : Rate of reaction doubles when concentration of reactant is doubled if it is a first order reaction.

Reason : Rate constant also doubles.

Ans. Correct option : (c)

Explanation : For first order reaction

$$\text{Rate}_1 = k[A_1]$$
$$[A_2] = [2A_1]$$
$$\text{Rate}_2 = k[2A_1]$$
$$\text{Rate}_2 = k \times 2\,\text{Rate}_1$$

For a given reaction, rate constant is constant and independent of the concentration of reactant.

Q. 2. Assertion : The rate of reaction increases with increase in temperature.

Reason : The reactant molecules collide less frequently.

Ans. Correct option : (c)

Explanation : As the temperature of a reaction is increased, the rate of the reaction increases because the reactant molecules collide more frequently and with greater energy per collision.

Q. 3. Assertion : Dust particles suspended in the air inside unheated gain electrons can sometimes react explosively.

Reason : The dust particles have large surface area for the reaction.

Ans. Correct option : (a)

Explanation : Since the dust particles have large surface area for the reaction so these particles suspended in the air inside unheated gain electrons can sometimes react explosively.

[C] VERY SHORT ANSWER TYPE QUESTIONS :

Q. 1. Why the molecularity of a reaction can not be zero? A

Ans. The molecularity of a reaction is the number of total molecules taking part in elementary step of reaction. So, minimum one molecule is required for a reaction to occur. Hence, the value of molecularity is never zero.

Q. 2. Write the formula for expressing rate of the reaction.

$N_2 + 3H_2 \rightarrow 2NH_3$ U

Ans. $\underset{\text{(Reactants)}}{N_2 + 3H_2} \rightarrow \underset{\text{(Product)}}{2NH_3}$

$$\text{Rate of reaction} = \frac{-d[N_2]}{dt} = \frac{1}{3}\left(\frac{-d[H_2]}{dt}\right)$$
$$= \frac{1}{2}\left(\frac{d[NH_3]}{dt}\right)$$

Q. 3. The rate of reaction decreases with the progress of reaction. Why? U

Ans. The rate of reaction depends on the concentration of reactants. Since, the concentration of reactants decreases with time, so rate of reaction also decreases.

Q. 4. Reactions having molecularity more than three occur rarely. Why? R

Ans. It is because of the fact that collision of more than three molecules is not possible at a time.

Q. 5. If the rate equation is given below :

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

then what will be the unit of its rate and rate constant?

Ans. Unit of rate = mol $L^{-1}s^{-1}$ **[½]**

$$\text{Unit of rate constant (k)} = \frac{\text{Unit of rate}}{\text{Unit of }[A^2] \times \text{Unit of }[B]}$$
$$= \frac{\text{mol}\,L^{-1}s^{-1}}{(\text{mol}\,L^{-1})^2(\text{mol}\,L^{-1})}$$
$$= \text{mol}^{-2}\,L^2s^{-1}$$ **[½]**

Short Answer Type Questions-I **(2 marks each)**

AI **Q. 1. For a reaction,**

$$2H_2O_2 \xrightarrow[\text{alkaline medium}]{I^-} 2H_2O + O_2$$

The proposed mechanism is given below :

(1) $H_2O_2 + I^- \rightarrow H_2O + IO^-$ (slow)

(2) $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$ (fast)

(i) Write rate law of the reaction.

(ii) Write overall order of reaction.

(iii) Out of step (1) and (2), which one is rate determining step? U **[CBSE Delhi Set-1, 2019]**

Ans. **(i)** Rate = k $[H_2O_2]$ $[I^-]$ **[1]**

(ii) Order = 2 **[½]**

(iii) Step 1 **[½]**

[CBSE Marking Scheme, 2019]

Detailed Answer :

(i) The rate law for the reaction is

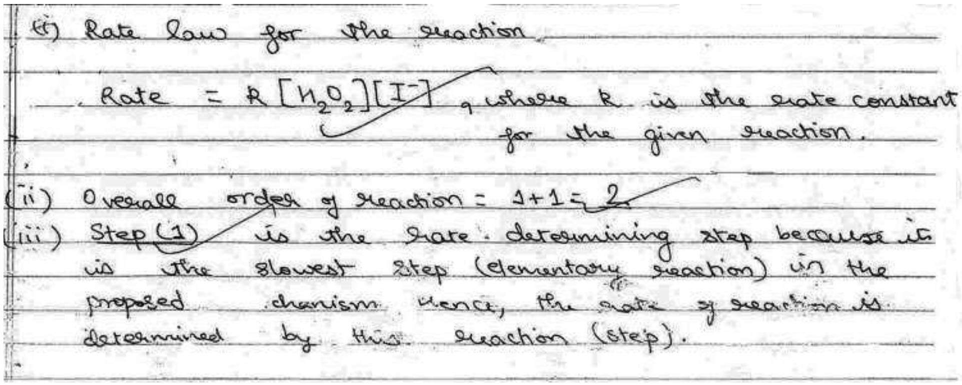
$$\text{rate} = -\frac{d[H_2O_2]}{dt} = k[H_2O_2][I^-]$$

(ii) This reaction is first order with respect to both H_2O_2 and I^-.

The overall order of the reaction is bimolecular, 2. The order of the reaction is determined from the slowest step of the reaction mechanism.

(iii) The first reaction is slow, so this is the rate determining step. **[2]**

OR



(i) Rate law for the reaction

Rate = $k[H_2O_2][I^-]$, where k is the rate constant for the given reaction.

(ii) Overall order of reaction = 1+1 = 2

(iii) Step (1) is the rate determining step because it is the slowest step (elementary reaction) in the proposed chanism. Hence, the rate of reaction is determined by this reaction (step).

[Topper's Answer 2019] [2]

Commonly Made Error

- Some students are not able to write correct expression for the rate of the reaction.

Answering Tip

- Learn and understand the rate law.

AI Q. 2. For the reaction

$$2N_2O_5\,(g) \longrightarrow 4NO_2\,(g) + O_2\,(g),$$

the rate of formation of NO_2 (g) is 2.8×10^{-3} M s^{-1}. Calculate the rate of disappearance of N_2O_5 (g).

U, A [CBSE, Delhi/Outside Delhi Set, 2018]

Ans. $$\text{Rate} = \frac{1}{4}\frac{\Delta(NO_2)}{\Delta t} = \frac{-1}{2}\frac{\Delta(N_2O_5)}{\Delta t} \quad ½$$

$$\frac{1}{4}(2.8\times10^{-3}) = \frac{-1}{2}\frac{\Delta(N_2O_5)}{\Delta t} \quad ½$$

$$\text{Rate of disappearance of } N_2O_5 \left(\frac{-\Delta(N_2O_5)}{\Delta t}\right)$$

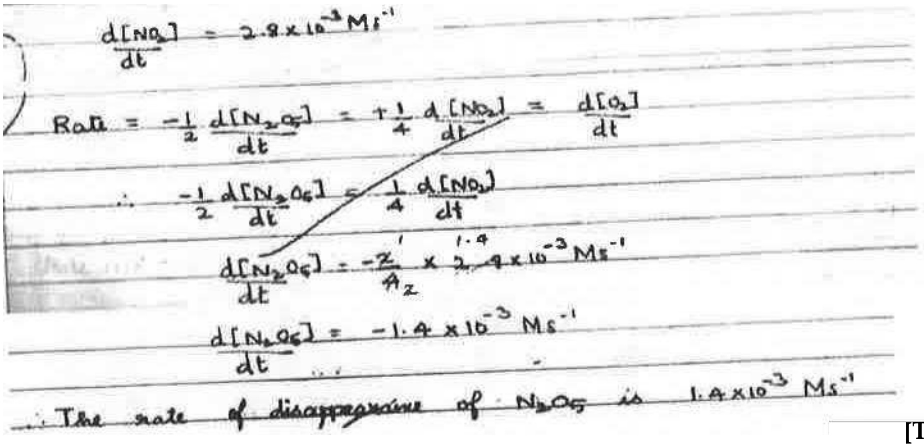
$$= 1.4\times10^{-3}\ \text{M/s} \quad 1$$

(Deduct half mark if unit is wrong or not written)

[CBSE Marking Scheme 2018]

OR

Ans.



$$\frac{d[NO_2]}{dt} = 2.8\times10^{-3}\ Ms^{-1}$$

$$\text{Rate} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

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

$$\frac{d[N_2O_5]}{dt} = -\frac{\cancel{2}^{1}}{\cancel{4}_{2}} \times \overset{1.4}{\cancel{2.8}}\times10^{-3}\ Ms^{-1}$$

$$\frac{d[N_2O_5]}{dt} = -1.4\times10^{-3}\ Ms^{-1}$$

∴ The rate of disappearance of N_2O_5 is $1.4\times10^{-3}\ Ms^{-1}$

[Topper's Answer 2018]

Commonly Made Error

- Students tend to forget specifically mentioning the formula and start the calculations or do not mention all the steps or specific units.

Answering Tip

- Pay special attention to writing of units in the answer as missing out units in the last step leads to deduction of marks.

Q. 3. For a reaction the rate law expression is represented as follows:

$$\text{Rate} = k\,[A][B]^{1/2}$$

(i) Interpret whether the reaction is elementary or complex. Give reason to support your answer.

(ii) Write the unit of rate constant for this reaction if concentration of A and B is expressed in moles/L. **U [CBSE SQP, 2020-21]**

Ans. **(i)** This is a complex reaction. **[½]**

Order of reaction is 1.5. Molecularity cannot be 1.5, it has no meaning for this reaction. The reaction occurs in steps, so it is a complex reaction. **[½]**

(ii) Rate = $k[A][B]^{[1/2]}$

Unit of Rate constant (k)

$$= \frac{\text{Unit of rate}}{\text{Unit of [A]} \times \text{Unit of [B]}^{1/2}}$$

$$= \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})(\text{mol L}^{-1})^{1/2}}$$

$$= \text{mol}^{-1/2}\,\text{L}^{1/2}\text{s}^{1}$$ **[1]**

Q.4. The following results have been obtained during the kinetic studies for the reaction :

$P + 2Q \rightarrow R + 2S$

Exp.	Initial P(mol/L)	Initial Q (mol/L)	Init. Rate of Formation of R (M min^{-1})
1	0.10	0.10	3.0×10^{-4}
2	0.30	0.30	9.0×10^{-4}
3	0.10	0.30	3.0×10^{-4}
4	0.20	0.40	6.0×10^{-4}

Determine the rate law expression for the reaction.

$\boxed{A}$ **[CBSE SQP, 2020-21]**

Ans. Let the rate law expression be Rate = $k\,[P]^x\,[Q]^y$ from the table we know that

Rate 1 = $3.0 \times 10^{-4} = k\,(0.10)^x\,(0.10)^y$

Rate 2 = $9.0 \times 10^{-4} = k\,(0.30)^x\,(0.30)^y$

Rate 3 = $3.0 \times 10^{-4} = k\,(0.10)^x\,(0.30)^y$

Rate 1/ Rate 3 = $(1/3)^y$ or $1 = (1/3)^y$

So $y = 0$ **[½]**

Rate 2/ Rate 3 = $(3)^x$ or $3 = (3)^y$

So $x = 1$ **[½]**

Rate = k [P] **[1]**

Q.5. For a reaction : $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$

Rate = k

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

(ii) Write the unit of k.

$\boxed{A}$ **[CBSE, Outside Delhi Set 1, 2016]**

Ans. (i) Zero order reaction, Molecularity is 2 / bimolecular reaction. **[[½] + [½]]**

(ii) mol L^{-1} s^{-1}. **[1]**

[CBSE Marking Scheme, 2016]

Commonly Made Error

- Some students get confused to write correct unit of rate constant for the reaction.

Answering Tip

- Understand the unit of rate constant for different orders of reaction.

