12. **Which of the following is a zero order reaction?**
(a) Decomposition of N_2O_5
(b) Decomposition of NH_3
(c) Decomposition of N_2O
(d) Radioactive decay of unstable nuclei

13. **Diazonium salt decomposes as**

$$C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$$

at 0° C. The evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore it is
(a) a first order reaction
(b) a second order reaction
(c) independent of the initial concentration of the salt
(d) a zero order reaction

14. **In the graph plotted between ln [R] and t for a first order reaction, the intercept on y-axis is**
(a) $-k$
(b) $[R]_0$
(c) $\ln [R]_0$
(d) $k/2.303$

15. **If 75% of the first-order reaction was completed in 32 minutes, 50% of the same reaction would be completed in:**
(a) 8 min
(b) 4 min
(c) 16 min
(d) 24 min

16. **The half life of a first order reaction is 69.35 sec. The value of rate constant of the reaction is**
(a) 1.0 s^{-1}
(b) 0.1 s^{-1}
(c) 0.01 s^{-1}
(d) 0.001 s^{-1}

17. **Consider a first order gas phase decomposition reaction given below:** *[NCERT Exemplar]*

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

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 _____ **.**

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

18. **The activation energy of a reaction is zero. The rate of the reaction**
(a) increases with increase of temperature
(b) decreases with decrease of temperature
(c) decreases with increase of temperature
(d) is nearly independent of temperature

19. **The activation energy of a reaction can be determined from the slope of which of the following graphs?**

(a) $\ln k$ vs $\dfrac{1}{T}$

(b) $\dfrac{T}{\ln k}$ vs $\dfrac{1}{T}$

(c) $\ln k$ vs T

(d) $\dfrac{\ln k}{T}$ vs T

20. **Consider figure and mark the correct option.**
[NCERT Exemplar]
(a) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.
(b) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant.
(c) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product.
(d) Activation energy of backward reaction is E_1 and product is more stable than reactant.
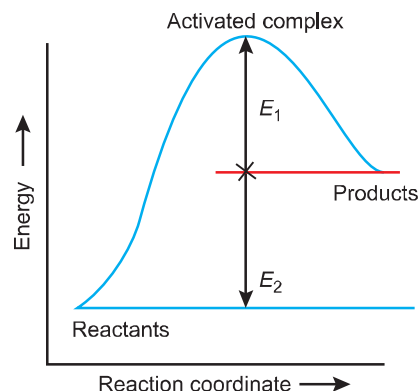
21. **The role of a catalyst is to change** _____. [*NCERT Exemplar*]
    (*a*) gibbs energy of reaction (*b*) enthalpy of reaction
    (*c*) activation energy of reaction (*d*) equilibrium constant

22. **In the presence of a catalyst, the heat evolved or absorbed during the reaction** _____.

    [*NCERT Exemplar*]

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

Answers

1. (*d*)	**2.** (*c*)	**3.** (*b*)	**4.** (*d*)	**5.** (*d*)	**6.** (*c*)	**7.** (*a*), (*d*)	**8.** (*b*)	**9.** (*c*)	**10.** (*a,c,d*)
11. (*c*)	**12.** (*b*)	**13.** (*a*)	**14.** (*c*)	**15.** (*c*)	**16.** (*c*)	**17.** (*b*)	**18.** (*d*)	**19.** (*a*)	**20.** (*a*)
21. (*c*)	**22.** (*c*)								

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(*a*) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

(*b*) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

(*c*) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

(*d*) *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. **Assertion** (*A*) : Instantaneous rate is used to predict the rate of a reaction at a particular moment of time.
   Reason (*R*) : Average rate is constant for the time interval for which it is calculated.

2. **Assertion** (*A*) : For the reaction, $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$, rate $= k[CHCl_3][Cl_2]^{1/2}$
   Reason (*R*) : Rate law for any reaction can be predicted with the help of a balanced chemical equation.

3. **Assertion** (*A*) : The rate of the reaction is the rate of change of concentration of a reaction or a product.
   Reason (*R*) : Rate of reaction remains constant during the course of reaction.

4. **Assertion** (*A*) : Order of the reaction can be zero or fractional.
   Reason (*R*) : We cannot determine order from balanced chemical equation.

5. **Assertion** (*A*) : Order and molecularity are same.
   Reason (*R*) : Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step.

6. **Assertion** (*A*) : For the reaction
   $$2N_2O_5 \longrightarrow 4NO_2 + O_2;$$
   $$Rate = k[N_2O_5].$$
   Reason (*R*) : Rate of decomposition of N_2O_5 is determined by slow step.

7. **Assertion** (*A*) : The inversion of cane sugar,
   $$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
   is a pseudo first order reaction.
   Reason (*R*) : H_2O in this reaction is present in very less amount as compared to $C_{12}H_{22}O_{11}$.

8. **Assertion** (*A*) : For each ten degree rise of temperature the specific rate constant is nearly doubled.
   Reason (*R*) : Energy-wise distribution of molecules in a gas is an experimental function of temperature.

9. **Assertion** (*A*) : If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.
   Reason (*R*) : Lower the activation energy, faster is the reaction.

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10. **Assertion (A) :** Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.

    Reason (R) : Reactant molecules undergo chemical change irrespective of their orientation during collision.

11. **Assertion (A) :** The enthalpy of reaction remains constant in the presence of a catalyst.

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

12. **Assertion (A) :** All collision of reactant molecules lead to product formation.

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

Answers

1. (*b*)	**2.** (*c*)	**3.** (*c*)	**4.** (*b*)	**5.** (*d*)	**6.** (*b*)	**7.** (*c*)	**8.** (*b*)	**9.** (*c*)	**10.** (*c*)
11. (*a*)	**12.** (*d*)								

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

The rate of a chemical reaction is expressed either in terms of decrease in the concentration of a reactant per unit time or increase in the concentration of a product per unit time. Rate of the reaction depends upon the nature of reactants, concentration of reactants, temperature, presence of catalyst, surface area of the reactants and presence of light. Rate of reaction is directly related to the concentration of reactant. Rate law states that the rate of reaction depends upon the concentration terms on which the rate of reaction actually depends, as observed experimentally. The sum of powers of the concentration of the reactants in the rate law expression is called order of reaction while the number of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction is called molecularity of the reaction.

1. **Express the rate of the following reaction in terms of different reactants and products.**

    $$4NH_3(g) + 5O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(g)$$

Ans. Rate of reaction $= -\dfrac{1}{4}\dfrac{d[NH_3]}{dt}$

$$= -\dfrac{1}{5}\dfrac{d[O_2]}{dt} = +\dfrac{1}{4}\dfrac{d[NO_2]}{dt} = +\dfrac{1}{6}\dfrac{d[H_2O]}{dt}$$

2. **Why do pieces of wood burn faster than a log of wood of the same mass?**

Ans. Pieces of wood have larger surface area than the log of wood of the same mass. Greater the surface area, faster is the reaction.

3. **Why does the rate of any reaction generally decrease during the course of the reaction?**

Ans. The rate of reaction depends on the concentration of reactants. As the reaction progresses, reactants start getting converted to products so the concentration of reactants decreases hence the rate of reaction decreases.

4. **Why is molecularity applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?**

Ans. A complex reaction proceeds through several elementary reactions. Number of molecules involved in each elementary reaction may be different, *i.e.*, the molecularity of each step may be different. Therefore, discussion of the molecularity of overall complex reaction is meaningless. On the other hand, order of a complex reaction is determined by the slowest step in its mechanism and is not meaningless even in the case of complex reactions.

5. **The kinetics of the reaction**

$$mA + nB + pC \longrightarrow m'X + n'Y + p'Z$$

obey the rate expression $dx/dt = k[A]^m[B]^n$

Calculate total order and molecularity of the reaction.

Ans. The total order of reaction = $m + n$

The molecularity of the reaction = $m + n + p$

PASSAGE–2

Temperature has a marked effect on the rate of reaction. For most of the reactions, the rate of reaction becomes nearly double for every 10 degree rise in temperature. The effect of temperature is usually expressed in terms of temperature coefficient. The quantitative dependence of reaction rate on temperature was first explained by Swante Arrhenius. Arrhenius proposed a simple equation known as Arrhenius equation

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

This equation provides a relationship between the rate constant (k) of a reaction and the temperature of the system. A is the Arrhenius factor or pre-exponential factor, E_a is the activation energy and R is the gas constant.

1. **Define 'activation energy' of a reaction.** **[CBSE (AI) 2011]**
Ans. The energy required to form the intermediate called activated complex is known as activation energy.

