CHAPTER

3 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, no mathematical treatment). Activation energy, Arrhenius equation.*

Chapter Analysis

List of Topics	2016		2017		2018
	D	OD	D	OD	D/OD
Order and Molecularity of reaction	1 Q. (2 marks)	1 Q. (2 marks)	1 Q. (1 mark)		
Catalyst				1 Q. (1 mark)	1 Q. (1 mark)
Numerical on Activation Energy, Rate Constant, Order of Reaction, Half-life and Rate of Disappearance	1 Q. (3 marks)	1 Q. (3 marks)	1 Q. (3 marks)	1 Q. (3 marks)	1 Q. (2 marks) 1 Q. (3 marks)

On the basis of above analysis, it can be said that from exam point of view, Order and Molecularity of reaction, Catalyst and numerical on Order of Reaction, Half-life and Activation Energy are the most important topics of the chapter.

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.

$$A + B \rightarrow C$$

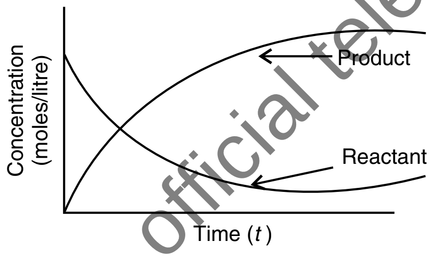
$$\text{Rate of reaction, A} = \frac{\text{Decrease in concentration of A}}{\text{Time taken}} = \frac{-\Delta A}{\Delta t}$$

$$\text{Similarly for reaction, B} = \frac{-\Delta B}{\Delta t} \text{ and for product C} = \frac{\Delta C}{\Delta t}$$

- **Unit of rate reaction :** mol L^{-1} s^{-1} or mol L^{-1} min^{-1} (in liquid), atm s^{-1} or atm m^{-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.

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

- **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 of the reaction :** 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 of the reaction :** 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 the velocity 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 :** Those 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. It states that the rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to some power which may or may not be equal to stereochemistry experimentally.

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

- **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.

Know the Terms

- **Catalyst :** A substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change.
- **Photochemical reactions :** The chemical reaction whose rate is influenced by radiations, particularly from ultraviolet and visible light is known as photochemical reaction.

Very Short Answer-Objective Type Questions (1 mark each)

A. Multiple choice Questions:

Q. 1. In the presence of a catalyst, heat evolved or absorbed during reaction :

(a) increases.
(b) decreases.
(c) remains unchanged.
(d) may increase or decrease.

U [NCERT Exemp. Q. 2, Page 47]

Ans. Correct option : (c)

Explanation : There is no effect on heat evolved or absorbed during the reaction in the presence of a catalyst. It is because catalyst influence the rate of reaction and does not participate in the reaction.

Q. 2. Rate law for the reaction A+2B- → C, is found to be Rate =k[A][B]. If the concentration of reactant B is doubled keeping the concentration of A constant, the value of rate constant will be :

(a) the same. **(b) doubled.**
(c) quadrupled. **(d) halved.**

A&E [NCERT Exemp. Q. 14, Page 51]

Ans. Correct option : (a)

Explanation : Rate constant of a reaction does not depend upon concentration of the reactants.

Q. 3. Which of the following expressions is correct for the rate of reaction given below?

$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

(a) $\frac{\Delta[Br^-]}{\Delta t} = 5\frac{\Delta[H^+]}{\Delta t}$ (b) $\frac{\Delta[Br^-]}{\Delta t} = \frac{6}{5}\frac{\Delta[H^+]}{\Delta t}$

(c) $\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$ (d) $\frac{\Delta[Br^-]}{\Delta t} = 6\frac{\Delta[H^+]}{\Delta t}$

A [NCERT Exemp. Q. 12, Page 50]

Ans. Correct option : (c)

Explanation : Rate law expression for the above equation is written as :

$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq.) + 3H_2O(l)$

Rate law expression for the above equation can be presented as :

$$\frac{+1}{5}\frac{\Delta(Br^-)}{\Delta t} = \frac{\Delta[BrO_3^-]}{\Delta t} = \frac{+1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{-1}{3}\frac{\Delta[Br_2]}{\Delta t}$$

$$\frac{\Delta[Br^-]}{\Delta t} = \frac{\Delta[BrO_3^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$$

$$\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$$

B. Match the following :

Q. 1. Match the items of Column I and Column II.

	Column I		Column II
(i)	Diamond	(a)	short interval of time
(ii)	Instantaneous rate	(b)	ordinarily rate of conversion is imperceptible
(iii)	Average rate	(c)	long duration of time

[NCERT Exemp. Q. 51, Page 40]

Ans. Correct option :

(ii) → (a)
(i) → (b)
(iii) → (c)

Explanation : (i) Diamond cannot be converted into graphite under ordinary condition.

(ii) Instantaneous rate of reaction complete at very short span of time.

(iii) Average rate of reaction occurs for a long duration of time.

C. Answer the following:

Q. 1. Define rate constant (*k*).

R [CBSE Comptt. OD 2016]

Ans. Rate constant is the rate of reaction when the concentration of reactant is unity. **1**

[CBSE Marking Scheme 2016]

Q. 2. Express the rate of the following reaction in terms of the formation of ammonia :

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

U [CBSE Comptt. OD 2013]

Ans. Rate of the reaction.

$$= \frac{-d[N_2]}{dt}$$

$$= \frac{-1}{3}\frac{d[H_2]}{dt} = \frac{+1}{2}\frac{d[NH_3]}{dt}$$ **1**

Answering Tip

- Read the question carefully, only give the expression as asked.

Short Answer Type Questions (2 marks each)

Q. 1. What is meant by rate of a reaction ? Differentiate between average rate and instantaneous rate of a reaction. **R + U [CBSE Comptt. OD 2012]**

Ans. Rate of a reaction is defined as the change in concentration of reactant or product in a chemical reaction at particular time interval.

Rate of reaction

$$= \frac{\text{Change in concentration}}{\text{Time taken}}$$

S. No.	**Instantaneous Rate**	**Average Rate**
(i)	It is defined as the rate of change in concentration of any one of the reactant or product in a chemical reaction at particular time.	It is defined as the rate of reaction measured over a long time interval.
	Let us consider reaction $A + B \rightarrow C$	
(ii)	Instantaneous rate for the above reaction would be, $\frac{dx}{dt} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{+d[C]}{dt}$	Average rate for the above reaction would be $= \frac{\Delta x}{\Delta t}$, where Δx is change in concentration in given time; Δt is time taken.

2

Commonly Made Error

- Some students just defined the terms. The concept of instantaneous rate and average rate are not clear to many students. Some students interchange the difference.

AI Q. 2. For the reaction

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

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).

