

CHM406

REACTION KINETICS



Course video is available on our app

Course code: CHM 406

Course Title: Reaction Kinetics

Course Unit: (2 Units C: LH 30)

List of Series:

1. **Series 1: Rate Equations and Reaction Orders**
 2. **Series 2: Integrated Rate Laws and Reaction Half-Life**
 3. **Series 3: Collision Theory, Activation Energy, and the Arrhenius Equation**
 4. **Series 4: Catalysis, Reaction Mechanisms, and Enzymatic Processes**
 5. **Series 5: Photochemical Reactions and Chemical Warfare Agents**
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Suggested Outline

Part 1: Fundamentals of Rate Equations

- 1.1.1 Definition of rate of reaction
- 1.1.2 Expressing rate using concentration changes
- 1.1.3 Relationship between balanced chemical equations and rate expressions

Part 2: Orders of Reaction

- 1.2.1 First-order reactions and their characteristics
- 1.2.2 Second-order reactions and their characteristics
- 1.2.3 Third-order reactions and their characteristics

Part 3: Instantaneous and Average Rates

- 1.3.1 Graphical representation of reaction rates
- 1.3.2 Distinguishing instantaneous rate from average rate
- 1.3.3 Practical applications of rate determination

Part 4: Determining Rate Laws from Experimental Data

- 1.4.1 Initial rate method
- 1.4.2 Determining order with respect to each reactant
- 1.4.3 Overall order of reaction and rate constant with units

Introduction

Chemical reactions are not only about what substances are transformed but also about how fast these transformations occur. The study of reaction rates provides valuable insights into the mechanisms of chemical change and helps chemists predict and control processes in both



laboratory and industrial settings. Understanding rate equations and reaction orders is therefore a fundamental starting point in reaction kinetics, as it lays the groundwork for more advanced topics such as integrated rate laws, activation energy, and catalysis.

The aim of this Series is to introduce you to the principles of rate equations and reaction orders, equipping you with the skills to express reaction rates, classify reactions by order, and determine rate laws from experimental data.

We shall commence this Series by exploring the fundamentals of rate equations, including how reaction rates are expressed in terms of concentration changes. Next, we will move on to examine first, second, and third-order reactions, highlighting their distinct characteristics. Following that, we will consider instantaneous and average rates, using graphical methods to distinguish between them. Finally, we will wrap up by studying how rate laws are determined experimentally, focusing on the initial rate method and the calculation of overall order and rate constants. This progression will ensure you gain a solid foundation in the quantitative aspects of reaction kinetics.

Series Learning Outcomes

Upon completing this Series, you should be able to:

- **SLO 1.1** define the rate of a chemical reaction and express it in terms of concentration changes,
- **SLO 1.2** explain how coefficients in a balanced chemical equation relate to the rate expression,
- **SLO 1.3** describe the characteristics of first-order reactions,
- **SLO 1.4** describe the characteristics of second-order reactions,
- **SLO 1.5** describe the characteristics of third-order reactions,
- **SLO 1.6** distinguish between instantaneous and average rates using graphical methods,
- **SLO 1.7** demonstrate how to determine reaction rates from concentration–time graphs,
- **SLO 1.8** apply the initial rate method to determine the order of reaction with respect to each reactant,
- **SLO 1.9** calculate the overall order of a reaction and the rate constant with appropriate units.

1.1 Fundamentals of Rate Equations

1.1.1 Definition of rate of reaction

The **rate of reaction** is defined as the change in concentration of a reactant or product per unit time. It provides a measure of how quickly a chemical process occurs. Rates can be expressed in terms of either the disappearance of reactants or the appearance of products.

Fill in the blank: The rate of reaction is defined as the change in _____ of a reactant or product per unit time.



Figure 1.1. Rate of reaction expressed as change in concentration per unit time

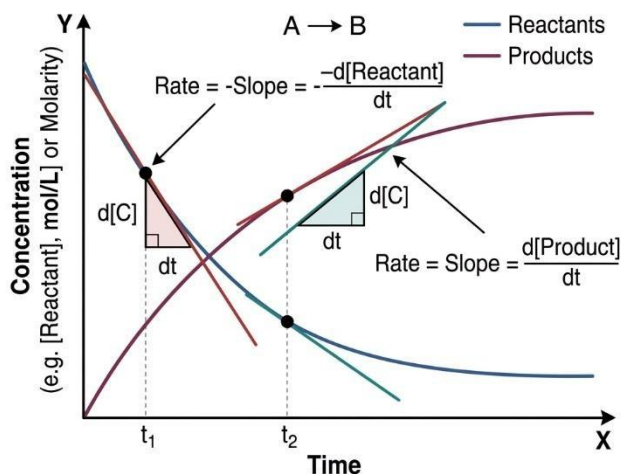


Figure 1.1. Rate of reaction expressed as change in concentration per unit time

Diagram showing concentration changes of reactants and products over time.

Figure 1.1: Rate of reaction expressed as change in concentration per unit time.

1.1.2 Expressing rate using concentration changes

The rate of a reaction is often expressed mathematically as:

$$\left[\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt} \right]$$

Here, **[A]** represents the concentration of reactant A, **[B]** represents the concentration of product B, and **a** and **b** are the stoichiometric coefficients from the balanced chemical equation. The negative sign indicates that the concentration of reactants decreases with time.

Fill in the blank: The negative sign in the rate expression indicates that the concentration of _____ decreases with time.



Plate 1.1: Expressing rate using stoichiometric coefficients.

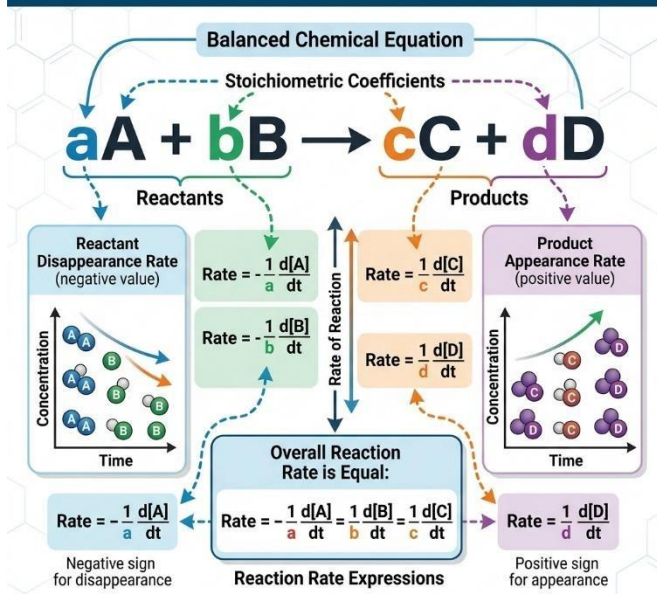


Image showing a balanced chemical equation with rate expressions derived from stoichiometric coefficients.

Plate 1.1: Expressing rate using stoichiometric coefficients.

1.1.3 Relationship between balanced chemical equations and rate expressions

A **balanced chemical equation** provides the stoichiometric relationship between reactants and products. This relationship is essential for writing correct rate expressions. For example, in the reaction:



The rate can be expressed as:

$$[\text{Rate} = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt}]$$

This ensures that the rate is consistent regardless of whether it is expressed in terms of reactants or products.

Fill in the blank: A balanced chemical equation provides the _____ relationship between reactants and products.



GUIDE: STOICHIOMETRIC COEFFICIENTS IN RATE EXPRESSIONS

HOW STOICHIOMETRIC COEFFICIENTS ARE USED

1. FOR THE OVERALL REACTION:

They determine the relationship between the rates of disappearance of reactants and appearance of products. The rate is typically expressed as:

$$\text{Rate} = -\frac{(1/a)\Delta[A]}{\Delta t} = -\frac{(1/b)\Delta[B]}{\Delta t} = \frac{(1/c)\Delta[C]}{\Delta t} = \frac{(1/d)\Delta[D]}{\Delta t},$$

for a reaction $aA + bB \rightarrow cC + dD$.



Important: For complex reactions, the rate law *must* be determined experimentally, not just from coefficients.

EXAMPLES

GENERAL RELATIVE RATES

Reaction:



Relative Rates:

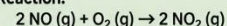
$$-\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

Interpretation:

NO_2 forms 4 times faster than O_2 ; N_2O_5 disappears twice as fast as O_2 forms.

ELEMENTARY REACTION RATE LAW (IF ELEMENTARY)

Reaction:



Proposed Rate Law (assuming elementary):

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

Experimental data confirms this for this specific reaction.

SOURCE: GENERAL CHEMISTRY OER RESOURCES

Box 1.1: Key points on rate expressions and balanced equations

Box summarising how stoichiometric coefficients are used in rate expressions.

Pilot questions 1.1

- The rate of reaction is defined as the change in _____ per unit time.
 - Pressure
 - Concentration
 - Temperature
 - Volume
- The negative sign in the rate expression indicates that the concentration of _____ decreases with time.
 - Products
 - Reactants
 - Catalysts
 - Enzymes
- In the reaction $(2A + B \rightarrow 3C)$, the rate expressed in terms of A is:
 - $(-\frac{d[A]}{dt})$
 - $(-\frac{1}{2}\frac{d[A]}{dt})$
 - $(\frac{d[A]}{dt})$
 - $(\frac{1}{2}\frac{d[A]}{dt})$
- A balanced chemical equation provides the _____ relationship between reactants and products.
 - Random
 - Stoichiometric
 - Empirical
 - Approximate



5. Which of the following can be used to express the rate of a reaction?
- A. Disappearance of reactants
 - B. Appearance of products
 - C. Both A and B
 - D. Neither A nor B

1.2 Orders of Reaction

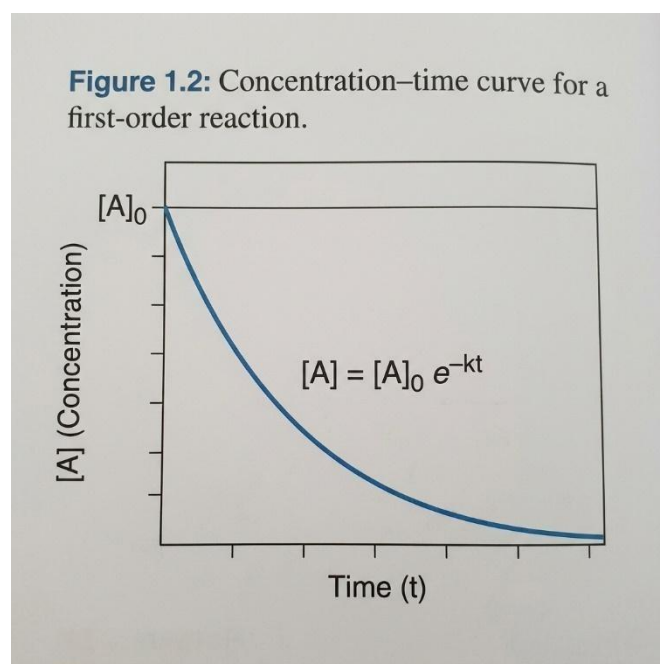
1.2.1 First-order reactions and their characteristics

A **first-order reaction** is one in which the rate depends linearly on the concentration of a single reactant. This means that if the concentration of the reactant is doubled, the rate of reaction also doubles. Mathematically, the rate law can be expressed as:

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

where **k** is the rate constant and **[A]** is the concentration of the reactant. First-order reactions are common in processes such as radioactive decay and certain unimolecular reactions.

Fill in the blank: In a first-order reaction, if the concentration of the reactant is doubled, the rate of reaction _____.



Short description: Graph showing concentration versus time for a first-order reaction.

Caption: Figure 1.2: Concentration–time curve for a first-order reaction.

AI prompt: “Generate a graph showing exponential decay of concentration versus time for a first-order reaction.”

Search string: “first-order reaction concentration time graph OER”



1.2.2 Second-order reactions and their characteristics

A **second-order reaction** is one in which the rate depends on the square of the concentration of a single reactant, or on the product of the concentrations of two different reactants. The rate law can be expressed as:

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

Second-order reactions are often observed in bimolecular processes where two particles must collide for the reaction to occur.

Fill in the blank: A second-order reaction may depend on the square of the concentration of one reactant or on the _____ of two reactants.

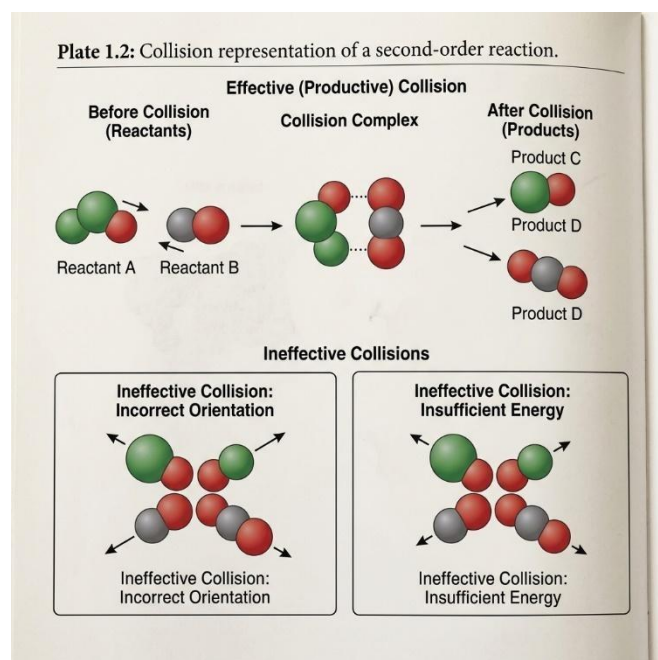


Image showing two molecules colliding to represent a bimolecular second-order reaction.
Plate 1.2: Collision representation of a second-order reaction.

1.2.3 Third-order reactions and their characteristics

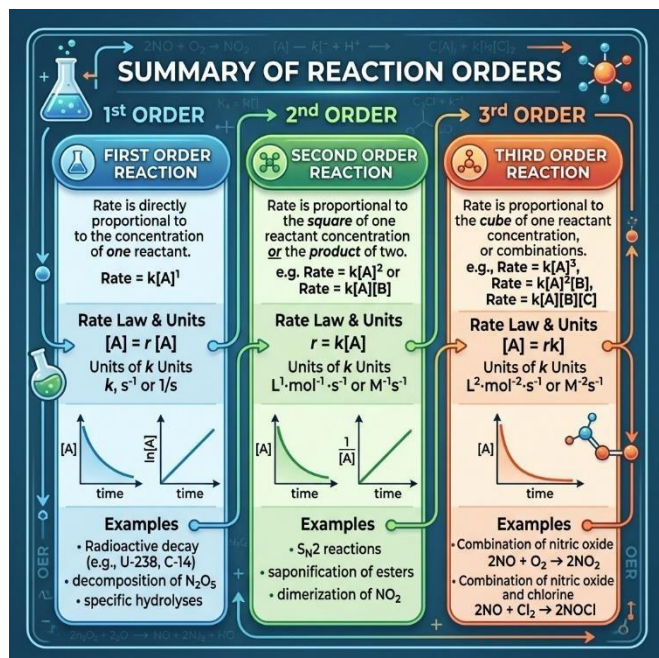
A **third-order reaction** is one in which the rate depends on the cube of the concentration of a single reactant, or on a combination of concentrations that add up to three. The rate law can be expressed as:

$$[\text{Rate}] = k[A]^3 \quad \text{or} \quad \text{Rate} = k[A]^2[B] \quad \text{or} \quad \text{Rate} = k[A][B][C]$$

Third-order reactions are less common because the probability of three particles colliding simultaneously is very low. They are usually observed in complex mechanisms rather than simple reactions.



Fill in the blank: Third-order reactions are less common because the probability of _____ particles colliding simultaneously is very low.



Box 1.2: Key points on orders of reaction

Short description: Box summarising the characteristics of first, second, and third-order reactions.

Pilot questions 1.2

- In a first-order reaction, doubling the concentration of the reactant will:
 - Halve the rate
 - Double the rate
 - Quadruple the rate
 - Leave the rate unchanged
- A second-order reaction may depend on:
 - The square of one reactant's concentration
 - The product of two reactants' concentrations
 - Both A and B
 - Neither A nor B
- Which of the following is a correct rate law for a third-order reaction?
 - ($\text{Rate} = k[A]^3$)
 - ($\text{Rate} = k[A]^2[B]$)
 - ($\text{Rate} = k[A][B][C]$)
 - All of the above
- Third-order reactions are rare because:
 - They require catalysts
 - They involve three particles colliding simultaneously



- C. They occur only at high temperatures
 - D. They are forbidden by chemical laws
5. Which order of reaction is most commonly observed in radioactive decay?
- A. Zero-order
 - B. First-order
 - C. Second-order
 - D. Third-order

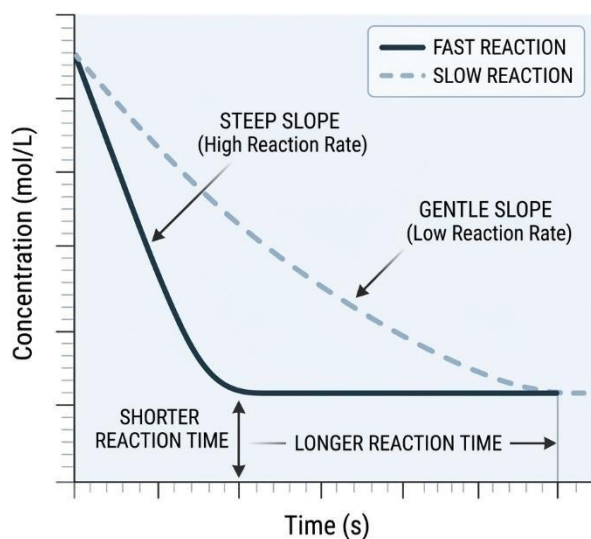
1.3 Instantaneous and Average Rates

1.3.1 Graphical representation of reaction rates

The **reaction rate** can be visualised using a graph of concentration versus time. The slope of the curve at any point represents the rate of change of concentration. A steep slope indicates a fast reaction, while a gentle slope shows a slower reaction.

Fill in the blank: On a concentration–time graph, the slope of the curve at any point represents the _____ of change of concentration.

Figure 1.3: Graphical representation of reaction rates



Graph showing concentration versus time with slopes indicating reaction rates.

Figure 1.3: Graphical representation of reaction rates.

1.3.2 Distinguishing instantaneous rate from average rate

The **instantaneous rate** is the rate of reaction at a specific moment in time, determined by the tangent to the curve at that point. The **average rate** is the overall change in concentration over a given time interval, calculated by dividing the change in concentration by the change in time.

Fill in the blank: The instantaneous rate is determined by the tangent to the curve at a specific point, while the average rate is calculated over a _____ interval.



Plate 1.3 Distinguishing instantaneous and average rates.

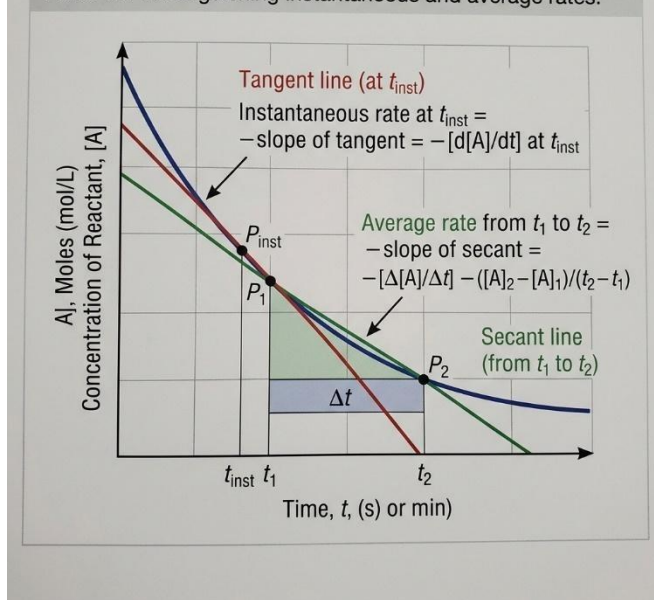


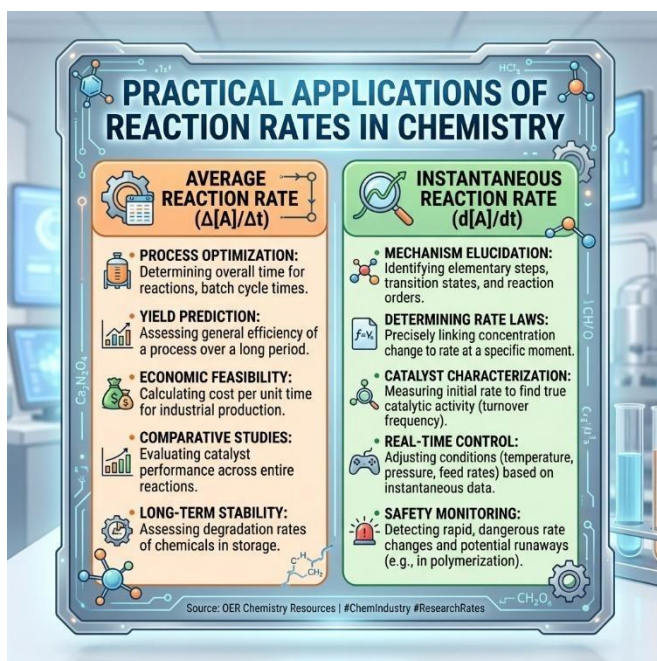
Image showing tangent line to a curve for instantaneous rate and secant line for average rate.
Plate 1.3: Distinguishing instantaneous and average rates.