Activation energy = Threshold energy – Average energy of the reactants

2. **How does a catalyst affect the rate of a reaction? Explain with respect to the Arrhenius equation.**
Ans. A catalyst decreases the activation energy. According to Arrhenius equation, lower the activation energy, greater will be the rate constant and thus the rate of reaction increases.

3. **Can a reaction have zero activation energy? Justify.**
Ans. No, $E_a \neq 0$.

If $E_a = 0$, then according to Arrhenius equation,

$$k = Ae^{-Ea/RT}$$
$$k = Ae^0 = A,$$

i.e., Rate constant = Collision frequency

This means every collision results into a chemical reaction which cannot be true.

4. **The plot of log k vs X is linear with slope $= -E_a/2.303R$. What is X?**
Ans. $1/T$

5. **What is the fraction of molecules having energy greater than activation energy, E_a?**
Ans. $e^{-Ea/RT}$ at temperature T.

Very Short Answer Questions   [1 mark]

Q. 1. For the assumed reaction $X_2 + 3Y_2 \longrightarrow 2XY_3$, write the rate of equation in terms of rate of disappearance of Y_2. **[HOTS]**

Ans.
$$\text{Rate} = -\frac{d[X_2]}{dt} = -\frac{1}{3}\frac{d[Y_2]}{dt} = +\frac{1}{2}\frac{d[XY_3]}{dt}$$

$$\text{Rate of disappearance of } Y_2 = -\frac{d[Y_2]}{dt} = -3\frac{d[X_2]}{dt} = +\frac{3}{2}\frac{d[XY_3]}{dt}$$

Q. 2. **Why does the rate of a reaction increase with rise in temperature?** **[NCERT Exemplar]**
Ans. At higher temperatures, larger fraction of colliding particles can cross the energy barrier (*i.e.*, the activation energy), which leads to faster rate.

Q. 3. **Define 'order of a reaction'.** **[CBSE 2019 (56/2/1)]**
Ans. Order of a reaction may be defined as the sum of the powers of the concentration terms of the reactants in the rate law expression.

Chemical Kinetics

Q. 4. Identify the order of reaction from the following unit for its rate constant:
$$L\ mol^{-1}s^{-1}$$ [*CBSE (F) 2010*]

Ans. Second order.

Q. 5. For the reaction $A \longrightarrow B$, the rate of reaction becomes three times when the concentration of A is increased by nine times. What is the order of reaction? [*HOTS*]

Ans. Let, $\qquad r = k\,[A]^n \qquad$ …(i)

Given, $\qquad 3r = k\,[9A]^n \qquad$ …(ii)

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

$$\frac{3r}{r} = \frac{k[9A]^n}{k[A]^n} = \frac{9^n k[A]^n}{k[A]^n}$$

$$3 = 9^n \qquad \text{or} \qquad 3^1 = 3^{2n}$$

$$\Rightarrow \qquad 2n = 1 \qquad \text{or} \qquad n = \frac{1}{2}$$

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

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

Q. 6. For which type of reactions, order and molecularity have the same value? [*NCERT Exemplar*]

Ans. If the reaction is an elementary reaction, order is same as molecularity.

Q. 7. Why is the probability of reaction with molecularity higher than three very rare? [*NCERT Exemplar*]

Ans. The probability of more than three molecules colliding simultaneously is very small. Hence, possibility of molecularity being three is very low.

Q. 8. For a reaction, $A + B \longrightarrow$ Products, the rate law is Rate $= k[A][B]^{3/2}$. Can the reaction be an elementary reaction? Explain. [*HOTS*]

Ans. During an elementary reaction, the number of atoms or ions colliding to react is referred to as molecularity. Had this been an elementary reaction the order of reaction with respect to B would have been 1, but in the given rate law it is $\frac{3}{2}$. This indicates that the reaction is not an elementary reaction.

Q. 9. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of the reaction? [*HOTS*]

Ans. As $t_{75\%} = 2t_{50\%}$

Therefore, it is a first order reaction.

Q. 10. What is the effect of adding a catalyst on
  (i) Activation energy (E_a), and
  (ii) Gibbs energy (ΔG) of a reaction? [*CBSE Delhi 2017; (AI) 2017*]

Ans. (i) Decreases
  (ii) No effect

Q. 11. Define threshold energy of a reaction.

Ans. Threshold energy is the minimum energy which must be possessed by reacting molecules in order to undergo effective collision which leads to formation of product molecules.

Q. 12. Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of one example. [*NCERT Exemplar*]

Ans. Thermodynamically the conversion of diamond to graphite is highly feasible but this reaction is very slow because its activation energy is high.

Q. 13. In some cases, it is found that a large number of colliding molecules have energy more than threshold value, yet the reaction is slow. Why? [*CBSE Delhi 2013*]

Ans. This is due to improper orientation of the colliding molecules at the time of collision.

Q. 1. For the reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ the rate of formation of $NO_2(g)$ is $2.8 \times 10^{-3} \, Ms^{-1}$. Calculate the rate of disappearance of $N_2O_5(g)$. **[CBSE 2018]**

Ans. $Rate = \dfrac{-1}{2} \dfrac{\triangle(N_2O_5)}{\triangle t} = +\dfrac{1}{4} \dfrac{\triangle(NO_2)}{\triangle t} = +\dfrac{\triangle(O_2)}{\triangle t}$

Rate of disappearance of $N_2O_5 = -\dfrac{\triangle(N_2O_5)}{\triangle t} = \dfrac{1}{2}\dfrac{\triangle(NO_2)}{\triangle t}$

$= \dfrac{1}{2} \times 2.8 \times 10^{-3} \, Ms^{-1} = \mathbf{1.4 \times 10^{-3} \, Ms^{-1}}$

Q. 2. The rate law for the reaction: $\quad Ester + H^+ \longrightarrow Acid + Alcohol$ is:

$$\dfrac{dx}{dt} = k \, [Ester] \, [H^+]^0$$

What would be the effect on the rate if (*i*) concentration of the ester is doubled? (*ii*) concentration of H^+ is doubled?

Ans. (*i*) The rate of reaction will be doubled. (*ii*) No effect on rate.

Q. 3. Differentiate between rate of reaction and reaction rate constant.

Ans.

S. No.	Rate of Reaction	Reaction Rate Constant
(*i*)	Rate of reaction is the change in concentration of a reactant or product in a unit interval of time.	It is the rate of reaction when the molar concentration of each of the reactants is unity.
(*ii*)	The rate of reaction at any instant of time depends upon the molar concentrations of the reactants at that time.	The rate constant does not depend upon the concentrations of the reactants.
(*iii*)	Its units are always mol litre^{-1} time^{-1}.	Its units depend upon the order of reaction.

Q. 4. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is reduced to half? What is the unit of rate constant for such a reaction? **[CBSE (AI) 2011]**

Ans. Consider the reaction $nR \longrightarrow Products$

As the reaction is of second order

$\therefore \qquad\qquad Rate, \, r = k \, [R]^2 \qquad\qquad\qquad ...(i)$

If the concentration of the reactant reduced to half, then

$\qquad\qquad Rate, \, r' = k\left[\dfrac{R}{2}\right]^2 \qquad\qquad\qquad ...(ii)$

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

$$\dfrac{r'}{r} = \dfrac{k\,[R]^2}{4k\,[R]^2} = \dfrac{1}{4}$$

$r' = \dfrac{1}{4}r$, *i.e.*, rate of reaction becomes $\dfrac{1}{4^{th}}$ of the initial rate.

The unit of rate constant is $\mathbf{mol^{-1} \, L \, s^{-1}}$.

Q. 5. 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 constant are: **[CBSE (AI) 2011]**

(*i*) $L^{-1} \, mol \, s^{-1}$ (*ii*) $L \, mol^{-1} \, s^{-1}$.

Ans. An experimentally determined expression which relates the rate of reaction with the concentration of reactants is called rate law while the rate of reaction when concentration of each reactant is unity in a rate law expression is called rate constant.