Short Answer Type Questions-II

(3 marks each)

Q. 1. For the reaction R → P, the concentration of a reactant changes from 0.03 to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds. $\boxed{A}$

Ans. $R \rightarrow P$

$[R_1] = 0.03$ M

$[R_2] = 0.02$ M

$\Delta t = 25$ min

$$\text{Average rate} = -\frac{\Delta[R]}{\Delta t}$$

$$= -\left[\frac{[R_2]-[R_1]}{\Delta t}\right]$$

$$= -\left[\frac{0.02-0.03}{25}\right]$$

$$= -\left[\frac{-0.01}{25}\right]$$

$$= 4 \times 10^{-4}\,\text{mol L}^{-1}\text{min}^{-1}$$ **[2]**

$$= \frac{4 \times 10^{-4}}{60}\text{mol L}^{-1}\text{s}^{-1}$$

$$= 6.66 \times 10^{-6}\,\text{mol L}^{-1}\text{s}^{-1}$$ **[1]**

Q. 2. For the reaction

$2A + B \rightarrow A_2B$

Rate = $k[A]\,[B]^2$, $k = 2.0 \times 10^{-6}$ mol^{-2}L^{2}s^{-1} Calculate the initial rate of the reaction when [A] = 0.1 mol L^{-1} and [B] = 0.2 mol L^{-1}. Calculate the rate of reaction after [A] is reduced to 0.06 mol L^{-1}. $\boxed{A}$

Ans. $2A + B \rightarrow A_2B$

Initial rate = $k[A]\,[B]^2$

$= 2.0 \times 10^{-6} \times 0.1 \times (0.2)^2$

$= 8.0 \times 10^{-9}$ mol L^{-1} **[1]**

When concentration of [A] is reduced from 0.10 mol L^{-1} to 0.06 mol L^{-1} i.e. 0.04 mol L^{-1}, concentration of A has been used in the reaction. Therefore, the concentration of B

$$= \frac{1}{2} \times 0.04$$

$= 0.02$ mol L^{-1} **[½]**

Hence, [B] = 0.2 – 0.02

$= 0.18$ mol L^{-1} **[½]**

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

$= 2.0 \times 10^{-6} \times 0.06 \times (0.18)^2$

$= 3.89 \times 10^{-9}$ mol L^{-1} s^{-1} **[1]**

Q.3. **The decomposition of NH_3 on platinum surface is a zero order reaction. What will be rate of production of N_2 and H_2 when the value of k is 2.5×10^{-9} mol L^{-1} s^{-1}?** $\boxed{A}$

Ans.

$$2NH_3 \rightarrow N_2 + 3H_2$$

$$\text{Rate of reaction} = -\frac{1}{2}\left(\frac{d[NH_3]}{dt}\right) = \frac{d[N_2]}{dt}$$

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

∵ Reaction is zero order, so, the rate of reaction

$$= k[NH_3]^0$$

$$= k = 2.5 \times 10^{-4}\ \text{mol}\ L^{-1}s^{-1}$$ **[1]**

Rate of production of N_2

∵ Rate of reaction = Rate of production of N_2

∴ Rate of production of $N_2 = 2.5 \times 10^{-9}$ mol $L^{-1}s^{-1}$ **[1]**

Rate of production of H_2

∵ Rate of reaction $= \frac{1}{3} \times$ Rate of production of H_2

∴ Rate of production of H_2 = 3 × Rate of reaction

$= 3 \times 2.5 \times 10^{-4}$

$= 7.5 \times 10^{-4}$ mol L^{-1} s^{-1}

[1]

Commonly Made Error

- Some students find it difficult to calculate rate of production of the reaction products.

Answering Tip

- Students must be clear about the concept of rate of reaction.

Long Answer Type Questions

(5 marks each)

Q. 1. **A reaction is of first order with respect to A and second order with respect to B**

(i) Write differential rate equation.

(ii) How is the rate effected when the concentration of B is tripled?

(iii) How is the rate affected when the concentration of both A and B is doubled? $\boxed{U}$ + $\boxed{A}$

Ans. (i) Differential rate equation

$$\frac{dx}{dt} = k[A][B]^2$$ **[1]**

(ii) Let [A] = a, [B] = b

If [B] increases three times

[B] = 3b

∴ Rate = $k[A][B]^2$

$Rate_1 = k \times a \times b^2$ …(i)

$Rate_2 = k \times a \times (3b)^2$ …(ii)

From eq (i) and (ii)

$$\frac{Rate_2}{Rate_1} = \frac{k \times a \times (3b)^2}{k \times a \times b}$$

$$Rate_2 = 9 \times Rate_1$$

∴ The rate becomes nine times when the concentration of B is tripled. **[2]**

(iii) If [A] and [B] is doubled then [A] = 2*a* [B] = 2*b*

$Rate_1 = k \times a \times b$ …(i)

$Rate_2 = k \times (2a) \times (2b)$ …(ii)

From eq. (i) & (ii)

$$\frac{Rate_2}{Rate_1} = \frac{k \times (2a) \times (2b)^2}{k \times a \times b^2}$$

$$= 8$$

$$Rate_2 = 8 Rate_1$$

∴ The rate becomes eight times when the concentration of both A and B is doubled. **[2]**

Q.2. **(a) Reaction 2A + B + C → D + 2E shows first order with respect to A, second order with respect to B and zero order with respect to C. Determine :**

(i) Rate law of reaction

(ii) What will be the rate of reaction on doubling of concentration of A, B and C?

(b) For the reaction,

$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$$

The rate of dissociation of N_2O_5 is 5.65×10^{-5} mol L^{-1} s^{-1}. Determine :

(i) Rate of reaction

(ii) Rate of formation of NO_2

(iii) Rate of formation of O_2 $\boxed{U}$

Ans. (a) (i) 2A + B + C → D + 2E

Rate Law

Rate (*r*) = $k[A]^1 [B]^2[C]^0$ **[1]**

(ii) If concentration of A, B & C is doubled

$r_1 = k[A]^1 [B]^2[C]^0$ …(i)

$r_2 = k[2A]^1 [2B]^2[2C]^0$ …(ii)

From equation (i) & (ii)

$$\frac{r_1}{r_2} = \frac{k[A]^1[B]^2[C]^0}{k[2A]^1[2B]^2[2C]^0} = \frac{1}{8}$$

∴ $r_2 = 8 \times r_1$

Hence rate of reaction becomes eight times. **[1]**

(b) (i) $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$

$$\text{Rate of reaction} = \frac{-d[N_2O_5]}{dt} = \frac{1}{2}\left(\frac{d[NO_2]}{dt}\right)$$

$$= 2\left(\frac{d[O_2]}{dt}\right)$$

Rate of reaction = Rate of dissociation of N_2O_5

$= 5.65 \times 10^{-5}$ mol $L^{-1}s^{-1}$ **[1]**

(ii) Rate of dissociation of N_2O_5

$$= \frac{1}{2} \times \text{Rate of formation of } NO_2$$

Rate of dissociation of NO_2

$$= 2 \times \text{Rate of formation of } N_2O_5$$

$$= 2 \times 5.65 \times 10^{-5}$$

$$= 11.3 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$ **[1]**

(iii) Rate of dissociation of N_2O_5 = 2 × Rate of formation of O_2

Rate of formation of O_2

$$= \frac{1}{2} \times \text{Rate of dissociation of } N_2O_5$$

$$= \frac{1}{2} \times 5.65 \times 10^{-5}$$

$$= 2.825 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$ **[1]**

TOPIC-2

Order of a Reaction, Integrated Rate Equations and Half-life of a Reaction

Revision Notes

- **Order of reaction :** Order is defined as the sum of powers of concentration of the reactants in the experimentally derived rate equation or rate law expression. Order of reaction is experimentally determined and is not written from the balanced chemical equation. Order of reaction can be whole number, zero or fractional.
- **Zero order reaction :** The rate of reaction does not change with the concentration of the reactants.

  i.e. Rate $= k\,[A]^0$,

  $$k = \frac{[A]_0 - [A]}{t}$$, where 'k' is rate constant, $[A]_0$ is initial concentration of reactant.

  Unit of the rate constant k is mol L^{-1} s^{-1}. This reaction will be zero order reaction. Decomposition of gaseous ammonia on hot platinum, thermal decomposition of HI on gold surface and photochemical reaction between hydrogen and chlorine are examples of zero order reaction.
- **First order reaction :** The rate of reaction is directly proportional to the first power of the concentration of reacting substance. Rate constant of the first order reaction is

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

  $$\Rightarrow \quad k = \frac{2.303}{t}\log\frac{[A_0]}{[A]},$$

  where 'a' is initial concentration and $(a - x)$ is the concentration after time 't'.
  Unit of 'k' is s^{-1} or min^{-1}.
  Decomposition of N_2O_5 and N_2O are examples.
- **Pseudo first order reaction :** If a reaction is not truly of the first order but under certain conditions becomes reaction of first order is called pseudo first order reaction, *e.g.*, acidic hydrolysis of ester (ethyl acetate).

  $$CH_3COOC_2H_5 + H_2O \xrightleftharpoons{H+} CH_3COOH + C_2H_5OH$$
- **Second order reaction :** The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 2.

  $$\therefore \quad \frac{dx}{dt} = k[A]\,[B]$$

  Unit of rate constant is mol^{-1} L s^{-1} or M^{-1} s^{-1}, where M is molarity.

Reaction	Order	Unit of rate constant	Example
Zero order	0	$mol^{-1}\,L^{-1}\,s^{-1}$	$H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$
First order	1	s^{-1}	$2N_2O_5 \rightarrow 4NO_2 + O_2$
Pseudo first order	1	s^{-1}	$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$
Second order	2	$mol^{-1}\,L\,s^{-1}$	$H_2 + I_2 \rightarrow 2HI$

- **Equation for typical first order gas phase reaction :** $A(g) \rightarrow B(g) + C(g)$

$$k = \frac{2.303}{t}\log\frac{p_i}{p_A}$$

or

$$k = \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)}$$

where p_i is the initial pressure of A at time, $t = 0$ and p_t is the total pressure at time t.

- **Half-life of a reaction :** The time taken for a reaction when half of the initial value has reacted is called **half-life of a reaction.**

For zero order reaction, $$t_{1/2} = \frac{[A]_0}{2k},$$

where $[A]^0$ is initial and last concentration of reaction it means there is no change in concentration and 'k' is rate constant.

For 1st order reaction, $$t_{1/2} = \frac{0.693}{k}$$

- **n^{th} order reaction :** In general for n^{th} order reaction of the type

$$A \rightarrow \text{products, where, } \frac{dx}{dt} = k[A]^n$$

$$k_n = \frac{1}{t(n-1)}\left[\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{\ n-1}}\right]$$

where $[A]_0$ is initial concentration, [A] is final concentration after time t and n can have all the values except 1.

- **Half-life of a reaction of n^{th} order :**

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

$t_{1/2} \propto [A]$ for zero order

$t_{1/2}$ is independent of [A] for 1st order

$t_{1/2} \propto \frac{1}{[A]}$ for 2nd order

$t_{1/2} \propto \frac{1}{[A]^2}$ for 3rd order

Amount of substances left after n half-lives $= \frac{[A]_0}{2^n}$

- **Integrated rate laws for the reactions of zero and first order :**

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half Life	Units of k
0	$A \rightarrow P$	$\frac{d[A]}{dt} = -k$	$kt = [A]_0 - [A]$	[A] vs. t	$\frac{[A]_0}{2k}$	conc. time^{-1}
1	$A \rightarrow P$	$\frac{d[A]}{dt} = -k[A]$	$[A] = [A]_0\, e^{-kt}$ $kt = \frac{ln[A]_0}{[A]}$	ln [A] vs. t	$ln\,\frac{2}{k}$	time^{-1}

- **Life time :** The time in which 98% of the reaction is completed is called life time.

Mnemonics

- **Concept:** Zero order
- Mnemonics : ZOR don't CCR
- Interpretation : In zero order reaction, the rate of reaction does not change with concentration of the reactants.

Know the Formulae

- **Integrated Rate Equations :**

  (i) For a zero order reaction :

$$t = \frac{[R]_0 - [R]}{k} \text{ and } t_{[½]} = \frac{[R]_0}{2k}$$

  (ii) For a first order reaction :

$$t = \frac{2.303}{k}\log\frac{[R]_0}{[R]} \text{ and } t_{[½]} = \frac{0.693}{k}$$

- Temperature coefficient $= \dfrac{k\,(T+10)}{k\,(T)}$

Objective Type Questions

(1 mark each)

[A] MULTIPLE CHOICE QUESTIONS :

Q. 1. In a chemical reaction X → Y, it is found that the rate of reaction doubles when the concentration of X is increased four times. The order of the reaction with respect to X is $\boxed{A}$ **[CBSE, Delhi Set-2, 2020]**

(a) 1 **(b) 0**

(c) 2 **(d) 1/2**

Ans. Correct option : (d)

Explanation : X → Y

Rate(r) ∝ $[X]^n$ [Where n = Order of reaction]

If the concentration X is increased by 4 times

$X' = 4X$

Then, Rate(r') ∝ $[X']^n$

$$\frac{r'}{r} = \frac{[4X]^n}{[X]^n} = 2$$

r' is new rate, X′ is a new concentration

$[4]^n = 2$

$$\therefore n = \frac{1}{2}$$

$$\text{Order of reaction} = \frac{1}{2}$$

Q. 2. The half-life period for a zero order reaction is equal to

(a) $\dfrac{0.693}{k}$ **(b)** $\dfrac{2k}{[R]_0}$

(c) $\dfrac{2.303}{k}$ **(d)** $\dfrac{[R]_0}{2k}$

(where $[R]_0$ is initial concentration of reactant and k is rate constant).