A [CBSE Delhi/OD 2018]

Ans.

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

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

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

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

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

[CBSE Marking Scheme 2018]

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.

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. $\text{Rate} = k\,[A]_0$,

  $$k = \frac{[A]_0 - [A]}{t},$$

  where 'k' is rate constant and unit of the rate constant k is mol L^{-1} s^{-1}.

  This reaction will be zero order reaction.

  Photosynthesis of HCl(g) is an example of zero order reaction.
- **First order reaction :** The rate of reaction is directly proportional to the one 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'.

  The unit of 'k' is s^{-1} or min^{-1}

  Decomposition of NH_4NO_2 is the example.
- **Pseudo first order reaction :** If a reaction is not truly of the first order but under certain conditions become 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.

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

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

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

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

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

  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, $$t_{1/2} = \frac{[\mathrm{A}]_0}{2k},$$

  where $[\mathrm{A}]_0$ 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

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

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

  where $[\mathrm{A}]_0$ 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 :**

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

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

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

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

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

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

- **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.

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** $= \frac{k\ (T+10)}{k\ (T)}$

Know the Terms

- **Intermediates :** The species which are produced in one step and consumed in another.
- **Simple or elementary reaction :** When a reaction completes in a single step is called as simple or elementary reaction.
- **Complex reaction :** When number of elementary reactions (steps) are combined together and complete the reaction is called complex reaction.
- **Differential rate equation :** The concentration dependence of rate is called differential rate equation.

Very Short Answer-Objective Type Questions (1 mark each)

A. Multiple choice Questions:

Q. 1. The value of rate constant of a pseudo first order reaction :

(a) depends on the concentration of reactants present in small amount.

(b) depends on the concentration of reactants present in excess.

(c) is independent of the concentration of reactants.

(d) depends only on temperature.

U [NCERT Exemp. Q. 19, Page 52]

Ans. Correct option : (b)

Explanation : Rate constant of a pseudo first order reaction depends on the concentration of reactants present in excess.

Q. 2. A first order reaction is 50% completed in 1.26 × 10^{14} s. How much time would it take for 100% completion?

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

(c) 2.52 × 10^{28} s **(d) Infinite**

A [NCERT Exemp. Q. 16, Page 51]

Ans. Correct option : (d)

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

Q. 3. Consider a first order gas phase decomposition reaction given below :

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

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 ___________.

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

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

(c) $k = \frac{2.303}{t} \log \frac{P_i}{P_i + P_i}$

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

$\boxed{\text{A}}$ **[NCERT Exemp. Q. 5, Page 48]**

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

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

B. Answer the following:

Q. 1. For a reaction R → P, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants . What is the order of reaction?

$\boxed{\text{A}}$ **[CBSE Delhi Set-1, 2 2017]**

Ans. First order. **1**

[CBSE Marking Scheme 2017]

Q. 2. Write the unit of rate constant for a zero order reaction. $\boxed{\text{U}}$ **[CBSE Comptt. OD 2013]**

Ans. Unit is mol L^{-1} s^{-1}. **1**

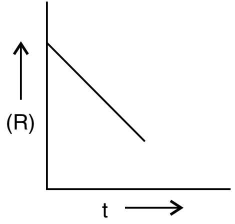
Q. 3. For the reaction A → B, the rate of reaction becomes three times when the concentration of A is increased by nine times. What is the order of reaction?

$\boxed{\text{A}}$ **[CBSE Comptt. Delhi/OD 2018]**

Ans. Order of reaction = 1/2 **1**

[CBSE Marking Scheme 2018]

Q. 4. For a chemical reaction R → P, the variation in the concentration (R) vs. time (t) plot is given as :



(i) Predict the order of the reaction.

(ii) What is the slope of the curve ?

$\boxed{\text{A}}$ **[CBSE OD 2014]**

Ans. (i) The reaction is a zero order reaction.

(ii) The slope of curve is $(-k)$ *i.e.*, negative of rate constant. **½ × 2**

Commonly Made Error

- Students get confused with the order. They do not give proper attention towards the coordinates.

Answering Tip

- Give stress on the variables taken on the coordinates.

Q. 5. If the rate constant of a reaction is $k = 3 \times 10^{-4}$ s^{-1}, then identify the order of the reaction.

$\boxed{\text{A}}$ **[CBSE Comptt. OD 2013]**

Ans. On the basis of unit of rate constant (s^{-1}), the order of reaction is first order. **1**

Commonly Made Error

- Incorrect unit.

Answering Tip

- General formula $(\text{mol } L^{-1})^{1-n}$ s^{-1} to write units for rate constant of any order (n is the order of the reaction).

AI **Q. 6. For a reaction, A + B → Product, the rate law is given by $r = k\,[A]^{1/2}\,[B]^2$. What is the order of the reaction ?** $\boxed{\text{A}}$ **[CBSE SQP 2016; DDE]**

Ans. Order of reaction $= \frac{1}{2} + 2$

$$= \frac{1+4}{2} = \frac{5}{2} = 2.5 \quad \mathbf{1}$$

Short Answer Type Questions (2 marks each)

Q. 1. Define the following terms :

(i) Pseudo first order reaction

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

$\boxed{\text{R}}$ **[CBSE Delhi 2014]**

Ans. (i) Pseudo first order reaction : If a reaction is not truly of the first order but under certain conditions become reaction of first order is called pseudo first order reaction. **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.

[CBSE Marking Scheme 2014] 1

Answering Tip

- Write only the definition of each as the question is of 2 marks.

Q. 2. 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. 3. Write two differences between 'order of reaction' and 'molecularity of reaction'.
U **[CBSE Delhi 2014]**

Ans. (i) Order of a reaction is meant for elementary as well as for complex reactions but molecularity is for elementary reactions. **1**

(ii) Order can be zero or fraction but molecularity cannot be zero or fraction. (or any other difference) **[CBSE Marking Scheme 2014] 1**

Commonly Made Error

- Some students just define the terms. A few students interchange the difference.

Q. 4. What do you understand by the rate law and rate constant of a reaction ? Identify the order of a reaction if the units of its rate constants are :
(i) L^{-1} mol s^{-1}
(ii) L mol^{-1} s^{-1} R + U **[CBSE Delhi 2012]**

Ans. The representation of rate of reaction in terms of concentration of the reactants is known as rate law. The rate constant is defined as the rate of reaction when the concentration of each reactant is unity. **1**
(i) Zero order ½
(ii) Second order ½

Commonly Made Error

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

Q. 5. 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

- Students get confused in order of reactions.