1.3.3 Practical applications of rate determination

Determining reaction rates is crucial in chemical industries, pharmaceuticals, and environmental studies. For example, knowing the instantaneous rate helps in controlling processes that require precise timing, while average rates are useful for monitoring long-term changes.

Fill in the blank: Instantaneous rates are useful for controlling processes that require precise





Box 1.3: Applications of instantaneous and average rates
Box summarising practical uses of instantaneous and average rates in industry and research.

Pilot questions 1.3

- On a concentration–time graph, the slope of the curve represents:
 - Temperature change
 - Rate of change of concentration
 - Pressure change
 - Energy released
- The instantaneous rate of reaction is determined by:
 - The tangent to the curve at a point
 - The secant line over an interval
 - The overall change in concentration
 - The equilibrium constant
- The average rate of reaction is calculated by:
 - Dividing the change in concentration by the change in time
 - Measuring the tangent slope at a point
 - Using the Arrhenius equation
 - Calculating activation energy
- Instantaneous rates are particularly useful for:
 - Monitoring long-term changes
 - Controlling processes requiring precise timing
 - Calculating equilibrium constants
 - Measuring catalyst efficiency



5. Average rates are most useful for:
 - A. Short-term control of reactions
 - B. Monitoring long-term changes in concentration
 - C. Determining activation energy
 - D. Studying enzyme specificity

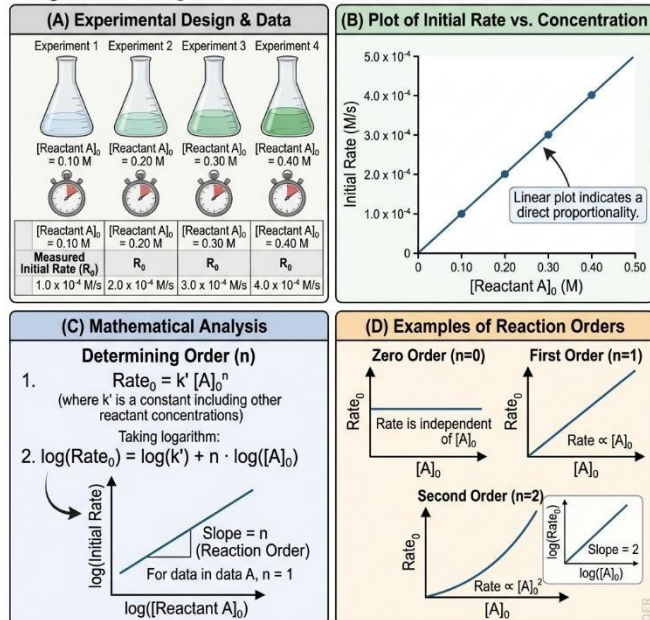
1.4 Determining Rate Laws from Experimental Data

1.4.1 Initial rate method

The **initial rate method** is a technique used to determine the order of a reaction by measuring how the rate changes when the concentration of one reactant is varied while others are kept constant. By comparing the change in rate with the change in concentration, the order with respect to that reactant can be deduced.

Fill in the blank: The initial rate method involves measuring how the rate changes when the _____ of one reactant is varied while others are kept constant.

Figure 1.4: Using the initial rate method to determine reaction order.



Graph showing initial rate data plotted against concentration of a reactant.

Figure 1.4: Using the initial rate method to determine reaction order.

1.4.2 Determining order with respect to each reactant

The **order of reaction with respect to a reactant** is the power to which its concentration is raised in the rate law. For example, if doubling the concentration of reactant A doubles the rate, the order with respect to A is one. If doubling the concentration quadruples the rate, the order with respect to A is two.

Fill in the blank: The order of reaction with respect to a reactant is the _____ to which its concentration is raised in the rate law.



Plate 1.4: Determining order with respect to each reactant

Trial Number	Initial Concentration of Reactant A ($[A]_0$, M)	Initial Concentration of Reactant B ($[B]_0$, M)	Initial Reaction Rate (M/s)
1	0.100	0.100	2.0×10^{-4}
2	0.200	0.100	4.0×10^{-4}
3	0.100	0.200	8.0×10^{-4}
4	0.200	0.200	1.6×10^{-3}

Analysis of Data to Determine Order

Comparing Trials 1 & 3:
[A] is constant. [B] doubles, and Rate quadruples ($2^2 = 4$). Reaction is 2nd order with respect to B ($y=2$).

Comparing Trials 1 & 2:
[B] is constant. [A] doubles, and Rate doubles. ($2^1 = 2$). Reaction is 1st order with respect to A ($x=1$).

Overall Rate Law:
Rate = $k[A]^1[B]^2$
Overall order = 3

Image showing experimental data table with concentration changes and rate changes for different reactants.

Plate 1.4: Determining order with respect to each reactant.

1.4.3 Overall order of reaction and rate constant with units

The **overall order of reaction** is the sum of the orders with respect to each reactant. The **rate constant (k)** is a proportionality factor in the rate law that links concentration and rate. Its units depend on the overall order of the reaction. For example, for a first-order reaction, k has units of s^{-1} , while for a second-order reaction, k has units of $L \cdot mol^{-1} \cdot s^{-1}$.

Fill in the blank: The overall order of reaction is the _____ of the orders with respect to each reactant.



Summary of Rate Constant Units by Reaction Order		
Reaction Order General Form	Units (Molarity & Seconds)	Alternative Units (e.g., minutes)
First-Order ($n = 1$)	s^{-1}	min^{-1}
Second-Order ($n = 2$)	$M^{-1} \cdot s^{-1}$	$(mol/L)^{-1} \cdot min^{-1}$
Third-Order ($n = 3$)	$M^{-2} \cdot s^{-1}$	$(mol/L)^{-2} \cdot min^{-1}$

General Rate Law: $Rate = k[A]^n$

General formula for rate constant units (k): $[M]^{1-n} \cdot time^{-1}$
 where n is the reaction order

Box 1.4: Units of rate constants for different reaction orders

Box summarising the units of rate constants for first, second, and third-order reactions.

Pilot questions 1.4

- The initial rate method involves:
 - Measuring the rate at equilibrium
 - Measuring the rate at the start of the reaction
 - Measuring the rate after completion
 - Measuring the rate at half-life
- The order of reaction with respect to a reactant is:
 - The coefficient in the balanced equation
 - The power to which its concentration is raised in the rate law
 - Always equal to one
 - Independent of experimental data
- If doubling the concentration of reactant A quadruples the rate, the order with respect to A is:
 - Zero
 - One
 - Two
 - Three
- The overall order of reaction is:
 - The highest order among reactants
 - The sum of the orders with respect to each reactant
 - Always equal to two
 - Independent of reactant concentrations



5. For a second-order reaction, the units of the rate constant are:
- A. s^{-1}
 - B. $L \cdot mol^{-1} \cdot s^{-1}$
 - C. $mol \cdot L^{-1} \cdot s^{-1}$
 - D. $L^2 \cdot mol^{-2} \cdot s^{-1}$

Series Summary

This Series has introduced you to the foundations of reaction kinetics by focusing on rate equations and reaction orders. We began by defining the rate of reaction and expressing it in terms of concentration changes, then examined how balanced chemical equations provide the stoichiometric basis for rate expressions. Following that, we explored first, second, and third-order reactions, highlighting their distinct characteristics and mathematical forms. We then distinguished between instantaneous and average rates using graphical methods, before concluding with experimental approaches to determining rate laws, including the initial rate method, orders with respect to each reactant, and the calculation of overall order and rate constants.

By completing this Series, you should now be able to define and express reaction rates (SLOs 1.1 and 1.2), describe the characteristics of first, second, and third-order reactions (SLOs 1.3–1.5), distinguish between instantaneous and average rates (SLOs 1.6 and 1.7), and apply experimental methods to determine rate laws and calculate rate constants (SLOs 1.8 and 1.9). These outcomes provide you with a strong foundation for analysing chemical reactions quantitatively and prepare you for more advanced topics in reaction kinetics.

Glossary of Terms

- **Average rate:** The overall change in concentration of a reactant or product divided by the time interval during which the change occurs.
- **Balanced chemical equation:** A chemical equation in which the number of atoms of each element is the same on both sides, showing the stoichiometric relationship between reactants and products.
- **First-order reaction:** A reaction in which the rate depends linearly on the concentration of a single reactant.
- **Initial rate method:** An experimental technique used to determine reaction order by measuring how the rate changes when the concentration of one reactant is varied while others are kept constant.
- **Instantaneous rate:** The rate of reaction at a specific moment in time, determined by the slope of the tangent to a concentration–time curve.
- **Overall order of reaction:** The sum of the orders with respect to each reactant in the rate law.
- **Rate constant (k):** A proportionality factor in the rate law that links concentration and rate, with units that depend on the overall order of the reaction.
- **Rate of reaction:** The change in concentration of a reactant or product per unit time.



- **Rate law:** A mathematical expression that relates the rate of a reaction to the concentrations of reactants, each raised to a power corresponding to its order.
- **Reaction order:** The power to which the concentration of a reactant is raised in the rate law, indicating how strongly the rate depends on that reactant.
- **Second-order reaction:** A reaction in which the rate depends either on the square of the concentration of one reactant or on the product of the concentrations of two reactants.
- **Stoichiometric coefficient:** The number in front of a chemical species in a balanced equation, used to relate the rate of change of reactants and products.
- **Third-order reaction:** A reaction in which the rate depends on the cube of the concentration of one reactant or on a combination of concentrations that add up to three.

Concept Check Questions [Series 1]

Objective Questions

1. The rate of reaction is defined as the change in _____ per unit time.
(Linked to SLO 1.1)
2. In a first-order reaction, doubling the concentration of the reactant will:
 - A. Halve the rate
 - B. Double the rate
 - C. Quadruple the rate
 - D. Leave the rate unchanged
 (Linked to SLO 1.3)
3. The order of reaction with respect to a reactant is:
 - A. The coefficient in the balanced equation
 - B. The power to which its concentration is raised in the rate law
 - C. Always equal to one
 - D. Independent of experimental data
 (Linked to SLO 1.4)
4. The instantaneous rate of reaction is determined by:
 - A. The tangent to the curve at a point
 - B. The secant line over an interval
 - C. The overall change in concentration
 - D. The equilibrium constant
 (Linked to SLO 1.6)
5. For a second-order reaction, the units of the rate constant are:
 - A. s^{-1}
 - B. $L \cdot mol^{-1} \cdot s^{-1}$
 - C. $mol \cdot L^{-1} \cdot s^{-1}$
 - D. $L^2 \cdot mol^{-2} \cdot s^{-1}$
 (Linked to SLO 1.9)



Short-Answer Questions

6. Define the term “rate law” in the context of chemical kinetics.
(Linked to SLO 1.8)
7. Explain why third-order reactions are rare in practice.
(Linked to SLO 1.5)
8. State one difference between instantaneous rate and average rate.
(Linked to SLO 1.6)
9. What is meant by the overall order of a reaction?
(Linked to SLO 1.9)
10. Give one practical application of determining reaction rates in industry.
(Linked to SLO 1.7)

Long-Answer Questions

11. Analyse how stoichiometric coefficients in a balanced chemical equation are used to express rate equations.
(Linked to SLO 1.2)
 - **Basic response:** Explain that coefficients provide the proportional relationship between the rate of disappearance of reactants and the rate of appearance of products.
 - **Value-added response:** Extend by discussing how this ensures consistency in rate expressions, with examples showing how coefficients normalise rates across different species.
12. Evaluate the usefulness of the initial rate method in determining reaction orders.
(Linked to SLO 1.8)
 - **Basic response:** Describe how varying the concentration of one reactant while keeping others constant allows the order with respect to that reactant to be deduced.
 - **Value-added response:** Discuss limitations such as experimental error, side reactions, and the need for precise measurement, while highlighting its importance in mechanistic studies.
13. Demonstrate how graphical methods can be used to distinguish between instantaneous and average rates.
(Linked to SLO 1.6)
 - **Basic response:** Show that the tangent to a concentration–time curve gives the instantaneous rate, while the slope of a secant line over an interval gives the average rate.
 - **Value-added response:** Provide examples of when each method is most useful, such as instantaneous rates in fast reactions and average rates in monitoring environmental processes.
14. Assess the importance of calculating the rate constant and its units for different orders of reaction.
(Linked to SLO 1.9)



- **Basic response:** Explain that the rate constant links concentration and rate, and its units vary depending on the overall order of the reaction.
- **Value-added response:** Discuss how knowing the rate constant and its units helps in comparing reactions, designing industrial processes, and predicting reaction behaviour under different conditions.

Answers to Concept Check Questions [Series 1]

Objective Questions

1. Concentration
2. B. Double the rate
3. B. The power to which its concentration is raised in the rate law
4. A. The tangent to the curve at a point
5. B. $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$

Short-Answer Questions

6. A rate law is a mathematical expression that relates the rate of a reaction to the concentrations of reactants, each raised to a power corresponding to its order.
7. Third-order reactions are rare because the probability of three particles colliding simultaneously is very low.
8. Instantaneous rate is measured at a specific moment using a tangent, while average rate is measured over a time interval using a secant.
9. The overall order of a reaction is the sum of the orders with respect to each reactant.
10. Reaction rate determination is applied in chemical industries to control production speed and ensure safety in processes.

Long-Answer Questions

11. **Basic response:** Stoichiometric coefficients show the proportional relationship between reactant consumption and product formation.

Value-added response: They ensure consistency in rate expressions, allowing rates to be compared across species, for example in reactions like $2\text{A} + \text{B} \rightarrow 3\text{C}$.

12. **Basic response:** The initial rate method helps deduce reaction order by varying one reactant's concentration while keeping others constant.

Value-added response: It is widely used but requires precise measurements and can be limited by side reactions or experimental error.

13. **Basic response:** Graphical methods use tangents for instantaneous rates and secants for average rates.

Value-added response: Instantaneous rates are useful in fast reactions, while average rates are valuable in monitoring long-term processes such as environmental changes.

14. **Basic response:** The rate constant links concentration and rate, with units depending on reaction order.

Value-added response: Knowing the rate constant and its units allows chemists to compare reactions, design efficient processes, and predict behaviour under varying conditions.



Part 1: Fundamentals of Rate Equations

1. Concentration
2. Reactants
3. $(-\frac{1}{2}\frac{d[A]}{dt})$
4. Stoichiometric
5. Both A and B

Part 2: Orders of Reaction

1. Double the rate
2. Product
3. All of the above
4. Three
5. First-order

Part 3: Instantaneous and Average Rates

1. Rate of change of concentration
2. Tangent to the curve at a point
3. Dividing the change in concentration by the change in time
4. Precise timing
5. Monitoring long-term changes in concentration

Part 4: Determining Rate Laws from Experimental Data

1. Measuring the rate at the start of the reaction
2. The power to which its concentration is raised in the rate law
3. Two
4. The sum of the orders with respect to each reactant
5. $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$

References and Attributions [Series 1]

This section compiles all references, attributions, and illustration sources used or suggested in **Series 1: Rate Equations and Reaction Orders**. Entries are presented in APA style for clarity and consistency.

Textual References

- Atkins, P., & de Paula, J. (2018). *Physical Chemistry* (11th ed.). Oxford University Press.
- Housecroft, C. E., & Constable, E. C. (2010). *Chemistry: An Introduction to Organic, Inorganic and Physical Chemistry* (4th ed.). Pearson.
- Laidler, K. J. (1997). *Chemical Kinetics* (3rd ed.). Pearson.

Illustrations (Figures, Plates, Boxes)



- Figure 1.1: Rate of reaction expressed as change in concentration per unit time*
 AI-generated using prompt: “Generate a diagram showing concentration changes of reactants decreasing and products increasing over time to illustrate rate of reaction.”
 Suggested OER search string: “rate of reaction concentration time diagram OER”.
- Plate 1.1: Expressing rate using stoichiometric coefficients*
 AI-generated using prompt: “Create an image showing a balanced chemical equation with arrows linking coefficients to rate expressions.”
 Suggested OER search string: “rate expression stoichiometric coefficients chemistry OER”.
- Box 1.1: Key points on rate expressions and balanced equations*
 AI-generated using prompt: “Create a text box summarising how stoichiometric coefficients are used in rate expressions with examples.”
 Suggested OER search string: “balanced chemical equation rate expression summary OER”.
- Figure 1.2: Concentration–time curve for a first-order reaction*
 AI-generated using prompt: “Generate a graph showing exponential decay of concentration versus time for a first-order reaction.”
 Suggested OER search string: “first-order reaction concentration time graph OER”.
- Plate 1.2: Collision representation of a second-order reaction*
 AI-generated using prompt: “Create an image showing two molecules colliding to represent a bimolecular second-order reaction.”
 Suggested OER search string: “second-order reaction bimolecular collision OER”.
- Box 1.2: Key points on orders of reaction*
 AI-generated using prompt: “Create a text box summarising the characteristics of first, second, and third-order reactions with examples.”
 Suggested OER search string: “orders of reaction summary chemistry OER”.
- Figure 1.3: Graphical representation of reaction rates*
 AI-generated using prompt: “Generate a graph of concentration versus time showing steep and gentle slopes to illustrate fast and slow reaction rates.”
 Suggested OER search string: “reaction rate concentration time graph OER”.
- Plate 1.3: Distinguishing instantaneous and average rates*
 AI-generated using prompt: “Create an image showing a concentration–time curve with a tangent line for instantaneous rate and a secant line for average rate.”
 Suggested OER search string: “instantaneous average reaction rate tangent secant OER”.
- Box 1.3: Applications of instantaneous and average rates*
 AI-generated using prompt: “Create a text box summarising practical applications of instantaneous and average rates in chemical industries and research.”
 Suggested OER search string: “applications instantaneous average reaction rates chemistry OER”.
- Figure 1.4: Using the initial rate method to determine reaction order*
 AI-generated using prompt: “Generate a graph showing initial rate data plotted against



concentration of a reactant to illustrate determination of reaction order.”

Suggested OER search string: “initial rate method reaction order graph OER”.

- *Plate 1.4: Determining order with respect to each reactant*
AI-generated using prompt: “Create an image showing a data table of concentration changes and rate changes used to determine reaction order.”
Suggested OER search string: “reaction order experimental data table chemistry OER”.
- *Box 1.4: Units of rate constants for different reaction orders*
AI-generated using prompt: “Create a text box listing the units of rate constants for first, second, and third-order reactions.”
Suggested OER search string: “rate constant units reaction order summary OER”.

Course code: CHM 406

Course Title: Reaction Kinetics

Course Unit: (2 Units C: LH 30)

List of Series:

1. **Series 1: Rate Equations and Reaction Orders**
2. **Series 2: Integrated Rate Laws and Reaction Half-Life**
3. **Series 3: Collision Theory, Activation Energy, and the Arrhenius Equation**
4. **Series 4: Catalysis, Reaction Mechanisms, and Enzymatic Processes**
5. **Series 5: Photochemical Reactions and Chemical Warfare Agents**

For **CHM 406: Reaction Kinetics (2-credit course)**, each Series should contain **3 to 5 main Parts**. Based on the scope of **Series 2: Integrated Rate Laws and Reaction Half-Life**, here is a suggested outline that conforms to the guideline:

Suggested Outline of Main Parts and Sub-Parts

Part 1: Integrated First-Order Rate Laws

- 2.1.1 Mathematical form of the first-order integrated rate law
- 2.1.2 Graphical representation of first-order reactions
- 2.1.3 Applications of first-order integrated laws

Part 2: Integrated Second-Order Rate Laws

- 2.2.1 Mathematical form of the second-order integrated rate law
- 2.2.2 Graphical representation of second-order reactions
- 2.2.3 Applications of second-order integrated laws



Part 3: Reaction Half-Life

- 2.3.1 Definition and concept of half-life
- 2.3.2 Relationship between half-life and rate constant for first-order reactions
- 2.3.3 Relationship between half-life and rate constant for second-order reactions

Part 4: Determining Reaction Order from Concentration–Time Plots

- 2.4.1 Concentration versus time plots
- 2.4.2 $\ln(\text{concentration})$ versus time plots
- 2.4.3 $1/\text{concentration}$ versus time plots

Introduction

In the last Series, we explored rate equations and reaction orders, laying the foundation for understanding how chemical reactions are quantified. Building on that knowledge, we now turn to integrated rate laws, which allow us to describe how concentrations of reactants change over time. This Series also introduces the concept of half-life, a practical measure of how long it takes for a reactant to reduce to half its initial concentration, making it particularly relevant in fields such as pharmacology, environmental chemistry, and nuclear science.

