

Chapter	7 Reaction Kinetics	Class	1 st Year	Subject	Chemistry
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Give Short Answers of the Following Questions

1. Differentiate between instantaneous and average rate of reaction.

Ans. Differences between Instantaneous and Average Rate of Reaction:

Average Rate	Instantaneous Rate
"The rate at any one instant during the interval is called the instantaneous rate".	"The rate of reaction between two specific time intervals is called average rate".
Instantaneous rate = $\frac{dx}{dt}$	Average rate = $\frac{\Delta x}{\Delta t}$
At first instantaneous rate is higher than average rate.	At the end, average rate is higher than instantaneous rate.

2. Differentiate between rate and rate constant of a reaction.

Ans. Differences between rate and rate constant of a reaction.

Rate of reaction	Rate constant
(i) It is the speed at which the reactants are converted into the products.	It is a constant of proportionality in the rate law expression.
(ii) Rate = $\frac{\Delta x}{\Delta t}$	Rate = $k[\text{Reactants}] \Rightarrow k = \frac{\text{Rate}}{[\text{Reactants}]}$
(iii) It depends upon the concentration of reactant species at that moment.	It refers to the rate of reaction at specific point when concentration of every reaction species is unity.
(iv) It decreases with the progress of reaction generally.	It is a constant and does not depend on the progress of the reaction.

3. Radioactive decay is always first order reaction. Justify.

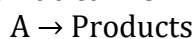
Ans. A radioactive substance has a single species at a moment, whose nucleus under goes disintegration. As only one reactant is involved, so it follows 1st order mechanism.

e.g., Half-life of $^{235}_{92}\text{U}$ is 710 million years. It means if one kg uranium is present at start, after 710 million years, 0.5kg of it will disintegrate and after next 710million years 0.25 kg of it will disintegrate and so on. Therefore we can say that half-life of a radioactive decay is always a 1st order reaction.

4. What is zero order reaction? Give one example.

Ans. Zero Order Reaction:"The reaction which is entirely independent of the concentration of reactant molecules is called zero order reaction"

Mathematical Form:



$$\text{Rate} = k[A]^0$$

$$\text{Rate} = k$$

Example: All photosynthetic reactions are usually zero order reactions.

5. The order of reaction may be in fraction. Explain.

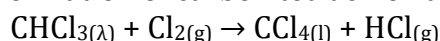
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Ans. Fractional Order Reaction:

The order of a reaction is usually positive integer or a zero, but it can also be in fraction or can have a negative value.

Example:

Consider the formation of carbon tetrachloride from chloroform.



$$\text{Rate} = k [\text{CHCl}_3] [\text{Cl}_2]^{1/2}$$

The sum of exponents will be $1 + 1/2 = 1.5$ so,

Order of reaction = 1.5

6. Differentiate between order of reaction and rate of reaction

Ans. Order of Reaction:

"The number of reacting molecules whose concentration alters as a result of the chemical change is called order of reaction."

OR

"The sum of all the exponents to which the concentration in the rate equation are raised is called order of reaction."

Rate of Reaction:

(i) It is the speed at which the reactants are converted into the products.

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

(iii) It depends upon the concentration of reactant species at that moment.

(iv) It decreases with the progress of reaction generally.

7. Define half-life period of a reaction. Give one example.

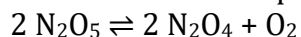
Ans. Half-life period:

"The time which is required to convert 50% of the reactants into products is called half-life period ($t_{1/2}$)."

Example:

Decomposition of N_2O_5

The half-life period for the decomposition of N_2O_5 at 45°C is 24 minutes.



$$t_{1/2} = 24 \text{ min at } 45^\circ\text{C}$$

[1st order reaction]

Importance:

- We can use the rate of decay of an item to determine the age of item.
- We can predict the amount of radioactive material that will remain after a given amount of time.

8. What is rate determining step? Give a suitable example.

Ans. Rate Determining Step:

"A slowest step in reaction mechanism which can determine the overall rate of reaction called rate determining step."

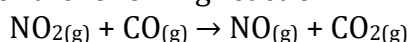
Rate Determining Step:

"Rate determining step is that step of a chemical reaction which controls the rate of reaction."