$\boxed{R}$ **[CBSE Outside Delhi Set-2, 2020]**

Ans. Correct option : (d)

Explanation : Half life period of a zero order reaction $= \dfrac{[R]_0}{2k}$

Where $[R]_0$ = initial concentration of reactant

k = Rate constant

Q. 3. For a zero order reaction, the slope in the plot of [R] vs. time is

(a) $\dfrac{-k}{2.303}$ **(b)** $-k$

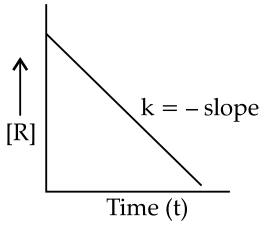
(c) $\dfrac{+k}{2.303}$ **(d)** $+k$

(where [R] is the final concentration of reactant)

$\boxed{R}$ **[CBSE Outside Delhi Set-3, 2020]**

Ans. Correct option : (b)

Explanation :



Q. 4. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion ? $\boxed{U}$

(a) 1.26×10^{15} s **(b) 2.52×10^{14} s**

(c) 2.52×10^{28} s **(d) Infinite**

Ans. Correct option : (d)

Explanation : The reaction will be 100% complete only after infinite time.

Q. 5. Consider a first order gas phase decomposition reaction given below :

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

The initial pressure of the system before decomposition of A was 'p_i'. After lapse of time 't', total pressure of the system increased by x units and became 'p_t'. The rate constant k for the reaction is given as : $\boxed{A}$

(a) $k = \dfrac{2.303}{t}\log\dfrac{p_i}{p_i - x}$

(b) $k = \dfrac{2.303}{t}\log\dfrac{p_i}{2p_i - p_t}$

(c) $k = \dfrac{2.303}{t}\log\dfrac{p_i}{2p_i + p_t}$

(d) $k = \frac{2.303}{t} \log \frac{p_i}{p_i + x}$

Ans. Correct option : (b)

Explanation : Let us consider a first order gas phase decomposition reaction :

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

The initial pressure of the system before decomposition of A is 'P_i.' After lapse of time 't', total pressure of the system increased by x units and became 'P_t'.

Hence, the pressure of A decreased by x atom.

Initial pressure :	P_i atom	0	0
Pressure after time t :	$(P_i - x)$	x atm	x atm

$$P_t = (P_i - x) + x + x$$
$$= P_i + x \text{ atm.}$$
$$x = P_t - P_i$$
$$= P_i - (P_t + P_i)$$
$$P_A = 2P_i - P_t$$
$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$
$$= \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$$

Q. 6. For the reaction A → B, the rate of reaction becomes three times when the concentration of A is increased by nine times. What is the order of reaction ? A

(a) 1 **(b) 2**

(c) 1/2 **(d) 0**

Ans. Correct option : (c)

Explanation : A → B

Rate of reaction $r \propto [A]^n$ ...(i)

If concentration of A is increased by nine times, then rate of reaction becomes three times,

$$r' = 3r$$
$$A' = 9A$$
$$r' \propto [A']^n$$
$$3r' \propto [9A]^n \qquad \text{...(ii)}$$

From eq. (i) and (ii)

$$\frac{r}{3r} = \frac{[A]^n}{[9A]^n}$$
$$\frac{1}{3} = \left(\frac{1}{3}\right)^{2n}$$
$$1 = 2n$$
$$n = 1/2$$

∴ Order of reaction = [½]

[B] ASSERTION AND REASON TYPE QUESTIONS :

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

Q. 1. Assertion : Hydrolysis of an ester follows first order kinetics.

Reason : Concentration of water remains nearly constant during the course of the reaction.

[CBSE, Outside Delhi Set 1, 2020]

Ans. Correct option : (a)

Explanation :

$$\underset{\text{ester}}{CH_3COOC_2H_5} + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

Hydrolysis of an ester follows first order kinetics as $[H_2O]$ remains nearly constant during the course of the reaction. It is pseudo first order reaction.

Q. 2. Assertion : For complex reactions molecularity and order are not same.

Reason : Order of reaction may be zero.

Ans. Correct option : (b)

Explanation : For a complex reaction,

Order of overall reaction = molecularity of slowest step

As rate of overall reaction depends upon total number of molecules involved in slowest step of the reaction. Hence, for complex reaction, molecularity and order are not same.

Q. 3. Assertion : Order of the reaction can be zero or fractional.

Reason : We cannot determine order from balanced chemical equation.

Ans. Correct option : (b)

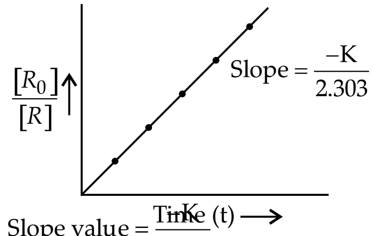
Explanation : Order of a reaction may be zero or fractional. It can be determined through the rate law expression by sum of power of reactants. **[1]**

[C] VERY SHORT ANSWER TYPE QUESTIONS :

Q. 1. Write the slope value obtained in the plot of log $[R_0] / [R]$ vs. time for a first order reaction.

R **[CBSE, Delhi Set 1, 2020]**

Ans.



Slope value = $\frac{-K}{2.303}$

Q. 2. For which reaction, the rate of reaction does not decrease with time? U

Ans. For zero order reaction the rate of reaction does not decrease with time because it does not depend on concentration of reactants

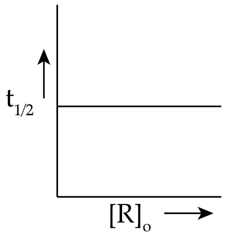
Q. 3. What is the order of photochemical reaction? R

Ans. Zero Order reaction

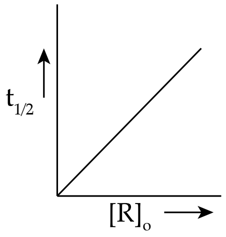
Short Answer Type Questions-I (2 marks each)

AI **Q. 1. Define order of reaction. Predict the order of reaction in the given graphs:**

(a)



(b)



Where $[R]_0$ is the initial concentration of reactant and $t_{1/2}$ is half life.

U **[CBSE, Outside Delhi set 2, 2019]**

Ans. Order of reaction is defined as the sum of powers to which the concentration terms are raised in the rate law equation. **[1]**

(a) First order (b) zero order [½]+[½]

[CBSE Marking Scheme 2019]

Commonly Made Error

- Sometimes students can not predict the order of reaction from the given graph.

Answering Tip

- Do practice to interpret the graph between initial concentration and half life for a particular order of reaction

AI **Q. 2. For a reaction : $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$; Rate $= k$;**

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

(ii) Write the unit of k.

U **[CBSE, Delhi Set 1, 2016]**

Ans. (i) Zero order, bimolecular / unimolecular. [½], [½]

(ii) mol L^{-1} s^{-1}. **[1]**

[CBSE Marking Scheme, 2016]

AI **Q. 3. Explain the following terms :**

(i) Rate constant (k)

(ii) Half-life period of reaction ($t_{1/2}$).

R **[CBSE Comptt. OD 2015]**

Ans. (i) Rate constant (k) : Rate constant is rate of the reaction when the concentration of reactants is unity. **[1]**

(ii) Half-life period of a reaction ($t_{1/2}$) : Half-life of a reaction is the time in which the concentration of a reactant is reduced to half of its original value. **[1]**

Q. 4. Write units of rate constants for zero order and for the second order reactions if the concentration is expressed in mol L^{-1} and time in second.

U **[CBSE Comptt. OD 2015]**

Ans. Zero order : mol $L^{-1}s^{-1}$ **[1]**

Second order : L $mol^{-1}s^{-1}$ **[1]**

[CBSE Marking Scheme 2015]

Commonly Made Error

- The concept of rate law and determination of order of reaction is not clear to many students. Hence, students make errors in identifying order of reaction.

Answering Tip

- Learn the units of various order reactions and also try and understand the underlying concept.

Q. 5. (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?

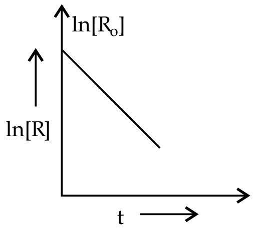
A **[CBSE Comptt. OD Set-3 2017]**

Ans. (i) Zero Order **[1]**

(ii) Pseudo-first Order **[1]**

[CBSE Marking Scheme 2017]

Q. 6. For a chemical reaction $R \rightarrow P$, variation in ln $[R]$ vs time (t) plot is given below:



For this reaction :

(i) Predict the order of reaction.

(ii) What is the unit of rate constant (k)?

A **[CBSE Comptt. Delhi Set-1, 2 2017]**

Ans. (i) First order. **[1]**

(ii) s^{-1}/time^{-1} **[1]**

[CBSE Marking Scheme 2017]

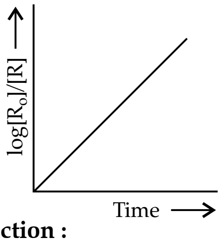
Commonly Made Error

- Students often misinterpret graph either in hurry or overlook the details.

Answering Tip

- Read the concept, understand and practice the interpretation of graphs of various orders.

Q. 7. For a chemical reaction $R \rightarrow P$, variation in log $[R_o]/[R]$ vs time plot is given below:



For this reaction :

(i) Predict the order of reaction

(ii) What is the unit of rate constant (k)?

$\boxed{\text{A}}$ **[CBSE Comptt. Delhi Set-3 2017]**

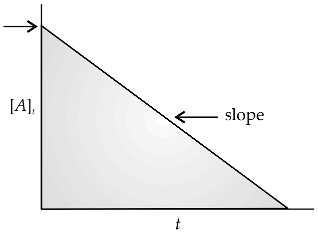
Ans. (i) First order. **[1]**

(ii) $s^{-1}/time^{-1}$ **[1]**

[CBSE Marking Scheme 2017]

Q. 8. For a certain chemical reaction variation in concentration [A] vs. time (s) plot is given below:

(i) Predict the order of the given reaction?



(ii) What does the slope of the line and intercept indicate?

(iii) What is the unit of rate constant k? $\boxed{\text{A}}$

Ans. (i) Zero order reaction **[½]**

(ii) Slope represents –k ; Intercept represents $[R]_0$ **[½] +[½]**

(iii) mol L^{-1} s^{-1} **[½]**

Q. 9. (i) Explain why H_2 and O_2 do not react at room temperature.

(ii) Write the rate equation for the reaction $A_2+3B_2 \rightarrow 2C$, if the overall order of the reaction is zero. $\boxed{\text{A\&E+A}}$

Ans. (i) Due to high activation energy **[1]**

(ii) Rate = k $[A_2]^0[B_2]^0$ **[1]**

Q. 10. Derive integrated rate equation for rate constant of a first order reaction.

$\boxed{\text{C}}$ **[CBSE Comptt. OD Set-1, 2 2017]**

Ans.

$$R \rightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

or

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

Integrating this equation, we get

$$\text{In } [R] = -kt + \text{I} \qquad \ldots(i)$$

$$\text{When } t = 0, R = [R]_0,$$

where $[R]_0$ is the initial concentration of the reactant.