Answering Tip

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

Q. 6. For a reaction : $H_2 + Cl_2 \xrightarrow{hv} 2HCl$
Rate = *k*
(i) Write the order and molecularity of this reaction,
(ii) Write the unit of *k*. A **[CBSE OD 2016]**

Ans. (i) It is a zero order reaction, molecularity = 2 (Bimolecular reaction)
(ii) Units of *k* = mol L^{-1} s^{-1}. **1 × 2 = 2**
[CBSE Marking Scheme 2016]

Q. 7. (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 ∝ [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]

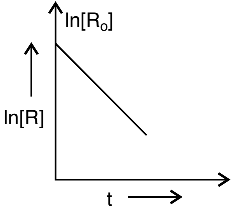
Commonly Made Error

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



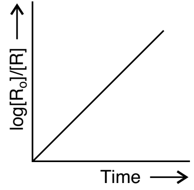
For this reaction :
(i) Predict the order of reaction
(ii) What is the unit of rate constant (*k*)?
A **[CBSE Comptt. Delhi Set-1, 2 2017]**

Ans. (i) First order. **1**
(ii) s^{-1}/time^{-1} **1**
[CBSE Marking Scheme 2017]

Commonly Made Error

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

Q. 9. 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*)?
A **[CBSE Comptt. Delhi Set-3 2017]**

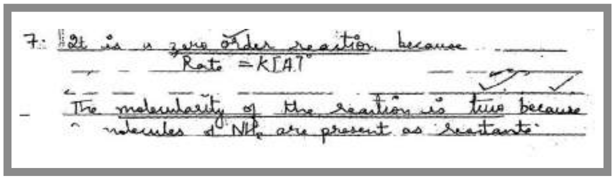
Ans. (i) First order. **1**
(ii) s^{-1}/time^{-1} **1**
[CBSE Marking Scheme 2017]

Q.10. **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. A **[CBSE Delhi 2016]**

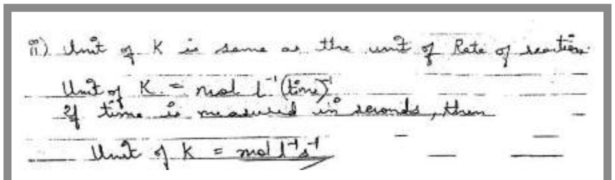
Ans.



7: It is a zero order reaction because

Rate $= K[A]^0$

The molecularity of the reaction is two because molecules of NH_3 are present as reactants



ii) Unit of K is same as the unit of Rate of reaction

Unit of K = mol L^{-1} $(time)^{-1}$

If time is measured in seconds, then

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

[Topper's Answers 2016] 2

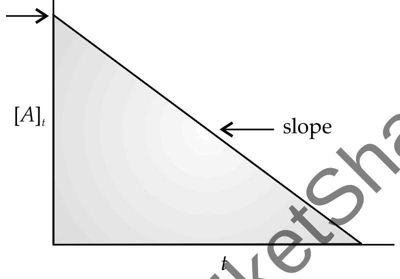
Detailed Answer :

(i) Order – Zero, Molecularity – Two ½+½

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

Q. 11. **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?

A **[CBSE SQP 2018-2019]**

Ans. (i) Zero order reaction ½

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

(iii) mol L^{-1} s^{-1} ½

[CBSE Marking Scheme 2014] 1

Q. 12. **(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. A&E+A

OR

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

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

Ans. (i) Due to high activation energy 1

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

OR

$$R \rightarrow P$$

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

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

Integrating this equation, we get

$$\text{In}[R] = -kt + I \qquad (4.8)$$

When $t = 0, R = [R]_0$,

where $[R]_0$ is the initial concentration of the reactant. Therefore, equation (4.8) can be written as

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

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

Substituting the value of I in equation (4.8)

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

Rearranging this equation (4.9)

$$\text{In}\frac{[R]}{[R]_0} = -kt$$ 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. 13. **State a condition under which a bimolecular reaction is kinetically first order reaction.**

C **[NCERT Exemplar]**

Ans. Let us take a biomolecular 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 biomolecular but is of first order. 2

Long Answer Type Questions-I (3 marks each)

Q. 1. **A reaction is first order in A and second order in B**

(i) Write the differential rate equation.

(ii) How is the rate affected on increasing the concentration of B three times ?

(iii) How is the rate affected when the concentration of both A and B are doubled ?

A **[CBSE Comptt. Delhi/OD 2018]**

Ans. (i) Rate = $k[A][B]^2$ 1

(ii) Rate becomes 9 times 1

(iii) Rate becomes 8 times 1

[CBSE Marking Scheme 2018]

Q. 2. **The following data were obtained during the first order thermal decomposition of $N_2O_5(g)$ at a**

constant volume:

$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$

S. No.	Time (sec.)	Total pressure (atm)
1.	0	0.5
2.	100	0.512

Calculate the rate constant.

A [CBSE SQP 2018-2019][CBSE Delhi 2014]

Ans.

	$2N_2O_5(g)$	$\rightarrow 2N_2O_4(g)$	$+ O_2(g)$
At t = 0	0.5 atm	0 atm	0 atm
At time t	0.5–2x atm	2x atm	x atm

$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$

$$= (0.5-2x) + 2x + x = 0.5+x \quad ½$$

$$x = pt - 0.5$$

$$p_{N_2O_5} = 0.5 - 2x$$

$$= 0.5 - 2(p_t - 0.5) \quad ½$$

$$= 1.5 - 2p_t$$

At t=100 s; pt = 0.512 atm

$$p_{N_2O_5} = 1.5-2 \times 0.512$$

$$= 0.476 \text{ atm}$$

$$k = \frac{2.303}{t}\log\frac{p_i}{p_A} \quad ½$$

$$k = \frac{2.303}{100\,\text{s}}\log\frac{0.5\text{ atm}}{0.476\,\text{atm}} \quad ½$$

$$k = 2.303 \times 0.0216 \times 10^{-2}$$

$$= 4.98 \times 10^{-4}\ s^{-1} \quad 1$$

[CBSE Marking Scheme 2018]

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.

$$t = \frac{2.303}{k}\log\frac{[A]_0}{A} \quad ½$$

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

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

Dividing equation (i) by (ii)

$$\frac{20}{t} = \frac{\frac{2.303}{k}\log\frac{100}{75}}{\frac{2.303}{k}\log\frac{100}{25}} = \frac{\log 4/3}{\log 4} \quad ½$$

$20/t = 0.1250/0.6021$

$t = 96.3$ min **1**

(or any other correct procedure)

[CBSE Marking Scheme 2017]