- If a reaction occurs in several steps, one of the steps is the slowest.
- The rate of this step determines the overall rate of reaction.

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- This slowest step is called the rate determining or rate limiting step.
- The total number of molecules taking part in the rate determining step-appear in the rate equation of the reaction.
- Let us consider the following reaction



The rate equation of the reaction is found to be:

$$\text{Rate} = K[\text{NO}_2]^2$$

- The reaction is second order with respect to $\text{NO}_{2(g)}$. Experiment shows that $\text{CO}_{(g)}$ is not taking part in the rate determining step. The proposed mechanism for this reaction is as follows:

Step 1: $\text{NO}_{2(g)} + \text{NO}_{2(g)} \xrightarrow{\text{Slow}} \text{NO}_{3(g)} + \text{NO}_{(g)}$ (It is a slow hence rate determining step)

Step 2: $\text{NO}_{3(g)} + \text{CO}_{2(g)} \xrightarrow{\text{fast}} \text{NO}_{2(g)} + \text{CO}_{2(g)}$

- The first step is the rate determining step and NO_3 which does not appear in the balanced equation, is called the reaction intermediate.
- The reaction intermediate has a temporary existence and it is unstable relative to the reactants and the products.

9. Differentiate between fast step and the rate determining step.

Ans.

Fast Step	Rate Determining Step
i. A step in a chemical reaction which proceeds so fastly that we are unable to determine the rate of reaction is called fast step. It has no effect on overall rate of reaction.	A slowest step in reaction mechanism which can determine the overall rate of reaction is called rate determining step.
ii. For example: For a reaction $2\text{NO}_{(g)} + 2\text{H}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(g)} + \text{N}_{2(g)}$ The steps of reaction mechanism are a. $2\text{NO}_{(g)} + \text{H}_2 \xrightarrow{\text{Slow}} \text{H}_2\text{O}_{2(g)} + \text{N}_{2(g)}$ b. $\text{H}_{2(g)} + \text{H}_2\text{O}_{2(g)} \xrightarrow{\text{fast}} 2\text{H}_2\text{O}_{(g)}$ Step (b) is fast step.	In the example given in left column, step (a) is the rate determining step. $2\text{NO}_{(g)} + \text{H}_2 \xrightarrow{\text{Slow}} \text{H}_2\text{O}_{2(g)} + \text{N}_{2(g)}$ It is experimentally determined. It involves 2 moles NO and one mole H_2 .
iii. Reactants of fast step are eliminated from rate equation. Moreover, in a multistep reaction, number of fast steps can be one or more than one.	Reactants of slow step are present in rate equation i.e., $\text{Rate} = k[\text{H}_2][\text{NO}_2]^2$.
iv. Fast step is unable to determine order of reaction.	Sum of reactant coefficients of slowest step is the order of reaction. E.g. in the above reaction: Order of reaction = $2 + 1 = 3$

10. The sum of the co-efficient of a balanced chemical equation is not necessarily important to give the order of reaction. Give reasons in support of your answer.

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Ans. Order of a chemical reaction is not necessarily the sum of the coefficients of the balanced chemical equation because the order of reaction is determined experimentally and not from the balanced chemical equation.

e.g., $2\text{H}_2 + 2\text{NO}_2 \rightarrow 2\text{H}_2\text{O}_2 + \text{N}_2$

For this reaction, the sum of coefficients of balanced equation is $2 + 2 = 4$ but the reaction is 3rd order. It is experimentally verified that rate of reaction is directly related to conc. of H_2 and to the square of concentration of NO_2 . So the rate equation of this reaction is

$$\text{Rate} \propto [\text{H}_2]^1[\text{NO}_2]^2$$

$$\text{Rate} = [\text{H}_2]^1[\text{NO}_2]^2$$

Order of reaction is sum of exponents of rate equation. So,

$$\text{Order of reaction} = 1 + 2 = 3$$

11. Define energy of activation. How is it affected by temperature?

Ans. Energy of Activation:

The minimum amount of energy in addition to average kinetic energy which is just sufficient to convert the reactants into products is called energy of activation (E_a).