Therefore, equation (i) can be written as

$$\text{In } [R]_0 = -k \times 0 + \text{I}$$

$$\text{In } [R]_0 = \text{I}$$

Substituting the value of I in equation (i)

$$\text{In } [R] = -kt + \text{ln}[R]_0$$

Rearranging this equation

$$\text{In} \frac{[R]}{[R]_0} = -kt \qquad \textbf{[1]}$$

$$k = \frac{1}{t} \text{In} \frac{[R]_0}{[R]}$$

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

[CBSE Marking Scheme 2017] [1]

Q. 11. State a condition under which a bimolecular reaction is kinetically first order reaction. $\boxed{\text{C}}$

Ans. Let us take a bimolecular reaction :

$A + B \rightarrow$ Product

Rate = k $[A]$ $[B]$

When concentration of $[B]$ is taken in excess then rate law will become :

Rate = k $[A]$

where, k = constant

The rate depends only on one of the reactant as there is negligible change in its concentration so it is bimolecular but is of first order. **[2]**

Q. 12. The C-14 content of an ancient piece of wood was found to have three tenths of that in living trees. How old is that piece of wood? (log 3= 0.4771, log 7 = 0.8540 , Half-life of C-14 = 5730 years) $\boxed{\text{A}}$

Ans. $k = 0.693/t_{1/2}$

$k = 0.693/5730 \text{ years}^{-1}$ [½]

$$t = \frac{2.303}{k} \log \frac{C_o}{C_t} \qquad [½]$$

Let $C_o = 1$ and $C_t = 3/10$

so $C_o/C_t = 1/(3/10) = 10/3$

$$t = \frac{2.303}{0.693} \times 5730 \log \frac{10}{3} \qquad [½]$$

t = 19042 × (1-0.4771) = 9957 years [½]

Q. 13. (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 ? $\boxed{\text{U}}$

Ans. (i) Zero order **[1]**

(ii) Pseudo-first order **[1]**

Commonly Made Error

- Student get confused in order of reactions.

Answering Tip

- Learn the units of various order reactions and also try and understand the underlying concept.

Q. 14. A first-order reaction has a rate constant $1.15 \times 10^{-3}\ s^{-1}$. How long will 5 g of this reactant take to reduce to 3 g ? $\boxed{\text{A}}$

Ans. Initial amount = 5 g

Final concentration = 3 g

Rate constant = $1.15 \times 10^{-3}\ s^{-1}$

We know that for a First order reaction,

$$t = \frac{2.303}{k}\log\frac{[R_{initial}]}{[R_{final}]}$$

$$= \frac{2.303}{1.15\times10^{-3}}\log\frac{5}{3}$$

$$= \frac{2.303}{1.15\times10^{-3}}\times0.2219$$

= 444.379 s **[2]**

Short Answer Type Questions-II

(3 marks each)

Q. 1. The following data were obtained for the reaction :

A + 2B → C

Experiment	[A]/M	[B]/M	Initial rate of formation of C/M min^{-1}
1	0.2	0.3	4.2×10^{-2}
2	0.1	0.1	6.0×10^{-3}
3	0.4	0.3	1.68×10^{-1}
4	0.1	0.4	2.40×10^{-2}

(a) Find the order of reaction with respect to A and B.

(b) Write the rate law and overall order of reaction.

(c) Calculate the rate constant (k).

[CBSE, Outside Delhi Set-2, 2019]

Ans. Rate = $k[A]^p[B]^q$

On solving

(a) Order with respect to A=2 , B=1 **[½] + [½]**

(b) Rate = $k[A]^2[B]^1$; overall order = 3 **[½] + [½]**

(c) Experiment 1 : $4.2 \times 10^{-2} = k\,(0.2)^2\,(0.3)$; k=3.5

Experiment 2 : $6.0 \times 10^{-3} = k\,(0.1)^2\,(0.1)$; k=6 **[1]**

(Full marks may be awarded for any one correct answer)

[CBSE Marking Scheme 2019]

Detailed Answer :

Let the order of reaction with respect to A be x and with respect to B be y.

∴ Rate of reaction = $k[A]^x[B]^y$

According to details given ,

$4.2 \times 10^{-2} = k[0.2]^x\,[0.3]^y$ …(i)

$6.0 \times 10^{-3} = k[0.1]^x\,[0.1]^y$ …(ii)

$1.68 \times 10^{-1} = k[0.4]^x\,[0.3]^y$ …(iii)

$2.40 \times 10^{-2} = k[0.1]^x\,[0.4]^y$ …(iv)

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

$$\frac{2.40\times10^{-2}}{6.0\times10^{-3}} = \frac{k[0.1]^x[0.4]^y}{k[0.1]^x[0.1]^y}$$

$$4 = \frac{[0.4]^y}{[0.1]^y}$$

$$(4)^1 = (4)^y$$

$$y = 1$$

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

$$\frac{4.2\times10^{-2}}{1.68\times10^{-1}} = \frac{k[0.2]^x[0.3]^y}{k[0.4]^x[0.3]^y}$$

$$0.25 = \frac{[0.1]^x}{[0.2]^x}$$

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

$$(0.5)^2 = (0.5)^x \qquad x = 2$$

(i) So the rate of reaction with respect to A is 2 and with respect to B is 1.

(ii) Rate law = $k[A]^2[B]$

Overall order of reaction is 3.

(iii) Rate constant, $K = \dfrac{\text{Rate}}{[A]^2[B]}$

$$= \frac{6.0\times10^{-3}}{(0.1)^2(0.1)}$$

$$= 6.0\ \text{mol}^{-2}\ \text{L}^2\ \text{min}^{-1}$$ **[3]**

Q. 2. Following data are obtained for the reaction :

$N_2O_5 \rightarrow 2NO_2 + ½O_2$

t/s	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(a) Show that it follows first order reaction.

(b) Calculate the half-life.

(Given log 2 = 0.3010, log 4 = 0.6021) **[3]**

[CBSE, Delhi set 1, 2017]

Ans. **(a)** $$k = \frac{2.303}{t}\log\frac{[A]_o}{[A]}$$ **[½]**

$$= \frac{2.303}{300}\log\frac{1.6\times10^{-2}}{0.8\times10^{-2}}$$

$$= \frac{2.303}{300}\log 2 = 2.31 \times 10^{-3}\ s^{-1}$$ **[½]**

At 600 s, $k = \frac{2.303}{t}\log\frac{[A]_o}{[A]}$ **[½]**

$$= \frac{2.303}{600}\log\frac{1.6\times10^{-2}}{0.4\times10^{-2}}$$

$$= 2.31\times10^{-3}\ s^{-1}$$

k is constant when using first order equation therefore it follows first order kinetics. **[½]**

OR

In equal time interval, half of the reactant gets converted into product and the rate of reaction is independent of concentration of reactant, so it is a first order reaction.

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

$= 0.693/2.31\times10^{-3}$

$= 300$ s

(If student writes directly that half life is 300 s, award full marks). **[1]**

[CBSE Marking Scheme, 2017]

Detailed Answer :

(a) For first order reaction the integral rate law is :

$$k_t = \ln\frac{a_0}{a_1}$$

Given, $a_0 = 1.6\times10^{-2}$ mol L^{-1}

For $t = 300\ s$, $a_t = 0.8\times10^{-2}$ mol L^{-1}

For $t = 600\ s$, $a_t = 0.4\times10^{-2}$ mol L^{-1}

Using first set of data in the rate law,

$$k\times300 = \ln\frac{1.6\times10^{-2}}{0.8\times10^{-2}}$$

$$k = 0.00231\ s^{-1}$$

Using second set of data in the rate law,

$$k\times600 = \ln\frac{1.6\times10^{-2}}{0.4\times10^{-2}}$$

$$\boldsymbol{k} = 0.00231\ s^{-1}$$

The value of k is consistent, therefore it follows first order reaction. **[1½]**

(b) The half-life of first order reaction is given by the following equation :

$$t_{[½]} = \frac{\ln 2}{k} = 2.303\times\frac{\log 2}{k}$$

$$\therefore\quad t_{[½]} = 2.303\times\frac{\log 2}{0.00231} = 300.08\ s.$$ **[1½]**

Commonly Made Error

- Some students get confused to show the order of reaction from the given data of a reaction.

Answering Tip

- Do practice to solve the numericals and be precise in your answer.

Q. 3. 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) A **[CBSE OD Set-1, 2, 3 2017]**

Ans. $t = \frac{2.303}{k}\log\frac{[A]^0}{A}$ **[½]**

$20\text{ min} = \frac{2.303}{k}\log\frac{100}{75}$ ...(i) **[½]**

$t = \frac{2.303}{k}\log\frac{100}{25}$ ...(ii) **[½]**

Divide (i) equation by (ii)

$$\frac{20}{t} = \frac{\frac{2.303}{k}\log\frac{100}{75}}{\frac{2.303}{k}\log\frac{100}{25}}$$

$$= \frac{\log 4/3}{\log 4}$$ **[½]**

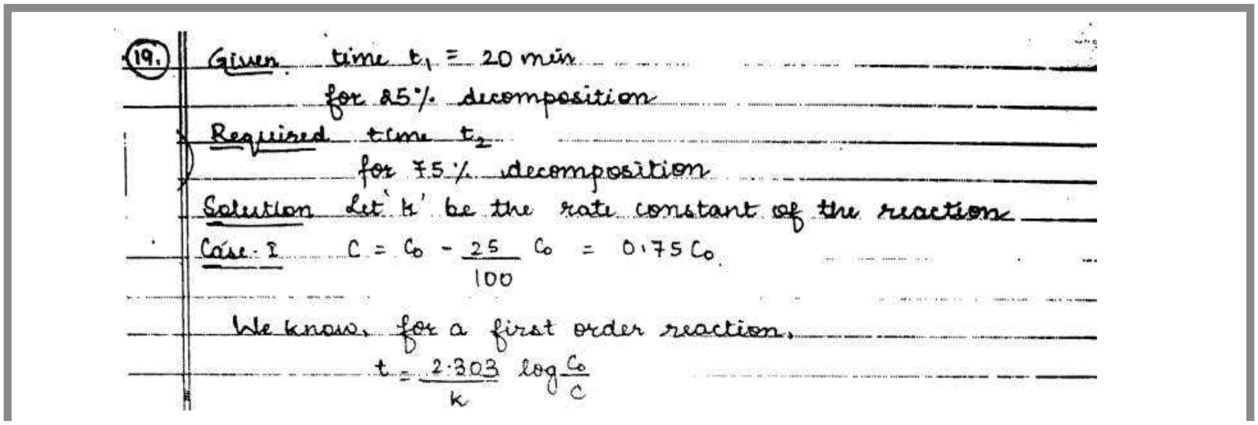
$20/t = 0.1250/0.6021$

$t = 96.3$ min **[1]**

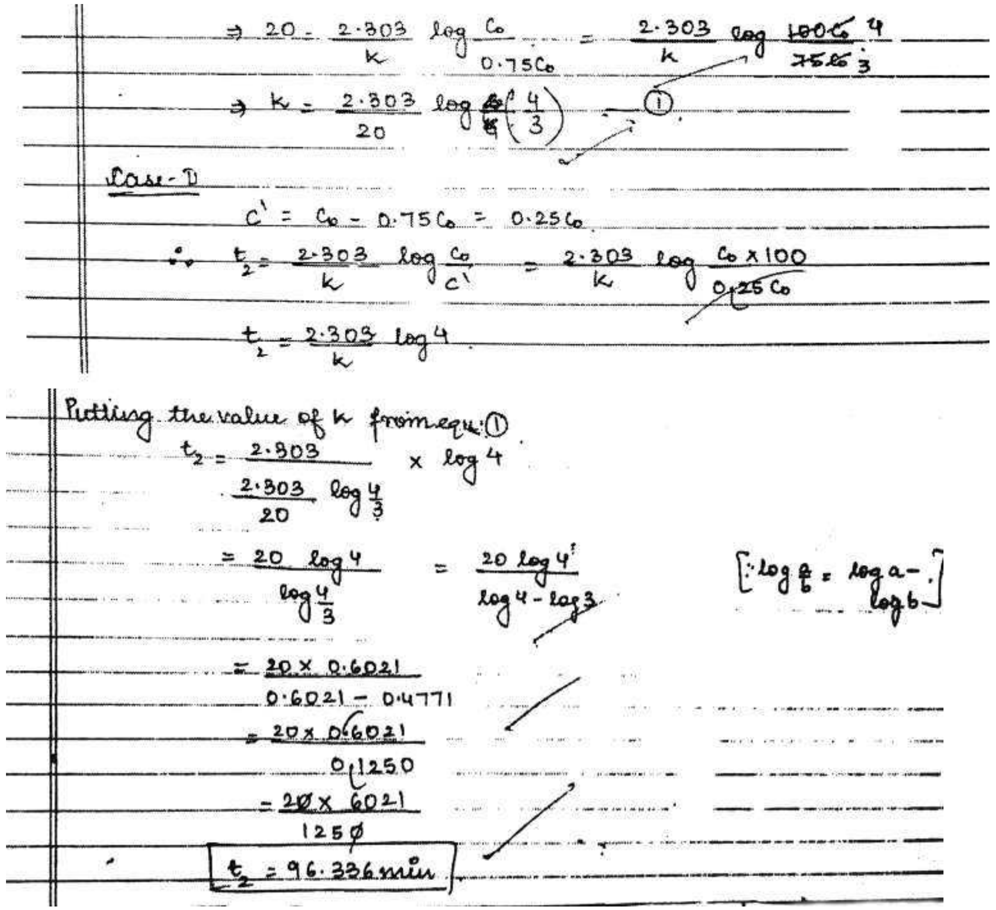
(or any other correct procedure)