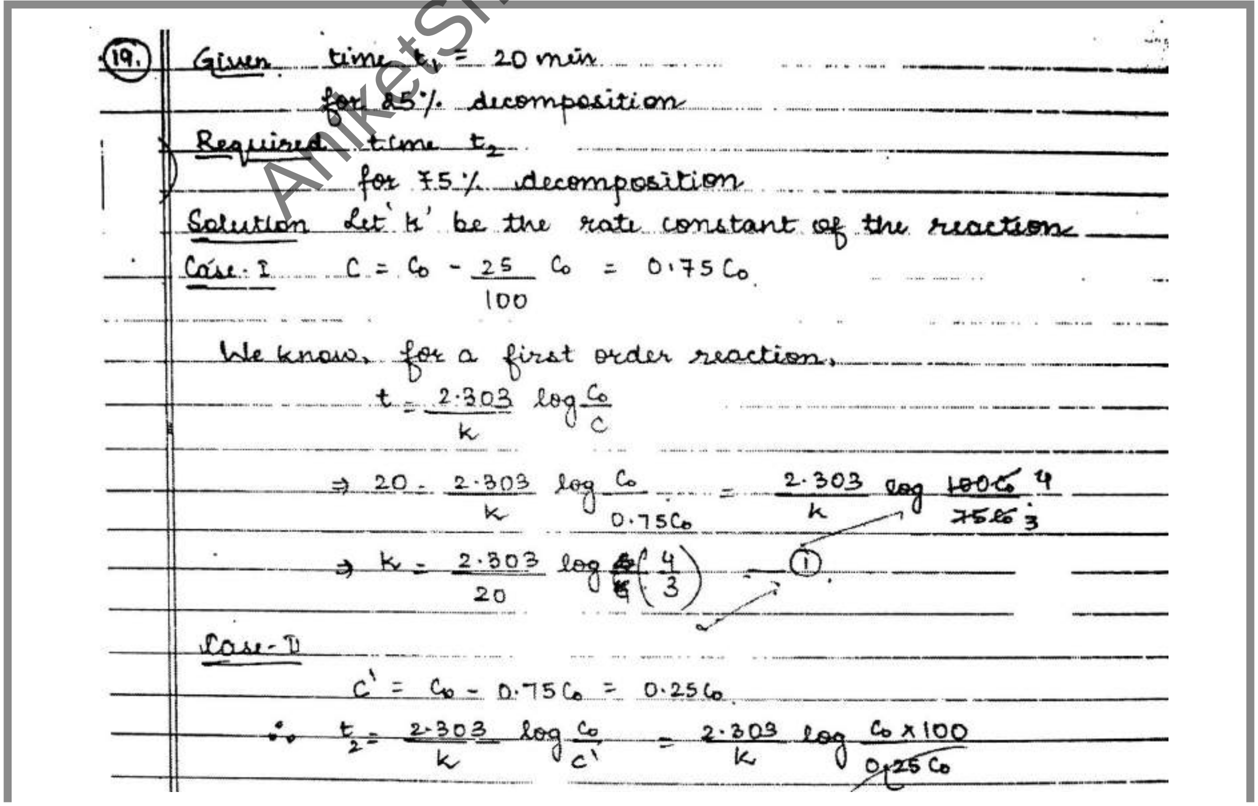
Commonly Made Error

- Incorrect values for concentration terms.

Answering Tip

- In the first order reactions, [A] given in the denominator is the concentration of the reactant present at that given time.

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,

$t = \frac{2.303}{k} \log\frac{C_0}{C}$

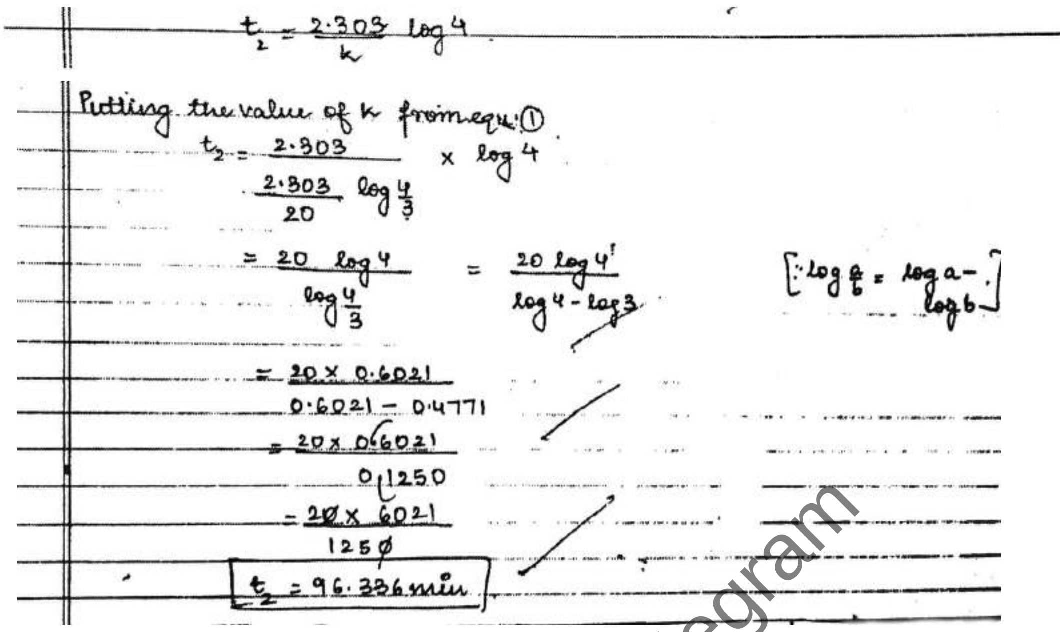
$\Rightarrow 20 = \frac{2.303}{k} \log\frac{C_0}{0.75C_0} = \frac{2.303}{k} \log \frac{\cancel{100C_0}\ 4}{\cancel{75C_0}\ 3}$

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

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

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

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

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

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

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

3

[Topper's Answer 2017]

Q. 4. Following data are obtained for the reaction:

$N_2O_5 \rightarrow 2NO_2 + {}^1\!/_2\, O_2$

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

(i) Show that it follows first order reaction.

(ii) Calculate the half-life.

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

A [CBSE Delhi Set-1, 2, 3 2017]

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

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

$= \frac{2.303}{300}\log 2 = 2.31\times10^{-3}s^{-1}$ ½

At 600 s, $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$ 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.

(ii) $t_{1/2} = 0.693/\text{k}$

$= 0.693/2.31 \times 10^{-3}$

$= 300$ s

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

[CBSE Marking Scheme 2017]

Commonly Made Error

- Incorrect values for the concentration terms. In first order reactions, the denominator is the concentration of the reactant present at that given time.

Q. 5. Half-life for a first order reaction is 693 s. Calculate the time required for 90% completion of this reaction. **A [CBSE Comptt. OD Set-3 2017]**

Ans. $t_{1/2} = \frac{0.693}{k}$ ½

$k = \frac{0.693}{693\ s}$

$= 0.001\ s^{-1}$ **1**

$k = \frac{2.303}{t}\log[R]_0/[R]$ ½

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

$= \frac{2.303}{0.001}\log 100/10$

$t = 2303\ s^{-1}$ **1**

[CBSE Marking Scheme 2017]

Commonly Made Error

- Incorrect values for concentration terms.