The aim of this Series is to equip you with the ability to apply integrated rate laws to first- and second-order reactions, interpret concentration–time plots, and calculate half-life values in relation to reaction order and rate constants.

We shall commence this Series by examining the integrated rate law for first-order reactions, including its mathematical form and graphical representation. Next, we will move on to integrated second-order rate laws, highlighting their distinct features and applications. Following that, we will explore the concept of reaction half-life, considering its relationship with rate constants for both first- and second-order reactions. Finally, we will wrap up by learning how to determine reaction order from concentration–time plots, using graphical methods to distinguish between different reaction types. This progression will ensure you gain both theoretical and practical skills in analysing reaction kinetics.

Series Learning Outcomes

Upon completing this Series, you should be able to:

- **SLO 2.1** derive the mathematical form of the integrated first-order rate law,
- **SLO 2.2** demonstrate how to represent first-order reactions graphically,
- **SLO 2.3** apply the integrated first-order rate law to practical chemical processes,
- **SLO 2.4** derive the mathematical form of the integrated second-order rate law,
- **SLO 2.5** demonstrate how to represent second-order reactions graphically,
- **SLO 2.6** apply the integrated second-order rate law to practical chemical processes,
- **SLO 2.7** define the concept of reaction half-life,
- **SLO 2.8** calculate half-life values for first-order reactions using the rate constant,



- **SLO 2.9** calculate half-life values for second-order reactions using the rate constant,
- **SLO 2.10** analyse concentration–time plots to determine reaction order,
- **SLO 2.11** distinguish between concentration, $\ln(\text{concentration})$, and $1/\text{concentration}$ plots in identifying reaction order.

2.1 Integrated First-Order Rate Laws

2.1.1 Mathematical form of the first-order integrated rate law

A **first-order reaction** is one in which the rate depends linearly on the concentration of a single reactant. The integrated form of the rate law shows how the concentration changes with time and is expressed as:

$$\ln[A] = \ln[A]_0 - kt$$

Here, $[A]$ is the concentration of the reactant at time (t), $[A]_0$ is the initial concentration, k is the rate constant, and t is time. This equation allows us to calculate concentrations at any point during the reaction.

Fill in the blank: The integrated first-order rate law is expressed as ($\ln[A] = \ln[A]_0 -$ _____).

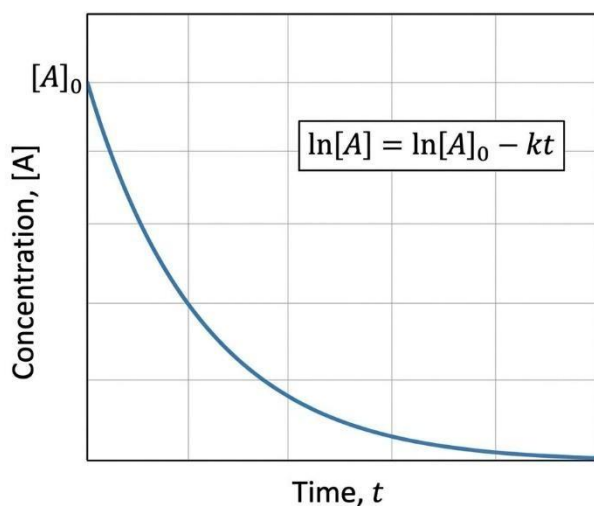


Figure 2.1: Mathematical representation of the integrated first-order rate law.

Graph showing exponential decay of concentration with time for a first-order reaction.

Figure 2.1: Mathematical representation of the integrated first-order rate law.

2.1.2 Graphical representation of first-order reactions



The integrated first-order rate law can be represented graphically by plotting ($\ln [A]$) against time. This produces a straight line with a slope of ($-k$) and an intercept of ($\ln [A]_0$). The linearity of this plot is a key indicator that a reaction follows first-order kinetics.

Fill in the blank: A plot of ($\ln [A]$) versus time for a first-order reaction gives a _____ line.

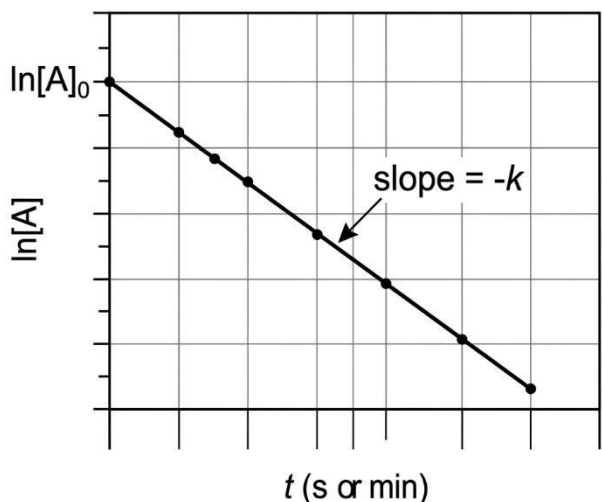


Plate 2.1: Graphical representation of a first-order reaction.

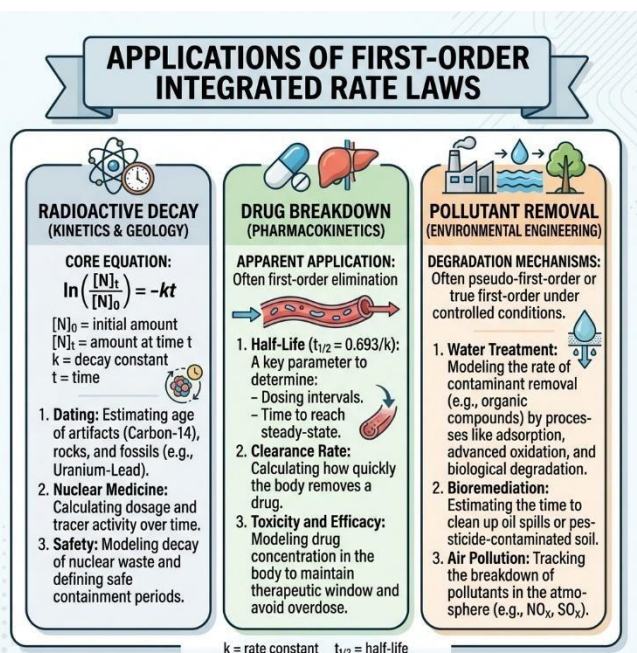
Image showing a straight-line plot of $\ln[A]$ versus time with slope $-k$.
Plate 2.1: Graphical representation of a first-order reaction.

2.1.3 Applications of first-order integrated laws

First-order integrated laws are widely applied in chemical and natural processes. For example, radioactive decay follows first-order kinetics, as does the breakdown of many pharmaceuticals in the body. These laws allow chemists to predict how long a substance will last under given conditions and to calculate half-life values.

Fill in the blank: Radioactive decay is an example of a process that follows _____ kinetics.





Box 2.1: Applications of first-order integrated laws

Box summarising practical applications of first-order integrated laws in chemistry, medicine, and environmental science.

Pilot questions 2.1

- The integrated first-order rate law is expressed as:
 - $[A] = [A]_0 - kt$
 - $\ln [A] = \ln [A]_0 - kt$
 - $[A] = [A]_0 e^{-kt}$
 - $\ln [A] = kt$
 (Linked to SLO 2.1)
- A plot of $(\ln [A])$ versus time for a first-order reaction gives:
 - A curve
 - A straight line
 - A parabola
 - A horizontal line
 (Linked to SLO 2.2)
- The slope of the straight line in a first-order plot is equal to:
 - $[A]_0$
 - $(-k)$
 - (t)
 - $(\ln [A])$
 (Linked to SLO 2.2)
- Radioactive decay is an example of a process that follows:
 - Zero-order kinetics
 - First-order kinetics



- C. Second-order kinetics
- D. Third-order kinetics
- (Linked to SLO 2.3)

5. Which of the following is a practical application of first-order integrated laws?
- A. Predicting catalyst efficiency
 - B. Calculating half-life of drugs
 - C. Measuring equilibrium constants
 - D. Determining molecular geometry
- (Linked to SLO 2.3)

2.2 Integrated Second-Order Rate Laws

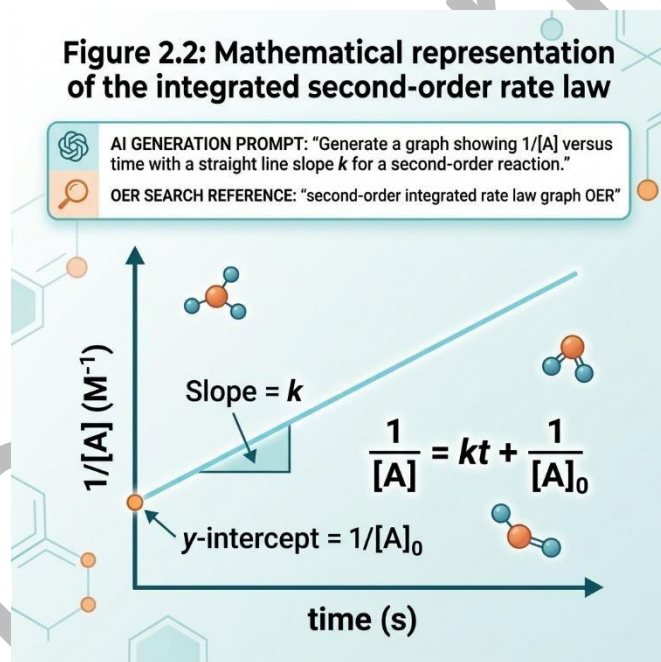
2.2.1 Mathematical form of the second-order integrated rate law

A **second-order reaction** is one in which the rate depends either on the square of the concentration of a single reactant or on the product of the concentrations of two reactants. For a reaction involving one reactant, the integrated form of the rate law is:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

Here, **[A]** is the concentration of the reactant at time (t), **[A]₀** is the initial concentration, **k** is the rate constant, and **t** is time. This equation shows that the reciprocal of concentration increases linearly with time.

Fill in the blank: The integrated second-order rate law for a single reactant is expressed as ($\frac{1}{[A]} = \frac{1}{[A]_0} + \underline{\hspace{2cm}}$).



[Insert figure here]

Graph showing reciprocal of concentration versus time for a second-order reaction.

Figure 2.2: Mathematical representation of the integrated second-order rate law.



2.2.2 Graphical representation of second-order reactions

The integrated second-order rate law can be represented graphically by plotting ($1/[A]$) against time. This produces a straight line with slope (k) and intercept ($1/[A]_0$). The linearity of this plot is a clear indicator that a reaction follows second-order kinetics.

Fill in the blank: A plot of ($1/[A]$) versus time for a second-order reaction gives a _____ line.

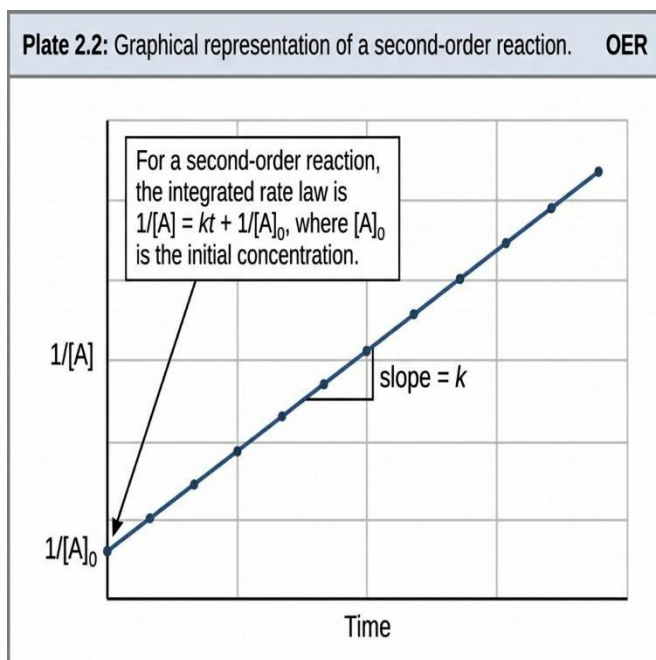


Image showing a straight-line plot of $1/[A]$ versus time with slope k .

Plate 2.2: Graphical representation of a second-order reaction.

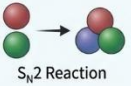
2.2.3 Applications of second-order integrated laws

Second-order integrated laws are particularly useful in studying bimolecular reactions, where two particles must collide for the reaction to occur. These laws are applied in areas such as atmospheric chemistry, where reactions between molecules determine pollutant behaviour, and in organic chemistry, where bimolecular substitution reactions follow second-order kinetics.

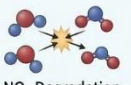
Fill in the blank: Bimolecular substitution reactions in organic chemistry often follow _____ kinetics.



APPLICATIONS OF SECOND-ORDER INTEGRATED RATE LAWS



S_N2 Reaction



NO_2 Degradation

- **Bimolecular Substitution (S_N2) Reactions:** Calculating the reaction rate and species concentrations over time for common organic reactions like haloalkane substitutions. Understanding how reactant concentration affects reaction progress.
- **Atmospheric Reactions:** Modeling and predicting the rates of degradation of pollutants, such as NO_2 and O_3 , which often follow second-order kinetics. Crucial for understanding air quality and ozone layer dynamics.
- **Environmental Remediation:** Designing treatment systems for removing contaminants, like certain pesticides or industrial chemical waste, from water. The rate of destruction often depends on the square of a reactant's concentration.
- **Polymerization Processes:** Controlling the synthesis of polymers where mono-linkage steps follow second-order kinetics, directly influencing chain length and material properties.
- **Dimerization and Condensation Reactions:** Analyzing common chemical processes, such as the formation of certain esters or the coupling of identical reactant molecules.



Box 2.2: Applications of second-order integrated laws

Box summarising practical applications of second-order integrated laws in atmospheric and organic chemistry.

Pilot questions 2.2

- The integrated second-order rate law for a single reactant is expressed as:
 - $[A] = [A]_0 - kt$
 - $\ln [A] = \ln [A]_0 - kt$
 - $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
 - $[A] = [A]_0 e^{-kt}$
 (Linked to SLO 2.4)
- A plot of $(1/[A])$ versus time for a second-order reaction gives:
 - A curve
 - A straight line
 - A parabola
 - A horizontal line
 (Linked to SLO 2.5)
- The slope of the straight line in a second-order plot is equal to:
 - $[A]_0$
 - k
 - t
 - $\ln [A]$
 (Linked to SLO 2.5)
- Bimolecular substitution reactions in organic chemistry often follow:
 - Zero-order kinetics
 - First-order kinetics



- C. Second-order kinetics
- D. Third-order kinetics
- (Linked to SLO 2.6)

5. Which of the following is a practical application of second-order integrated laws?
- A. Predicting catalyst efficiency
 - B. Studying atmospheric reactions
 - C. Measuring equilibrium constants
 - D. Determining molecular geometry
- (Linked to SLO 2.6)

2.3 Reaction Half-Life

2.3.1 Definition and concept of half-life

The **half-life** of a reaction is defined as the time required for the concentration of a reactant to decrease to half of its initial value. It provides a convenient way to describe how quickly a reaction proceeds without needing to know the exact concentrations at every point in time. Half-life is particularly useful in processes such as radioactive decay and drug metabolism.

Fill in the blank: The half-life of a reaction is the time required for the concentration of a reactant to decrease to _____ of its initial value.

Figure 2.3: Concept of half-life in chemical reactions

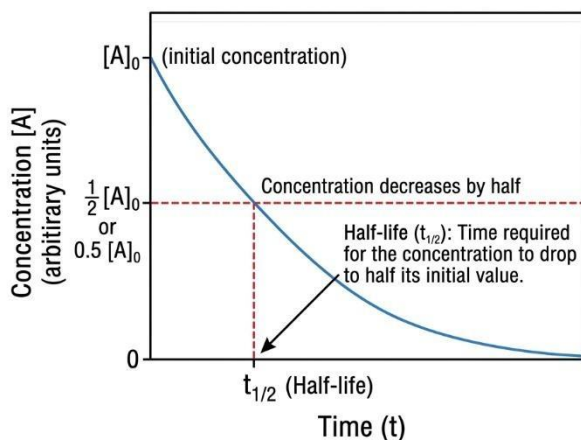


Figure 2.3: Concept of half-life in chemical reactions

[Insert figure here]

Diagram showing concentration decreasing to half its initial value over time.
Figure 2.3: Concept of half-life in chemical reactions.



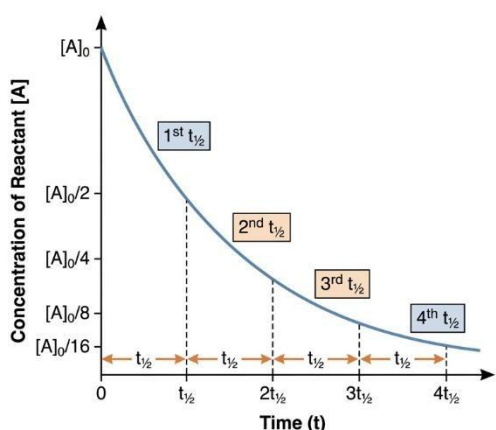
2.3.2 Relationship between half-life and rate constant for first-order reactions

For a **first-order reaction**, the half-life is independent of the initial concentration and is given by the formula:

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

Here, $t_{1/2}$ is the half-life and k is the rate constant. This means that the half-life remains constant throughout the reaction, making first-order kinetics easy to apply in practical situations such as pharmacology.

Fill in the blank: For a first-order reaction, the half-life is independent of the _____ concentration.



In a first-order reaction, the half-life ($t_{1/2}$) is constant and independent of the initial concentration.

Plate 2.3: Half-life intervals in a first-order reaction.

Half-Life Intervals in a First-Order Reaction

Image showing exponential decay curve with constant half-life intervals marked.
Plate 2.3: Half-life intervals in a first-order reaction.

2.3.3 Relationship between half-life and rate constant for second-order reactions

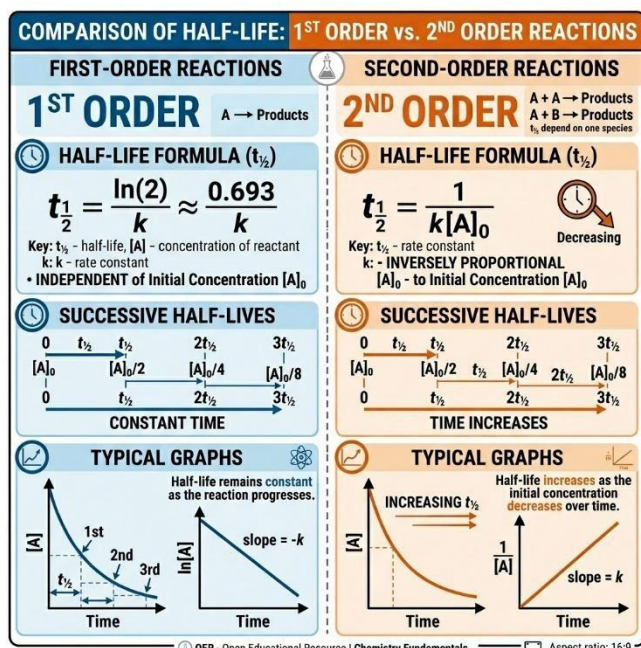
For a **second-order reaction**, the half-life depends on the initial concentration and is given by the formula:

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

Here, $t_{1/2}$ is the half-life, k is the rate constant, and $[A]_0$ is the initial concentration. This means that as the initial concentration increases, the half-life decreases, making second-order kinetics more sensitive to starting conditions.

Fill in the blank: For a second-order reaction, the half-life depends on the _____ concentration.