(*i*) Comparing power of mole in $L^{-1} \, mol \, s^{-1}$ and $(mol \, L^{-1})^{1-n} \, s^{-1}$,

We get

$$1 = 1 - n \quad \Rightarrow \quad n = 0 \text{ } i.e., \text{ zero order reaction}$$

(*ii*) Again comparing power of mole in $L \, mol^{-1}s^{-1}$ and $(mol \, L^{-1})^{1-n}s^{-1}$, we get

$$-1 = 1 - n \quad \Rightarrow \quad n = 2, \text{ } i.e., \text{ second order reaction}$$

Chemical Kinetics

Q. 6. Calculate the overall order of a reaction which has the rate expression,

(i) Rate = $k[A]^{1/2}[B]^{3/2}$ (ii) Rate = $k[A]^{3/2}[B]^{-1}$

Ans. (i) Order = $\dfrac{1}{2} + \dfrac{3}{2} = 2$, *i.e.*, second order.

(ii) Order = $\dfrac{3}{2} + (-1) = \dfrac{1}{2}$, *i.e.*, half order.

Q. 7. Write two differences between 'order of reaction' and 'molecularity of reaction'. [*CBSE Delhi 2014*]

Ans. Differences between order and molecularity of reaction:

S.No.	Order	Molecularity
(i)	It is the sum of the powers of the concentration of the reactants in the rate law expression.	It is the number of reacting species taking part in an elementary reaction, which must collide simultaneously so as to result into a chemical reaction.
(ii)	It is determined experimentally.	It is a theoretical concept.
(iii)	It can be zero or a fraction.	It cannot be zero or a fraction.
(iv)	Order is applicable to elementary as well as complex reactions.	Molecularity is applicable only for elementary reactions. For complex reactions it has no meaning.

(Any two)

Q. 8. For a reaction: $2NH_3(g) \xrightarrow{\text{Pt}} N_2(g) + 3H_2(g)$

Rate = k

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

(ii) Write the unit of k.   [*CBSE South 2016*]

Ans. (i) Zero order, bimolecular

(ii) $mol\ L^{-1}\ s^{-1}$

Q. 9. Why is molecularity applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?   [*NCERT Exemplar*]

Ans. A complex reaction proceeds through several elementary reactions. Number of molecules involved in each elementary reaction may be different, *i.e.*, the molecularity of each step may be different. Therefore, discussion of molecularity of overall complex reaction is meaningless. On the other hand, order of a complex reaction is determined by the slowest step in its mechanism and is not meaningless even in the case of complex reactions.

Q. 10. Consider the decomposition of hydrogen peroxide in alkaline medium which is catalysed by iodide ions.

$$2H_2O_2 \xrightarrow{\text{OH}^-} 2H_2O + O_2$$

This reaction takes place in two steps as given below:

Step-I $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ (slow)

Step-II $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ (fast)

(i) Write the rate law expression and determine the order of reaction w.r.t. H_2O_2.

(ii) What is the molecularity of each individual step?

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

Order of reaction w.r.t $H_2O_2 = 1$

(ii) Molecularity of step I = 2 and step II = 2.

Q. 11. For a chemical reaction $R \rightarrow P$, the variation in the concentration (R) vs. time (t) plot is given alongside.
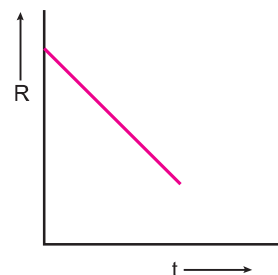
(i) Predict the order of the reaction.

(ii) What is the slope of the curve?   [*CBSE (AI) 2014*]

Ans. (i) Order of the reaction is zero.

(ii) Slope = $\dfrac{d[R]}{dt} = -k$

Q. 12. The rate constant for a reaction of zero order in A is 0.0030 mol L^{-1} s^{-1}. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M?

Ans. $k = 0.0030$ mol $L^{-1}s^{-1}$, $[R]_0 = 0.10$ M, $[R] = 0.075$ M

We know that

$$[R] = -kt + [R]_0$$

$$0.075 = -0.0030t + 0.10$$

$\Rightarrow$ $\qquad\qquad\qquad 3t = 100 - 75 \quad \Rightarrow \quad t = \textbf{8.33 seconds}$

Q. 13. Define the following terms:

    (i) Pseudo first order reaction

    (ii) Half life period of reaction $(t_{1/2})$ **[CBSE Delhi 2014]**

Ans.   (i) A reaction which is not truely of first order but under certain conditions becomes a reaction of first order is called pseudo first order reaction, *e.g.*, acid hydrolysis of ethyl acetate.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{\;\;H^+\;\;} CH_3COOH + C_2H_5OH$$
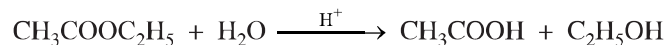
Rate $\propto [CH_3COOC_2H_5]$ as H_2O is in excess.

  (ii) The half life $(t_{1/2})$ of a reaction is the time in which the concentration of reactant is reduced to one half of its initial concentration $[R]_0$.

For a first order reaction, $t_{1/2} = \dfrac{0.693}{k}$, *i.e.*, independent of $[R]_0$.

For a zero order reaction, $t_{1/2} = \dfrac{[R]_0}{2k}$, *i.e.*, $t_{1/2} \propto [R]_0$.

Q. 14. For a reaction: $A + H_2O \longrightarrow B$, Rate $\propto [A]$.

What is its **(i) molecularity (ii) order of reaction?**

Ans.   (i) Pseudo unimolecular

  (ii) Order = 1.

Q. 15. The rate for the reaction $R \longrightarrow P$ is rate $= k[R]$. It has been shown graphically alongside. What is rate constant for the reaction?

Ans. From the graph

Case I: Rate $= k[A]$

1×10^{-2} mol L^{-1} $s^{-1} = k$ (0.1 mol L^{-1})

$\therefore$ $k = \dfrac{1 \times 10^{-2} \text{ mol } L^{-1} \text{ s}^{-1}}{0.1 \text{ mol } L^{-1}} = 0.1 \text{ s}^{-1}$
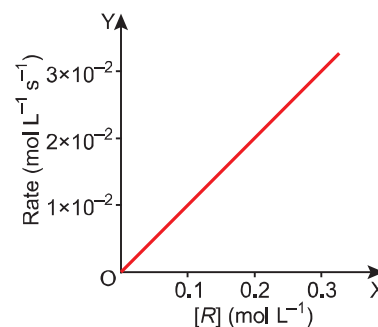
Case II:

3×10^{-2} mol $L^{-1}s^{-1} = k$ (0.3 mol L^{-1})

$k = \dfrac{3 \times 10^{-2} \text{ mol } L^{-1} \text{ s}^{-1}}{0.3 \text{ mol } L^{-1}} = 0.1 \text{ s}^{-1}$

Hence, $\boldsymbol{k = 0.1 \text{ s}^{-1}}$

Q. 16. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to $\dfrac{1}{10}$ th of its initial value?   **[CBSE (F) 2013]**

Ans. $t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]}$ as $[R] = \dfrac{[R]_0}{10}$

$\therefore$ $t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{\dfrac{[R]_0}{10}} = \dfrac{2.303}{60} \times \log 10 = \dfrac{2.303}{60} \times 1 = \textbf{3.838} \boldsymbol{\times 10^{-2}} \textbf{ s}$

Chemical Kinetics

Q. 17. (*i*) **For a reaction $A + B \longrightarrow P$, the rate law is given by,**
$$r = k[A]^{1/2}[B]^2.$$
What is the order of this reaction?

(*ii*) **A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14}$ s^{-1}. Find the half life of the reaction.** [*CBSE (AI) 2013*]

Ans. (*i*) Order of reaction $= \dfrac{1}{2} + 2 = \dfrac{5}{2}$

(*ii*) Radioactive decay follows first order kinetics.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.5 \times 10^{-14}} \text{ s} = \mathbf{1.26 \times 10^{13} \text{ s}}$$

Q. 18. **87.5% of the substance disintegrated in 45 minutes (first order reaction). What is its half-life?**

Ans. $\left(\dfrac{1}{2}\right)^n = \dfrac{12.5}{100}$ because 87.5% has disintegrated, amount left is 12.5%.