Answering Tip

- In the first order reactions, [R] given in the denominator is the concentration of the reactant present at that given time. Do not miss to write the unit with the numeric value.

Q. 6. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce 1 g of the reactant to 0.0625 g? $\boxed{\text{A}}$ **[CBSE SQP 2017]**

Ans. $t = \dfrac{2.303}{k}\log\dfrac{[R]_0}{[R]}$ 1

$t = \dfrac{2.303}{60}\log\dfrac{1}{0.0625}$ 1

$t = 0.0462\ s$ 1

[CBSE Marking Scheme 2017]

Q. 7. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

Experiment	**Time (s)**	**Total pressure (atm)**
1	**0**	**0.4**
2	**100**	**0.7**

Calculate the rate constant (k)

[Given: log 2 = 0.3010; log 4 = 0.6021]

$\boxed{\text{A}}$ **[CBSE Comptt. Delhi Set-1 2017; Delhi/OD 2014]**

Ans. $P_A = 2P_0 - P_t$ ½

$= (2 \times 0.4) - 0.7 = 0.1$ ½

$k = \dfrac{2.303}{t}\log P_0 / P_A$

$k = \dfrac{2.303}{100}\log 0.4 / 0.1$

$k = \dfrac{2.303}{100}\times 0.6021$ 1

$= 1.39 \times 10^{-2}\ s^{-1}$ 1

[CBSE Marking Scheme 2017]

Answering Tip

- Read the question carefully to write the correct values of concentration.

Q. 8. For the first order thermal decomposition reaction, the following data were obtained :

$C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$

Time / sec	**Total pressure / atm**
0	**0.30**
300	**0.50**

Calculate the rate constant.

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

$\boxed{\text{A}}$ **[CBSE OD 2016]**

Ans. $P_0 = 0.30$ atm $P_t = 0.50$ atm $t = 300$ s

Rate constant, $k = \dfrac{2.303}{t}\log\dfrac{P_0}{2P_0 - P_t}$ 1

$= \dfrac{2.303}{300}\log\dfrac{0.30}{2\times 0.30 - 0.50}$

$= \dfrac{2.303}{300}\log\dfrac{0.30}{0.60 - 0.50}$

$= \dfrac{2.303}{300}\log\dfrac{0.30}{0.10}$

$= \dfrac{2.303}{300}\log 3$ 1

$= \dfrac{2.303}{300}\times 0.4771 = \dfrac{1.099}{300}\ s^{-1}$

$= 0.0036\ s^{-1} = 3.6 \times 10^{-3}\ s^{-1}$ 1

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.

Q. 9. The rate constant for the first order decomposition of H_2O_2 is given by the following equation :

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

Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes.

(Given : R = 8.314 $JK^{-1}\ mol^{-1}$) $\boxed{\text{A}}$ **[CBSE Delhi 2016]**

Ans. $\log k = \dfrac{\log A - E_a}{2.303\ RT}$ ½

$\dfrac{E_a}{2.303\ RT} = \dfrac{k1.0\times 10^4}{T}$

$E_a = 1.0 \times 10^4 \times 2.303 \times 8.314$ 1

$= 191471.4$ J/mol ½

$t_{½} = \dfrac{0.693}{k}$

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

$= 0.0034\ \text{min}^{-1}$ or $3.4 \times 10^{-3}\ \text{min}^{-1}$ 1

[CBSE Marking Scheme 2016]

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.

Q. 10. Rate constant k for a first order reaction has been found to be 2.54 × 10^{-3}, sec^{-1}. Calculate its 3/4th life. (log 4 = 0.6020) $\boxed{\text{A}}$ **[CBSE Comptt. OD 2013]**

Ans. $k = 2.54 \times 10^{-3}\ \text{sec}^{-1}$

For a first order reaction, $t = \dfrac{2.303}{k}\log\dfrac{a}{a-x}$ ½

For 3/4th life $a - x = a - \dfrac{3}{4}a$

On substitution these values,

$t_{3/4} = \dfrac{2.303}{2.54\times 10^{-3}}\log\dfrac{a}{a-\frac{3}{4}a}$ ½

$= \dfrac{2.303}{2.54\times 10^{-3}}\log\dfrac{a}{\frac{1}{4}a}$ ½

$= \dfrac{2.303}{2.54\times 10^{-3}}\log 4$ ½

$= \dfrac{2.303}{2.54\times 10^{-3}}\times 0.6020$

$= 545.82$ sec 1

AI Q. 11. A first order gas phase reaction :

$$A_2B_2(g) \rightarrow 2A(g) + 2B(g)$$

at the temperature 400°C has the rate constant k = 2.0 × 10⁻⁴ sec⁻¹. What percentage of A_2B_2 is decomposed on heating for 900 seconds ? [Antilog 0.0781 = 1.197] A **[CBSE Comptt. OD 2013]**

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

$$\Rightarrow \quad 2\times10^{-4} = \frac{2.303}{900}\log\frac{100}{100-x}$$

$$\log\frac{100}{100-x} = \frac{9}{115.15} = 0.0781$$

$$\Rightarrow \quad \frac{100}{100-x} = \text{Antilog }(0.0781)$$

$$\Rightarrow \quad 100 = 1.197\,[100-x]$$

$$\Rightarrow \quad 100 = 119.7 - 1.197x$$

$$\Rightarrow \quad 1.197x = 19.7$$

$$\therefore \quad x = \frac{19.7}{1.197} = 16.45\%$$ 3

Commonly Made Error

- Choosing incorrect values for the concentration terms.

Answering Tip

- Understand that in the first order reactions, the denominator is the concentration of the reactant present at that given time.

Q. 12. Why molecularity is applicable only for elementary reactions and order is applicable for elementary as well as complex reactions ?

A&E **[NCERT Exemp. Q. 51, Page 56]**

Ans. A complex reaction occurs through several elementary reactions. Numbers of molecules involved in each elementary reaction may be different, that is, the molecularity of each step may be different. Therefore, the molecularity of overall complex reaction is meaningless. On the other hand, order of a complex reaction is experimentally determined by the slowest step in its mechanism and is therefore, applicable even in the case of complex reactions. 3

Long Answer Type Questions-II (5 marks each)

Q. 1. (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

$$\Rightarrow \quad t_{1/2} = \frac{2.303}{k}\log 2$$ ½

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

$$\Rightarrow \quad t_{1/2} = \frac{0.693}{k}$$ ½

The above equation shows that half-life 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

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

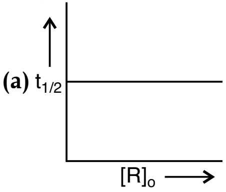
$$t_{99\%} = 2\times t_{90\%}$$ ½

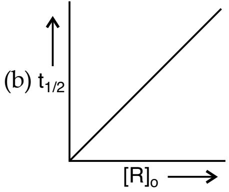
Commonly Made Error

- Incorrect values for concentration terms.