Box 2.3: Comparison of half-life in first- and second-order reactions

Box summarising differences between half-life behaviour in first- and second-order reactions.

Pilot questions 2.3

- The half-life of a reaction is defined as:
 - The time required for the concentration to double
 - The time required for the concentration to halve
 - The time required for the rate constant to change
 - The time required for equilibrium to be reached
 (Linked to SLO 2.7)
- For a first-order reaction, the half-life formula is:
 - $(t_{1/2} = \frac{1}{k[A]_0})$
 - $(t_{1/2} = \frac{0.693}{k})$
 - $(t_{1/2} = \frac{[A]_0}{k})$
 - $(t_{1/2} = \frac{1}{k})$
 (Linked to SLO 2.8)
- The half-life of a first-order reaction is:
 - Dependent on initial concentration
 - Independent of initial concentration
 - Dependent on temperature only
 - Always equal to one second
 (Linked to SLO 2.8)
- For a second-order reaction, the half-life formula is:
 - $(t_{1/2} = \frac{0.693}{k})$
 - $(t_{1/2} = \frac{1}{k[A]_0})$
 - $(t_{1/2} = \frac{[A]_0}{k})$



D. $(t_{1/2} = \frac{1}{k})$
(Linked to SLO 2.9)

5. The half-life of a second-order reaction:
- A. Increases with increasing initial concentration
 - B. Decreases with increasing initial concentration
 - C. Remains constant regardless of concentration
 - D. Is always equal to the rate constant
- (Linked to SLO 2.9)

2.4 Determining Reaction Order from Concentration–Time Plots

2.4.1 Concentration versus time plots

A **concentration–time plot** shows how the concentration of a reactant changes as the reaction progresses. For a zero-order reaction, the plot is a straight line with a negative slope, while for a first-order reaction, the plot is a curve showing exponential decay. Second-order reactions also produce curved plots, but with a different shape that reflects the reciprocal relationship.

Fill in the blank: A concentration–time plot for a zero-order reaction gives a _____ line with a negative slope.

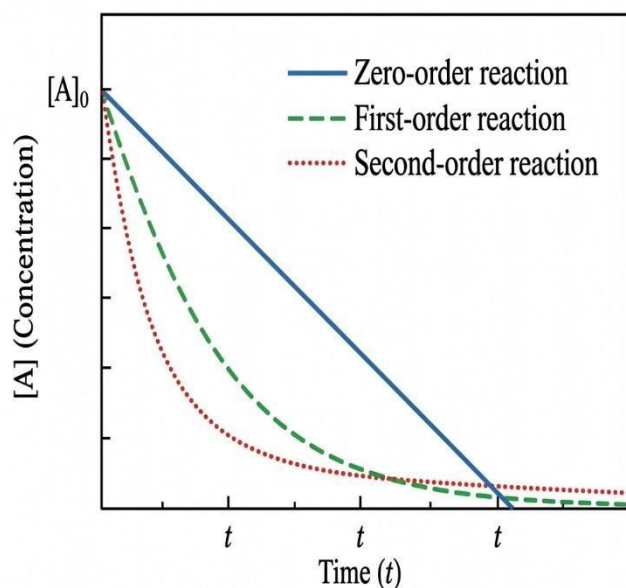


Figure 2.4: Concentration–time plots for different reaction orders.

Graph showing concentration versus time for zero-, first-, and second-order reactions.

Figure 2.4: Concentration–time plots for different reaction orders.

2.4.2 $\ln(\text{concentration})$ versus time plots

For a **first-order reaction**, plotting the natural logarithm of concentration against time produces a straight line. The slope of this line is equal to $(-k)$, the rate constant, and the intercept corresponds to $(\ln [A]_0)$. This linearity is a strong indicator of first-order kinetics and is often used to confirm reaction order experimentally.



Fill in the blank: A plot of $\ln(\text{concentration})$ versus time for a first-order reaction gives a _____ line.

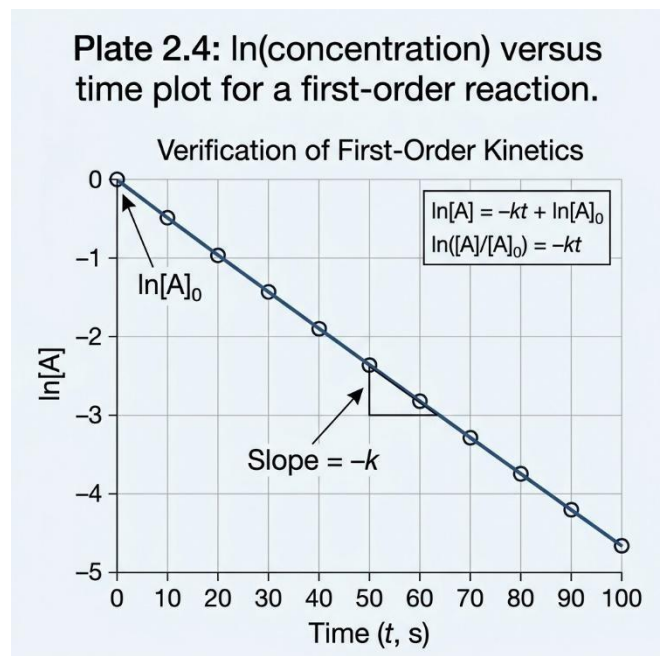


Image showing $\ln[A]$ versus time plot with slope $-k$.

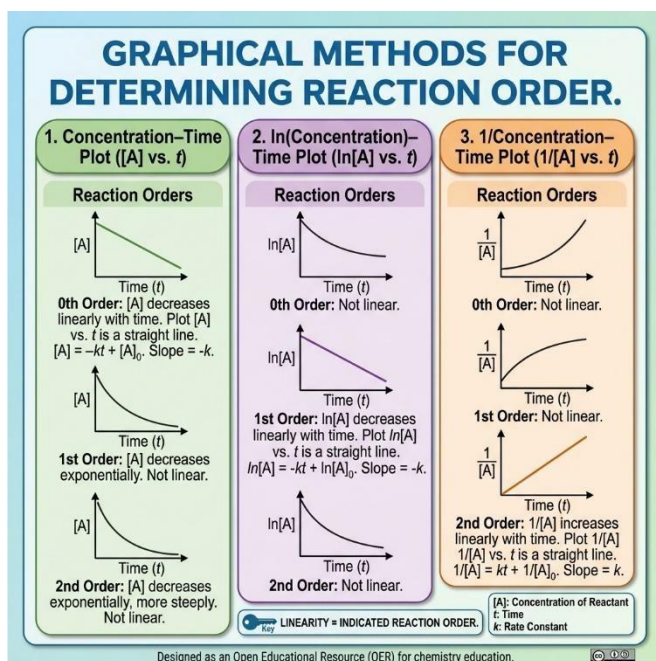
Plate 2.4: $\ln(\text{concentration})$ versus time plot for a first-order reaction.

2.4.3 $1/\text{concentration}$ versus time plots

For a **second-order reaction**, plotting the reciprocal of concentration against time produces a straight line. The slope of this line is equal to (k) , the rate constant, and the intercept corresponds to $(1/[A]_0)$. This method provides a clear way to distinguish second-order kinetics from other reaction types.

Fill in the blank: A plot of $1/\text{concentration}$ versus time for a second-order reaction gives a _____ line.





Box 2.4: Summary of graphical methods for determining reaction order

Box listing concentration–time, ln(concentration)–time, and 1/concentration–time plots with their corresponding reaction orders.

Pilot questions 2.4

- A concentration–time plot for a zero-order reaction gives:
 - A straight line with a negative slope
 - A curve showing exponential decay
 - A straight line with a positive slope
 - A reciprocal curve
 (Linked to SLO 2.10)
- A plot of ln(concentration) versus time for a first-order reaction gives:
 - A curve
 - A straight line
 - A parabola
 - A horizontal line
 (Linked to SLO 2.11)
- The slope of the ln(concentration) versus time plot for a first-order reaction is equal to:
 - $[A]_0$
 - $(-k)$
 - (t)
 - $(\ln [A])$
 (Linked to SLO 2.11)
- A plot of 1/concentration versus time for a second-order reaction gives:
 - A curve
 - A straight line



- C. A parabola
 - D. A horizontal line
- (Linked to SLO 2.11)

5. Which graphical method is used to confirm second-order kinetics?
- A. Concentration versus time plot
 - B. $\ln(\text{concentration})$ versus time plot
 - C. $1/\text{concentration}$ versus time plot
 - D. Rate versus concentration plot
- (Linked to SLO 2.11)

Series Summary

This Series has focused on integrated rate laws and the concept of reaction half-life, building directly on the foundations of rate equations and reaction orders. We began by deriving and applying the integrated first-order rate law, showing how concentration changes exponentially with time and how this can be represented graphically. We then moved on to integrated second-order rate laws, highlighting their distinct mathematical form and linear reciprocal plots. Following that, we explored the concept of half-life, comparing its behaviour in first-order reactions, where it remains constant, with second-order reactions, where it depends on the initial concentration. Finally, we examined how concentration–time plots can be used to determine reaction order, distinguishing between zero-, first-, and second-order kinetics through graphical methods.

By completing this Series, you should now be able to derive and apply integrated rate laws (SLOs 2.1–2.6), define and calculate half-life for different reaction orders (SLOs 2.7–2.9), and analyse concentration–time plots to determine reaction order (SLOs 2.10–2.11). These outcomes provide you with practical tools for interpreting experimental data and predicting reaction behaviour, strengthening your ability to apply chemical kinetics in both academic and real-world contexts.

Glossary of Terms

- **Concentration–time plot:** A graph showing how the concentration of a reactant changes as a reaction progresses, used to identify reaction order.
- **First-order reaction:** A reaction in which the rate depends linearly on the concentration of a single reactant.
- **Half-life:** The time required for the concentration of a reactant to decrease to half of its initial value.
- **Integrated rate law:** A mathematical expression that relates the concentration of a reactant to time, derived from the differential rate law.
- **Natural logarithm ($\ln$):** A mathematical function used in first-order integrated rate laws, where plotting $\ln(\text{concentration})$ against time produces a straight line.
- **Rate constant (k):** A proportionality factor in the rate law that links concentration and rate, with units depending on the reaction order.
- **Reaction order:** The power to which the concentration of a reactant is raised in the rate law, indicating how strongly the rate depends on that reactant.



- **Reciprocal concentration plot ($1/[A]$):** A graph used in second-order reactions where plotting the reciprocal of concentration against time produces a straight line.
- **Second-order reaction:** A reaction in which the rate depends either on the square of the concentration of one reactant or on the product of the concentrations of two reactants.
- **Zero-order reaction:** A reaction in which the rate is independent of the concentration of the reactant, producing a straight-line concentration–time plot with a negative slope.

Concept Check Questions [Series 2]

Objective Questions

- The integrated first-order rate law is expressed as:
 - $[A] = [A]_0 - kt$
 - $\ln [A] = \ln [A]_0 - kt$
 - $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
 - $[A] = [A]_0 e^{-kt}$
 (Linked to SLO 2.1)
- A plot of $\ln(\text{concentration})$ versus time for a first-order reaction gives:
 - A curve
 - A straight line
 - A parabola
 - A horizontal line
 (Linked to SLO 2.2)
- The integrated second-order rate law for a single reactant is expressed as:
 - $[A] = [A]_0 - kt$
 - $\ln [A] = \ln [A]_0 - kt$
 - $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
 - $[A] = [A]_0 e^{-kt}$
 (Linked to SLO 2.4)
- For a first-order reaction, the half-life formula is:
 - $t_{1/2} = \frac{1}{k[A]_0}$
 - $t_{1/2} = \frac{0.693}{k}$
 - $t_{1/2} = \frac{[A]_0}{k}$
 - $t_{1/2} = \frac{1}{k}$
 (Linked to SLO 2.8)
- A plot of $1/\text{concentration}$ versus time for a second-order reaction gives:
 - A curve
 - A straight line
 - A parabola
 - A horizontal line
 (Linked to SLO 2.11)



Short-Answer Questions

6. Define the term “integrated rate law”.
(Linked to SLO 2.1)
7. Explain why the half-life of a first-order reaction is independent of initial concentration.
(Linked to SLO 2.8)
8. State one practical application of second-order integrated laws.
(Linked to SLO 2.6)
9. What graphical method is used to confirm second-order kinetics?
(Linked to SLO 2.11)
10. Give one example of a process that follows first-order kinetics.
(Linked to SLO 2.3)

Long-Answer Questions

11. Derive the integrated first-order rate law and explain how it can be applied to experimental data.
(Linked to SLO 2.1, 2.3)
 - **Basic response:** Show the derivation from the differential rate law and explain how concentration changes exponentially with time.
 - **Value-added response:** Extend by discussing how experimental data can be fitted to $\ln(\text{concentration})$ versus time plots to determine the rate constant.
12. Analyse the differences between half-life behaviour in first-order and second-order reactions.
(Linked to SLO 2.7–2.9)
 - **Basic response:** Explain that first-order half-life is constant, while second-order half-life depends on initial concentration.
 - **Value-added response:** Provide examples from pharmacology and atmospheric chemistry to illustrate practical implications of these differences.
13. Evaluate the usefulness of concentration–time plots in determining reaction order.
(Linked to SLO 2.10–2.11)
 - **Basic response:** Describe how zero-, first-, and second-order reactions produce distinct plots that can be used to identify reaction order.
 - **Value-added response:** Discuss limitations such as experimental error and overlapping behaviours, and suggest complementary methods like initial rate analysis.

Answers to Concept Check Questions [Series 2]

Objective Questions

1. B. $\ln [A] = \ln [A]_0 - kt$
2. B. A straight line



3. C. $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
4. B. $t_{1/2} = \frac{0.693}{k}$
5. B. A straight line

Short-Answer Questions

6. An integrated rate law is a mathematical expression that relates the concentration of a reactant to time.
7. Because the exponential decay of concentration in first-order reactions ensures that half-life depends only on the rate constant, not on starting concentration.
8. Studying bimolecular substitution reactions in organic chemistry.
9. Plotting $1/\text{concentration}$ versus time.
10. Radioactive decay.

Long-Answer Questions

11. **Basic response:** Derived by integrating the differential rate law, showing exponential decay.

Value-added response: Applied by plotting $\ln(\text{concentration})$ versus time to determine the rate constant experimentally.

12. **Basic response:** First-order half-life is constant, second-order half-life decreases with increasing initial concentration.

Value-added response: Examples include constant half-life in radioactive decay and variable half-life in atmospheric reactions.

13. **Basic response:** Distinct plots (linear or curved) allow identification of reaction order.

Value-added response: Limitations include experimental noise; complementary methods can strengthen conclusions.

Answers to Pilot Questions [Series 2]

Part 1: Integrated First-Order Rate Laws

1. $\ln [A] = \ln [A]_0 - kt$
2. A straight line
3. Radioactive decay
4. Exponential decay with slope $(-k)$
5. Practical application: drug breakdown

Part 2: Integrated Second-Order Rate Laws

1. $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
2. A straight line
3. Slope $= (k)$
4. Second-order kinetics
5. Studying atmospheric reactions

Part 3: Reaction Half-Life



1. The time required for concentration to halve
2. $(t_{1/2} = \frac{0.693}{k})$
3. Independent of initial concentration
4. $(t_{1/2} = \frac{1}{k[A]_0})$
5. Decreases with increasing initial concentration

Part 4: Determining Reaction Order from Concentration–Time Plots

1. A straight line with a negative slope
2. A straight line
3. Slope = $(-k)$
4. A straight line
5. $1/\text{concentration}$ versus time plot

References and Attributions [Series 2]

This section compiles all references, attributions, and illustration sources used or suggested in **Series 2: Integrated Rate Laws and Reaction Half-Life**. Entries are presented in APA style for clarity and consistency.

Textual References

- Atkins, P., & de Paula, J. (2018). *Physical Chemistry* (11th ed.). Oxford University Press.
- Housecroft, C. E., & Constable, E. C. (2010). *Chemistry: An Introduction to Organic, Inorganic and Physical Chemistry* (4th ed.). Pearson.
- Laidler, K. J. (1997). *Chemical Kinetics* (3rd ed.). Pearson.

Illustrations (Figures, Plates, Boxes)

- *Figure 2.1: Mathematical representation of the integrated first-order rate law*
AI-generated using prompt: “Generate a graph showing exponential decay of concentration versus time with the equation $\ln[A] = \ln[A]_0 - kt$.”
Suggested OER search string: “first-order integrated rate law graph OER”.
- *Plate 2.1: Graphical representation of a first-order reaction*
AI-generated using prompt: “Create an image showing a straight-line plot of $\ln[A]$ versus time with slope $-k$ and intercept $\ln[A]_0$.”
Suggested OER search string: “first-order reaction $\ln[A]$ vs time plot OER”.
- *Box 2.1: Applications of first-order integrated laws*
AI-generated using prompt: “Create a text box summarising applications of first-order integrated laws such as radioactive decay, drug breakdown, and pollutant removal.”
Suggested OER search string: “applications of first-order integrated rate law OER”.
- *Figure 2.2: Mathematical representation of the integrated second-order rate law*
AI-generated using prompt: “Generate a graph showing $1/[A]$ versus time with a straight line slope k for a second-order reaction.”
Suggested OER search string: “second-order integrated rate law graph OER”.



- *Plate 2.2: Graphical representation of a second-order reaction*
AI-generated using prompt: "Create an image showing a straight-line plot of $1/[A]$ versus time with slope k and intercept $1/[A]_0$."
Suggested OER search string: "second-order reaction $1/[A]$ vs time plot OER".
- *Box 2.2: Applications of second-order integrated laws*
AI-generated using prompt: "Create a text box summarising applications of second-order integrated laws such as bimolecular substitution and atmospheric reactions."
Suggested OER search string: "applications of second-order integrated rate law OER".
- *Figure 2.3: Concept of half-life in chemical reactions*
AI-generated using prompt: "Generate a diagram showing concentration versus time with a marker at half of the initial concentration to illustrate half-life."
Suggested OER search string: "reaction half-life concentration time diagram OER".
- *Plate 2.3: Half-life intervals in a first-order reaction*
AI-generated using prompt: "Create an image showing exponential decay with equal half-life intervals marked along the curve."
Suggested OER search string: "first-order reaction half-life exponential decay OER".
- *Box 2.3: Comparison of half-life in first- and second-order reactions*
AI-generated using prompt: "Create a text box comparing half-life formulas and behaviour for first-order and second-order reactions."
Suggested OER search string: "comparison half-life first second order reactions OER".
- *Figure 2.4: Concentration–time plots for different reaction orders*
AI-generated using prompt: "Generate a graph showing concentration versus time for zero-, first-, and second-order reactions with distinct shapes."
Suggested OER search string: "concentration time plots reaction order OER".
- *Plate 2.4: $\ln(\text{concentration})$ versus time plot for a first-order reaction*
AI-generated using prompt: "Create an image showing a straight-line plot of $\ln[A]$ versus time with slope $-k$ and intercept $\ln[A]_0$."
Suggested OER search string: "first-order reaction $\ln[A]$ vs time plot OER".
- *Box 2.4: Summary of graphical methods for determining reaction order*
AI-generated using prompt: "Create a text box summarising graphical methods for determining reaction order using concentration–time, $\ln(\text{concentration})$ –time, and $1/\text{concentration}$ –time plots."
Suggested OER search string: "graphical methods determining reaction order OER".



Course code: CHM 406

Course Title: Reaction Kinetics

Course Unit: (2 Units C: LH 30)

List of Series:

1. **Series 1: Rate Equations and Reaction Orders**
2. **Series 2: Integrated Rate Laws and Reaction Half-Life**
3. **Series 3: Collision Theory, Activation Energy, and the Arrhenius Equation**
4. **Series 4: Catalysis, Reaction Mechanisms, and Enzymatic Processes**
5. **Series 5: Photochemical Reactions and Chemical Warfare Agents**

Suggested Outline

Part 1: Fundamentals of Collision Theory

- 3.1.1 Basic assumptions of collision theory
- 3.1.2 Effective collisions and orientation factor
- 3.1.3 Limitations of collision theory

Part 2: Concept of Activation Energy

- 3.2.1 Definition and significance of activation energy
- 3.2.2 Energy profile diagrams
- 3.2.3 Factors influencing activation energy

Part 3: The Arrhenius Equation

- 3.3.1 Mathematical form of the Arrhenius equation
- 3.3.2 Role of frequency factor and exponential term
- 3.3.3 Determining activation energy from experimental data

Part 4: Applications of Collision Theory and Arrhenius Equation

- 3.4.1 Temperature dependence of reaction rates
- 3.4.2 Industrial and laboratory applications
- 3.4.3 Case studies in chemical kinetics

Introduction

In the last Series, we examined integrated rate laws and reaction half-life, learning how to describe concentration changes over time and how to determine reaction order from experimental plots. We now move into a deeper exploration of the molecular basis of reaction rates. This Series introduces collision theory, activation energy, and the Arrhenius equation, which together



explain why reactions occur at different speeds and how temperature influences these rates. These ideas are central to chemical kinetics and have wide applications in both laboratory and industrial contexts.