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

Number of half lives = 3

$$t_{1/2} = \frac{45}{3} = \mathbf{15 \text{ minutes}}$$

Q. 19. **After 24 hrs, only 0.125 gm out of the initial quantity of 1 gm of a radioactive isotope remains behind. What is its half life period?** [*CBSE Sample Paper 2017*]

Ans. Here, $[R]_0 = 1$ g, $[R] = 0.125$ g, $t = 24$ h

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

$$k = \frac{2.303}{24} \log \frac{1}{0.125} \quad \Rightarrow \quad k = \frac{2.303}{24} \log 8$$

$$k = \frac{2.303}{24} \times 0.9031 \quad \Rightarrow \quad k = 0.0866 \text{ h}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} \qquad \Rightarrow \quad t_{1/2} = \frac{0.693}{0.0866 \text{ h}^{-1}} \text{ or } t_{1/2} = \mathbf{8 \text{ h}}$$

Q. 20. **Show that in a first order reaction, time required for completion of 99.9% is 10 times that of half-life ($t_{1/2}$) of the reaction.** [*CBSE (F) 2016*]

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

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{\dfrac{2.303}{k} \log \dfrac{100}{100 - 99.9}}{\dfrac{2.303}{k} \log \dfrac{100}{100 - 50}} = \frac{\log \dfrac{100}{0.1}}{\log \dfrac{100}{50}} = \frac{\log 10^3}{\log 2} = \frac{3 \log 10}{0.3010}$$

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{30}{3.01} \simeq 10$$

$$t_{99.9\%} = 10 \, t_{50\%}$$

Q. 21. **Rate constant k for first order reaction has been found to be 2.54×10^{-3} s^{-1}. Calculate its three-fourth life.** [*CBSE Sample Paper 2013*]

Ans. $t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]}$ ...(*i*)

$$k = 2.54 \times 10^{-3} \text{ s}^{-1}; [R] = \frac{[R]_0}{4}$$

Substituting these values in equation (i), we get

$$t_{3/4} = \frac{2.303}{2.54 \times 10^{-3}} \log \frac{[R]_0}{\dfrac{[R]_0}{4}} = 0.9066 \times 10^3 \log 4$$

$$t_{3/4} = 0.9066 \times 10^3 \times 0.6021 \text{ s}$$
$$= \mathbf{5.46 \times 10^2 \text{ s}}$$

Q. 22. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time/second^{-1}	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

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

Ans.
$$k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

Here, $P_0 = 0.4$ atm, $t = 100$ s, $P_t = 0.7$ atm

$$\therefore \qquad k = \frac{2.303}{100} \log \frac{0.4}{2 \times 0.4 - 0.7}$$

$$= \frac{2.303}{100} \log \frac{0.4}{0.1} = \frac{2.303}{100} \log 4$$

$$= \frac{2.303}{100} \times 0.6021$$

$$k = \mathbf{1.386 \times 10^{-2} \text{ s}^{-1}}$$

Q. 23. (i) **Explain why H_2 and O_2 do not react at room temperature.**

(ii) **Write the rate equation for the reaction $A_2 + 3B_2 \longrightarrow 2C$, if the overall order of the reaction is zero.** **[CBSE (AI) 2017]**

Ans. (i) Due to high activation energy for the reaction.

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

Q. 24. **Answer the following questions on the basis of the given plot of potential energy vs reaction coordinate:**

(i) **What is the threshold energy for the reaction?**

(ii) **What is the activation energy for forward reaction?**

(iii) **What is the activation energy for backward reaction?**

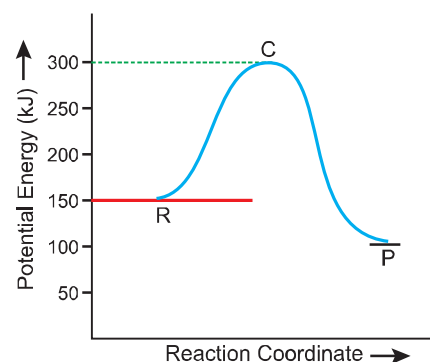(iv) **What is enthalpy change for the forward reaction?**

Ans. (i) Threshold energy for the reaction = 300 kJ mol^{-1}

(ii) Activation energy for the forward reaction = 300 – 150
$$= 150 \text{ kJ mol}^{-1}$$

(iii) Activation energy for the backward reaction = 300 – 100
$$= 200 \text{ kJ mol}^{-1}$$

(iv) Enthalpy change for the forward reaction $\Delta_r H = 100 - 150$
$$= -50 \text{ kJ mol}^{-1}$$

Chemical Kinetics

Q. 25. A graph between $\ln k$ and $\dfrac{1}{T}$ for a reaction is given.
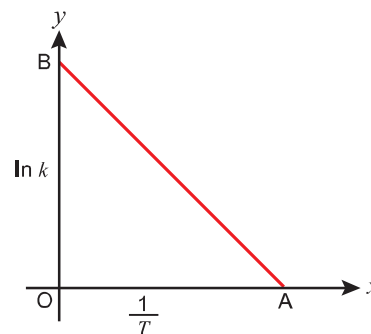
Here k is rate constant and T is temperature in kelvin.
If $OA = a$ and $OB = b$, answer the following:

(*i*) What is the activation energy (E_a) of the reaction?

(*ii*) What is the frequency factor (A) for the reaction?

[*HOTS*]

Ans. According to Arrhenius equation, $\ln\ k = -\dfrac{E_a}{RT} + \ln A$

(*i*) Slope $= -\dfrac{OB}{OA} = -\dfrac{b}{a} = -\dfrac{E_a}{R}$ or $E_a = \dfrac{b}{a}\,R$

(*ii*) Intercept on y-axis $= OB = b = \ln A$ or $A = e^b$

Short Answer Questions–II [3 marks]

Q. 1. $A + 2B \longrightarrow 3C + 2D$. The rate of disappearance of B is 1×10^{-2} mol L^{-1} s^{-1}. What will be

(*i*) Rate of the reaction (*ii*) Rate of change in concentration of A and C?

Ans. (*i*) As $\dfrac{-d\,[B]}{dt} = 1 \times 10^{-2}$ mol L^{-1} s^{-1}

$\therefore$ Rate $= -\dfrac{1}{2}\dfrac{d\,[B]}{dt} = \dfrac{1}{2} \times 1 \times 10^{-2} = \mathbf{0.5 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}}$

(*ii*) Rate $= -\dfrac{d\,[A]}{dt} = -\dfrac{1}{2}\dfrac{d\,[B]}{dt} = +\dfrac{1}{3}\dfrac{d\,[C]}{dt}$

Rate of change in concentration of A

$= -\dfrac{d\,[A]}{dt} = -\dfrac{1}{2}\dfrac{d\,[B]}{dt}$

$= \mathbf{0.5 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}}$

Rate of change in concentration of C

$= +\dfrac{d\,[C]}{dt} = -\dfrac{3}{2}\dfrac{d\,[B]}{dt} = \dfrac{3}{2} \times 1 \times 10^{-2}$

$= \mathbf{1.5 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}}$

Q. 2. The rate of reaction, $2NO + Cl_2 \longrightarrow 2NOCl$ is doubled when concentration of Cl_2 is doubled and it becomes eight times when concentration of both NO and Cl_2 are doubled. Deduce the order of the reaction. [*HOTS*]

Ans. Let

$r = k\,[NO]^x\,[Cl_2]^y$ …(*i*)

$2r = k\,[NO]^x\,[2Cl_2]^y$ …(*ii*)

$8r = k\,[2NO]^x\,[2Cl_2]^y$ …(*iii*)

Dividing (*iii*) by (*ii*), we get

$\dfrac{8r}{2r} = \dfrac{k\,[2NO]^x\,[2Cl_2]^y}{k\,[NO]^x\,[2Cl_2]^y}$

$2^2 = [2]^x$

$x = 2$

Putting the value of x in (*i*) and (*ii*), we get

$r = k\,[NO]^2\,[Cl_2]^y$

$2r = k\,[NO]^2\,[2Cl_2]^y$

$\dfrac{2r}{r} = \dfrac{[2Cl_2]^y}{[Cl_2]^y}$

$$2 = [2]^y$$
$$y = 1$$
$$\text{Rate} = k\,[NO]^2\,[Cl_2]^1$$

Overall order of reaction = $x + y = 2 + 1 = $ **3**

Q. 3. **Following reaction takes place in one step:**
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
How will the rate of the above reaction change if the volume of the reaction vessel is reduced to one-third of its original volume? Will there be any change in the order of the reaction with reduced volume? *[HOTS]*

Ans.
$$\text{Rate} = k\,[NO]^2\,[O_2]$$

Let initially, moles of NO = a, moles of $O_2 = b$, volume of the vessel = V. Then
$$[NO] = \frac{a}{V}\,M, \; [O_2] = \frac{b}{V}\,M$$

$\therefore$
$$\text{Rate}\,(r_1) = k\left(\frac{a}{V}\right)^2\left(\frac{b}{V}\right) = k\frac{a^2 b}{V^3} \qquad \ldots(i)$$

Now, new volume = $\dfrac{V}{3}$

$\therefore$ New concentrations:
$$[NO] = \frac{a}{V/3} = \frac{3a}{V}$$
$$[O_2] = \frac{b}{V/3} = \frac{3b}{V}$$

$\therefore$
$$\text{New rate}\,(r_2) = k\left(\frac{3a}{V}\right)^2\left(\frac{3b}{V}\right) = \frac{27ka^2 b}{V^3} \qquad \ldots(ii)$$

$\therefore$
$$\frac{r_2}{r_1} = 27 \qquad \text{or} \qquad r_2 = 27r_1,\; i.e.,\; \text{rate becomes } \textbf{27 times}.$$

Thus, there is no effect on the order of reaction.