Q. 2. (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)

OR

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) $k = \dfrac{2.303}{t}\log\dfrac{[A]_0}{[A]}$ ½

$= \dfrac{2.303}{40}\log\dfrac{100}{25}$ ½

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

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

$k = 0.0347\ min^{-1}$ ½

$t_{1/2} = \dfrac{0.693}{k}$ ½

$t_{1/2} = \dfrac{0.693}{0.0347\,min^{-1}} = 19.98\ min = 20\ min$ 1

(ii) (a) First order reaction 1

(b) Zero order reaction 1

OR

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

$7.2 \times 10^{-2} = k[0.3]^x[0.2]^y$ Eqn (1)

$6.0 \times 10^{-3} = k[0.1]^x[0.1]^y$ Eqn (2)

$2.88 \times 10^{-1} = k[0.3]^x[0.4]^y$ Eqn (3)

$2.40 \times 10^{-2} = k[0.4]^x[0.1]^y$ 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 $k = \dfrac{rate}{[NO]^1[O_2]^2} = \dfrac{7.2\times10^{-2}}{0.3\times(0.2)^2}$

$k = 6.0\ mol^{-2}\ L^2\ min^{-1}$ 1

[CBSE Marking Scheme 2017]

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.

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

  It is observed that for a chemical reaction with rise in temperature by 10°, 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 a reaction cannot be zero. It is not possible that every collision between molecules will be effective. E_a cannot 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.
- **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

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

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

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

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

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

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

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

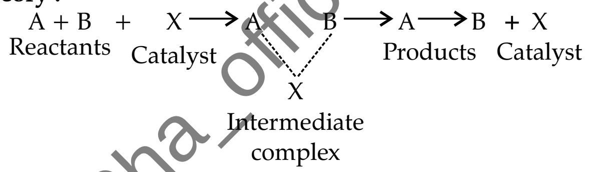
  where '*z*' is collision frequency and '*F*' is fraction of collisions, which are effective.
- The number of collisions that take place per second per unit volume of the reaction mixture is called collision frequency. It is represented by 'Z'.
- Activated complex is defined as unstable intermediate formed 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 :



Characteristics of catalyst :

(i) Catalyses only the spontaneous reaction.
(ii) Does not change the equilibrium constant.
(iii) Catalyses 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.

Know the Formulae

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

  where Z is the collision frequency, f is the fraction of collisions.
- Arrhenius equation :

  $$k = Ae^{-E_a/RT}$$
- $$\text{Rate} = PZ_{AB}e^{-E_a/RT}$$

Know the Terms

- **Effective collisions :** Collisions in which molecules collide with sufficient kinetic energy and proper orientation and result in a reaction.
- **Collision frequency :** Number of collisions per second per unit volume of the reaction mixture.

Very Short Answer-Objective Type Questions (1 mark each)

A. Multiple choice Questions:

Q. 1. Mark the incorrect statements :

(a) Catalyst provides an alternative pathway to reaction mechanism.

(b) Catalyst raises the activation energy.

(c) Catalyst lowers the activation energy.

(d) Catalyst alters enthalpy change of the reaction.

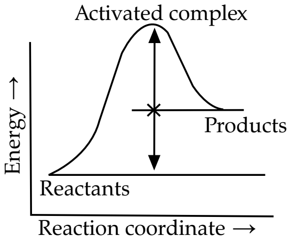
U [NCERT Exemp. Q. 30, Page 54]

Ans. Correct option : (b) and (d)

Explanation : **(i)** When catalyst is added in reaction medium, the rate of reaction increases by decreasing activation energy of the molecule. Hence, it follows an alternative pathway.

(ii) Catalyst does not change the enthalpy change of reaction. Energy of reactant and product remain same in both catalysed and uncatalysed reaction. Therefore, (b) and (d) are incorrect statements.

Q. 2. 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.

U [NCERT Exemp. Q. 4, Page 47]

Ans. Correct option : (a)

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.

Q. 3. The role of a catalyst is to change ______________.

(a) Gibbs energy of reaction.

(b) enthalpy of reaction.

(c) activation energy of reaction.

(d) equilibrium constant.

U [NCERT Exemp. Q. 1, Page 47]

Ans. Correct option : (c)

Explanation : A catalyst lowers the activation energy of a reaction.

Q. 4. Activation energy of a chemical reaction can be determined by

(a) determining the rate constant at standard temperature.

(b) determining the rate constants at two temperatures.

(c) determining probability of collision.

(d) using catalyst. U [NCERT Exemp. Q. 3, Page 47]

Ans. Correct option : (b)

Explanation : Activation energy of a chemical reaction is linked to rate constant of a reaction at two different temperatures that is k_1 and k_2,

$$\log\frac{k_2}{k_1} = \frac{E_0}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where, E_a = Activation energy
T_2 = Higher temperature
T_1 = Lower temperature
k_1 = Rate constant at temperature T_1
k_2 = Rate constant at temperature T_2

This equation is know as 'Arrhenius equation.'

Q. 5. Which of the following statement is not correct for the catalyst?

(a) It catalyses the forward and backward reactions to the same extent.

(b) It alters Gibbs energy (ΔG) of the reaction.

(c) It is a substance that does not change the equilibrium constant of a reaction.

(d) It provides an alternate mechanism by reducing activation energy between reactants and products.

U [NCERT Exemp. Q. 18, Page 52]

Ans. Correct option : (b)

Explanation : The characteristics of catalysts are given below :

(i) It catalyses the forward and backward reactions to the same extent as it decreases energy of activation hence, increases the rate of both the reactions

(ii) Catalyst does not alter Gibbs free energy as it is related reaction quotient.

(iii) It does not alter equilibrium of reaction as equilibrium constant (K_c) is also dependent on concentration.

(iv) It provides an alternate mechanism by reducing activation energy between reactants and product.

B. Answer the following:

Q. 1. What is the effect of catalyst on

(i) Gibbs energy (ΔG) and

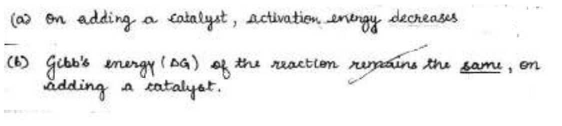
(ii) activation energy of a reaction?