[CBSE Marking Scheme 2017]

OR



(19.) Given. time t_1 = 20 min
for 25% decomposition
Required time t_2
for 75% decomposition
Solution Let 'k' be the rate constant of the reaction
Case-I $C = C_0 - \frac{25}{100}C_0 = 0.75\,C_0$
We know, for a first order reaction,
$t = \frac{2.303}{k}\log\frac{C_0}{C}$



$$\Rightarrow 20 = \frac{2.303}{k} \log \frac{C_0}{0.75C_0} = \frac{2.303}{k} \log \frac{\cancel{100C_0}\ 4}{\cancel{75C_0}\ 3}$$

$$\Rightarrow k = \frac{2.303}{20} \log \left(\frac{4}{3}\right) \text{ — ①}$$

Case - II

$$C' = C_0 - 0.75C_0 = 0.25C_0$$

$$\therefore t_2 = \frac{2.303}{k} \log \frac{C_0}{C'} = \frac{2.303}{k} \log \frac{C_0 \times 100}{0.25 C_0}$$

$$t_2 = \frac{2.303}{k} \log 4$$

Putting the value of k from equ: ①

$$t_2 = \frac{2.303}{\frac{2.303}{20} \log \frac{4}{3}} \times \log 4$$

$$= \frac{20 \log 4}{\log \frac{4}{3}} = \frac{20 \log 4}{\log 4 - \log 3} \qquad \left[\because \log \frac{a}{b} = \log a - \log b\right]$$

$$= \frac{20 \times 0.6021}{0.6021 - 0.4771}$$

$$= \frac{20 \times 0.6021}{0.1250}$$

$$= \frac{2\cancel{0} \times 6021}{125\cancel{0}}$$

$$\boxed{t_2 = 96.336 \text{ min}}$$

[3]

[Topper's Answer 2017]

Q. 4. For the first order thermal decomposition reaction, the following data were obtained :

$$\mathbf{C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)}$$

Time / sec	Total pressure / atm
0	0.30
300	0.50

Calculate the rate constant

(Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021)

[CBSE, Outside Delhi Set 1, 2016]

Ans. Given : Initial pressure,

$P_0 = 0.30$ atm

$P_t = 0.50$ atm

$t = 300\ s$

$$\text{Rate constant, } k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t} \qquad \textbf{[1]}$$

$$= \frac{2.303}{300\,\text{s}} \log \frac{0.30}{2 \times 0.30 - 0.50}$$

$$= \frac{2.303}{300\,\text{s}} \log \frac{0.30}{0.60 - 0.50}$$

$$= \frac{2.303}{300\,\text{s}} \log \frac{0.30}{0.10}$$

$$= \frac{2.303}{300\,\text{s}} \log 3 \qquad \textbf{[1]}$$

$$= \frac{2.303}{300\,\text{s}} \times 0.4771$$

$$= \frac{1.099}{300\,\text{s}}$$

$$= 0.0036\text{s}^{-1}$$

$$= 3.6 \times 10^{-3}\ \text{s}^{-1}$$

(deduct [½] mark if unit is not written) **[1]**

[CBSE Marking Scheme, 2016]

Commonly Made Error

- Students tend to overlook or incorrectly copy the data.

Answering Tip

- Read the question carefully to write the correct values of concentration. Write working formula followed by substitution of values. Do not forget to mention unit with the answer.

Long Answer Type Questions

(5 marks each)

Q. 1. (a) A first order reaction is 25% complete in 40 minutes. Calculate the value of rate constant. In what time will the reaction be 80% completed?

(b) Define order of reaction. Write the condition under which a bimolecular reaction follows first order kinetics.

[CBSE, Delhi set 1, 2020]

Ans. (a) $t=\frac{2.303}{k}\log\frac{[A]_0}{[A]}$

(i) $40\,\text{min}=\frac{2.303}{k}\log\frac{100}{75}$ ...(i)

(ii) $t=\frac{2.303}{k}\log\frac{100}{20}$ ...(ii)

Dividing (i) by (ii)

$$\frac{40}{t}=\frac{2.303}{k}\log\frac{100}{75}\Big/\frac{2.303}{k}\log\frac{100}{20}$$

$$\frac{40}{t}=\frac{\frac{2.303}{k}\log\frac{4}{3}}{2.303\log 5}$$

$$\frac{40}{t}=\frac{0.6021/4.771}{0.6991}$$

$$\frac{40}{t}=\frac{0.1250}{0.6991}$$

$$t=\frac{0.6691\times 40}{0.1250}=223.712\text{ min.}$$

$$k=\frac{2.303}{t}\log\frac{100}{100-0.25}=\frac{2.303}{40}\log\frac{100}{75}$$

$$=\frac{2.303}{40}(\log 4-\log 3)$$

$$=\frac{2.303}{40}(0.6021-0.4771)$$

$$=\frac{2.303}{40}\times 0.125=0.007196$$

$$=7.196\times 10^{-3}\text{ min}^{-1}$$ **[3]**

(b) Order of reaction : The sum of the coefficients of the reacting species that are involved in the rate equation for the reaction, is called order of reaction.

The condition under which a bimolecular reaction follows first order kinetics is when one of the reactants is taken in large excess that its concentration hardly changes. **[2]**

Q. 2. (i) Write the rate law for a first order reaction. Justify the statement that half life for a first order reaction is independent of the initial concentration of the reactant.

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

C+A **[CBSE Comptt. OD Set-1, 2 2017]**

Ans. (i) For a first order reaction

$$k=\frac{2.303}{t}\log\frac{[R]_0}{[R]},$$

where $[R]_0$ = initial concentration, [R] = conc. after time t

When half of the reaction is completed, $[R]=[R]_0/2$. Representing, the time taken for half of the reaction to be completed, by $t_{1/2}$, equation becomes :

$$k=\frac{2.303}{t_{1/2}}\log\frac{[R]_0}{[R]_0/2}$$ **[½]**

$$\Rightarrow t_{1/2}=\frac{2.303}{k}\log 2$$ **[½]**

$$\Rightarrow t_{1/2}=\frac{2.303}{k}\times 0.3010$$

$$\Rightarrow t_{1/2}=\frac{0.693}{k}$$ **[½]**

The above equation shows that half-life of first order reaction is independent of the initial concentration of the reactant. **[½]**

(ii) For a first order reaction

$$t=\frac{2.303}{k}\log\frac{a}{a-x}$$ **[½]**

$$t_{99\%}=\frac{2.303}{k}\log\frac{100}{1}$$ **[½]**

$$=\frac{2.303}{k}\log 100$$

$$=\frac{2.303\times 2}{k}$$

$$=\frac{4.606}{k}$$ **[½]**

and $$t_{90\%}=\frac{2.303}{k}\log\frac{100}{10}$$ **[½]**

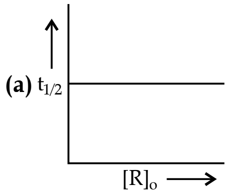
$$=\frac{2.303}{k}\log 10=\frac{2.303}{k}$$ **[½]**

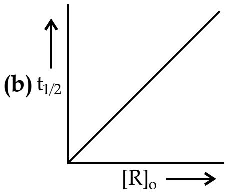
$$\frac{t_{99\%}}{t_{90\%}}=2$$

$$t_{99\%}=2\times t_{90\%}$$ **[½]**

Q. 3. (i) A first order reaction is 75% completed in 40 minutes. Calculate its $t_{1/2}$.

(ii) Predict the order of the reaction in the given plots:





where $[R]_0$ is the initial concentration of reactant.

(Given : log 2 = 0.3010, log 4 = 0.6021)

[CBSE Foreign Set-1, 2, 3 2017]

Ans. (i) $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$ **[½]**

$= \frac{2.303}{40}\log\frac{100}{25}$ **[½]**

$= \frac{2.303}{40}\log 4$

$= \frac{2.303}{40}\times 0.6021$

$k = 0.0347\ \text{min}^{-1}$ **[½]**

$t_{1/2} = \frac{0.693}{k}$ **[½]**

$t_{1/2} = \frac{0.693}{0.0347\,\text{min}^{-1}} = 19.98\ \text{min} = 20\ \text{min}$ **[1]**

(ii) (a) First order reaction **[1]**

(b) Zero order reaction **[1]**

[CBSE Marking Scheme 2017]

Q. 4. The following data were obtained for the reaction:

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

Experiment	**[NO]/M**	**$[O]^2$/M**	**Initial rate of formation of NO_2/M min^{-1}**
1	0.3	0.2	7.2×10^{-2}
2	0.1	0.1	6.0×10^{-3}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.40×10^{-2}

(i) Find the order of reaction with respect to NO and O_2.

(ii) Write the rate law and overall order of reaction.

(iii) Calculate the rate constant (*k*).

A **[CBSE Foreign Set-1, 2, 3 2017]**

Ans. (i) Rate $= k[NO]^x[O_2]^y$

$7.2\times10^{-2} = k[0.3]^x[0.2]^y$ Eqn (1)

$6.0\times10^{-3} = k[0.1]^x[0.1]^y$ Eqn (2)

$2.88\times10^{-1} = k[0.3]^x[0.4]^y$ Eqn (3)

$2.40\times10^{-2} = k[0.4]^x[0.1]^y$ Eqn (4)

Dividing eqn 4 by eqn 2

$$\frac{2.40\times10^{-2}}{6.0\times10^{-3}} = \frac{k[0.4]^x[0.1]^y}{k[0.1]^x[0.1]^y}$$

$x = 1$ **[1]**

Dividing eqn 3 by eqn 1

$$\frac{2.88\times10^{-1}}{7.2\times10^{-2}} = \frac{k[0.3]^x[0.4]^y}{k[0.3]^x[0.2]^y}$$

$y = 2$ **[1]**

order w.r.t. NO = 1, order w.r.t. O_2 is 2. **[½]+[½]**

(ii) Rate law

Rate $= k[NO]^1[O_2]^2$, overall order of the reaction is 3. **[½]+[½]**

(iii) Rate constant $k = \frac{\text{rate}}{[NO]^1[O_2]^2} = \frac{7.2\times10^{-2}}{0.3\times(0.2)^2}$

$k = 6.0\ \text{mol}^{-2}\ \text{L}^2\ \text{min}^{-1}$ **[1]**

[CBSE Marking Scheme 2017]

Q. 5. (i) For a reaction A + B → P, the rate is given by Rate = k[A] $[B]^2$

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

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

(ii) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction. (log 2 = 0.3010) U **[Question for Green board]**

Ans. (i) A + B → P

Rate $= k[A]\,[B]^2$

(a) When concentration of B is doubled it means concentration of B becomes 2 times.

Thus, Rate $= k[A]^1\,[2B]^2$

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

So, the rate becomes 4 times. **[1]**

(b) Order of reaction is the number of molecules whose concentration alters after the reaction. If A is present in excess *i.e.,* its concentration is unaffected.

So, rate depends only on the concentration of B. as $k = [B]^2$

Thus, the reaction is of second order. **[1]**

(ii) STEP 1 : For the 1st order reaction :

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

$$t = 30\times60 = 1800\ \text{s}$$

$$k = \frac{2.303}{1800}\log\frac{100}{100-50}$$

$$= \frac{2.303}{1800}\log 2$$

$$= \frac{2.303}{1800} \times 0.3010$$ **[1]**

STEP 2 : and $$t = \frac{2.303}{k} \log \frac{a}{(a-x)}$$

$$= \frac{2.303}{k} \log \frac{100}{100-90}$$

$$= \frac{2.303}{k} \log 10 = \frac{2.303}{k}$$ **[1]**

STEP 3 : By putting the value of k here, we get

$$\Rightarrow \quad t = \frac{2.303 \times 1800}{2.303 \times 0.3010}$$

$$= 5.98 \times 10^3 \text{ s}$$ **[1]**

TOPIC-3
Concept of Collision Theory, Activation Energy and Arrhenius Equation

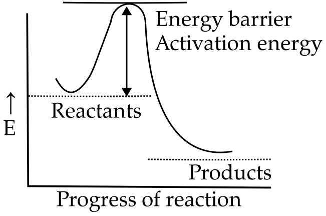
Revision Notes

- The rate of reaction is dependent on temperature. This is expressed in terms of temperature coefficient.

  $$\text{Temperature coefficient} = \frac{\text{Rate constant at 308 K}}{\text{Rate constant at 298 K}}$$

  It is observed that for a chemical reaction with rise in temperature by 10°C, the rate constant is nearly doubled.
- **Activation energy :** It is an extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to the formation of product molecules.
- Activation energy (E_a) for n reaction can not be zero. It is not possible that every collision between molecules will be effective. E_a can not have negative value.
- **Threshold energy :** The minimum energy that the reacting species must possess in order to undergo effective collision to form product molecules is called threshold energy.