Effect of Temperature:

According to Arrhenius Equation:

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

K is exponentially related to activation energy E_a and temperature T. the equation shows that the increase in temperature, increase the rate constant and the reaction of high activation energy low "k" values. It means that if we increase the temperature the activation energy of the reaction decreases.

Activated complex is an unstable combination of all the atoms involved in the reaction for which the energy is maximum. It is a short lived species and decomposes into products immediately. It has a transient existence that is why it is also called a transition state.

12. Describe Half Life Method to determine order of reaction.

Ans. Half-Life Method:

"Half-life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction."

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

Let us perform a reaction twice by taking two different initial concentrations a_1 and a_2 and their half-life periods are found to be t_1 and t_2 respectively.

$$T_1 \propto \frac{1}{a_1^{n-1}} \quad \text{and} \quad T_2 \propto \frac{1}{a_2^{n-1}}$$

Dividing the above two equations:

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking log on both sides, we have

$$\log\left(\frac{t_1}{t_2}\right) = \log\left[\left(\frac{a_2}{a_1}\right)^{n-1}\right]$$

$$\log\left(\frac{t_1}{t_2}\right) = (n-1)\log\left(\frac{a_2}{a_1}\right)$$

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$$n = 1 + \frac{\log \frac{t_1}{t_2}}{\log \frac{a_2}{a_1}}$$

Where, n = order of reaction

13. Define Catalysis. Write two characteristics of a catalyst.

Ans. Catalysis:

“The process, which takes place in the presence of a catalyst, is called catalysis.”

Characteristics of a Catalyst.

1. Unchanged chemical composition:

A catalyst remains unchanged in mass and chemical composition at the end of reaction. It may not remain in the same physical state.

Examples:

(i) MnO₂ is added as a catalyst for the decomposition of KClO₃. But MnO₂ is regenerated at the end in the form of a fine powder.

(ii) In some cases, the shining surfaces of the solid catalyst become dull.

2. Effectiveness of a Catalyst:

Sometimes, we use a trace of metal catalyst to effect very large amount of reactants.

Examples:

(i) 1 mg of fine platinum powder can convert 2.5 dm³ of H₂ and 1.25 dm³ of O₂ to water.

(ii) Dry HCl and NH₃ don't combine, but in the presence of trace of moisture, they give dense white fumes of NH₄Cl.

(iii) Thousands of dm³ of H₂O₂ can be decomposed in the presence of 1 g of colloidal platinum.

14. Define catalysis. Give its different types with one example in each case.

Ans. Catalysis:

“The process, which takes place in the presence of a catalyst, is called catalysis.”

Types of Catalysis:

(a) Homogeneous Catalysis

(b) Heterogeneous Catalysis

(a) Homogeneous Catalysis:

“When the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout, then it is called homogeneous catalysis.”

The catalyst is distributed uniformly throughout the system.

Examples:

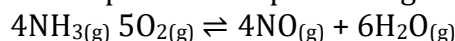
The formation of SO₃ from SO₂ and O₂ in lead chamber process for the manufacture of sulphuric acid needs NO as a catalyst. Both the reactants and the catalyst are gases.

(b) Heterogeneous Catalysis

“When the catalyst and the reactants are in different phases, then it is called heterogeneous catalysis.”

Examples:

Oxidation of ammonia to NO in the presence of platinum gauze helps us to manufacture HNO₃.



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15. Differentiate between homogeneous and heterogeneous catalysis. Give example.

Ans.

Homogeneous Catalysis	Heterogeneous Catalysis
(i) It is catalysis in which the catalyst and reacting substances are in same physical state/phase.	(i) It is catalyst in which the catalyst and reacting substances are in different phases.
(ii) Catalyst is uniformly distributed.	(ii) No uniform distribution of catalyst.
(iii) Mostly liquid or gaseous catalysts are used in homogeneous catalysis.	(iii) Catalyst is solid and reacting substances and either liquids or gases.
(iv) e.g., $2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$	e.g., $4\text{NH}_{3(g)} + 5\text{O}_{2(g)} \rightleftharpoons 4\text{NO}_{(g)} + 6\text{H}_2\text{O}_{(g)}$

16. Describe the effects of catalyst on reversible reaction.

Ans. Effects of Catalyst

In Reversible chemical reaction, catalyst suitable for forward reaction may be used to carry out back reaction as it increases the rate of both forward and reverse processes by lowering the activation energy of both forward and reverse steps by giving new path to the reaction. This reduces the time to attain the equilibrium state. It does not affect the equilibrium state K_c .