U [CBSE Delhi Set-3 2017/OD Set-1 2013]

Ans. **(i)** No effect. ½
(ii) Decreases ½

[CBSE Marking Scheme 2017]

OR



(a) On adding a catalyst, activation energy decreases

(b) Gibb's energy (ΔG) of the reaction remains the same, on adding a catalyst.

[Topper's Answer 2017] 1

Q. 2. In the Arrhenius equation, what does the factor $e^{-Ea/RT}$ corresponds to? U [CBSE SQP 2017]

Ans. $e^{-Ea/RT}$ corresponds to the fraction of molecules that have kinetic energy greater than E_a **1**

[CBSE Marking Scheme 2017]

AI Q. 3. On increasing temperature, activation energy of a reaction decreases, why ? A&E **[CBSE SQP 2016]**

Ans. Because temperature and activation energy are inversely proportional to each other. 1

Q. 4. In some cases, it is found that a large number of colliding molecules have energy more than threshold energy yet the reaction is slow why ? A&E **[CBSE Delhi 2013]**

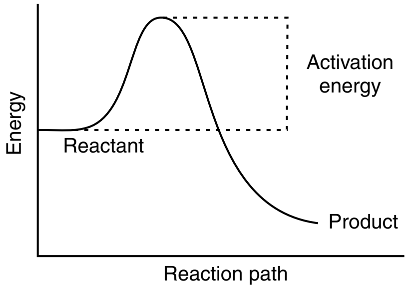
Ans. It is due to improper orientation. Because energy more than threshold energy and proper orientation, are the two main factors which are responsible for a reaction to occur. 1

Short Answer Type Questions (2 marks each)

Q. 1. With the help of a diagram, explain the physical significance of energy of activation (E_a) in chemical reactions. C **[CBSE Comptt. OD 2013]**

Ans. The excess energy which must be supplied to the reactants to undergo chemical reactions is called activation energy E_a. It is equal to the difference between the threshold energy E_P, needed for the reaction and the average of all the reacting molecules, E_R.

Activation energy = Threshold energy – Average kinetic energy of the reacting molecule. 1



1

Commonly Made Error

- Some students write incorrect formula.
- Many students do not plot the graph. Some students do not mention the axis of the graph. In some cases, the slope is not marked.

Q. 2. The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of activation (E_a) of the reaction assuming that it does not change with temperature.
[R = 8.314 JK^{-1} mol^{-1}, log 4 = 0.6021] A **[CBSE OD 2013]**

Ans. Given if rate at 293 K is R thus at 313 K rate becomes 4R

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 \times T_2}\right] \quad ½$$

$$\Rightarrow \log\frac{4R}{R} = \frac{E_a}{2.303 \times 8.314}\left[\frac{313-293}{293 \times 313}\right] ½$$

$$\Rightarrow \log 4 = \frac{E_a}{19.1471}\left[\frac{20}{91709}\right]$$

$$\Rightarrow 0.6021 = \frac{E_a}{19.1471}\left[\frac{20}{91709}\right]$$

$$\Rightarrow \frac{0.6021 \times 19.1471 \times 91709}{20} = E_a$$

$$\Rightarrow E_a = 52863.2177 \text{ J mol}^{-1}$$

$$= 52.863 \text{ kJ mol}^{-1} \quad 1$$

Commonly Made Error

- Incorrect data in the working formula.

Answering Tip

- Mention the working formula. Check the numerical values and units in the working formula.

Long Answer Type Questions-I (3 marks each)

Q. 1. The rate of most reactions becomes double when their temperature is raised from 298 K to 308 K. Calculate their activation energy.
[Given R = 8.314 J mol^{-1} K^{-1}]
A **[CBSE Comptt. OD 2016; DDE]**

Ans. $T_1 = 298$ K, $T_2 = 308$ K.
$R = 8.314$ J mol^{-1} K^{-1}

Activation energy

$$k_2 = 2k_1$$

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

$$\Rightarrow \log 2 = \frac{E_a}{19.15 \text{ J mol}^{-1}}\left[\frac{1}{298} - \frac{1}{308}\right]$$

$$E_a = \frac{0.3010 \times 19.15 \times 298 \times 308}{10} \text{ J mol}^{-1} \quad 1$$

$$E_a = 52905 \text{ J mol}^{-1} \text{ or } 52.905 \text{ kJ mol}^{-1} \quad 1$$

[CBSE Marking Scheme 2016]

Commonly Made Error

- Incorrect data in the working formula.

Answering Tip

- Mention the working formula. Check the numerical values and units in the working formula.

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}) A **[CBSE Delhi/OD 2018]**

Ans.

$$k_2 = 0.693/20, \qquad \tfrac{1}{2}$$

$$k_1 = 0.693/40 \qquad \tfrac{1}{2}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} - \left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \tfrac{1}{2}$$

$$k_2/k_1 = 2$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \frac{[320 - 300]}{320 \times 300} \qquad \tfrac{1}{2}$$

$$E_a = 27663.8 \text{ J/mol or } 27.66 \text{ kJ/ mol} \qquad 1$$

[CBSE Marking Scheme 2018]

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})

A [CBSE SQP 2018-2019]

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

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

For reaction (i) $\log k_1 = \log A - \dfrac{E_a(1)}{2.303RT}$ 1

For reaction (ii) $\log k_2 = \log A - \dfrac{E_a(2)}{2.303RT}$ 1

Subtracting (i) from (ii)

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

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

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

$$= 4.342$$

$$\frac{k_1}{k_2} = \text{antilog } (4.342) = 2.198 \text{ x } 10^4$$

1

[CBSE Marking Scheme 2018]

Commonly Made Error

- Incorrect data in the working formula.

Answering Tip

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

Long Answer Type Questions-II

(5 marks each)

Q. 1. (i) For the reaction A→B, the rate of reaction becomes twenty seven times when the concentration 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 kJmol^{-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 ? A [CBSE SQP 2016]

Ans. (i) $r = k[R]^n$

When concentration is increased three times,

$$[R] = 3a \qquad \tfrac{1}{2}$$

$$27r = k(3a)^n$$

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

$$= 3^n \text{ or } 3^3 = 3^n \qquad \tfrac{1}{2}$$

$$\Rightarrow \quad n = 3 \qquad 1$$

(ii) According to Arrhenius equation,

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

For uncatalysed reaction

$$\log k_1 = \log A - \frac{E_a(1)}{2.303RT} \quad \text{....(i) } \tfrac{1}{2}$$

For catalysed reaction

$$\log k_2 = \log A - \frac{E_a(2)}{2.303RT} \quad \text{....(ii) } \tfrac{1}{2}$$

A is equal for both the reactions.

Subtracting equation (i) from equation (ii)

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

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

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

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

$$= 2.45 \times 10^4$$

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

AI Q. 2. (i) The decomposition of A into products has a value of k as 4.5×10^3 s^{-1} at 10°C and energy of activation 60 kJ mol^{-1}. At what temperature would k be 1.5×10^4 s^{-1} ?