The aim of this Series is to help you understand how molecular collisions lead to chemical reactions, explain the role of activation energy in determining reaction feasibility, and apply the Arrhenius equation to quantify the effect of temperature on reaction rates.

We shall commence this Series by exploring the fundamentals of collision theory, focusing on effective collisions and the importance of molecular orientation. Next, we will move on to the concept of activation energy, using energy profile diagrams to illustrate how it acts as a barrier to reaction. Following that, we will study the Arrhenius equation, examining its mathematical form and how activation energy can be determined from experimental data. Finally, we will wrap up by considering practical applications of collision theory and the Arrhenius equation, including temperature dependence of reaction rates and case studies in industrial and laboratory settings. This progression will equip you with both theoretical insight and practical tools for analysing chemical kinetics.

Series Learning Outcomes

Upon completing this Series, you should be able to:

- **SLO 3.1** define the basic assumptions of collision theory,
- **SLO 3.2** explain the role of effective collisions and molecular orientation in reaction rates,
- **SLO 3.3** evaluate the limitations of collision theory in explaining complex reactions,
- **SLO 3.4** define activation energy and explain its significance in chemical reactions,
- **SLO 3.5** interpret energy profile diagrams to illustrate activation energy,
- **SLO 3.6** analyse factors that influence activation energy in different reactions,
- **SLO 3.7** derive the mathematical form of the Arrhenius equation,
- **SLO 3.8** explain the role of the frequency factor and exponential term in the Arrhenius equation,
- **SLO 3.9** calculate activation energy from experimental data using the Arrhenius equation,
- **SLO 3.10** apply collision theory and the Arrhenius equation to explain the temperature dependence of reaction rates,
- **SLO 3.11** evaluate industrial and laboratory applications of collision theory and the Arrhenius equation through case studies.

3.1 Fundamentals of Collision Theory

3.1.1 Basic assumptions of collision theory

Collision theory is a model that explains how chemical reactions occur and why reaction rates differ. It is based on the idea that molecules must collide with sufficient energy and proper orientation to react. The basic assumptions are that particles are in constant motion, collisions occur frequently, and only a fraction of these collisions lead to reactions.

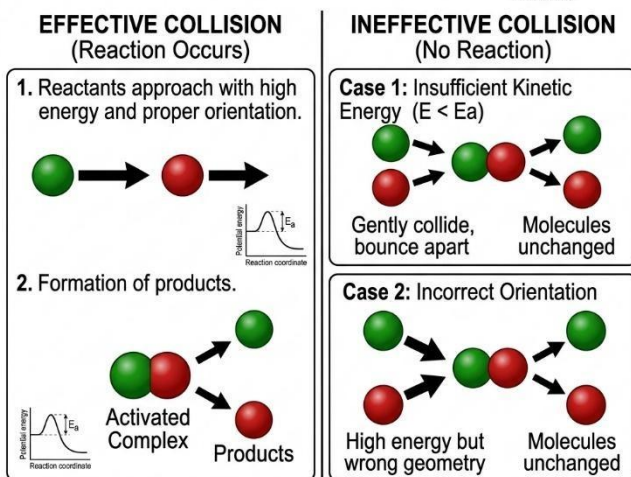


Fill in the blank: According to collision theory, only collisions with sufficient energy and proper _____ lead to reactions.

Figure 3.1: Basic assumptions of collision theory

For a chemical reaction to occur, reactant molecules must collide with:

1. **Sufficient Energy** ($\geq$ Activation Energy)
2. **Correct Orientation**.



Short description: Diagram showing

molecules colliding, with some collisions leading to reaction and others not.

Caption: Figure 3.1: Basic assumptions of collision theory.

AI prompt: "Generate a diagram showing molecules colliding, with some collisions leading to reaction and others bouncing apart."

Search string: "collision theory diagram OER"

3.1.2 Effective collisions and orientation factor

An **effective collision** is one that results in a chemical reaction. For a collision to be effective, two conditions must be met: the colliding particles must have energy equal to or greater than the activation energy, and they must collide with the correct orientation. The **orientation factor** refers to the way molecules must align during collision to allow bonds to break and new ones to form.

Fill in the blank: A collision that results in a chemical reaction is called an _____ collision.



Figure 3.1: Basic assumptions of collision theory.

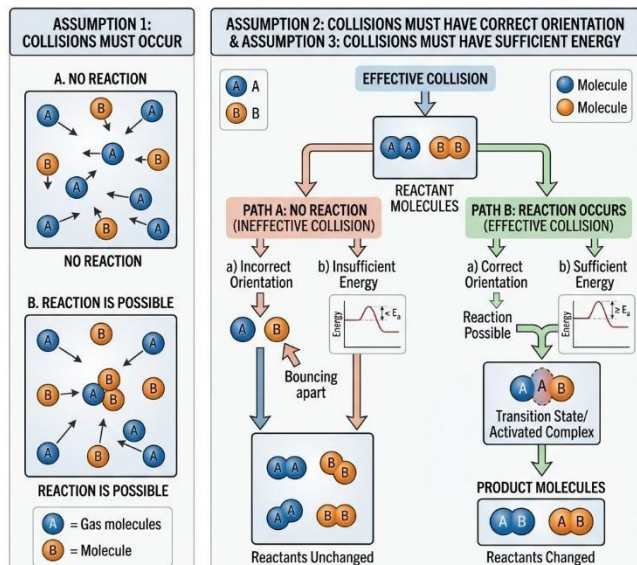


Image showing correct and incorrect molecular orientations during collision.

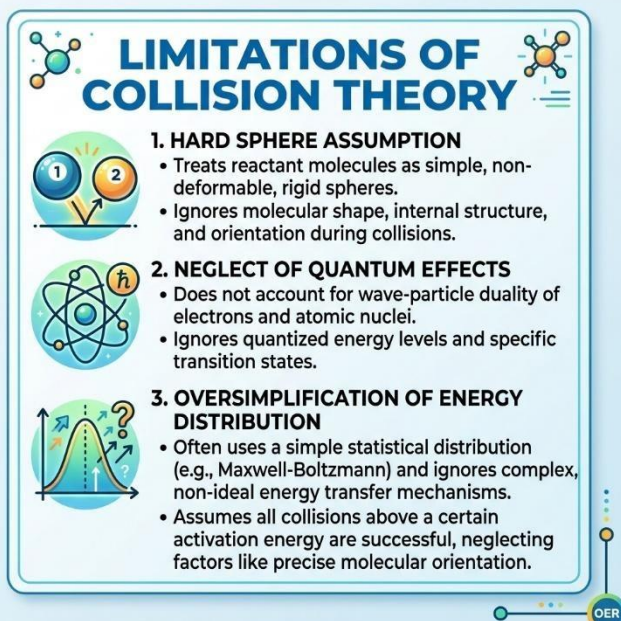
Plate 3.1: Effective collisions and orientation factor.

3.1.3 Limitations of collision theory

While collision theory provides a useful framework, it has limitations. It assumes that molecules are hard spheres and does not account for quantum effects or complex molecular structures. It also oversimplifies the role of energy distribution among molecules. More advanced models, such as transition state theory, provide a more accurate description of reaction mechanisms.

Fill in the blank: Collision theory assumes molecules behave like hard _____ spheres.





Caption: Box 3.1: Limitations of collision theory

Short description: Box summarising key limitations of collision theory, including oversimplification of molecular behaviour and neglect of quantum effects.

AI prompt: “Create a text box listing limitations of collision theory such as hard sphere assumption, neglect of quantum effects, and oversimplification of energy distribution.”

Search string: “limitations of collision theory OER”

Pilot questions 3.1

- According to collision theory, only collisions with sufficient energy and proper orientation lead to:
 - Effective collisions
 - Ineffective collisions
 - Random collisions
 - Elastic collisions
 (Linked to SLO 3.2)
- A collision that results in a chemical reaction is called:
 - Elastic collision
 - Effective collision
 - Ineffective collision
 - Random collision
 (Linked to SLO 3.2)
- The orientation factor refers to:
 - The speed of molecules
 - The alignment of molecules during collision
 - The size of molecules
 - The number of collisions per second
 (Linked to SLO 3.2)



4. Collision theory assumes molecules behave like:
 - A. Flexible chains
 - B. Hard spheres
 - C. Quantum particles
 - D. Soft shells
 (Linked to SLO 3.3)
5. Which of the following is a limitation of collision theory?
 - A. It accounts for quantum effects
 - B. It explains complex molecular structures
 - C. It oversimplifies energy distribution
 - D. It describes transition states accurately
 (Linked to SLO 3.3)

3.2 Concept of Activation Energy

3.2.1 Definition and significance of activation energy

Activation energy is the minimum amount of energy required for a chemical reaction to occur. It represents the energy barrier that reactants must overcome to be transformed into products. Without sufficient activation energy, collisions between molecules will not result in a reaction, even if they occur frequently. This concept is crucial because it explains why some reactions are slow at room temperature but faster when heated.

Fill in the blank: The minimum amount of energy required for a chemical reaction to occur is called _____.

Figure 3.2: Activation energy as an energy barrier in chemical reactions.

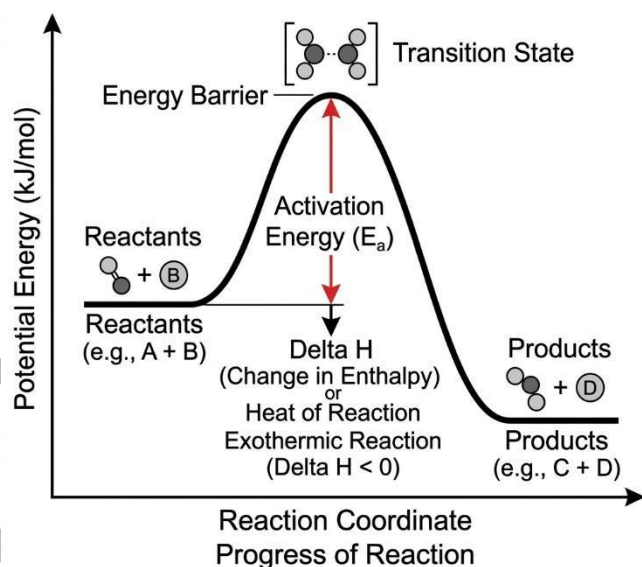


Diagram showing reactants needing to overcome an energy barrier to form products.
Figure 3.2: Activation energy as an energy barrier in chemical reactions.



3.2.2 Energy profile diagrams

An **energy profile diagram** is a graphical representation of the energy changes during a chemical reaction. It shows the energy of reactants, the peak representing the activation energy, and the energy of products. Exothermic reactions release energy, so the products lie lower than the reactants, while endothermic reactions absorb energy, placing the products higher. These diagrams help visualise the role of activation energy in determining reaction feasibility.

Fill in the blank: In an exothermic reaction, the products lie _____ than the reactants on an energy profile diagram.

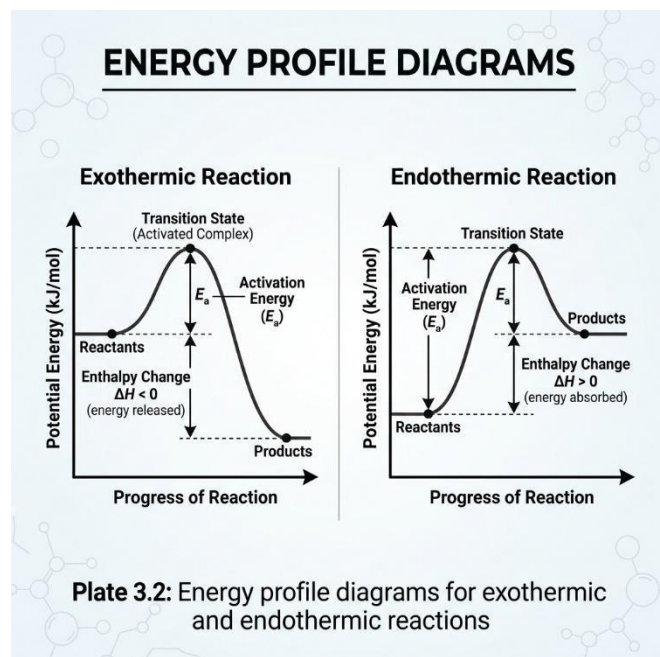


Image showing energy profile diagrams for exothermic and endothermic reactions.

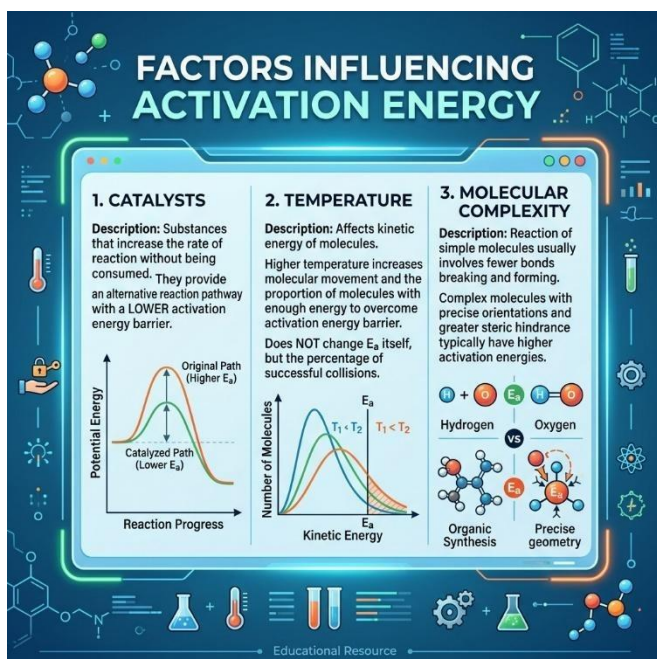
Plate 3.2: Energy profile diagrams for exothermic and endothermic reactions.

3.2.3 Factors influencing activation energy

Several factors can influence activation energy. The nature of the reactants plays a role, as complex molecules often require more energy to rearrange bonds. The presence of a **catalyst** can lower activation energy by providing an alternative pathway for the reaction. Temperature also affects the proportion of molecules with sufficient energy to overcome the barrier. These factors explain why some reactions proceed rapidly while others are slow.

Fill in the blank: A substance that lowers the activation energy of a reaction by providing an alternative pathway is called a _____.





Box 3.2: Factors influencing activation energy

Box summarising factors such as nature of reactants, catalysts, and temperature.

Pilot questions 3.2

- The minimum amount of energy required for a chemical reaction to occur is called:
 - Collision energy
 - Activation energy
 - Reaction energy
 - Potential energy
 (Linked to SLO 3.4)
- In an exothermic reaction, the products lie:
 - Higher than the reactants
 - Lower than the reactants
 - At the same level as the reactants
 - At the activation energy peak
 (Linked to SLO 3.5)
- Which of the following is represented by the peak in an energy profile diagram?
 - Reactants
 - Products
 - Activation energy
 - Catalyst
 (Linked to SLO 3.5)
- A substance that lowers the activation energy of a reaction is called a:
 - Reactant
 - Product
 - Catalyst



D. Inhibitor
(Linked to SLO 3.6)

5. Which factor influences activation energy by providing an alternative pathway for the reaction?
- A. Temperature
 - B. Catalyst
 - C. Pressure
 - D. Concentration
- (Linked to SLO 3.6)

3.3 The Arrhenius Equation

3.3.1 Mathematical form of the Arrhenius equation

The **Arrhenius equation** is a mathematical expression that relates the rate constant of a reaction to temperature and activation energy. It is written as:

$$[k = Ae^{\{-\frac{E_a}{RT}\}}]$$

Here, **k** is the rate constant, **A** is the frequency factor (sometimes called the pre-exponential factor), **E_a** is the activation energy, **R** is the gas constant, and **T** is the absolute temperature. This equation shows that as temperature increases, the rate constant also increases, making reactions faster.

Fill in the blank: The Arrhenius equation is expressed as ($k = A e^{\{-\frac{E_a}{RT}\}}$), where (A) is the _____ factor.

Figure 3.3: Mathematical form of the Arrhenius equation.

The diagram shows the Arrhenius equation $k = A * \exp\left(\frac{-E_a}{R \cdot T}\right)$ with arrows pointing to each term and its definition:

- k = Rate Constant** (with a flask and reaction icon)
- E_a = Activation Energy (J/mol)** (with a graph icon)
- R = Ideal Gas Constant (8.314 J/(mol·K))** (with a thermometer icon)
- A = Pre-exponential Factor (or Frequency Factor)** (with a flask and reaction icon)
- T = Absolute Temperature (Kelvin, K)** (with a thermometer icon)

Diagram showing the Arrhenius equation with labelled terms.

Figure 3.3: Mathematical form of the Arrhenius equation.



3.3.2 Role of frequency factor and exponential term

The **frequency factor (A)** represents the number of collisions between molecules with the correct orientation per unit time. It accounts for how often molecules collide in a way that could lead to reaction. The **exponential term ($e^{-E_a/RT}$)** represents the fraction of molecules that have enough energy to overcome the activation barrier. Together, these terms explain why both collision frequency and energy distribution are essential for reaction rates.

Fill in the blank: The exponential term in the Arrhenius equation represents the fraction of molecules with sufficient _____ to react.

Plate 3.3: Role of frequency factor and exponential term.

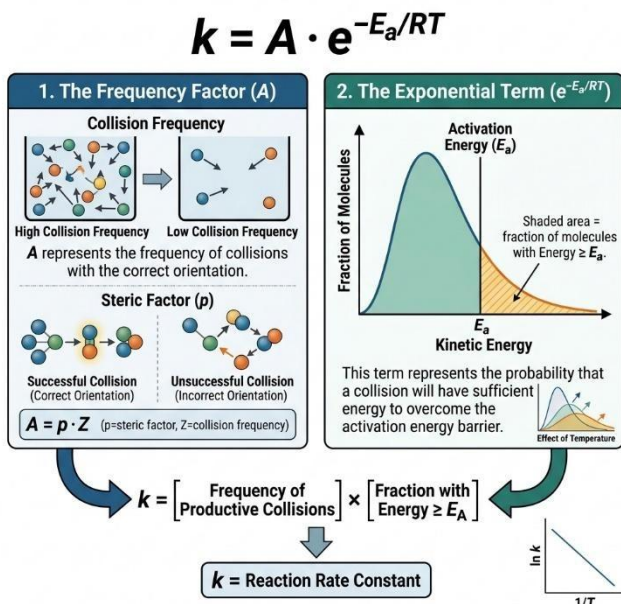


Image showing the relationship between collision frequency and energy distribution in the Arrhenius equation.

Plate 3.3: Role of frequency factor and exponential term.

3.3.3 Determining activation energy from experimental data

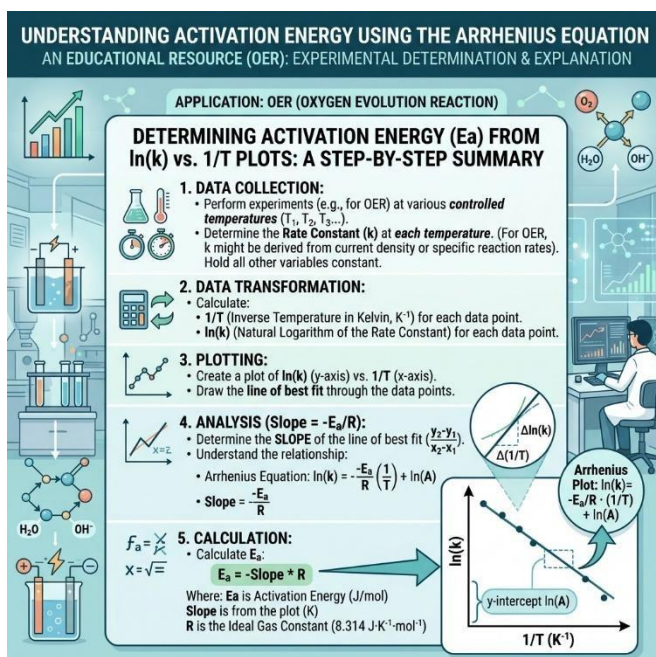
The Arrhenius equation can be rearranged into a linear form:

$$[\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}]$$

By plotting ($\ln k$) against ($1/T$), a straight line is obtained with slope ($-E_a/R$) and intercept ($\ln A$). This method allows chemists to determine activation energy experimentally by measuring rate constants at different temperatures.