17. What do you understand by the rate of a reaction?

Ans. The rate of a reaction refers to how fast or slow a chemical reaction occurs. It is defined as the change in concentration of a reactant or product per unit time.

Mathematically, the rate of reaction can be expressed as:

$$\text{Rate of reaction} = \frac{\text{Change in concentration of the substance}}{\text{Time taken for the change}}$$

$$\text{Rate of reaction} = \frac{\Delta x}{\Delta t}$$

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18. Give the difference between enthalpy change of reaction and energy of activation of reaction.

Ans. Difference between Enthalpy Change of Reaction and Energy of Activation of Reaction:

Property	Enthalpy of Reaction (ΔH)	Activation Energy (E_a)
Definition	The total heat change during a chemical reaction at constant pressure.	The minimum energy required for a reaction to occur.
Significance	It indicates whether a reaction is exothermic ($\Delta H < 0$) or endothermic ($\Delta H > 0$).	It represents the energy barrier that must be overcome for a reaction to proceed.
Effect on Reaction	Reflects the overall energy change between products and reactants.	Affects the rate of the reaction; higher E_a means slower reaction.
Energy Direction	ΔH can be positive (endothermic) or negative (exothermic).	E_a is always positive, indicating an energy input is needed.
Measurement	It is the difference in the enthalpy between reactants and products.	It is determined experimentally by studying reaction rates.
Example	In the combustion of methane: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	For a reaction to occur, molecules must first overcome the activation

19. Differentiate clearly between order and molecularity of a reaction.

Ans. Difference between Order and Molecularity

Property	Order and a Reaction	Molecularity of a Reaction
Definition	The power to which the concentration of a reactant is raised in the rate law expression.	The number of reacting species (atoms, molecules, or ions) involved in the elementary step of a reaction.
Dependence on Concentration	Order depends on the experimental observation of how reaction rate changes with concentration of reactants.	Molecularity is based on the stoichiometric coefficients in the elementary reaction step.
Nature	Experimental: Determined by experimental data, can be fractional or zero.	Theoretical: Based on the nature of the reaction mechanism and the elementary steps.
Units	Depends on the rate law and overall reaction rate, and can vary with different reactions.	Always an integer (1, 2, 3, etc.) indicating the number of molecules or ions reacting in an elementary steps.
Example	For $A \rightarrow \text{products}$, if $\text{rate} = k[A]^2$, the order is 2.	For $A + B \rightarrow \text{products}$, the molecularity is 2 (because two molecules are involved).
Can It Be Fractional?	Yes, order can be fractional, zero, or a whole number.	No, molecularity must always be a whole number (1, 2, 3, ...).
Reactions	The order applies to overall reactions and depends on how concentration affects the rate.	Molecularity applies to the elementary step of a reaction mechanism.

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20. Why the instantaneous rate changes during a reaction?

Ans. The instantaneous rate of a reaction changes during the course of the reaction because:

1. Concentration of Reactants Changes:

- As the reaction proceeds, reactant molecules are consumed to form products. This causes a decrease in the concentration of the reactants over time.
- According to the rate law, the rate of reaction depends on the concentration of reactants. As the concentration decreases, the rate of the reaction generally slows down (in the case of most reactions).

2. Effect on Rate Law:

- The rate of the reaction is often directly proportional to the concentration of reactants raised to some power (the order of the reaction).
- For example, if the rate law is $\text{rate} = k[A]^n$, as $[A]$ decreases, the rate will decrease accordingly. This change in concentration over time causes the instantaneous rate to change as well.