  Activation theory (E_a) = Threshold energy (E_T) – Average energy of the reactions (E_R)



- **Arrhenius equation :** Activated complex is defined as unstable intermediate formed between reacting molecules. It is highly unstable and readily changes into product. Arrhenius equation gives the relation between rate of reaction and temperature.

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

  where k = Rate constant

  A = Frequency factor (Arrhenius factor)

  E_a = Activation Energy.

  R = Gas constant

  T = Temperature in Kelvin

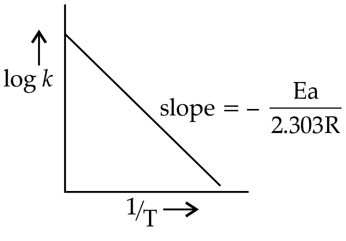
  $$\ln k = \ln A - E_a / RT$$

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

  A plot of log k with 1/T gives a straight line with slope $= -\frac{E_a}{2.303\,R}$

  If k_2 and k_1 are rate constants at temperature T_2 and T_1 respectively, then

  $$\log \frac{k_2}{k_1} = -\frac{E_a}{2.303\,R}\left|\frac{T_2 - T_1}{T_1 - T_2}\right|$$



- Those collisions which lead to the formation of product molecules are called effective collisions.

$$\text{Rate of reaction} = f \times z,$$

  where 'z' is collision frequency and 'f' is fraction of collisions which are effective.
- The number of collisions that take place per second per unit volume of the reaction mixture is called collision frequency. It is represented by 'Z'.
- Activated complex is defined as unstable intermediate formed between reacting molecules. It is highly unstable and readily changes into product.
- According to the collision theory, rate of reaction depends on the collision frequency and effective collisions.

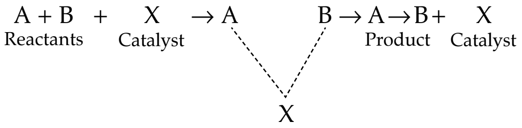
$$\text{Rate} = Z_{AB} e^{-E_a/RT},$$

  where Z_{AB} represents the collision frequency of reactants A and B. $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a.
- According to collision theory, another factor P which is called steric factor refers to the orientation of molecules which collide, is important and contributes to effective collision,

$$k = PZ_{AB} e^{-E_a/RT}$$

- **Catalyst :** A catalyst is a substance that alters the rate of reaction without itself undergoing any chemical change at the end of reaction.

  Intermediate complex theory :



$$\underset{\text{Reactants}}{A + B} + \underset{\text{Catalyst}}{X} \rightarrow A \qquad B \rightarrow \underset{\text{Product}}{A \rightarrow B} + \underset{\text{Catalyst}}{X}$$

Intermediate complex

Characteristics of catalyst :

(i) Catalyzes only the spontaneous reaction.

(ii) Does not change the equilibrium constant.

(iii) Catalyzes both the forward and backward reactions.

(iv) Does not alter the free energy change (ΔG) of a reaction.

(v) A small amount of the catalyst can catalyse large amount of reactions.

Mnemonics

- **Concept:** Effect of Collision
- **Mnemonics :** ECFPM
- **Interpretation :** Effective collisions lead to formation of product molecules.
- **Concept:** Catalyst
- **Mnemonics :** CAR
- **Interpretation :** A catalyst alters the reaction

Know the Formulae

- Temperature coefficient $= \dfrac{\text{Rate constant at}\,(T+10)°}{\text{Rate constant at } T°}$
- Rate of reaction $= f \times Z$

  where Z is the collision frequency, f is the fraction of collisions.
- Arrhenius equation : $k = Ae^{-E_a/RT}$
- Rate $= PZe^{-E_a/RT}$

How is it done on the GREENBOARD?

Q. (i) For the reaction A → B, the rate of reaction becomes twenty seven times when the concentraion of A is increased three times. What is the order of the reaction ?

(ii) The activation energy of a reaction is 75.2 kJ mol^{-1} in the absence of a catalyst and it lowers to 50.14 kJ mol^{-1} with a catalyst. How many times will the rate of reaction grow in the presence of a catalyst if the reaction proceeds at 25°C?

Solution:

STEP - I : (i) $r = k[\mathrm{R}]^n$

When concentration is increased three times,

$$[\mathrm{R}] = 3a$$

$$27r = k(3a)^n$$ **[½]**

$$\frac{27}{r} = \frac{k(3a)^n}{ka^n} \text{ or } 27$$ **[½]**

$$= 3^n \text{ or } 3^3 = 3^n$$

$$n = 3$$ **[1]**

(ii) STEP - I : According to Arrhenius equation,

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

For uncatalysed reaction

$$\log k_1 = \log \mathrm{A} - \frac{E_a(1)}{2.303RT} \quad \text{...(i)}$$ **[½]**

STEP - II : For catalysed reaction

$$\log k_2 = \log \mathrm{A} - \frac{E_a(2)}{2.303RT} \quad \text{...(ii)}$$ **[½]**

STEP - III : A is equal for both the reactions.

Subtracting equation (i) from equation (ii)

$$\log\frac{k_2}{k_1} = \frac{E_a(1) - E_a(2)}{2.303RT}$$

$$\log\frac{k_2}{k_1} = \frac{(75.2 - 50.14)kJ\,\mathrm{mol}^{-1}}{2.303 \times 8.314\,JK^{-1}\mathrm{mol}^{-1} \times 298\,K}$$

$$\log\frac{k_2}{k_1} = 4.39$$

$$\frac{k_2}{k_1} = \text{antilog}(4.39)$$

$$= 2.45 \times 10^4$$ **[1]**

Rate of reaction increases by 2.45×10^4 times. **[1]**

Objective Type Questions

(1 mark each)

[A] MULTIPLE CHOICE QUESTIONS :

Q. 1. The slope in the plot of ln[R] vs. time gives

(a) $+k$ **(b)** $\frac{+k}{2.303}$

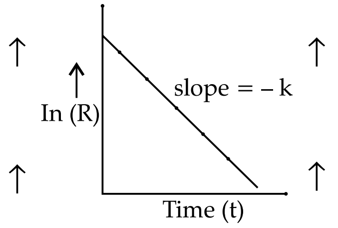
(c) $-k$ **(d)** $\frac{-k}{2.303}$

(where [R] is the final concentration of reactant.)

[CBSE, Outside Delhi Set 1, 2020]

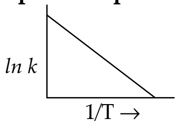
Ans. Correct option : (c)

Explanation :

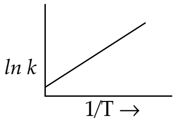


Q. 2. According to Arrhenius equation, rate constant k is equal to $Ae^{-E_a/RT}$. Which of the following options represent the graph of *ln k* versus 1/T ? $\boxed{A}$

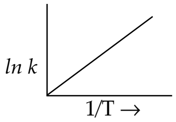
(a)



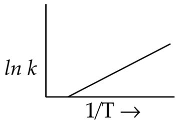
(b)



(c)



(d)



Ans. Correct option : (a)

Explanation : According to Arrhenius equation,

$$k = A.e^{-E_a/\text{RT}}$$

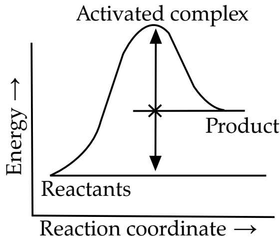
Taking log on both sides

$$\ln k = \ln\ A - \frac{E_a}{RT} = -\frac{-E_a}{R} \times \frac{1}{T} + \text{In}\ A$$

This equation can be related to equation of straight line, $y = mx + c$. It is evident that slope of the plot can be given as slope = $\frac{E_a}{R}$

Intercept = ln A.

Q. 3. Consider the following figure 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 is 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. $\boxed{U}$

Ans. Correct option : (c)

Explanation : Activation energy of forward reaction is $E_1 + E_2$ and their product is less stable than reactants.

E_a (forward) = $E_1 + E_2$

As energy of reactants is less than products and the product is less stable than the reactant.

[B] ASSERTION AND REASON TYPE QUESTIONS :

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

Q. 1. 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. Correct option : (c)

Explanation : According to Arrhenius equation, the rate constant determined is closely accurate for single as well as complex reaction because the reactant molecules with proper orientation and sufficient kinetic energy undergo a chemical change.

Q. 2. Assertion : The rate of reaction on also increase with its product if one of the product act as catalyst.

Reason: A catalyst lowers the activation energy of reaction.

Ans. Correct option: (a)

Explanation : A catalyst increases the rate of reaction by decreasing activation energy.

Q. 3. Assertion : There is no reaction known for which ΔG is positive, yet it is spontaneous.

Reason : For photochemical reaction, ΔG may or may not be negative.

Ans. Correct option: (a)

Explanation : For photochemical reaction, ΔG may or may not be negative. While for spontaneous reaction, ΔG is negative.

[C] VERY SHORT ANSWER TYPE QUESTIONS :

Q. 1. Define activation energy. $\boxed{R}$

Ans. The minimum extra energy over and above the average potential energy of the reactants which must be supplied to the reactants to enable them to cross over the energy barrier between reactants and product is called activation energy.

Q. 2. All collisions taking place between reactants do not form products. Why? $\boxed{U}$

Ans. Only those collisions are effective for a reaction which help reactant molecules to get threshold energy level.

Q. 3. What is the effect of (i) catalyst (ii) increase in temperature on activation energy? $\boxed{R}$

Ans. (i) A catalyst decreases the activation energy. **[½]**

(ii) An increase in temperature decreases the activation energy. **[½]**

Short Answer Type Questions-I

(2 marks each)

AI **Q. 1. What is the effect of adding a catalyst on**

(i) Activation energy (E_a), and

(ii) Gibb's energy (ΔG) of a reaction ?

[CBSE, Delhi Set 3/ Outside Delhi Set 1, 2017]

Ans. (i) Decreases [½]

(ii) No effect [½]

[CBSE Marking Scheme, 2017]

Detailed Answer :

(i) Adding of a catalyst lowers the activation energy (E_a) of reactants. [½]

(ii) Adding of a catalyst has no effect on Gibb's free energy. [½]

Q. 2. The activation energy for the reaction,

$2HI(g) \rightarrow H_2(g) + I_2(g)$

is 209.5 KJ mol^{-1} at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy. A&E

Ans.

$$x = \frac{n}{N} = e^{-E_a/Rt}$$

$$E_a = 209.5 \times 10^3 \text{ J mol}^{-1}$$

$$T = 581 \text{ K}$$

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

$$\log x = \frac{-E_a}{2.303RT}$$

$$= -\frac{209.5 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 581 \text{ K}}$$

$$= -18.8323$$

$$X = \text{Antilog } (-18.8323)$$

$$= \text{Antilog } \overline{19}.1677$$

$$= 1.471 \times 10^{-19}$$ [2]

Q. 3. The rate of a particular reaction quadruples on increasing temperature from 293K to 313K. For this reaction, calculate activation energy. A

Ans.

$$T_1 = 293 \text{ K}$$

$$T_2 = 313 \text{ K}$$

$$\frac{k_2}{k_1} = 4$$

According to Arhenius equation,

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

$$\log 4 = \frac{E_a}{2.303 \times 8.314}\left[\frac{313 - 293}{293 \times 313}\right]$$

$$0.6020 = \frac{E_a}{2.303 \times 8.314} \times \frac{20}{91709}$$

$$E_a = 528545 \text{ J mol}^{-1}$$

$$= 52.854 \text{ KJ mol}^{-1}$$ [2]

Short Answer Type Questions-II

(3 marks each)

Q. 1. The rate constant for the first order decomposition of N_2O_5 is given by the following equation : $k = (2.5 \times 10^{14} \text{ s}^{-1})\, e^{(-25000K)/T}$

Calculate E_a for this reaction and rate constant if its half-life period be 300 minutes.