Fill in the blank: A plot of $\ln(k)$ versus $1/T$ gives a straight line with slope equal to _____.





Box 3.3: Determining activation energy experimentally

Box summarising the steps for determining activation energy using the Arrhenius equation.

Pilot questions 3.3

- The Arrhenius equation is expressed as:
 - $k = Ae^{\{-\frac{E_a}{RT}\}}$
 - $k = \frac{E_a}{RT}$
 - $k = A + E_aRT$
 - $k = \ln A - \frac{E_a}{RT}$

(Linked to SLO 3.7)
- The frequency factor in the Arrhenius equation represents:
 - The slope of a plot
 - The number of effective collisions per unit time
 - The activation energy barrier
 - The gas constant

(Linked to SLO 3.8)
- The exponential term in the Arrhenius equation represents:
 - The fraction of molecules with sufficient energy
 - The number of collisions per second
 - The intercept of a plot
 - The rate constant at zero temperature

(Linked to SLO 3.8)
- A plot of $\ln(k)$ versus $1/T$ gives a straight line with slope equal to:
 - $(\ln A)$
 - $(-E_a/R)$
 - (k)



D. (T)

(Linked to SLO 3.9)

5. Which experimental method is used to determine activation energy from the Arrhenius equation?

A. Plotting $\ln(k)$ versus $1/T$

B. Plotting k versus T

C. Plotting A versus E_a

D. Plotting R versus T

(Linked to SLO 3.9)

3.4 Applications of Collision Theory and Arrhenius Equation

3.4.1 Temperature dependence of reaction rates

One of the most important applications of the **Arrhenius equation** is explaining how reaction rates change with temperature. As temperature increases, more molecules have sufficient energy to overcome the activation barrier, and the rate constant rises. This is why reactions often proceed faster when heated. Collision theory supports this by showing that higher temperatures increase both the frequency and energy of collisions.

Fill in the blank: As temperature increases, the proportion of molecules with sufficient _____ to react also increases.

Figure 3.4: Temperature dependence of reaction rates.

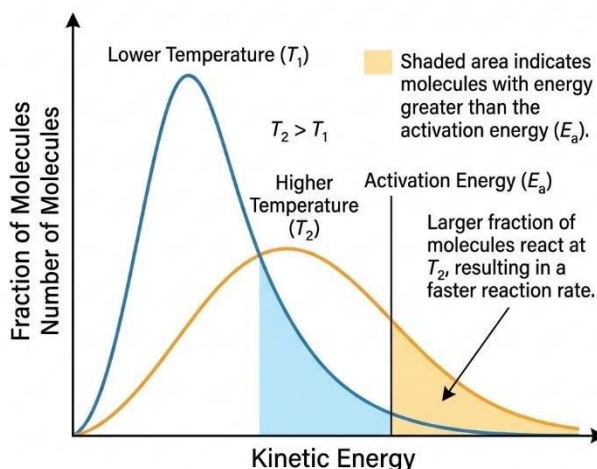


Figure 3.4: Temperature dependence of reaction rates.

Diagram showing the effect of temperature on the distribution of molecular energies.

Figure 3.4: Temperature dependence of reaction rates.

3.4.2 Industrial and laboratory applications



Collision theory and the Arrhenius equation are widely applied in industry and laboratory settings. In chemical manufacturing, controlling temperature allows optimisation of reaction rates for efficiency and safety. In pharmaceuticals, understanding activation energy helps design drugs with stable shelf lives. Laboratory experiments often use Arrhenius plots to determine activation energies, providing insight into reaction mechanisms.

Fill in the blank: In pharmaceutical science, activation energy is important for predicting the _____ of drugs.



Image showing laboratory and industrial settings where reaction rate control is applied.

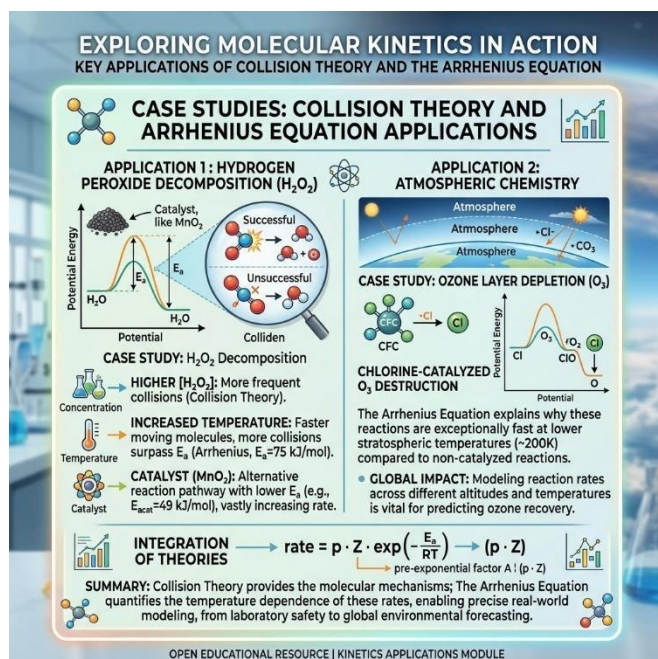
Plate 3.4: Industrial and laboratory applications of collision theory and Arrhenius equation.

3.4.3 Case studies in chemical kinetics

Case studies highlight how these theories are applied in practice. For example, the decomposition of hydrogen peroxide is accelerated by catalysts, demonstrating how activation energy can be lowered. In atmospheric chemistry, the Arrhenius equation helps explain how pollutants react at different temperatures. These examples show the practical relevance of collision theory and Arrhenius analysis in solving real-world problems.

Fill in the blank: The decomposition of hydrogen peroxide is accelerated by _____, which lower activation energy.





Box 3.4: Case studies in chemical kinetics

Box summarising examples such as hydrogen peroxide decomposition and atmospheric pollutant reactions.

Pilot questions 3.4

- As temperature increases, the proportion of molecules with sufficient energy to react:
 - Decreases
 - Remains constant
 - Increases
 - Becomes zero
 (Linked to SLO 3.10)
- In pharmaceutical science, activation energy is important for predicting:
 - Shelf life of drugs
 - Colour of drugs
 - Taste of drugs
 - Packaging of drugs
 (Linked to SLO 3.11)
- Which of the following is an industrial application of the Arrhenius equation?
 - Determining catalyst efficiency in chemical manufacturing
 - Measuring molecular geometry
 - Predicting atomic structure
 - Calculating molar mass
 (Linked to SLO 3.11)
- The decomposition of hydrogen peroxide is accelerated by:
 - Heat



- B. Catalysts
 - C. Pressure
 - D. Light only
- (Linked to SLO 3.11)

5. In atmospheric chemistry, the Arrhenius equation helps explain:
- A. The colour of pollutants
 - B. The rate of pollutant reactions at different temperatures
 - C. The density of gases
 - D. The molecular weight of pollutants
- (Linked to SLO 3.11)

Series Summary

This Series has explored collision theory, activation energy, and the Arrhenius equation, providing a molecular-level understanding of why reactions occur at different rates and how temperature influences them. We began with the fundamentals of collision theory, examining the assumptions, effective collisions, and orientation factor, before considering its limitations. We then moved on to the concept of activation energy, using energy profile diagrams to illustrate the energy barrier that must be overcome for reactions to proceed. Following that, we studied the Arrhenius equation, focusing on its mathematical form, the role of the frequency factor and exponential term, and how activation energy can be determined experimentally. Finally, we applied these ideas to real-world contexts, including temperature dependence of reaction rates, industrial and laboratory applications, and case studies in chemical kinetics.

By completing this Series, you should now be able to define and explain collision theory (SLOs 3.1–3.3), describe and interpret activation energy and its influencing factors (SLOs 3.4–3.6), derive and apply the Arrhenius equation (SLOs 3.7–3.9), and evaluate practical applications in both laboratory and industrial settings (SLOs 3.10–3.11). These outcomes equip you with both theoretical insight and practical skills, strengthening your ability to analyse and predict reaction behaviour in diverse chemical contexts.

Glossary of Terms

- **Activation energy:** The minimum amount of energy that reacting particles must have in order to successfully form products.
- **Arrhenius equation:** A mathematical expression that relates the rate constant of a reaction to temperature and activation energy.
- **Catalyst:** A substance that lowers the activation energy of a reaction by providing an alternative pathway, thereby increasing the rate of reaction.
- **Collision theory:** A model that explains reaction rates based on the frequency, energy, and orientation of molecular collisions.
- **Effective collision:** A collision between molecules that has sufficient energy and correct orientation to result in a chemical reaction.
- **Energy profile diagram:** A graphical representation showing the energy changes during a chemical reaction, including the activation energy barrier.



- **Exponential term (in Arrhenius equation):** The part of the equation, $(e^{-E_a/RT})$, that represents the fraction of molecules with enough energy to overcome the activation barrier.
- **Frequency factor (A):** A constant in the Arrhenius equation that represents the number of collisions with proper orientation per unit time.
- **Orientation factor:** The requirement that molecules must collide in a specific alignment for bonds to break and new ones to form.
- **Rate constant (k):** A proportionality factor in the rate law that indicates how quickly a reaction proceeds at a given temperature.

Concept Check Questions [Series 3]

Objective Questions

1. According to collision theory, only collisions with sufficient energy and correct orientation lead to:
 - A. Effective collisions
 - B. Ineffective collisions
 - C. Random collisions
 - D. Elastic collisions
 (Linked to SLO 3.2)
2. The minimum amount of energy required for a chemical reaction to occur is called:
 - A. Collision energy
 - B. Activation energy
 - C. Reaction energy
 - D. Potential energy
 (Linked to SLO 3.4)
3. The Arrhenius equation is expressed as:
 - A. $(k = Ae^{-\frac{E_a}{RT}})$
 - B. $(k = \frac{E_a}{RT})$
 - C. $(k = A + E_aRT)$
 - D. $(k = \ln A - \frac{E_a}{RT})$
 (Linked to SLO 3.7)
4. The exponential term in the Arrhenius equation represents:
 - A. The fraction of molecules with sufficient energy
 - B. The number of collisions per second
 - C. The intercept of a plot
 - D. The rate constant at zero temperature
 (Linked to SLO 3.8)
5. A plot of $\ln(k)$ versus $1/T$ gives a straight line with slope equal to:
 - A. $(\ln A)$
 - B. $(-E_a/R)$
 - C. (k)



D. (T)
(Linked to SLO 3.9)

Short-Answer Questions

6. Define collision theory.
(Linked to SLO 3.1)
7. Explain what is meant by an effective collision.
(Linked to SLO 3.2)
8. State one limitation of collision theory.
(Linked to SLO 3.3)
9. What does an energy profile diagram show?
(Linked to SLO 3.5)
10. Give one industrial application of the Arrhenius equation.
(Linked to SLO 3.11)

Long-Answer Questions

11. Derive the Arrhenius equation and explain the significance of each term.
(Linked to SLO 3.7–3.8)
 - **Basic response:** Present the mathematical form of the equation and describe the meaning of k , A , E_a , R , and T .
 - **Value-added response:** Extend by discussing how collision frequency and energy distribution combine to explain reaction rates, with examples from laboratory experiments.
12. Analyse the role of activation energy in determining reaction feasibility.
(Linked to SLO 3.4–3.6)
 - **Basic response:** Explain that activation energy is the minimum energy barrier that must be overcome for a reaction to occur.
 - **Value-added response:** Provide examples of how catalysts lower activation energy and discuss implications for industrial processes.
13. Evaluate the usefulness of collision theory and the Arrhenius equation in real-world applications.
(Linked to SLO 3.10–3.11)
 - **Basic response:** Describe how these theories explain temperature dependence of reaction rates and are applied in laboratory and industrial contexts.
 - **Value-added response:** Critically assess limitations, such as oversimplification of molecular behaviour, and suggest complementary models like transition state theory.



Objective Questions

1. A. Effective collisions
2. B. Activation energy
3. A. $(k = Ae^{\{-\frac{E_a}{RT}\}})$
4. A. The fraction of molecules with sufficient energy
5. B. $(-E_a/R)$

Short-Answer Questions

6. Collision theory is a model that explains reaction rates based on the frequency, energy, and orientation of molecular collisions.
7. An effective collision is one that has sufficient energy and correct orientation to result in a chemical reaction.
8. One limitation is that collision theory assumes molecules behave like hard spheres and neglects quantum effects.
9. An energy profile diagram shows the energy changes during a reaction, including the activation energy barrier.
10. One industrial application is optimising reaction rates in chemical manufacturing by controlling temperature.

Long-Answer Questions

11. **Basic response:** The Arrhenius equation ($k = Ae^{\{-\frac{E_a}{RT}\}}$) shows how rate constant depends on temperature and activation energy. Each term represents a physical factor influencing reaction rate.
Value-added response: Beyond the equation, collision frequency and energy distribution explain why reactions accelerate with temperature. Laboratory Arrhenius plots provide experimental determination of activation energy.
12. **Basic response:** Activation energy is the minimum energy required for reactants to form products, acting as a barrier to reaction.
Value-added response: Catalysts lower activation energy, enabling faster reactions. Industrial processes such as catalytic converters in cars demonstrate this principle.
13. **Basic response:** Collision theory and the Arrhenius equation explain temperature dependence and are applied in laboratory and industrial contexts.
Value-added response: They have limitations, such as oversimplification of molecular behaviour. Transition state theory provides a more detailed model, complementing these approaches in advanced chemical kinetics.

Part 1: Fundamentals of Collision Theory

1. Effective collisions
2. Effective collision
3. The alignment of molecules during collision
4. Hard spheres



5. It oversimplifies energy distribution

Part 2: Concept of Activation Energy

1. Activation energy
2. Lower than the reactants
3. Activation energy
4. Catalyst
5. Catalyst

Part 3: The Arrhenius Equation

1. $k = Ae^{-\frac{E_a}{RT}}$
2. The number of effective collisions per unit time
3. The fraction of molecules with sufficient energy
4. $(-E_a/R)$
5. Plotting $\ln(k)$ versus $1/T$

Part 4: Applications of Collision Theory and Arrhenius Equation

1. Increases
2. Shelf life of drugs
3. Determining catalyst efficiency in chemical manufacturing
4. Catalysts
5. The rate of pollutant reactions at different temperatures

References and Attributions [Series 3]

This section compiles all references, attributions, and illustration sources used or suggested in **Series 3: Collision Theory, Activation Energy, and the Arrhenius Equation**. Entries are presented in APA style for clarity and consistency.

Textual References

- Atkins, P., & de Paula, J. (2018). *Physical Chemistry* (11th ed.). Oxford University Press.
- Housecroft, C. E., & Constable, E. C. (2010). *Chemistry: An Introduction to Organic, Inorganic and Physical Chemistry* (4th ed.). Pearson.
- Laidler, K. J. (1997). *Chemical Kinetics* (3rd ed.). Pearson.

Illustrations (Figures, Plates, Boxes)

- *Figure 3.1: Basic assumptions of collision theory*
AI-generated using prompt: “Generate a diagram showing molecules colliding, with some collisions leading to reaction and others bouncing apart.”
Suggested OER search string: “collision theory diagram OER”.
- *Plate 3.1: Effective collisions and orientation factor*
AI-generated using prompt: “Create an image showing molecules colliding with correct



orientation leading to reaction and incorrect orientation failing to react.”
Suggested OER search string: “effective collision orientation factor OER”.

- *Box 3.1: Limitations of collision theory*

AI-generated using prompt: “Create a text box listing limitations of collision theory such as hard sphere assumption, neglect of quantum effects, and oversimplification of energy distribution.”

Suggested OER search string: “limitations of collision theory OER”.

- *Figure 3.2: Activation energy as an energy barrier in chemical reactions*

AI-generated using prompt: “Generate a diagram showing an energy profile with reactants, activation energy barrier, and products.”

Suggested OER search string: “activation energy energy profile diagram OER”.

- *Plate 3.2: Energy profile diagrams for exothermic and endothermic reactions*

AI-generated using prompt: “Create an image showing energy profile diagrams for exothermic and endothermic reactions, with activation energy marked.”

Suggested OER search string: “energy profile diagram exothermic endothermic OER”.

- *Box 3.2: Factors influencing activation energy*

AI-generated using prompt: “Create a text box listing factors that influence activation energy, including catalysts, temperature, and molecular complexity.”

Suggested OER search string: “factors influencing activation energy OER”.

- *Figure 3.3: Mathematical form of the Arrhenius equation*

AI-generated using prompt: “Generate a diagram showing the Arrhenius equation with labelled terms: k, A, Ea, R, and T.”

Suggested OER search string: “Arrhenius equation diagram OER”.

- *Plate 3.3: Role of frequency factor and exponential term*

AI-generated using prompt: “Create an image showing collision frequency and energy distribution as components of the Arrhenius equation.”

Suggested OER search string: “Arrhenius equation frequency factor exponential term OER”.

- *Box 3.3: Determining activation energy experimentally*

AI-generated using prompt: “Create a text box summarising steps for determining activation energy experimentally using $\ln(k)$ versus $1/T$ plots.”

Suggested OER search string: “Arrhenius equation activation energy determination OER”.

- *Figure 3.4: Temperature dependence of reaction rates*

AI-generated using prompt: “Generate a diagram showing Maxwell–Boltzmann energy distribution curves at two different temperatures, highlighting molecules above activation energy.”

Suggested OER search string: “temperature dependence reaction rate Maxwell Boltzmann OER”.

- *Plate 3.4: Industrial and laboratory applications of collision theory and Arrhenius equation*



AI-generated using prompt: “Create an image showing chemical manufacturing plant and laboratory experiment illustrating reaction rate control.”

Suggested OER search string: “industrial laboratory applications Arrhenius equation OER”.

- *Box 3.4: Case studies in chemical kinetics*

AI-generated using prompt: “Create a text box summarising case studies of collision theory and Arrhenius equation applications, including hydrogen peroxide decomposition and atmospheric chemistry.”

Suggested OER search string: “case studies Arrhenius equation collision theory OER”.

Course code: CHM 406

Course Title: Reaction Kinetics

Course Unit: (2 Units C: LH 30)

List of Series:

1. **Series 1: Rate Equations and Reaction Orders**
2. **Series 2: Integrated Rate Laws and Reaction Half-Life**
3. **Series 3: Collision Theory, Activation Energy, and the Arrhenius Equation**
4. **Series 4: Catalysis, Reaction Mechanisms, and Enzymatic Processes**
5. **Series 5: Photochemical Reactions and Chemical Warfare Agents**

Suggested Outline

Part 1: Fundamentals of Catalysis

- 4.1.1 Definition and types of catalysis
- 4.1.2 Homogeneous and heterogeneous catalysis
- 4.1.3 Role of catalysts in lowering activation energy

Part 2: Reaction Mechanisms

- 4.2.1 Elementary steps and molecularity
- 4.2.2 Rate-determining step
- 4.2.3 Chain reactions and intermediates

Part 3: Enzymatic Processes

- 4.3.1 Characteristics of enzymes as biological catalysts
- 4.3.2 Enzyme–substrate complex and active site
- 4.3.3 Factors affecting enzyme activity



Part 4: Applications of Catalysis and Enzymatic Processes

- 4.4.1 Industrial applications of catalysis
- 4.4.2 Enzyme applications in biotechnology and medicine
- 4.4.3 Case studies in catalysis and enzymatic kinetics

Introduction

In the last Series, we examined collision theory, activation energy, and the Arrhenius equation, gaining insight into how molecular collisions and energy barriers determine reaction rates. Building on that foundation, this Series introduces catalysis, reaction mechanisms, and enzymatic processes. These topics are central to understanding how reactions can be accelerated, controlled, and applied in both industrial and biological contexts, making them highly relevant to the overall study of chemical kinetics.

The aim of this Series is to equip you with the knowledge to explain how catalysts and enzymes influence reaction rates, analyse reaction mechanisms, and apply these concepts to practical and real-world scenarios.

We shall commence this Series by exploring the fundamentals of catalysis, including its types and the role of catalysts in lowering activation energy. Next, we will move on to reaction mechanisms, focusing on elementary steps, molecularity, and the rate-determining step. Following that, we will study enzymatic processes, examining the unique characteristics of enzymes, the enzyme–substrate complex, and factors affecting enzyme activity. Finally, we will wrap up by considering applications of catalysis and enzymatic processes, highlighting industrial uses, biotechnology, and case studies that demonstrate their importance in practice. This progression will provide you with both theoretical understanding and applied skills in chemical kinetics.