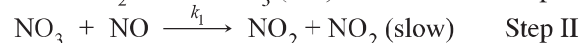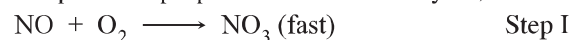**Q. 4.** **Nitric oxide, NO, reacts with oxygen to produce nitrogen dioxide.** *[HOTS]*
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
The rate law for this reaction is:
$$\text{Rate} = k\,[NO]^2\,[O_2]$$
Propose a mechanism for the reaction.

Ans. The probable proposed mechanism may be,

$NO + O_2 \longrightarrow NO_3$ (fast)   Step I
$NO_3 + NO \xrightarrow{\;k_1\;} NO_2 + NO_2$ (slow)   Step II

Since slowest reaction is the rate determining step, therefore
$$\text{Rate} = k_1\,[NO_3]\,[NO]$$
$$K = \frac{[NO_3]}{[NO][O_2]}$$
$$[NO_3] = K\,[NO]\,[O_2]$$
$$\text{Rate} = k_1 K\,[NO]\,[O_2]\,[NO] = K'[NO]^2\,[O_2], \text{ where } K' = k_1 . K$$

Q. 5. **The reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ contributes to air pollution whenever a fuel is burnt in air at a high temperature. At 1500 K, equilibrium constant K for it is 1.0×10^{-5}. Suppose in a case $[N_2] = 0.80$ mol L^{-1} and $[O_2] = 0.20$ mol L^{-1} before any reaction occurs. Calculate the equilibrium concentrations of the reactants and the product after the mixture has been heated to 1500 K.**

[CBSE (AI) 2012] [HOTS]

Ans.

	N_2	+	O_2	$\longrightarrow$	$2NO$
Initial conc. in mol L^{-1}	0.8		0.2		0
Change in conc. in mol L^{-1}	$-x$		$-x$		$+2x$
Equilibrium conc. in mol L^{-1}	0.8–x		0.2 – x		2x

$$K_C = \frac{[NO]^2}{[N_2][O_2]} \qquad \therefore \; 1 \times 10^{-5} = \frac{(2x)^2}{(0.8 - x)(0.2 - x)}$$

Chemical Kinetics

As $x << 0.2$, therefore $0.8 - x \approx 0.8$ and $0.2 - x \approx 0.2$

$$\therefore \qquad 1 \times 10^{-5} = \frac{4x^2}{0.16} \qquad \Rightarrow \qquad 4x^2 = 16 \times 10^{-7}$$

$$x = 6.324 \times 10^{-4} \text{ mol L}^{-1}$$

Thus at equilibrium,

$$[NO] = 2x = 2 \times 6.324 \times 10^{-4} = \textbf{12.648} \times \textbf{10}^{-4} \textbf{ mol L}^{-1}$$
$$[N_2] = 0.8 - 6.324 \times 10^{-4} \text{ mol L}^{-1} = \textbf{0.799 mol L}^{-1}$$
$$[O_2] = 0.2 - 6.324 \times 10^{-4} \text{ mol L}^{-1} = \textbf{0.199 mol L}^{-1}$$

Q. 6. **Define order of reaction. How does order of a reaction differ from molecularity for a complex reaction?** *[CBSE 2019 (56/3/2), 2020 (56/5/1)]*

Ans. ● The sum of powers of the concentration of the reactants in the rate law expression is known as order of that reaction.

Consider the general reaction,

$$aA + bB \longrightarrow cC + dD$$

Let

$$\text{Rate} = k[A]^x[B]^y$$

where x and y represent the order w.r.t. t. The reactants A and B respectively. Overall order of reaction $= x + y$.

● Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions.

For a complex reaction molecularity has no meaning and order is given by the slowest step. Molecularity of the slowest step is same as the order of the overall reaction.

Q. 7. **Observe the graph in diagram and answer the following questions.**
    (i) If slope is equal to $-2.0 \times 10^{-6} \text{ sec}^{-1}$, what will be the value of rate constant?
    (ii) How does the half-life of zero order reaction relate to its rate constant? *[CBSE Sample Paper 2017]*

Ans. (i) Slope $= -\dfrac{k}{2.303}$ or $k = -2.303 \times$ Slope

$$\therefore \qquad k = -2.303 \times (-2.0 \times 10^{-6} \text{ s}^{-1})$$
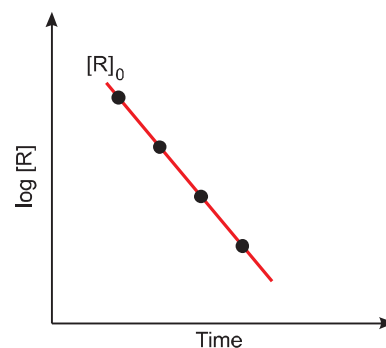$$k = \textbf{4.606} \times \textbf{10}^{-6} \textbf{ s}^{-1}$$

(ii) For a zero order reaction

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

$$\text{At } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

$$\therefore \qquad t_{1/2} = \frac{[R]_0 - \dfrac{[R]_0}{2}}{k} \qquad \text{or} \qquad t_{1/2} = \frac{[R]_0}{2k}$$

Q. 8. **A solution of H_2O_2 when titrated against $KMnO_4$ solution at different intervals of time gave the following results:**

Time (minutes)	0	10	20
Volume of $KMnO_4$ (mL)	23.8	14.7	9.1

Show that decomposition of H_2O_2 is first order reaction.

Ans. (i) $k = \dfrac{2.303}{10} \log \dfrac{23.8}{14.7} = \dfrac{2.303}{10} \times 0.2093 = \textbf{0.048 min}^{-1}$

(ii) $k = \dfrac{2.303}{20} \log \dfrac{23.8}{9.1} = \dfrac{2.303}{20} \times 0.4176 = \textbf{0.048 min}^{-1}$

Since the value of k comes out to be constant in both the cases, therefore the reaction is of first order.

Q. 9. Define half-life of a reaction. Write the expression of half-life for **[CBSE (F) 2014]**
　　　 (i) zero order reaction and (ii) first order reaction.

Ans. The half life ($t_{1/2}$) of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

　　　(i) $t_{1/2}$ for a zero order reaction = $\dfrac{[R]_0}{2k}$ where $[R]_0$ = initial concentration, k = rate constant

　　　(ii) $t_{1/2}$ for a first order reaction = $\dfrac{0.693}{k}$

Q. 10. **A first order reaction is 50% complete in 25 minutes. Calculate the time for 80% completion of the reaction.** **[CBSE 2019 (56/3/2)]**

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

$k = \dfrac{0.693}{25\text{ min}} = 2.772 \times 10^{-2}\text{ min}$

$[R] = [R]_0 - 80\%\text{ of }[R]_0$ or $[R] = [R]_0 - \dfrac{80 \times [R]_0}{100}$ or $[R] = 0.2[R]_0$

Substituting the value of k and $[R]$ in the expression

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

$$t = \frac{2.303}{2.772 \times 10^{-2}} \times \log \frac{[R]_0}{0.2[R]_0}$$

$$t = \frac{2.303}{2.772 \times 10^{-2}} \log 5$$

$$t = \frac{2.303 \times 0.699}{2.772 \times 10^{-2}} \text{ or } t = \mathbf{58.07\ min}$$

Q. 11. **Following data are obtained for the reaction:**

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

t/s	0	300	600
[N$_2$O$_5$]/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) **[CBSE Delhi 2017]**

Ans. (i) At 300 s,

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

$$= \frac{2.303}{300} \log \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}} = \frac{2.303}{300} \log 2$$

$$k = \frac{2.303}{300} \times 0.3010 = 2.31 \times 10^{-3}\ s^{-1}$$

At 600 s

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

$$= \frac{2.303}{600} \log \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}} = \frac{2.303}{600} \log 4$$

$$k = \frac{2.303}{600} \times 0.6021 = 2.31 \times 10^{-3}\ s^{-1}$$

Chemical Kinetics

k is constant and is equal to 2.31×10^{-3} s^{-1} when we use first order equation. Hence, it follows first order reaction.