(ii) (a) If half life period of a first order reaction is x and 3/4th life period of the same reaction is y, how are x and y related to each other ?

(b) In some cases it is found that a large number of colliding molecules have energy more than threshold energy, yet the reaction is slow. Why ? A + A&E [CBSE Comptt. Delhi 2013]

Ans. (i) We know that

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

$$\Rightarrow \quad \log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60{,}000}{2.303 \times 8.314}\left(\frac{T_2 - 283}{283 T_2}\right)$$

$$\Rightarrow \quad 0.5228 = 3133.62\left(\frac{T_2 - 283}{283 \text{ } T_2}\right)$$

$$\Rightarrow \quad \frac{0.5228}{3133.62} = \frac{T_2 - 283}{283 \text{ } T_2}$$

$$1.68 \times 10^{-4} = \frac{T_2 - 283}{283\, T_2}$$

$$0.04754\, T_2 = T_2 - 283$$

$$T_2 - 0.04754\, T_2 = 283$$

$$0.95246\, T_2 = 283$$

Hence, $T_2 = \frac{283}{0.95245} = 297.12 \text{ K}$ **3**

(ii) (a) $y = 2x$. This is because for 3/4th of the reaction to complete, time required = two half lives. **1**

(b) This is because of improper orientation of the colliding molecules at the time of collision. **1**

Commonly Made Error

- Incorrect data in the working formula.

Answering Tip

- Check the numerical values and units in the working formula. Pay special attention to the writing of units in the answer as missing out units in the last step leads to deduction of marks.

Q. 3. (i) A first order reaction takes 100 minutes for completion of 60% of the reaction. Find the time when 90% of the reaction will be completed.

(ii) With the help of diagram explain the role of activated complex in a reaction.

A&C [CBSE Comptt. Delhi 2013]

Ans. (i) (a) For the reaction of first order,

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

$$\Rightarrow \quad k = \frac{2.303}{100}\log\frac{100}{40} = 0.00916$$

(b)

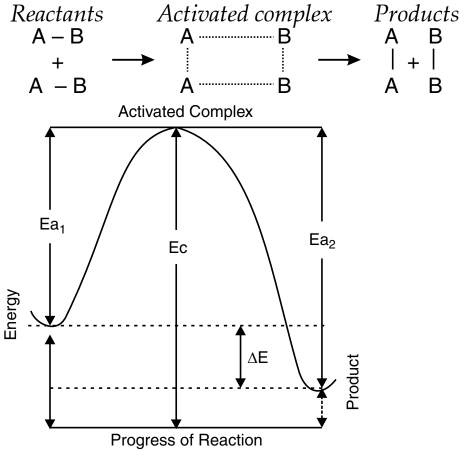
$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$\Rightarrow \quad 0.00916 = \frac{2.303}{t}\log\frac{100}{10}$$

$$\Rightarrow \quad t = \frac{2.303}{0.00916}\log 10$$

$$= 251.4 \text{ minutes}$$ **3**

(ii) It is believed that when the reactant molecules absorb energy, their bonds are loosened and new loose bonds are formed between them (A and B both). The intermediate thus formed is called an activated complex. It is unstable and immediately dissociated to form the stable products. **1**



1

Commonly Made Error

- Some students write incorrect formula.
- Many students do not plot the graph. Some students do not mention the axis of the graph. In some cases, the slope is not marked.

Q. 4. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained :

t/s	0	30	60
[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 to 60 seconds.

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

OR

AI (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 reactions. (log 2 = 0.3010)

A [CBSE Delhi 2015]

Ans. (i) For the first order reaction—

$$t_1 = 30 \text{ sec}$$

$$t_2 = 60 \text{ sec}$$

$$k_1 = \frac{2.303}{t_1}\log\frac{a}{(a-x)}$$

$$\Rightarrow \quad k_1 = \frac{2.303}{30}\log\frac{0.60}{0.30}$$

$$= \frac{2.303}{30}\log 2$$

$$\Rightarrow \quad k_1 = \frac{2.303}{30} \times 0.3010$$

$$= 0.0231 \text{ s}^{-1}$$

and

$$k_2 = \frac{2.303}{t_2}\log\frac{a}{(a-x)}$$

$$= \frac{2.303}{60}\log\frac{0.60}{0.15}$$

$$= \frac{2.303}{60}\log 2^2$$

$$\Rightarrow \quad k_2 = \frac{2.303 \times 2 \times 0.3010}{60}$$

$$= \frac{2.303 \times 0.3010}{30}$$

$$= 0.0231 \text{ s}^{-1}$$

$$\because \quad k_1 = k_2$$ **3**

Hence, the reaction is pseudo first order reaction.

(ii) $\text{Rate} = \frac{\Delta x}{\Delta t}$

$$= \frac{0.30-0.15}{60-30} = \frac{0.15}{30}$$

$= 0.005 \text{ mol L}^{-1} \text{ s}^{-1}$ **2**

OR

(i) A + B → P

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

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

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

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

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

(b) Order of reaction is the no. 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

$k = [\text{B}]^2$

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

(ii) For the 1st order reaction:

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

$$t = 30 \times 60 = 1800 \text{ sec}$$

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

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

$$= \frac{2.303}{1800} \times 0.3010 \quad \textbf{1}$$

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

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

$$= \frac{2.303}{k}\log 10 = \frac{2.303}{k} \quad \textbf{1}$$

By putting the value of k here, we get

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

$$= 5.98 \times 10^3 \text{ sec} \quad \textbf{1}$$

Commonly Made Error

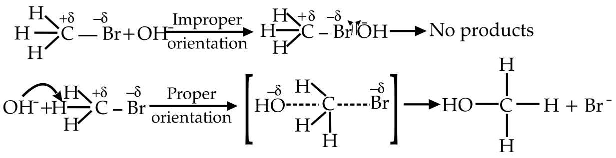
- Incorrect values of concentration/units and calculation errors while solving the problems.

Q. 5. All energetically effective collisions do not result in a chemical change. Explain with the help of an example. Ⓒ **[NCERT Exemp. Q. 62, Page 59]**

Ans. Effective collision leads to the formation of products implying that during collisions molecules collide with sufficient kinetic energy called threshold energy (Threshold Energy = Activation energy + Energy possessed by reacting species) and proper orientation leads to a chemical change because it enhance the old bond breaking between reactant molecules and formation of the new ones in products. For example : Formation of methanol from bromoethane depends upon the orientation of the reactant molecules. Proper orientation of reactant molecules leads to bond formation while improper orientation does not allow bond formation and hence no products are formed. To estimate effective collisions, another factor P which is called as probability or steric factor is introduced.

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

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$



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