3. Transition from Fast to Slow Reactions:

- In initial stages, when reactants are present in higher concentrations, the reaction proceeds faster.
- As reactants are consumed and their concentrations drop, the rate of reaction decreases.

4. Reverse Reaction (if applicable):

- In reversible reactions, as products form, they can also react to regenerate reactants. This can affect the overall rate, especially as the reaction approaches equilibrium.

21. Briefly summarize the effects of temperature and surface area on the rates of reaction.

Ans. 1. Effect of Temperature on Reaction Rate:

- Increase in Temperature $\Rightarrow$ Increase in Rate of reaction.
- At higher temperatures, molecules have more kinetic energy, leading to:
 - More frequent collisions between reactant molecules.
 - More energetic collisions, increasing the chances of successful reactions (i.e., Collisions with enough energy to overcome the activation energy barrier).
- Arrhenius Equation:** The rate constant (k) increases with temperature, generally leading to a faster reaction.

2. Effect of Surface Area on Reaction Rate:

- Increase in Surface Area $\Rightarrow$ Increase in Rate of reaction.
- Smaller particles or larger surface area of reactants result in:
 - More surface contact between reactants, leading to more collisions.
 - Faster reaction rate as more reactant particles are exposed to react with the other reactant molecules.
- Example:** Powdered solid reactants react faster than large chunks of the same substance because of the greater surface area available for collisions.

22. Justify that the radioactive decay is always a first order reaction.

Ans. Radioactive decay is always a first order reaction due to the nature of the process, which can be justified as follows:

First Order Reaction:

- A first order reaction is one where the rate reaction depends on the concentration of a single reactant raised to the power of 1.
- Mathematically: $\text{rate} = k[A]$, where $[A]$ is the concentration of the reactant, and k is the rate

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constant.

Dependence on the Number of Radioactive Nuclei:

- In radioactive decay, the rate at which substance decays depends on the number of radioactive nuclei present at any given time.
- The probability that a single nucleus will decay within a given time interval is constant and independent of the number of decays that have already occurred.
- The rate of decay is proportional to the number of radioactive atoms that are still intact at any moment, i.e., the concentration of the substance.
- The half life remains constant regardless of how much material is left, further proving that radioactive decay is a first order process.

23. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the square of the concentration is doubled and reduced to half?

Ans. For a second order reaction with respect to a reactant, the rate of the reaction is proportional to the square of the concentration of that reactant. This means that the rate law can be expressed as:

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

Where:

- k is the rate constant,
- $[A]$ is the concentration of the reactant.

24. What is meant by half-life and what is it used for?

Ans. Half-Life ($T_{1/2}$):

The half-life of a reaction is the time required for the concentration of a reactant to decrease to half of its initial value. It is a measure of how quickly a reaction occurs or how long it takes for a substance to undergo a certain amount of decay or transformation.

Uses:

It is used in various fields like radioactive decay, chemical reactions, and pharmacokinetics to measure the rate of processes or determine safe and effective dosages in medicine.

25. Why does wood burn more rapidly in pure oxygen than in air?

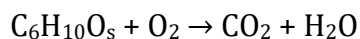
Ans. 1. Increased Oxygen Concentration:

- In air, oxygen makes up about 21% of the atmosphere, with the rest primarily consisting of nitrogen and trace gases.
- In pure oxygen, the oxygen concentration is 100%, meaning there is a much higher availability of oxygen molecules to react with the wood during combustion.
- More oxygen molecules allow the combustion reaction to proceed more quickly and at a higher rate, as there are more molecules available to support the chemical reaction.

2. Increased Rate of Combustion:

- Combustion is a chemical reaction between the fuel (in this case, wood) and oxygen. The reaction rate increases when the concentration of oxygen is higher.
 - Since the combustion of wood involves breaking bonds in the wood's cellulose structure, more oxygen molecules allow the reaction to happen more efficiently and rapidly.
- The general combustion reaction of wood (which primarily consists of cellulose) is:

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In pure oxygen, this reaction can proceed much faster than in air.

26. A catalyst lowers the activation energy of a chemical reaction. Illustrate it.

Ans. A catalyst is a substance that lowers the activation energy of a chemical reaction, thereby increasing the reaction rate without being consumed in the process.