(ii) $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{2.31 \times 10^{-3} \text{ s}^{-1}} = \mathbf{300\ s}$

Q. 12. $^{238}_{92}$U changes to $^{206}_{92}$Pb by successive radioactive decay. A sample of uranium ore was analysed and found to contain 1.0 g of ^{238}U and 0.1 g of ^{206}Pb had accumulated due to decay of ^{238}U, find out the age of the ore. (Half-life of ^{238}U = 4.5 × 10^9 years) **[HOTS]**

Ans. $[A]_0$ = Initial amount of ^{238}U = amount of ^{238}U left at time t + amount of ^{238}U decayed

$$[A]_0 = 1.0 + \text{amount of } {}^{238}\text{U decayed}$$

Now, amount of ^{238}U decayed $= \dfrac{0.1 \times 238}{206}$ g $= 0.1155$ g

∴ $[A]_0 = 1.0$ g $+ 0.1155$ g $= 1.1155$ g

Determination of k: $\quad k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{4.5 \times 10^9} = 0.154 \times 10^{-9}$ year^{-1}

Determination of time: $\quad t = \dfrac{2.303}{k} \log \dfrac{[A]_0}{[A]}$

Substituting the values of $[A]_0 = 1.1155$ g and $k = 0.154 \times 10^{-9}$ year^{-1}

$$t = \dfrac{2.303}{0.154 \times 10^{-9}} \log \dfrac{1.1155}{1}$$
$$= 0.7099 \times 10^9 \text{ year}$$
$$= \mathbf{7.099 \times 10^8 \text{ year}}$$

**Q. 13.** The following data were obtained during the first order thermal decomposition of N$_2$O$_5$(g) at a constant volume:

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

S. No.	Time/s	Total Pressure/atm
1.	0	0.5
2.	100	0.512

Calculate the rate constant. **[HOTS]**

Ans. Let the pressure of N$_2$O$_5$(g) decrease by $2x$ atm. As two moles of N$_2$O$_5$ decompose to give two moles of N$_2$O$_4$(g) and one mole of O$_2$(g), the pressure of N$_2$O$_4$(g) increases by $2x$ atm and that of O$_2$(g) increases by x atm.

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$
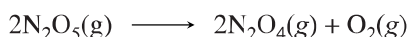
At $t = 0$ $\quad$ 0.5 atm $\quad\quad$ 0 atm $\quad$ 0 atm

At time t $\quad$ $(0.5 - 2x)$ atm $\quad$ $2x$ atm $\quad$ x atm

$$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$$
$$= (0.5 - 2x) + 2x + x = 0.5 + x$$
$$x = p_t - 0.5$$
$$p_{N_2O_5} = 0.5 - 2x = 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$$

At $t = 100$ s; $p_t = 0.512$ atm,

$$p_{N_2O_5} = 1.5 - 2 \times 0.512 = 0.476 \text{ atm}$$

Thus, $\quad k = \dfrac{2.303}{t} \log \dfrac{p_i}{p_A}$

$$= \dfrac{2.303}{100 \text{ s}} \log \dfrac{0.5 \text{ atm}}{0.476 \text{ atm}}$$
$$= \dfrac{2.303}{100 \text{ s}} \times 0.02136 = \mathbf{4.92 \times 10^{-4} \text{ s}^{-1}}$$

Q. 14. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

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

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

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

Ans. Comparing the equation, $\log k = 14.2 - \frac{1.0 \times 10^4}{T}$ K with the equation, $\log k = \log A - \frac{E_a}{2.303 \, RT}$, we get

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

$$E_a = 1.0 \times 10^4 \text{ K} \times 2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 19.1471 \times 10^4 \text{ J mol}^{-1} = \textbf{191.47 kJ mol}^{-1}$$

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

$\therefore$　　　　　　　　　　　$k = \frac{0.693}{200 \text{ min}} = \textbf{3.465} \times \textbf{10}^{-3} \textbf{ min}^{-1}$

Q. 15. The rate constant of a first order reaction increases from 2×10^{-2} to 4×10^{-2} when the temperature changes from 300 K to 310 K. Calculate the energy of activation (E_a).

　　　　　(log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)　　　　　　　　**[CBSE Patna 2015]**

Ans. Substituting $k_1 = 2 \times 10^{-2}$, $k_2 = 4 \times 10^{-2}$, $T_1 = 300$ K, $T_2 = 310$ K, $R = 8.314$ J K^{-1}mol^{-1} in the expression

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left(\frac{T_2 - T_1}{T_1 T_2}\right), \text{ we get}$$

$$\log \frac{4 \times 10^{-2}}{2 \times 10^{-2}} = \frac{E_a}{2.303 \times 8.314}\left(\frac{310 - 300}{300 \times 310}\right)$$

$$\log 2 = \frac{E_a}{19.147} \times \frac{10}{300 \times 310}$$

$$E_a = 0.3010 \times 19.147 \times 300 \times 31 = 53598 \text{ J mol}^{-1}$$

$$E_a = \textbf{53.598 kJ mol}^{-1}$$

Q. 16. For a reaction, the energy of activation is zero. What is the value of rate constant at 300 K, if $k = 1.6 \times 10^6$ s^{-1} at 280 K? [$R = 8.31$ J K^{-1} mol^{-1}]

Ans. Given $T_1 = 280$ K, $k_1 = 1.6 \times 10^6$ s^{-1}, $k_2 = ?$, $E_a = 0$, $T_2 = 300$ K.

By Arrhenius equation,

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

As, $E_a = 0$

$\therefore$　　　　　　　　　$\log \frac{k_2}{k_1} = 0$

or　　　　　　　　　　　$\frac{k_2}{k_1} = 1$　　or　　　$k_2 = k_1$

Thus, the rate constant at 300 K is $\textbf{1.6} \times \textbf{10}^6 \textbf{ s}^{-1}$.

Q. 17. A certain reaction is 50% complete in 20 minutes at 300 K and the same reaction is again 50% complete in 5 minutes at 350 K. Calculate the activation energy if it is a first order reaction.

[$R = 8.314$ J K^{-1} mol^{-1}; log 4 = 0.602]　　　　　　　　　　　　　　**[HOTS]**

Ans. For a first order reaction,　　　$k = \frac{0.693}{t_{1/2}}$

$T_1 = 300$ K,　　　　　　　　　$k_1 = \frac{0.693}{20} = 3.456 \times 10^{-2} \text{ min}^{-1}$

$$T_2 = 350 \text{ K}, \qquad k_2 = \frac{0.693}{5} = 1.386 \times 10^{-1} \text{ min}^{-1}$$

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

$$\log \frac{1.386 \times 10^{-1}}{3.465 \times 10^{-2}} = \frac{E_a}{2.303 \times 8.314}\left(\frac{350 - 300}{350 \times 300}\right)$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314}\left(\frac{50}{350 \times 300}\right)$$

$$0.602 = \frac{E_a}{19.147}\left(\frac{50}{350 \times 300}\right)$$

$$E_a = \frac{0.602 \times 19.147 \times 350 \times 300}{50}$$

$$= 24205.63 \text{ J mol}^{-1}$$

$$= \textbf{24.206 kJ mol}^{-1}$$

Q. 18. 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. **[*CBSE 2018*]**

(Given: log 2 = 0.3010, log 4 = 0.6021, $R = 8.314$ J K^{-1} mol^{-1})

Ans. For a first order reaction, $k = \dfrac{0.693}{t_{1/2}}$

So, $k_1 = \dfrac{0.693}{40}$ min^{-1} and $k_2 = \dfrac{0.693}{20}$ min^{-1}

$$\frac{k_2}{k_1} = \frac{0.693 \text{ min}^{-1}/20}{0.693 \text{ min}^{-1}/40} = 2$$

Here, $T_1 = 300$ K, $T_2 = 320$ K and $R = 8.314$ J K^{-1} mol^{-1}

Substituting these values in the expression

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left(\frac{T_2 - T_1}{T_1 T_2}\right), \text{ we get}$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1}\text{mol}^{-1}}\left(\frac{320 \text{ K} - 300 \text{ K}}{300 \text{ K} \times 320 \text{ K}}\right)$$