Series Learning Outcomes

Upon completing this Series, you should be able to:

- **SLO 4.1** define catalysis and distinguish between homogeneous and heterogeneous catalysis,
- **SLO 4.2** explain how catalysts lower activation energy and influence reaction rates,
- **SLO 4.3** describe the concept of elementary steps and molecularity in reaction mechanisms,
- **SLO 4.4** analyse the role of the rate-determining step in controlling overall reaction speed,
- **SLO 4.5** explain the significance of intermediates and chain reactions in complex mechanisms,
- **SLO 4.6** define enzymes as biological catalysts and describe their unique characteristics,
- **SLO 4.7** explain the formation of the enzyme–substrate complex and the role of the active site,
- **SLO 4.8** evaluate factors that affect enzyme activity such as temperature, pH, and inhibitors,



- **SLO 4.9** apply knowledge of catalysis to industrial processes for efficiency and sustainability,
- **SLO 4.10** assess applications of enzymes in biotechnology and medicine,
- **SLO 4.11** evaluate case studies that demonstrate the practical importance of catalysis and enzymatic kinetics.

4.1 Fundamentals of Catalysis

4.1.1 Definition and types of catalysis

Catalysis is the process by which the rate of a chemical reaction is increased by the presence of a substance called a **catalyst**, which itself is not consumed in the reaction. Catalysts work by lowering the activation energy, thereby making it easier for reactants to be converted into products. Catalysis can be broadly classified into two types: **homogeneous catalysis**, where the catalyst and reactants are in the same phase (such as liquid), and **heterogeneous catalysis**, where the catalyst is in a different phase from the reactants (such as a solid catalyst with gaseous reactants).

Fill in the blank: A catalyst increases the rate of a chemical reaction by lowering the _____ energy.

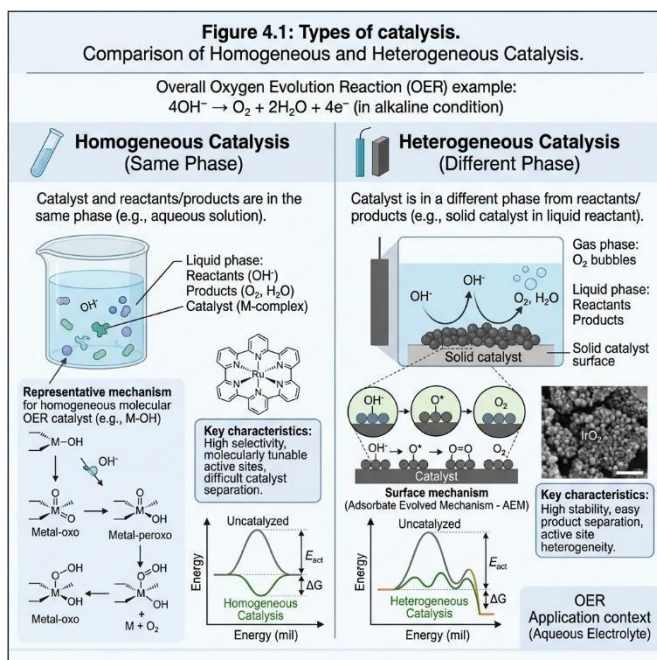


Diagram showing homogeneous and heterogeneous catalysis.

Figure 4.1: Types of catalysis.



4.1.2 Homogeneous and heterogeneous catalysis

In **homogeneous catalysis**, the catalyst interacts directly with reactants in the same phase, often forming intermediate species that facilitate the reaction. This type of catalysis is common in solution-phase reactions, such as acid-base catalysis. In **heterogeneous catalysis**, the catalyst provides a surface on which reactants can adsorb, react, and then desorb as products. Examples include the use of solid metal catalysts in industrial processes like the Haber process for ammonia synthesis.

Fill in the blank: In heterogeneous catalysis, reactants interact with the catalyst by _____ onto its surface.

Plate 4.1: Adsorption in Heterogeneous Catalysis

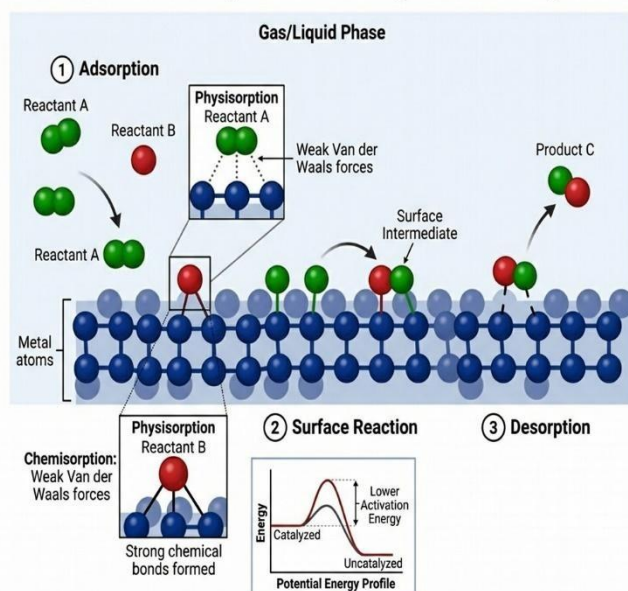


Image showing molecules adsorbing onto a solid catalyst surface.

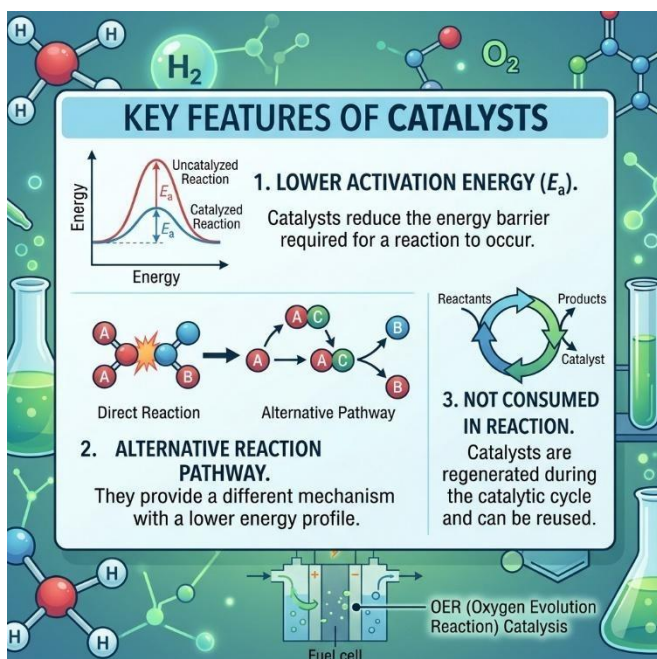
Plate 4.1: Adsorption in heterogeneous catalysis.

4.1.3 Role of catalysts in lowering activation energy

Catalysts function by providing an alternative reaction pathway with lower activation energy. This means that more molecules have sufficient energy to react at a given temperature, increasing the reaction rate without altering the overall thermodynamics of the reaction. Importantly, catalysts are not consumed in the reaction and can be reused.

Fill in the blank: Catalysts provide an alternative reaction _____ with lower activation energy.





Box 4.1: Key features of catalysts

Box summarising the main features of catalysts, including lowering activation energy, providing alternative pathways, and remaining unchanged after the reaction.

Pilot questions 4.1

- A catalyst increases the rate of a chemical reaction by lowering:
 - Potential energy
 - Activation energy
 - Reaction enthalpy
 - Collision frequency
 (Linked to SLO 4.2)
- In heterogeneous catalysis, reactants interact with the catalyst by:
 - Dissolving into the catalyst
 - Adsorbing onto its surface
 - Reacting without contact
 - Forming a new phase
 (Linked to SLO 4.1)
- Which of the following is true about catalysts?
 - They are consumed in the reaction
 - They increase activation energy
 - They provide an alternative pathway with lower activation energy
 - They change the overall thermodynamics of the reaction
 (Linked to SLO 4.2)
- Homogeneous catalysis occurs when:
 - Catalyst and reactants are in different phases
 - Catalyst and reactants are in the same phase



- C. Catalyst is solid and reactants are gaseous
 D. Catalyst is liquid and reactants are solid
 (Linked to SLO 4.1)

5. Which industrial process uses heterogeneous catalysis with solid metal catalysts?
 A. Haber process
 B. Electrolysis of water
 C. Fermentation of glucose
 D. Distillation of crude oil
 (Linked to SLO 4.1)

4.2 Reaction Mechanisms

4.2.1 Elementary steps and molecularity

A **reaction mechanism** is the sequence of elementary steps that together describe how a chemical reaction occurs at the molecular level. An **elementary step** is a single, simple reaction event that cannot be broken down further. Each step has its own rate law and contributes to the overall reaction. The **molecularity** of an elementary step refers to the number of reactant particles involved in that step, such as unimolecular (one particle), bimolecular (two particles), or termolecular (three particles).

Fill in the blank: The number of reactant particles involved in an elementary step is called its _____.

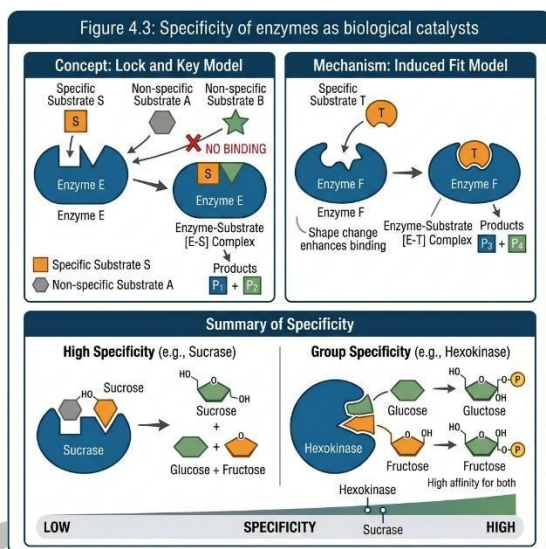


Diagram showing unimolecular, bimolecular, and termolecular elementary steps.

Figure 4.2: Types of molecularity in elementary steps.



4.2.2 Rate-determining step

The **rate-determining step** is the slowest step in a reaction mechanism. It acts as a bottleneck, controlling the overall rate of the reaction. Even if other steps are faster, the overall reaction cannot proceed faster than this limiting step. Identifying the rate-determining step is crucial for understanding reaction kinetics and predicting rate laws.

Fill in the blank: The slowest step in a reaction mechanism that controls the overall rate is called the _____ step.

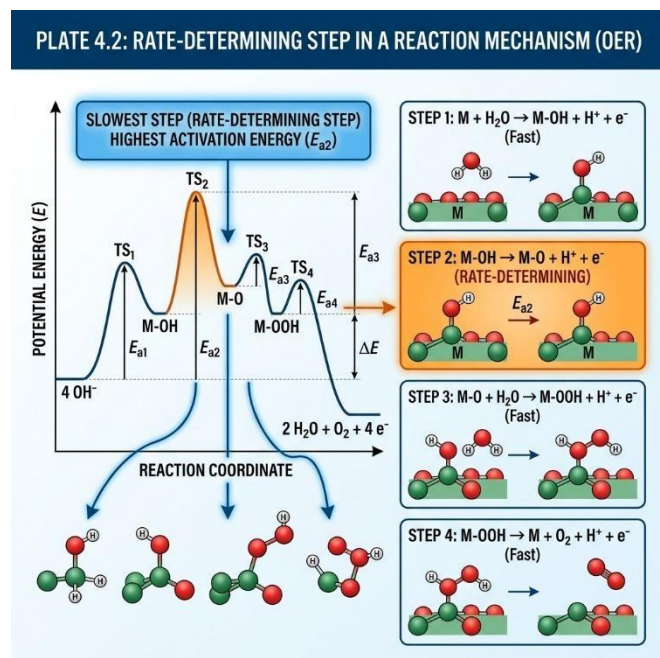


Image showing a multi-step reaction mechanism with the slowest step highlighted.

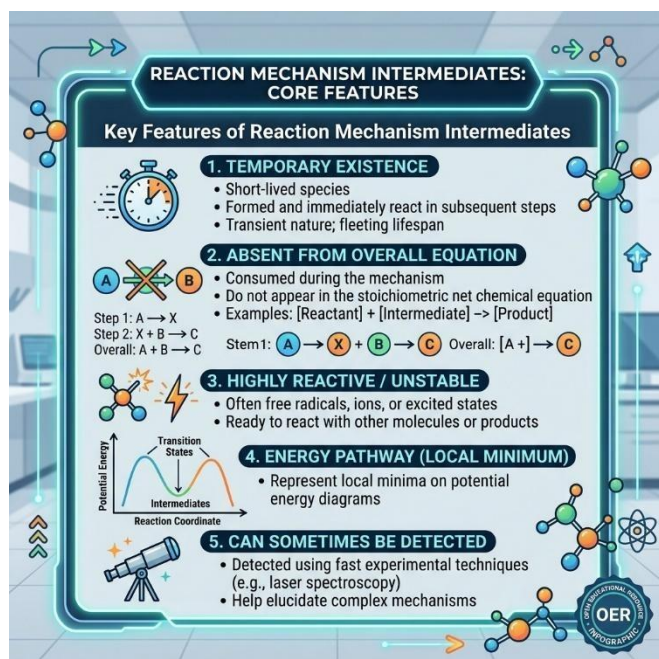
Plate 4.2: Rate-determining step in a reaction mechanism.

4.2.3 Chain reactions and intermediates

Some reactions proceed through **chain reactions**, where reactive intermediates are continuously regenerated, allowing the reaction to sustain itself. An **intermediate** is a species formed in one step of a mechanism and consumed in a later step. Intermediates do not appear in the overall balanced equation but are essential for understanding how the reaction progresses. Examples include free radicals in combustion reactions.

Fill in the blank: A species formed in one step of a mechanism and consumed in a later step is called an _____.





Box 4.2: Features of intermediates in reaction mechanisms

Box summarising key features of intermediates, including their temporary existence and absence from the overall equation.

Pilot questions 4.2

- The number of reactant particles involved in an elementary step is called:
 - Order
 - Molecularity
 - Frequency
 - Rate constant
 (Linked to SLO 4.3)
- The slowest step in a reaction mechanism is known as the:
 - Fast step
 - Intermediate step
 - Rate-determining step
 - Chain step
 (Linked to SLO 4.4)
- Which of the following is true about intermediates?
 - They appear in the overall balanced equation
 - They are consumed in the same step they are formed
 - They are formed in one step and consumed in another
 - They remain unchanged throughout the reaction
 (Linked to SLO 4.5)
- A chain reaction is characterised by:
 - The absence of intermediates
 - Continuous regeneration of reactive intermediates



- C. A single elementary step
 - D. A constant rate-determining step
- (Linked to SLO 4.5)

5. Which type of elementary step involves three reactant particles colliding simultaneously?
- A. Unimolecular
 - B. Bimolecular
 - C. Termolecular
 - D. Multimolecular
- (Linked to SLO 4.3)

4.3 Enzymatic Processes

4.3.1 Characteristics of enzymes as biological catalysts

Enzymes are specialised proteins that act as biological catalysts, speeding up chemical reactions in living organisms without being consumed in the process. They are highly specific, meaning each enzyme typically catalyses only one type of reaction or acts on a particular substrate. Enzymes function under mild conditions of temperature and pH, which makes them ideal for biological systems.

Fill in the blank: Enzymes are specialised _____ that act as biological catalysts in living organisms.

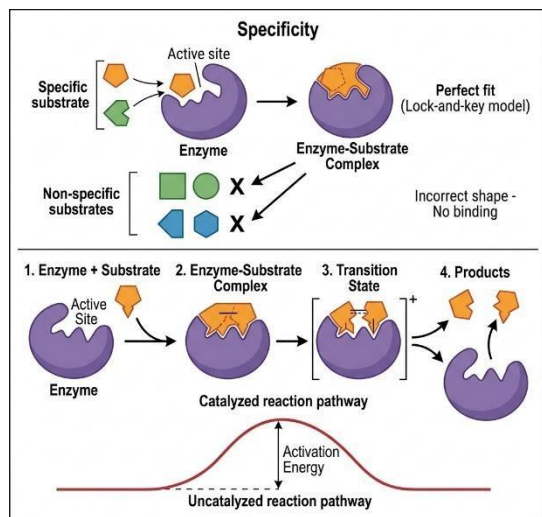


Figure 4.3: Specificity of enzymes as biological catalysts.

Diagram showing enzyme specificity with one enzyme acting on a specific substrate.

Figure 4.3: Specificity of enzymes as biological catalysts.

4.3.2 Enzyme–substrate complex and active site

The **enzyme–substrate complex** is formed when a substrate binds to the enzyme's **active site**, which is the region of the enzyme where the reaction takes place. The active site has a unique shape that complements the substrate, often described using the lock-and-key model. In some cases, the induced-fit model applies, where the enzyme slightly changes shape to better



accommodate the substrate. This binding lowers the activation energy, allowing the reaction to proceed more efficiently.

Fill in the blank: The region of the enzyme where the substrate binds and the reaction occurs is called the _____.

Plate 4.3: Models of enzyme–substrate interaction.

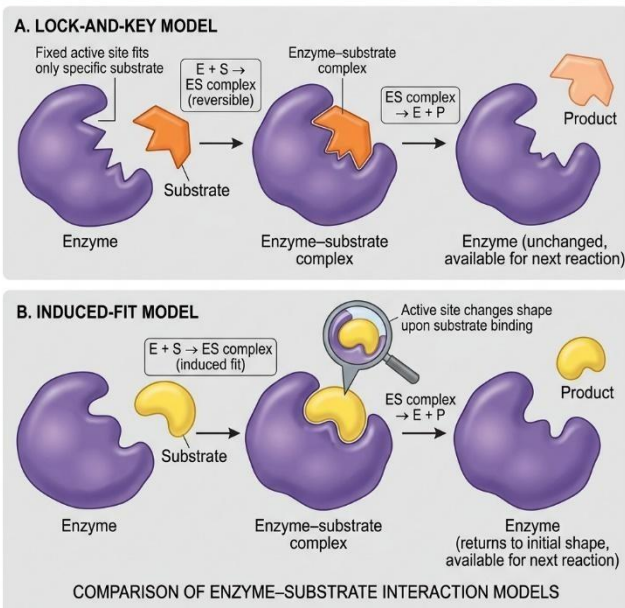


Image showing lock-and-key and induced-fit models of enzyme action.

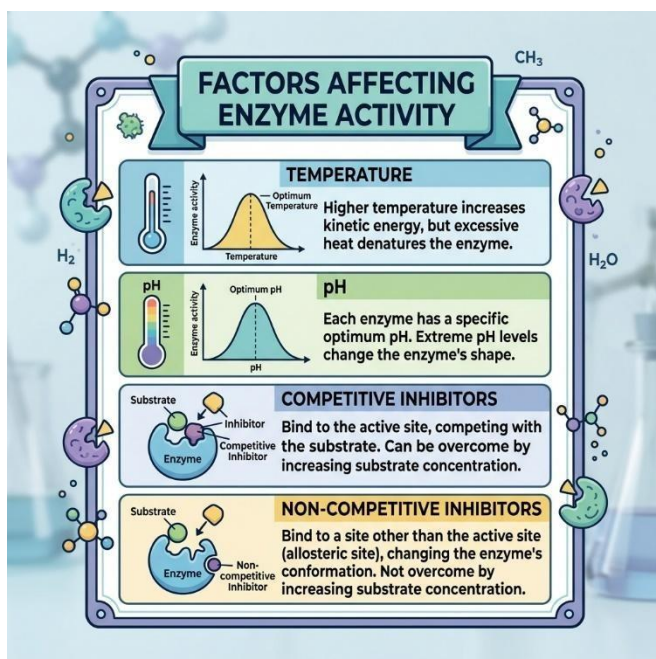
Plate 4.3: Models of enzyme–substrate interaction.

4.3.3 Factors affecting enzyme activity

Several factors influence enzyme activity. **Temperature** affects the kinetic energy of molecules; moderate increases speed up reactions, but excessive heat can denature enzymes. **pH** influences the ionisation of amino acids at the active site, affecting binding. **Inhibitors** are substances that reduce enzyme activity, either by binding to the active site (competitive inhibitors) or to another part of the enzyme (non-competitive inhibitors). These factors explain why enzymes work best under specific conditions.

Fill in the blank: Substances that reduce enzyme activity by binding to the enzyme are called _____.





Box 4.3: Factors affecting enzyme activity

Box summarising temperature, pH, and inhibitors as key factors influencing enzyme activity.