[CBSE, Outside Delhi Set 1, 2020]

Ans.

$$k = (2.5 \times 10^{14}\, l^{-1})\, e^{(-25000K)/T}$$

$$t_{1/2} = 300 \text{ minutes}$$

$$\frac{E_a}{R} = 25000K$$

$$E_a = 25000 \times R \times K$$

$$= 25000 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times K$$ [2]

$$= 207850 \text{ J mol}^{-1} = 207.850 \text{ KJ mol}^{-1}$$

$$t_{½} = \frac{0.693}{K} \Rightarrow K = \frac{0.693}{300} \text{min}^{-1}$$

$$= 0.231 \times 10^{-2}$$ [1]

$$= 2.31 \times 10^{-3} \text{ min}^{-1}$$

Q. 2. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction. (Given : log 2 = 0.3010, log 4 = 0.6021, R = 8.314 JK^{-1}mol^{-1}) **[CBSE, Outside Delhi, 2018]**

Ans.

$$k_2 = 0.693/20,$$

$$k_1 = 0.693/40$$

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

$$k_2/k_1 = 2$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\left[\frac{320 - 300}{320 \times 300}\right]$$

$$E_a = 27663.8 \text{ J/mol or } 27.66 \text{ kJ/ mol}$$ [3]

Q.3. Two reactions of the same order have equal pre exponential factors but their activation energies differ by 24.9 kJ mol^{-1}. Calculate the ratio between the rate constants of these reactions at 27°C. (Gas constant R = 8.314 J K^{-1} mol^{-1}) U

Ans. The Arrhenius equation : $k = Ae^{-E_a/RT}$

Taking log on both sides : $\log k = \log A - \frac{E_a}{2.303RT}$

For reaction (i) : $\log k_1 = \log A - \frac{E_a(1)}{2.303RT}$ [1]

For reaction (ii) : $\log k_2 = \log A - \frac{E_a(2)}{2.303RT}$ [1]

Subtracting (i) from (ii)

$$\frac{\log k_1}{\log k_2} = \frac{E_a(1) - E_a(2)}{2.303\,RT}$$

$$\frac{\log k_1}{\log k_2} = \frac{24.9 \times 1000}{2.303 \times 8.3 \times 300}$$

$$= 4.342$$

$$\frac{k_1}{k_2} = \text{antilog}(4.342) = 2.198 \times 10^4$$ **[1]**

Commonly Made Error

- Students often substitute incorrect data in the working formula leading to wrong result.

Answering Tip

- List the given data and carefully identify the values to be computed in the formula.

AI Q.4. The rate constant for the first order decomposition of H_2O_2 is given by the following equation :

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} K\,;$$

Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes.
(Given : $R = 8.314\ J\ K^{-1}\ mol^{-1}$)

U [CBSE, Delhi Set 1, 2016]

Ans.

$$\log k = \frac{\log A - E_a}{2.303RT}$$ **[½]**

$$\frac{E_a}{2.303\,RT} = \frac{1.0 \times 10^4\ K}{T}$$

$$E_a = 1.0 \times 10^4 \times 2.303 \times 8.314$$

$$= 191471.4\ J/mol$$ **1**

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$ **[½]**

$$k = \frac{0.693}{200}\ \text{min}$$

$$= 0.0034\ \text{min}^{-1}$$ **1**

[CBSE Marking Scheme, 2016]

Long Answer Type Questions

(5 marks each)

AI Q. 1. (a) A first order reaction is 50% completed in 30 minutes at 300 K and in 10 minutes at 320 K. Calculate activation energy (E_a) for the reaction. ($R = 8.314\ J\ K^{-1}\ mol^{-1}$)

(b) Write the two conditions for collisions to be effective collisions.

(c) How order of reaction and molecularity differ towards a complex reaction?

[Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021, log 5 = 0.6991]

A + U [CBSE, Delhi Set-1, 2 & 3, 2020]

Ans. (a) At 300K, $t_{1/2} = 30$ min.

$$t_{½} = \frac{0.693}{k} \text{ or } k = \frac{0.693}{t_{½}}$$

$$k_1 = \frac{0.693}{30} = 0.0231\,\text{min}^{-1}$$

At 320K, $t_{½} = 10\,\text{min}$

$$t_{½} = \frac{0.693}{k} \text{ or } k = \frac{0.693}{t_{½}}$$

$$k_2 = \frac{0.693}{10} = 0.0693\,\text{min}^{-1}$$

According to Arrhenius equation :

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

$$= \log\frac{0.0693}{0.0231} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$= \log\frac{0.0693}{0.0231} = \frac{E_a}{2.303 \times 8.314}\left[\frac{320 - 300}{300 \times 320}\right]$$

$$\left[\because R = 8.314\,JK^{-1}\ mol^{-1}\right]$$

$$= \log 3 = \frac{E_a \times 20}{2.303 \times 8.314 \times 300 \times 320}$$

$$E_a = \frac{\log 3 \times 2.303 \times 8.314 \times 300 \times 320}{20}$$

$[\because \log 3 = 0.4771]$

$$= \frac{0.4771 \times 2.303 \times 8.314 \times 300 \times 320}{20}$$

$= 43848.5\ J\ mol^{-1} = 43.85\ k\,J\ mol^{-1}$ **[2]**

(b) Two conditions for collisions to be effective collision are :

(i) The reactant molecules must have attained sufficient energy to break chemical bonds

(ii) The reactant molecules must have the proper orientation. **[2]**

(c) The number of the reacting species that collide simultaneously in a chemical reaction is called as molecularity of a reaction. The sum of the coefficients of the reacting species is the order of reaction.

For complex reactions, molecularity has no significance while the order of reaction is applicable. **[1]**

Visual Case-Based Questions

(4 marks each)

Q. 1. Read the passage given below and answer the following questions : 1×4=4

The rate of a reaction, which may also be called its velocity or speed, can be defined with relation to 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 c at 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 liter are employed for concentration and seconds for the time, the units for the rate are moles litre^{-1}sec^{-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 α^{th} power of the concentration of one of the reactants A, to the β^{th} power of the concentration of a second reactant B, and so forth, via.,

rate = $k\,C_A^{\alpha}\,C_A^{\beta}$

the over-all order of the reaction is simply

$n = \alpha + \beta +$ ----- (2)

Such a reaction is said to be of the α^{th} order with respect to the substance A, the β^{th} order with respect to B and so on...

(Laidler, K. J., & Glasstone, S. (1948). Rate, order and molecularity in chemical kinetics. Journal of Chemical Education, 25(7), 383.)

In the following questions, a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices on the basis of the above passage. (CBSE QB 2021)

(a) **Assertion and reason both are correct statements and reason is correct explanation for assertion.**

(b) **Assertion and reason both are correct statements but reason is not correct explanation for assertion.**

(c) **Assertion is correct statement but reason is wrong statement.**

(d) **Assertion is wrong statement but reason is correct statement.**

(i) **Assertion:** Rate of reaction is a measure of change in concentration of reactant with respect to time.

Reason: Rate of reaction is a measure of change in concentration of product with respect to time.

(ii) **Assertion:** For a reaction: P + 2Q → Products, Rate = k $[P]^{1/2}[Q]^1$ so the order of reaction is 1.5

Reason: Order of reaction is the sum of stoichiometric coefficients of the reactants.

(iii) **Assertion:** The unit of k is independent of order of reaction.

Reason: The unit of k is moles L^{-1}s^{-1}.

(iv) **Assertion:** Reactions can occur at different speeds.

Reason: Rate of reaction is also called speed of reaction.

Ans. **(i)** Correction option is **(b)**

(ii) Correction option is **(c)**

(iii) Correction option is **(d)**

(iv) Correction option is **(b)**

Q. 2. Read the passage given below and answer the following questions : (1 × 4 = 4)

The rate of the reaction is proportional to the concentration of the reactant. Hydrogenation of ethene results in the formation of ethane. The rate constant, k for the reaction was found to be 2.5×10^{-15}s^{-1}. The concentration of the reactant reduces to one-third of the initial concentration in 5 minutes.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) **Find the order of reaction :**

(a) Zero order **(b)** First order

(c) Second order **(d)** Fractional order

(ii) **The rate law equation is :**

(a) Rate = k $[C_2H_6]$ **(b)** Rate = k $[C_2H_4]^2$

(c) Rate = k $[C_2H_4]$ **(d)** Rate = k $[C_2H_4]^2$

(iii) **The half-life for the reaction is:**

(a) 2.772×10^{-24} s **(b)** 2.772×10^{-12} s

(c) 1.386×10^{-24} s **(d)** 1.386×10^{-12} s

(iv) **The rate constant of the reaction after 5 minutes is:**

(a) 0.4290 min^{-1} **(b)** 0.1297 min^{-1}

(c) 0.2197 min^{-1} **(d)** 0.6591 min^{-1}

OR

The slope of the curve in the reaction is :

(a) K **(b)** –K

(c) 2K **(d)** –2K

Ans.

(i) **Correct option: (b)**

Explanation : Since the rate of the reaction is proportional to the concentration for the reactant i.e. ethene so, it is first order reaction. **[1]**

(ii) **Correct option : (c)**

Explanation :

$$\underset{\text{Ethene}}{C_2H_4 + H_2} \xrightarrow{\text{Catalyst}} \underset{\text{Ethane}}{C_2H_6}$$

Rate law equation,

Rate = K $[C_2H_4]$ **[1]**

(iii) **Correct option : (a)**

Explanation : For first order reaction,

$$t_{1/2} = \frac{0.693}{K}$$
$$= \frac{0.693}{2.5 \times 10^{-15}\,s^{-1}}$$
$$= 2.772 \times 10^{-24}\,s$$

[1]

(iv) **Correct option : (c)**

Explanation : t = 5 min

$$\frac{[R]_0}{[R]} = 3$$

For first order reaction,

$$K \quad \frac{2.303}{t}\log\frac{[R]}{[R]}$$
$$\frac{2.303}{}\log 3$$
$$= \frac{2.303}{} \times 0.4771$$
$$0.2197\,\text{min}$$

[1]

OR

Correct option : (b)

Slope = –k **[1]**

Q. 3. Concentration dependence of rate is called differential rate equation. Integrated differential equations give relation between directly measured experimental data i.e. concentration at different times and rate constant. The integrated rate equations are different for the reactions of different reaction orders. The first-order reaction has a rate constant $1.15 \times 10^{-3} s^{-1}$.

The following questions are multiple choice questions. Choose the most appropriate answer:

(1 × 4 = 4)

(i) How long will 5g of this reactant take to reduce to 3g?

(a) 222.189 s **(b)** 444.379 s

(c) 111.095 s **(d)** 888.789 s

(ii) When the rate constant has same units as the rate of reaction, the order of the reaction is :

(a) Zero order **(b)** First order

(c) Second order **(d)** Fractional order

(iii) Under which condition a bimolecular reaction is kinetically first order reaction:

(a) When two reactants are involved.

(b) When one of the reactants is in excess.

(c) When one of the reactants does not involve in reaction.

(d) None of these.

(iv) For a reaction,

$A + H_2O \rightarrow B$

Rate ∝ [A]

The order of the reaction is:

(a) Zero order **(b)** Fractional order

(c) Pseudo first order **(d)** Second order

OR

The integrated rate equation for rate constant of a first order reaction is :

(a) $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

(b) $k = \frac{1}{t}\left[\frac{1}{[R]} - \frac{1}{[R]_0}\right]$

(c) $k = \frac{1}{2t}\left[\frac{1}{[R]^2} - \frac{1}{[R]_0^2}\right]$

(d) None of these

Ans.

(i) Correct option: (b)

Explanation : Initial amount= 5 g

Final concentration = 3 g

Rate constant= $1.15 \times 10^{-3}\ s^{-1}$

We know that for a First order reaction

$$t = \frac{2.303}{k} \log \frac{[R_{initial}]}{[R_{final}]}$$

$$= \frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3}$$

$$= \frac{2.303}{1.15 \times 10^{-3}} \times 0.2219$$

$$= 444.379\, s$$

[1]

(ii) Correct option: (a)

Explanation : In case of zero order reaction, the rate constant has same units as the rate of reaction.