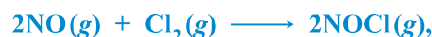$$0.3010 = \frac{E_a \times 20}{19.147 \text{ J mol}^{-1} \times 300 \times 320}$$

or $\qquad E_a = \dfrac{0.3010 \times 19.147 \times 300 \times 320 \text{ J mol}^{-1}}{20} = 27663.58 \text{ J mol}^{-1}$

$$E_a = \textbf{27.66 kJ mol}^{-1}$$

Long Answer Questions   [5 marks]

Q. 1. For the reaction,

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g),$$

the following data were collected. All the measurements were taken at 263 K:

Experiment	Initial [NO] (M)	Initial [Cl$_2$] (M)	Initial rate of disappearance of Cl$_2$ (M/min)
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

(*i*) **Write the expression for rate law.**

(*ii*) **Calculate the value of rate constant and specify its units.**

(*iii*) **What is the initial rate of disappearance of Cl_2 in experiment 4?**   [*CBSE Delhi 2012*]

Ans. Suppose order w.r.t. NO is m and order w.r.t. Cl_2 is n. Then the rate will be

$$\text{Rate } = k\,[NO]^m\,[Cl_2]^n$$

Substituting the values of experiment 1 to 3 in the rate expression, we get

$$0.60 = k(0.15)^m\,(0.15)^n \qquad\qquad ...(i)$$
$$1.20 = k(0.15)^m\,(0.30)^n \qquad\qquad ...(ii)$$
$$2.40 = k(0.30)^m\,(0.15)^n \qquad\qquad ...(iii)$$

Dividing equation (*iii*) by (*i*), we get

$$\frac{2.40}{0.60} = \frac{k\,(0.30)^m\,(0.15)^n}{k\,(0.15)^m\,(0.15)^n}$$

$$4 = 2^m \text{ or } 2^2 = 2^m \text{ or } m = 2$$

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

$$\frac{1.20}{0.60} = \frac{k\,(0.15)^m\,(0.30)^n}{k\,(0.15)^m\,(0.15)^n}$$

$$2 = 2^n \text{ or } n = 1$$

(*i*) Rate law expression is, Rate $= k[NO]^2\,[Cl_2]$

(*ii*) $0.60 \text{ mol L}^{-1}\text{ min}^{-1} = k(0.15 \text{ mol L}^{-1})^2\,(0.15 \text{ mol L}^{-1})$

$$k = \textbf{177.78 mol}^{-2}\,\textbf{L}^2\,\textbf{min}^{-1}$$

(*iii*) Rate $= 177.78 \text{ mol}^{-2}\text{ L}^2\text{ min}^{-1} \times (0.25 \text{ mol L}^{-1})^2\,(0.25 \text{ mol L}^{-1})$

$$= \textbf{2.778 mol L}^{-1}\,\textbf{min}^{-1}$$

Q. 2. **Consider the reaction $R \xrightarrow{k} P$. The change in concentration of R with time is shown in the following plot:**   [*CBSE 2019 (56/4/1)*]

(*i*) **Predict the order of the reaction.**

(*ii*) **Derive the expression for the time required for the completion of the reaction.**

(*iii*) **What does the slope of the above line indicate?**
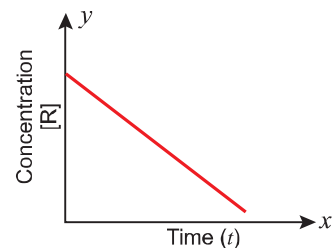
Ans. (*i*) The reaction $R \longrightarrow P$ is a zero order reaction.

(*ii*) For the reaction $R \xrightarrow{k} P$

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

$$d\,[R] = -k\,dt$$

Integrating both sides,

$$[R] = -kt + C, \qquad \text{where } C = \text{constant of integration} \quad ...(i)$$

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

Substituting this in equation (*i*)

$$C = [R]_0$$

Substituting the value of C in equation (*i*)

$$[R] = -kt + [R]_0 \qquad\qquad ...(ii)$$

$$kt = [R]_0 - [R]$$

$$\Rightarrow \qquad\qquad t = \frac{[R]_0 - [R]}{k}$$

On completion of reactions, $[R] = 0$

$$\therefore \qquad\qquad t = \frac{[R]_0}{k}$$

(*iii*) From equation (*ii*), we have slope of curve

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

Chemical Kinetics

Q. 3. For a certain chemical reaction variation in the concentration ln [R] vs. time plot is given alongside. **[HOTS]**

For this reaction
  (*i*) what is the order of the reaction?
  (*ii*) what are the units of rate constant *k*?
  (*iii*) give the relationship between *k* and $t_{1/2}$ (half-life period).
  (*iv*) what is the slope of the curve?
  (*v*) draw the plot log $[R]_0$ /[R] vs time *t*(s).
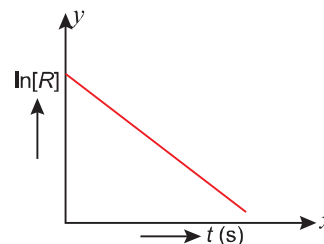
Ans. (*i*) First order   (*ii*) time^{-1} (s^{-1})

(*iii*) $k = \dfrac{0.693}{t_{1/2}}$ (*iv*) slope $= -k$ (rate constant)

(*v*)
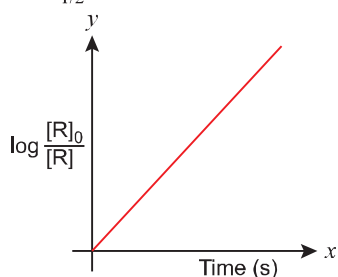
Q. 4. Nitrogen pentoxide decomposes according to equation:

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

This first order reaction was allowed to proceed at 40°C and the data below were collected:

$[N_2O_5]$ (M)	Time (min)
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

(*i*) Calculate the rate constant. Include units with your answer.
(*ii*) What will be the concentration of N_2O_5 after 100 minutes?
(*iii*) Calculate the initial rate of reaction.   *[CBSE Delhi 2011]*

Ans. (*i*) When $t = 20$ min, $[R] = 0.289$ mol L^{-1}

Also, $[R]_0 = 0.400$ mol L^{-1}

For a first order reaction

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

∴ $k = \dfrac{2.303}{20} \log \dfrac{0.400}{0.289}$ ⟹ $k = \dfrac{2.303}{20} \log \dfrac{4.00}{2.89}$

⟹ $k = \dfrac{2.303}{20} [\log 4.00 - \log 2.89]$ ⟹ $k = \dfrac{2.303}{20} [0.6021 - 0.4609]$

⟹ $k = \dfrac{2.303}{20} \times 0.1412$ ⟹ $k = 2.303 \times 0.00706 = 0.016259$ min^{-1}

⟹ $k = \mathbf{1.6259 \times 10^{-2}}$ **min^{-1}**

(*ii*) $t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]}$

Here, $[R]_0 = 0.400$ mol^{-1}, $t = 100$ min, $k = 1.626 \times 10^{-2}$ min^{-1}

$$100 = \frac{2.303}{1.626 \times 10^{-2}} \log \frac{0.400}{[R]}$$

$$\frac{100 \times 1.626 \times 10^{-2}}{2.303} = \log \frac{0.4}{[R]} \quad \Rightarrow \quad 0.7060 = \log \frac{0.4}{[R]}$$
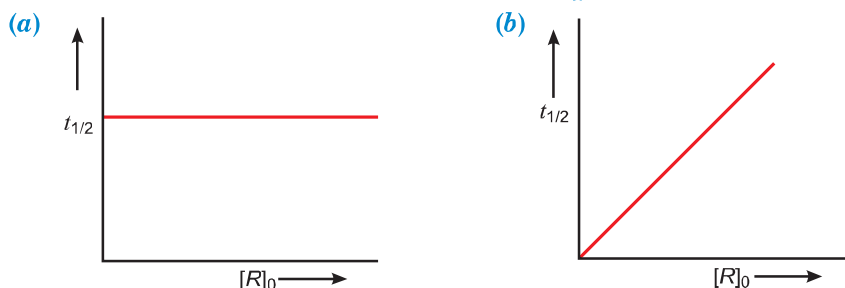
$$\text{Antilog } (0.7060) = \frac{0.4}{[R]}$$

$$5.082 = \frac{0.4}{[R]} \quad \Rightarrow \quad [R] = \frac{0.4}{5.082} = \mathbf{0.0787\ M}$$