27. The rate constant for a certain reaction is $3.5 \times 10^{-4} \text{ s}^{-1}$ at 25°C . What is the order of the reaction? Explain based on the units of the rate constant.

Ans. It seems to a reaction with a given rate constant ($k = 3.5 \times 10^{-4} \text{ s}^{-1}$) at a specific temperature (25°C). This rate constant suggests that the reaction may follow first-order kinetics, where the rate of reaction depends linearly on the concentration of the reactant.

Here are some key points about rate constants and their interpretation:

First Order Kinetics:

For a reaction with first-order kinetics, the rate law is given by:

$$\text{rate} = k[\text{A}]$$

Where:

- k is the rate constant (in this case, $3.5 \times 10^{-4} \text{ s}^{-1}$)
- $[\text{A}]$ is the concentration of the reactant.

The units of k for a first-order reaction are s^{-1} seconds inverse, which is consistent with the given rate constant.

“The number of reacting molecules whose concentration alters as a result of the chemical change is called order of reaction.”

OR

“The sum of all the exponents to which the concentrations in the rate equation are raised is called order of reaction.”

Order of a reaction decides the units of rate constant a reaction.

Explanation:

The units of the rate constant (k) reveal the reaction order:

- **First-Order (s^{-1}):** Rate depends linearly on concentration ($\text{Rate} = k[\text{A}]$).
- **Second-Order ($\text{dm}^3\text{mol}^{-1} \text{ s}^{-1}$):** Rate depends on concentration squared ($\text{Rate} = k[\text{A}]^2$).
- **Zero-Order ($k = \text{mol.dm}^3 \text{ s}^{-1}$):** Rate independent of concentration.

28. If the initial concentration of the reactant is 0.50 mol dm^{-3} , calculate the initial rate of the reaction.

Ans. For a first-order reaction, the rate law is:

$$\text{rate} = k[\text{A}]$$

Where:

- Rate is the initial rate of the reaction,
- k is the rate constant (given as $3.5 \times 10^{-4} \text{ s}^{-1}$)
- $[\text{A}]$ is the initial concentration of the reactant (given as 0.50 mol/dm^3).

Substitute the Given Values:

$$\text{Rate} = (3.5 \times 10^{-4} \text{ s}^{-1}) \times 0.50 \text{ mol/dm}^3$$

$$\text{Rate} = 1.75 \times 10^{-4} \text{ mol/dm}^3\text{s}$$

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29. How would the rate of this reaction change if the concentration of the reactant were double

Ans. The reaction is first-order the rate is directly proportional to the concentration of the reactant.

Rate law:

$$\text{rate} = k[A]$$

If the initial concentration is doubled, say from $[A]$ to $2[A]$, then:

$$\text{New rate} = k(2[A]) = 2 \cdot (k[A]) = 2 \times \text{original rate}$$

30. A certain first order reaction has a rate constant of $2.5 \times 10^{-4} \text{ s}^{-1}$. Calculate the half- life of the reaction in minutes.

Ans. Half- life formula (for first-order reaction):

$$t_{1/2} = \ln 2 / k$$

Where:

$$t_{1/2} = \text{half-life}$$

$$\ln 2 \approx 0.693$$

$$k = 2.5 \times 10^{-4} \text{ s}^{-1}$$

Calculate in seconds: $t_{1/2} = 0.693 / 2.5 \times 10^{-4} = 277.2 \text{ seconds}$

Convert seconds to minute: $t_{1/2} = 277.2 / 60 \approx 4.62 \text{ minute}$

31. A radioactive isotope decays by a first order process with a half -life of 12 hours. Calculate the rate constant for the decay in s^{-1} .

Ans. $k = \ln 2 / t_{1/2}$

Given: $t_{1/2} = 12 \text{ hours}$

Convert to seconds: $12 \text{ hours} = 12 \times 60 \times 60 = 43,200 \text{ s}$

$$k = 0.693 / 43,200 \approx 1.60 \times 10^{-5} \text{ s}^{-1}$$

The rate constant k is approximately $1.60 \times 10^{-5} \text{ s}^{-1}$