$r = k\,[A]^0$

$r = k$

Unit of rate = mol $L^{-1}s^{-1}$

Unit of k = mol $L^{-1}s^{-1}$ **[1]**

(iii) Correct option: (b)

Explanation : When one of the reactants is in excess, a bimolecular reaction is kinetically first order reaction. **[1]**

(iv) Correct option: (c)

Explanation : $A + H_2O \rightarrow B$

r ∝ [A] **($\because$ $[H_2O]$ = excess)**

It is called pseudo first order reaction. **[1]**

OR

Correct option: (a)

Explanation : A → products

For first order reaction,

Integrated rate equation is,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$ **[1]**

❑❑

Self Assessment Test - 4

Time : 1 Hour **Max. Marks : 25**

1. **Read the passage given below and answer the following questions : (1 × 4 = 4)**

The formation of product is possible only if the molecules of reactants collide. For the colliding molecules, the total number of collisions which occur among the reacting species per second per unit volume is called collision frequency. All the collisions in a reaction mixture which are effective in bringing about the chemical reaction are called effective collisions. The number of effective collisions is very less as compared to total number of collisions. A certain minimum energy is required for effective collisions between reactant molecules in a chemical reaction. This certain minimum energy is called threshold energy. Only those molecular collisions are effective whose energy is either equal to or more than threshold energy. For effective collision, we have to provide certain extra amount of energy to them, this extra amount of energy is called activation energy. In the chemical reaction, the colliding molecules must have proper orientation at the time of collision so that the old bonds breaks and the new bonds are formed.

In these questions, a statement of Assertion is followed by a statement of Reason is given. Choose the correct answer out of the following choices.

(a) **Assertion and reason both are correct statements and the reason is correct explanation for assertion.**

(b) **Assertion and reason both are correct statements and the reason is not correct explanation for assertion.**

(c) **Assertion is correct statement but reason is wrong statement.**

(d) **Assertion is wrong statement but reason is correct statement.**

(i) **Assertion :** The formation of product is possible only if the molecules of reactants collide.

Reason : In a chemical reaction, chemical bonds in the reactants are broken and new bonds in the products are formed.

(ii) **Assertion :** All the collisions in a reaction mixture are effective in bringing about the chemical reaction.

Reason : The collisions which bring about the chemical reaction is called effective collisions.

(iii) **Assertion :** The number of effective collisions is very less than total collisions.

Reason : First molecules come in activated state and only those molecules form products whose energy is equal to or more than threshold energy.

(iv) **Assertion :** Greater than concentration of reactants, smaller is the rate of the reaction.

Reason : The number of collisions between the reacting molecules increases on increasing concentration of reactants.

OR

Assertion : In some cases, the reactant molecules having equal to or greater than threshold energy do not form products.

Reason : They posses proper orientation.

The following question (No. 2 to 5) are Multiple Choice Questions carrying 1 mark each.

2. **Which of the following quantity changes by addition of catalyst in a chemical reaction?**

(a) Entropy **(b)** Internal energy
(c) Enthalpy **(d)** Activation energy R

3. **The initial concentration of the reactant becomes twice in a reaction, then half-life period of that reaction is not affected. The order of that reaction is**

(a) first
(b) second
(c) more than zero but less than one
(d) zero U

4. **The unit of rate constant for the zero order reaction is**

(a) L s^{-1} **(b)** L $mol^{-1}s^{-1}$
(c) mol L^{-1} s^{-1} **(d)** mol s^{-1} R

5. **The temperature dependence of the rate constant is given by the Arrhenius equation:**

(a) $\ln k = \ln A - \frac{E_a}{RT}$ **(b)** $\ln A = \ln k - \frac{E_a}{RT}$
(c) $\ln k = A\frac{E_a}{RT}$ **(d)** $\ln A = RT\ln E_a - \ln k$ R

The following questions (No. 6 & 7), a statement of Assertion is followed by a statement of Reason. Choose the correct answer out of the following choices.

(a) **Assertion and reason both are correct statements and reason is correct explanation for assertion.**

(b) **Assertion and reason both are correct statements but reason is not the correct explanation for assertion.**

(c) **Assertion is correct statement but reason is wrong statement.**

(d) **Assertion is wrong statement but reason is correct statement.**

6. **Assertion :** Half-life period is always independent of initial concentration.

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

7. **Assertion :** Order of a reaction cannot be written from the balanced equation of a reaction.

Reason: Rate law can provide some clue about the reaction mechanism.

The following questions (No. 8 & 9), are Short Answer Type-I and carry 2 marks each.

8. The rate of a reaction depends upon the temperature and is quantitatively expressed as :

(i) If a graph is plotted between log k and 1/T, write the expression for the slope of the reaction?

(ii) If at under different conditions Ea1 and Ea2 are the activation energy of two reactions. If Ea1 = 40J/mol and Ea2 = 80 J/mol. Which of the two has a larger value of the rate constant?

9. **(i)** Rate law $r = k[A]^{1/2}[B]^2$ is given for the reaction $A + B \rightarrow P$. What will be the order of the reaction?

(ii) The rate constant (k) is $5.5 \times 10^{-14} s^{-1}$ for a first order reaction. Calculate the half-time period of this reaction.

Q.No. 10 & 11 are Short Answer Type-II carrying 3 marks each.

10. For the reaction A + B → products, the following initial rates were obtained at various given initial concentrations :

S.No.	[A] mol/L	[B] mol/L	Initial rate M/s
1.	0.1	0.1	0.05
2.	0.2	0.1	0.10
3	0.1	0.2	0.05

Determine the half-life period. U

11. A first order reaction is 50% complete in 50 minutes at 300 K and the same reaction is again 50% complete in 25 minutes at 350 K. Calculate activation energy of the reaction. A&E

Q.No 12 is a Long Answer Type Question carrying 5 marks.

12. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained :

t/s	0	300	600
$[CH_3COOCH_3]$ / mol L^{-1}	0.60	0.30	0.15

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

(ii) Calculate the average rate of reaction between the time interval 30 lo 60 seconds.

(Given log 2 = 0.3010, log 4 = 0.6021)

OR

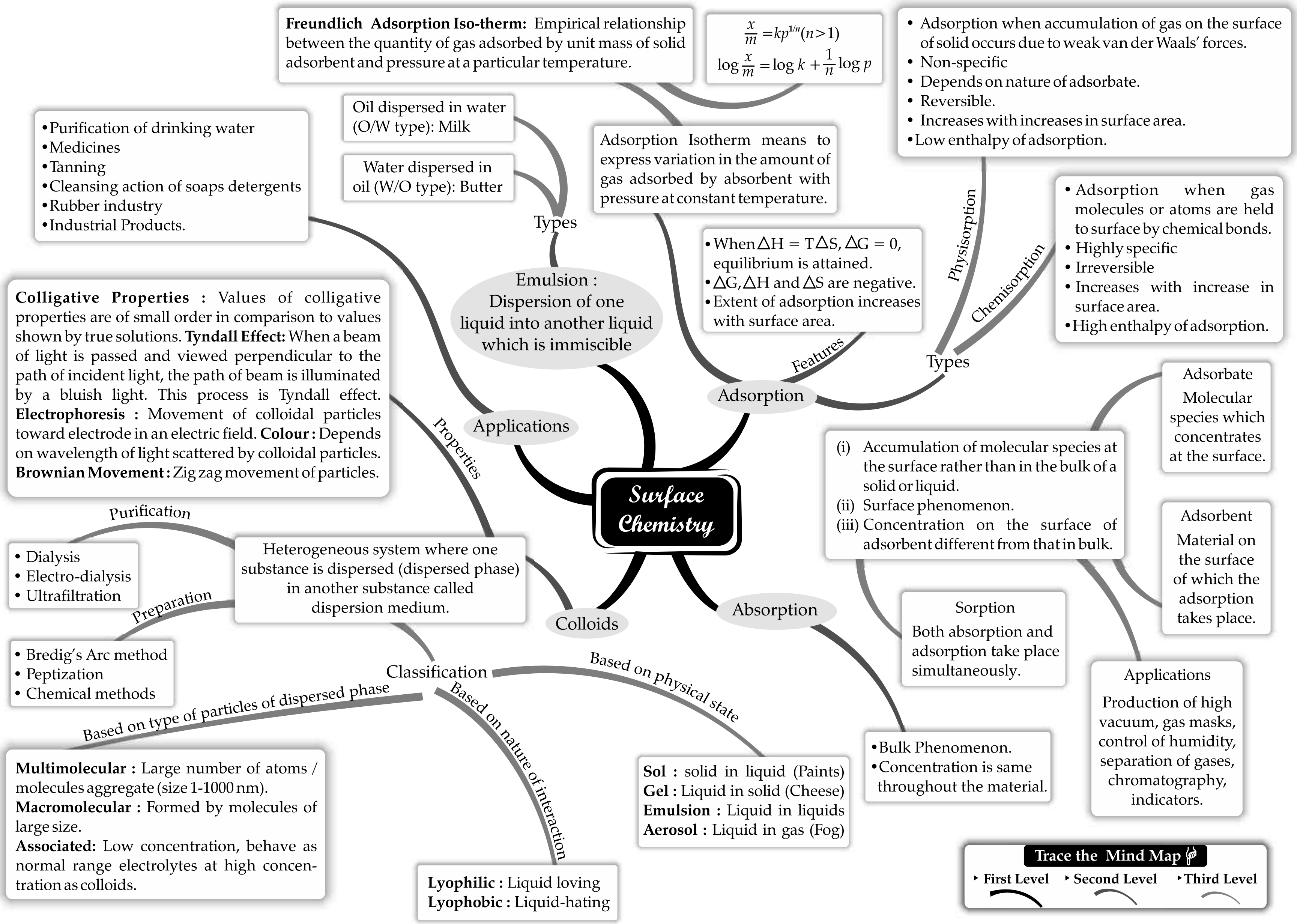
(i) For a reaction $A + B \rightarrow P$, the rate is given by

Rate = $k[A]\,[B]^2$

(a) How is the rate of reaction affocted if the concentration of B is doubled ?

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

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



Surface Chemistry

Adsorption

(i) Accumulation of molecular species at the surface rather than in the bulk of a solid or liquid.
(ii) Surface phenomenon.
(iii) Concentration on the surface of adsorbent different from that in bulk.

Adsorbate
Molecular species which concentrates at the surface.

Adsorbent
Material on the surface of which the adsorption takes place.

Applications
Production of high vacuum, gas masks, control of humidity, separation of gases, chromatography, indicators.

Features

- When $\Delta H = T\Delta S, \Delta G = 0$, equilibrium is attained.
- $\Delta G, \Delta H$ and ΔS are negative.
- Extent of adsorption increases with surface area.

Adsorption Isotherm means to express variation in the amount of gas adsorbed by absorbent with pressure at constant temperature.

Freundlich Adsorption Iso-therm: Empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.

$$\frac{x}{m} = kp^{1/n} (n > 1)$$

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

Types

Physisorption

- Adsorption when accumulation of gas on the surface of solid occurs due to weak van der Waals' forces.
- Non-specific
- Depends on nature of adsorbate.
- Reversible.
- Increases with increases in surface area.
- Low enthalpy of adsorption.

Chemisorption

- Adsorption when gas molecules or atoms are held to surface by chemical bonds.
- Highly specific
- Irreversible
- Increases with increase in surface area.
- High enthalpy of adsorption.

Absorption

- Bulk Phenomenon.
- Concentration is same throughout the material.

Sorption
Both absorption and adsorption take place simultaneously.

Applications

- Purification of drinking water
- Medicines
- Tanning
- Cleansing action of soaps detergents
- Rubber industry
- Industrial Products.

Emulsion : Dispersion of one liquid into another liquid which is immiscible

Types

Oil dispersed in water (O/W type): Milk

Water dispersed in oil (W/O type): Butter

Colloids

Heterogeneous system where one substance is dispersed (dispersed phase) in another substance called dispersion medium.

Properties

Colligative Properties : Values of colligative properties are of small order in comparison to values shown by true solutions. **Tyndall Effect:** When a beam of light is passed and viewed perpendicular to the path of incident light, the path of beam is illuminated by a bluish light. This process is Tyndall effect. **Electrophoresis :** Movement of colloidal particles toward electrode in an electric field. **Colour :** Depends on wavelength of light scattered by colloidal particles. **Brownian Movement :** Zig zag movement of particles.

Purification

- Dialysis
- Electro-dialysis
- Ultrafiltration

Preparation

- Bredig's Arc method
- Peptization
- Chemical methods

Classification

Based on type of particles of dispersed phase

Multimolecular : Large number of atoms / molecules aggregate (size 1-1000 nm).
Macromolecular : Formed by molecules of large size.
Associated: Low concentration, behave as normal range electrolytes at high concentration as colloids.

Based on nature of interaction

Lyophilic : Liquid loving
Lyophobic : Liquid-hating

Based on physical state

Sol : solid in liquid (Paints)
Gel : Liquid in solid (Cheese)
Emulsion : Liquid in liquids
Aerosol : Liquid in gas (Fog)

Trace the Mind Map
First Level
Second Level
Third Level