(*iii*) Initial rate, *i.e.*, rate of reaction when $t = 0$

When, $\qquad\qquad\qquad\qquad\qquad t = 0.00$ min, $[R] = 0.400$ mol L^{-1}

Also, $\qquad\qquad\qquad\qquad\qquad k = 1.626 \times 10^{-2}$ min^{-1}

$\therefore \qquad\qquad\qquad\qquad$ Initial rate $= k\,[R]$

$$= 1.626 \times 10^{-2}\ \text{min}^{-1} \times 0.400\ \text{mol}\ L^{-1}$$

$$= \mathbf{6.504 \times 10^{-3}\ mol\ L^{-1}\ min^{-1}}$$

Q. 5. (*i*) **A first order reaction is 75% completed in 40 minutes. Calculate its $t_{1/2}$. [CBSE (F) 2017]**

(*ii*) **Predict the order of the reaction in the given plots:** [*CBSE 2019 (56/2/1)*]

(*a*)

(*b*)

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

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

Ans. (*i*) For a first order reaction, $t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]}$

$$\therefore \qquad \frac{t_{3/4}}{t_{1/2}} = \frac{\dfrac{2.303}{k} \log \dfrac{100}{25}}{\dfrac{2.303}{k} \log \dfrac{100}{50}} = \frac{\log 4}{\log 2} = \frac{0.6021}{0.3010}$$

$$\frac{40 \text{ min}}{t_{1/2}} = 2 \qquad \text{or} \qquad t_{1/2} = \mathbf{20\ min.}$$

(*ii*) (*a*) First order $\qquad\qquad$ (*b*) Zero order

Q. 6. **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) [*CBSE Delhi 2015*]

Ans. (*i*) $k = \dfrac{2.303}{t} \log \dfrac{[R]_0}{[R]}$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ …(*i*)

Substituting $[R]_0 = 0.60$ mol L^{-1}, $[R] = 0.30$ mol L^{-1} and $t = 30$ s in equation (*i*), we get

$$k = \frac{2.303}{30} \log \frac{0.60}{0.30}$$

$$k = \frac{2.303}{30} \log 2 = \frac{2.303}{30} \times 0.3010$$

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

Chemical Kinetics

Again substituting, $[R]_0 = 0.60$ mol L^{-1}, $[R] = 0.15$ mol L^{-1} and $t = 60$ in equation (i), we get

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

$$k = \frac{2.303}{60}\times\log 4 = \frac{2.303}{60}\times 0.6021$$

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

As the value of k is same in both the cases, therefore, hydrolysis of methylacetate in aqueous solution follows pseudo first order reaction.

(ii) Average rate $= -\dfrac{\Delta[CH_3COOCH_3]}{\Delta t} = \dfrac{-[0.15 - 0.30]}{60 - 30} = \dfrac{0.15}{30}$

Average rate = **0.005 mol L^{-1} s^{-1}**

Q. 7. (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) **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?**

Ans. (i) Consider the first order reaction,

$$R \longrightarrow P$$

For this reaction, rate law which relates the rate of reaction to the concentration of reactants can be given as

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

For a first order reaction,

$t = \dfrac{2.303}{k}\log\dfrac{[R]_0}{[R]}$, where $[R]_0$ = initial concentration, $[R]$ = concentration at time t.

At $t_{1/2}$, $[R] = [R]_0/2$

So, the above equation becomes

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

$$t_{1/2} = \frac{2.303}{k}\log 2 \quad\text{or}\quad t_{1/2} = \frac{2.303}{k}\times 0.3010$$

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

This shows that half life of a first order reaction is independent of the initial concentration of the reactant.

(ii) According to Arrhenius equation,

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

For uncatalysed reaction,   For catalysed reaction,

$\log k_1 = \log A - \dfrac{E_{a_1}}{2.303\,RT}$ ...(i) $\log k_2 = \log A - \dfrac{E_{a_2}}{2.303\,RT}$ ...(ii)

A is equal for both reactions.

Subtracting equation (i) from equation (ii),

$$\log\frac{k_2}{k_1} = \frac{E_{a_1} - E_{a_2}}{2.303\,RT} = \frac{(75.2 - 50.14)\text{ kJ mol}^{-1}}{2.303\times 8.314\text{ JK}^{-1}\text{ mol}^{-1}\times 298\text{ K}} = 4.39$$

$$\frac{k_2}{k_1} = \text{antilog }(4.39) = \mathbf{2.45\times 10^4}$$

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

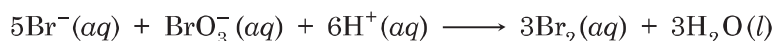*Choose and write the correct answer for each of the following.*   **(3 × 1 = 3)**

1. Rate law for the reaction $A + 2B \longrightarrow C$ is found to be

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

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

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

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

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

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

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

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

  (*b*) It alters ΔG of the reaction.

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

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

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

  (a) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

  (b) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

  (c) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

 **(d)** *Assertion (A) is incorrect, but Reason (R) is correct statement.*   **(3 × 1 = 3)**

4. **Assertion** (*A*) **:** Many of photochemical changes have positive sign of ΔG, yet they are spontaneous.

  Reason (*R*) **:** The activation energy in photochemical reactions is provided by light energy.

5. **Assertion** (*A*) **:** In a reversible endothermic reaction, E_{act} of the forward reaction is higher than that of the backward reaction.

  Reason (*R*) **:** The threshold energy of the forward reaction is more than that of the backward reaction.

6. **Assertion** (*A*) **:** The order of the reaction

$$2NO(g) + 2H_2(g) \longrightarrow 2H_2O(g) + N_2(g) \text{ is } 3.$$
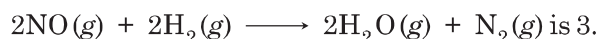
  Reason (*R*) **:** Order of reaction with respect to a given reactant is the power of the reactant's concentration in the rate equation.

Answer the following questions:

7. State a condition under which a bimolecular reaction is kinetically first order.   **(1)**

8. Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of one example. **(1)**

9. A first order reaction takes 40 minutes for 30% decomposition. Calculate $t_{1/2}$. **(2)**

10. For a zero order reaction will the molecularity be equal to zero? Explain. **(2)**

11. (i) The conversion of the molecule X to Y follows second order kinetics. If the concentration X is increased to three times, how will it affect the rate of formation of Y?

    (ii) The specific reaction rate of a reaction is 6.2×10^{-3} mol L^{-1} s^{-1}. What is the order of reaction? **(2)**

12. Derive an expression to calculate time required for completion of zero order reaction. **(2)**

13. The rate constant for the decomposition of ethyl iodide

$$C_2H_5I(g) \longrightarrow C_2H_4(g) + HI(g)$$
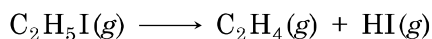
    at 600 K is 1.60×10^{-5} s^{-1}. Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700 K. **(3)**

14. For a general reaction A $\longrightarrow$ B, plot of concentration of A vs time is given in figure. Answer the following questions on the basis of this graph.
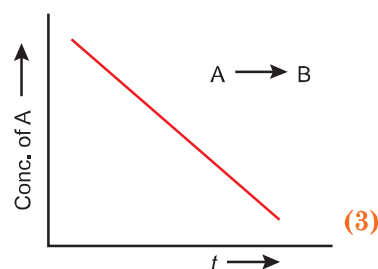
    (i) What is the order of the reaction?

    (ii) What is the slope of the curve?

    (iii) What are the units of rate constant? **(3)**

15. The following data were obtained for the reaction:

$$A + 2B \longrightarrow C$$

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}

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

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

    (iii) Calculate the rate constant (k). **(3)**

16. (i) For an elementary reaction

$$2A + B \longrightarrow 3C$$

    the rate of appearance of C at time 't' is 1.3×10^{-4} mol L^{-1} s^{-1}.

    Calculate at this time

    (a) rate of the reaction.

    (b) rate of disappearance of A.

    (ii) The decomposition of $N_2O_5(g)$ is a first order reaction with a rate constant of 5×10^{-4} s^{-1} at 45°C, i.e., $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$. If initial concentration of N_2O_5 is 0.25 M, calculate its concentration after 2 min. Also, calculate half-life for decomposition of $N_2O_5(g)$. **(5)**

Answers

1. (a)   **2.** (c)   **3.** (b)   **4.** (b)   **5.** (c)   **6.** (a)   **9.** 77.78 min   **13.** 6.36×10^{-3} s^{-1}

15. (iii) 6.0 L^2 mol^{-1} min^{-1} **16.** (i) (a) 0.43×10^{-4} mol L^{-1} s^{-1}, (b) 0.86×10^{-4} mol L^{-1} s^{-1} (ii) 0.235 M, 1386 s