Pilot questions 4.3

- Enzymes are specialised proteins that act as:
 - Substrates
 - Biological catalysts
 - Inhibitors
 - Products
 (Linked to SLO 4.6)
- The region of the enzyme where the substrate binds is called the:
 - Active site
 - Binding pocket
 - Reaction zone
 - Catalyst centre
 (Linked to SLO 4.7)
- Which model describes the enzyme–substrate interaction as a perfect fit?
 - Induced-fit model
 - Lock-and-key model
 - Chain reaction model
 - Rate-determining model
 (Linked to SLO 4.7)
- Excessive heat can reduce enzyme activity by:
 - Increasing molecular collisions
 - Denaturing the enzyme
 - Lowering activation energy



D. Expanding the active site
(Linked to SLO 4.8)

5. Substances that reduce enzyme activity by binding to the enzyme are called:

- A. Catalysts
- B. Inhibitors
- C. Substrates
- D. Products

(Linked to SLO 4.8)

4.4 Applications of Catalysis and Enzymatic Processes

4.4.1 Industrial applications of catalysis

Catalysis plays a vital role in industry by enabling reactions to occur more efficiently and under milder conditions. For example, in the **Haber process**, iron catalysts are used to synthesise ammonia from nitrogen and hydrogen, which is essential for fertiliser production. In petroleum refining, catalysts help in cracking large hydrocarbons into smaller, more useful molecules. These applications highlight how catalysis reduces costs, saves energy, and increases yields.

Fill in the blank: The industrial process that uses iron catalysts to synthesise ammonia is called the _____ process.

Generate a diagram showing the Haber process with nitrogen and hydrogen reacting over an iron catalyst to form ammonia.

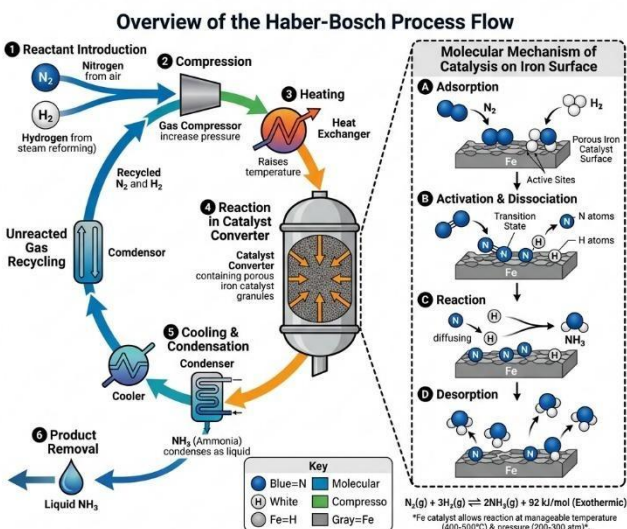


Figure 4.4: Industrial application of catalysis in the Haber process.

Diagram showing the Haber process with nitrogen, hydrogen, and iron catalyst producing ammonia.

Figure 4.4: Industrial application of catalysis in the Haber process.



4.4.2 Enzyme applications in biotechnology and medicine

Enzymes are widely applied in biotechnology and medicine due to their specificity and efficiency. In biotechnology, enzymes are used in food processing, such as amylases breaking down starch in brewing and baking. In medicine, enzymes serve as diagnostic tools, for example, measuring blood glucose levels with glucose oxidase. They are also used therapeutically, such as proteases in wound healing. These applications demonstrate the versatility of enzymes beyond natural biological systems.

Fill in the blank: The enzyme used to measure blood glucose levels in diagnostic tests is oxidase.

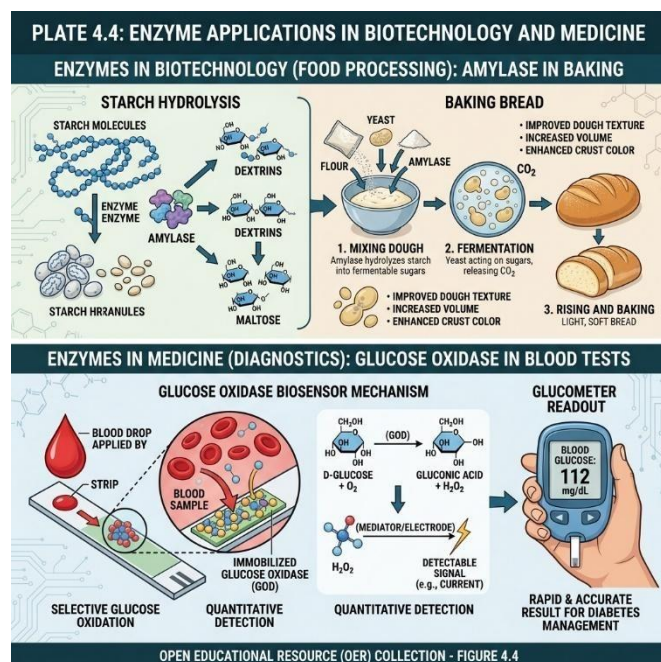


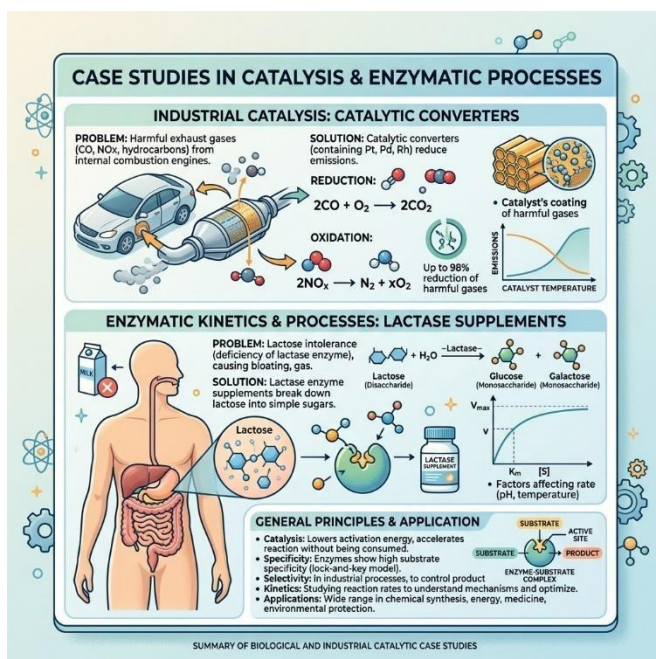
Image showing enzyme applications in food processing and medical diagnostics.
Plate 4.4: Enzyme applications in biotechnology and medicine.

4.4.3 Case studies in catalysis and enzymatic kinetics

Case studies provide practical insight into how catalysis and enzymatic processes are applied. For instance, catalytic converters in cars use platinum-based catalysts to reduce harmful emissions by converting carbon monoxide and nitrogen oxides into less harmful gases. In enzymatic kinetics, lactase supplements are used to help individuals digest lactose, demonstrating how enzyme activity can be harnessed to address dietary needs. These examples show the real-world impact of catalysis and enzymatic processes on health, environment, and industry.

Fill in the blank: The enzyme supplement used to help individuals digest lactose is called _____.





Box 4.4: Case studies in catalysis and enzymatic kinetics

Box summarising examples such as catalytic converters reducing emissions and lactase supplements aiding lactose digestion.

Pilot questions 4.4

- The industrial process that uses iron catalysts to synthesise ammonia is called the:
 - Haber process
 - Contact process
 - Fermentation process
 - Electrolysis process
 (Linked to SLO 4.9)
- The enzyme used to measure blood glucose levels in diagnostic tests is:
 - Amylase
 - Glucose oxidase
 - Protease
 - Lactase
 (Linked to SLO 4.10)
- Which of the following is an application of enzymes in food processing?
 - Catalytic cracking
 - Amylase in baking
 - Platinum in catalytic converters
 - Iron in ammonia synthesis
 (Linked to SLO 4.10)
- Catalytic converters in cars use platinum-based catalysts to:
 - Increase fuel efficiency



- B. Reduce harmful emissions
 - C. Produce ammonia
 - D. Break down starch
- (Linked to SLO 4.11)

5. The enzyme supplement used to help individuals digest lactose is called:
- A. Amylase
 - B. Lactase
 - C. Protease
 - D. Glucose oxidase
- (Linked to SLO 4.11)

Series Summary

This Series has focused on catalysis, reaction mechanisms, and enzymatic processes, showing how reactions can be accelerated, controlled, and applied in both industrial and biological contexts. We began by examining the fundamentals of catalysis, distinguishing between homogeneous and heterogeneous types and highlighting how catalysts lower activation energy. We then moved on to reaction mechanisms, where we explored elementary steps, molecularity, the rate-determining step, and the role of intermediates in chain reactions. Following that, we studied enzymatic processes, considering the unique characteristics of enzymes, the enzyme–substrate complex, and the factors that influence enzyme activity. Finally, we applied these concepts to real-world contexts, including industrial catalysis, biotechnology, medicine, and case studies that demonstrate their practical importance.

By completing this Series, you should now be able to define and explain catalysis (SLOs 4.1–4.2), describe and analyse reaction mechanisms (SLOs 4.3–4.5), explain and evaluate enzymatic processes (SLOs 4.6–4.8), and apply these ideas to industrial and medical contexts (SLOs 4.9–4.11). These outcomes ensure that you can connect theoretical principles with practical applications, equipping you with the skills to interpret, evaluate, and apply catalytic and enzymatic processes in diverse chemical and biological settings.

Glossary of Terms

- **Active site:** The specific region of an enzyme where the substrate binds and the chemical reaction takes place.
- **Catalysis:** The process of increasing the rate of a chemical reaction by using a catalyst, which is not consumed in the reaction.
- **Catalyst:** A substance that speeds up a chemical reaction by lowering the activation energy, while remaining unchanged at the end of the reaction.
- **Chain reaction:** A sequence of reactions in which reactive intermediates are continuously regenerated, allowing the reaction to sustain itself.
- **Enzyme:** A biological catalyst, usually a protein, that speeds up chemical reactions in living organisms under mild conditions of temperature and pH.
- **Enzyme–substrate complex:** A temporary structure formed when a substrate binds to the active site of an enzyme, enabling the reaction to proceed.



- **Heterogeneous catalysis:** A type of catalysis where the catalyst and reactants are in different phases, such as a solid catalyst with gaseous reactants.
- **Homogeneous catalysis:** A type of catalysis where the catalyst and reactants are in the same phase, often in solution.
- **Induced-fit model:** A model of enzyme action where the enzyme changes shape slightly to better fit the substrate.
- **Intermediate:** A species formed in one step of a reaction mechanism and consumed in a later step, not appearing in the overall balanced equation.
- **Lock-and-key model:** A model of enzyme action where the active site of the enzyme is a perfect fit for the substrate, like a key fitting into a lock.
- **Molecularity:** The number of reactant particles involved in a single elementary step of a reaction mechanism.
- **Rate-determining step:** The slowest step in a reaction mechanism that controls the overall rate of the reaction.
- **Substrate:** The reactant molecule that binds to an enzyme's active site and undergoes a chemical reaction.

Concept Check Questions [Series 4]

Objective Questions

1. Catalysts increase the rate of a chemical reaction by:
 - A. Raising activation energy
 - B. Lowering activation energy
 - C. Consuming reactants
 - D. Changing the products
 (Linked to SLO 4.2)
2. Homogeneous catalysis occurs when:
 - A. Catalyst and reactants are in different phases
 - B. Catalyst and reactants are in the same phase
 - C. Catalyst is solid and reactants are gaseous
 - D. Catalyst is liquid and reactants are solid
 (Linked to SLO 4.1)
3. The slowest step in a reaction mechanism is called the:
 - A. Intermediate step
 - B. Chain step
 - C. Rate-determining step
 - D. Fast step
 (Linked to SLO 4.4)
4. The region of the enzyme where the substrate binds is known as the:
 - A. Binding pocket
 - B. Active site
 - C. Reaction zone



D. Catalyst centre
(Linked to SLO 4.7)

5. The industrial process that uses iron catalysts to synthesise ammonia is the:
- A. Contact process
 - B. Haber process
 - C. Fermentation process
 - D. Electrolysis process
- (Linked to SLO 4.9)

Short-Answer Questions

6. Define catalysis.
(Linked to SLO 4.1)
7. Explain what is meant by molecularity in reaction mechanisms.
(Linked to SLO 4.3)
8. State one limitation of the lock-and-key model of enzyme action.
(Linked to SLO 4.7)
9. Give one example of an enzyme used in biotechnology.
(Linked to SLO 4.10)
10. What is an intermediate in a reaction mechanism?
(Linked to SLO 4.5)

Long-Answer Questions

11. Analyse the role of catalysts in lowering activation energy and explain why this is important in industrial processes.
(Linked to SLO 4.2, 4.9)

- **Basic response:** Describe how catalysts provide an alternative pathway with lower activation energy, increasing reaction rate.
- **Value-added response:** Extend by discussing specific industrial examples such as the Haber process and catalytic cracking, highlighting efficiency and sustainability benefits.

12. Evaluate the models of enzyme–substrate interaction (lock-and-key and induced-fit).
(Linked to SLO 4.7)

- **Basic response:** Explain the lock-and-key model as a perfect fit and the induced-fit model as a flexible adjustment.
- **Value-added response:** Critically assess the limitations of each model and discuss how modern structural biology supports the induced-fit concept.

13. Discuss the importance of intermediates and chain reactions in complex mechanisms.
(Linked to SLO 4.5)



- **Basic response:** Define intermediates and explain their temporary role in multi-step reactions.
- **Value-added response:** Provide examples such as free radicals in combustion and polymerisation, showing how chain reactions sustain processes.

Answers to Concept Check Questions [Series 4]

Objective Questions

1. B. Lowering activation energy
2. B. Catalyst and reactants are in the same phase
3. C. Rate-determining step
4. B. Active site
5. B. Haber process

Short-Answer Questions

6. Catalysis is the process of increasing the rate of a chemical reaction by using a catalyst that is not consumed in the reaction.
7. Molecularity refers to the number of reactant particles involved in a single elementary step of a reaction mechanism.
8. One limitation of the lock-and-key model is that it does not account for enzyme flexibility or conformational changes.
9. Amylase is an enzyme used in biotechnology, for example in baking and brewing.
10. An intermediate is a species formed in one step of a mechanism and consumed in a later step, not appearing in the overall balanced equation.

Long-Answer Questions

11. **Basic response:** Catalysts lower activation energy by providing an alternative pathway, increasing reaction rate.
Value-added response: In industry, catalysts such as iron in the Haber process reduce energy costs and improve efficiency, while catalytic cracking maximises fuel production.
12. **Basic response:** The lock-and-key model describes a perfect fit between enzyme and substrate, while the induced-fit model shows the enzyme adjusting shape.
Value-added response: Modern evidence supports induced-fit, showing enzymes are dynamic and flexible, which explains their high specificity and efficiency.
13. **Basic response:** Intermediates are temporary species that enable multi-step reactions, while chain reactions regenerate intermediates to sustain the process.
Value-added response: Examples include free radicals in combustion and polymerisation, which demonstrate how intermediates drive large-scale reactions.

Answers to Pilot Questions [Series 4]

Part 1: Fundamentals of Catalysis

1. Activation energy
2. Adsorbing
3. Provide an alternative pathway with lower activation energy
4. Catalyst and reactants are in the same phase



5. Haber process

Part 2: Reaction Mechanisms

1. Molecularity
2. Rate-determining step
3. Formed in one step and consumed in another
4. Continuous regeneration of reactive intermediates
5. Termolecular

Part 3: Enzymatic Processes

1. Biological catalysts
2. Active site
3. Lock-and-key model
4. Denaturing the enzyme
5. Inhibitors

Part 4: Applications of Catalysis and Enzymatic Processes

1. Haber process
2. Glucose oxidase
3. Amylase in baking
4. Reduce harmful emissions
5. Lactase

References and Attributions [Series 4]

This section compiles all references, attributions, and illustration sources used or suggested in **Series 4: Catalysis, Reaction Mechanisms, and Enzymatic Processes**. Entries are presented in APA style for clarity and consistency.

Textual References

- Atkins, P., & de Paula, J. (2018). *Physical Chemistry* (11th ed.). Oxford University Press.
- Housecroft, C. E., & Constable, E. C. (2010). *Chemistry: An Introduction to Organic, Inorganic and Physical Chemistry* (4th ed.). Pearson.
- Laidler, K. J. (1997). *Chemical Kinetics* (3rd ed.). Pearson.

Illustrations (Figures, Plates, Boxes)

- *Figure 4.1: Types of catalysis*
AI-generated using prompt: “Generate a diagram comparing homogeneous catalysis (same phase) and heterogeneous catalysis (different phase).”
Suggested OER search string: “homogeneous vs heterogeneous catalysis diagram OER”.
- *Plate 4.1: Adsorption in heterogeneous catalysis*
AI-generated using prompt: “Create an image showing molecules adsorbing onto a solid



catalyst surface and reacting.”

Suggested OER search string: “heterogeneous catalysis adsorption diagram OER”.

- *Box 4.1: Key features of catalysts*

AI-generated using prompt: “Create a text box listing key features of catalysts: lower activation energy, alternative pathway, not consumed in reaction.”

Suggested OER search string: “catalyst features activation energy OER”.

- *Figure 4.2: Types of molecularity in elementary steps*

AI-generated using prompt: “Generate a diagram showing unimolecular, bimolecular, and termolecular reaction steps with labelled reactants.”

Suggested OER search string: “reaction mechanism molecularity diagram OER”.

- *Plate 4.2: Rate-determining step in a reaction mechanism*

AI-generated using prompt: “Create an image showing a multi-step reaction mechanism with the slowest step highlighted as the rate-determining step.”

Suggested OER search string: “rate determining step reaction mechanism OER”.

- *Box 4.2: Features of intermediates in reaction mechanisms*

AI-generated using prompt: “Create a text box listing features of intermediates in reaction mechanisms, including temporary existence and absence from overall equation.”

Suggested OER search string: “reaction mechanism intermediates OER”.

- *Figure 4.3: Specificity of enzymes as biological catalysts*

AI-generated using prompt: “Generate a diagram showing an enzyme binding only to its specific substrate, highlighting specificity.”

Suggested OER search string: “enzyme specificity biological catalyst diagram OER”.

- *Plate 4.3: Models of enzyme–substrate interaction*

AI-generated using prompt: “Create an image showing lock-and-key and induced-fit models of enzyme–substrate binding.”

Suggested OER search string: “enzyme substrate complex lock and key induced fit OER”.

- *Box 4.3: Factors affecting enzyme activity*

AI-generated using prompt: “Create a text box listing factors affecting enzyme activity: temperature, pH, competitive inhibitors, non-competitive inhibitors.”

Suggested OER search string: “factors affecting enzyme activity OER”.

- *Figure 4.4: Industrial application of catalysis in the Haber process*

AI-generated using prompt: “Generate a diagram showing the Haber process with nitrogen and hydrogen reacting over an iron catalyst to form ammonia.”

Suggested OER search string: “Haber process catalysis diagram OER”.

- *Plate 4.4: Enzyme applications in biotechnology and medicine*

AI-generated using prompt: “Create an image showing enzymes used in food processing (amylase in baking) and medical diagnostics (glucose oxidase in blood tests).”

Suggested OER search string: “enzyme applications biotechnology medicine OER”.

- *Box 4.4: Case studies in catalysis and enzymatic kinetics*

AI-generated using prompt: “Create a text box summarising case studies of catalysis and



enzymatic processes, including catalytic converters and lactase supplements.”
Suggested OER search string: “case studies catalysis enzymatic kinetics OER”.

Course code: CHM 406

Course Title: Reaction Kinetics

Course Unit: (2 Units C: LH 30)

List of Series:

1. **Series 1: Rate Equations and Reaction Orders**
2. **Series 2: Integrated Rate Laws and Reaction Half-Life**
3. **Series 3: Collision Theory, Activation Energy, and the Arrhenius Equation**
4. **Series 4: Catalysis, Reaction Mechanisms, and Enzymatic Processes**
5. **Series 5: Photochemical Reactions and Chemical Warfare Agents**

Suggested Outline of Main Parts and Sub-Parts

Part 1: Fundamentals of Photochemical Reactions

- 5.1.1 Definition and principles of photochemistry
- 5.1.2 Role of light in chemical reactions
- 5.1.3 Examples of simple photochemical processes

Part 2: Mechanisms of Photochemical Reactions

- 5.2.1 Excited states and energy transfer
- 5.2.2 Photodissociation and radical formation
- 5.2.3 Photosensitisation and quenching

Part 3: Applications of Photochemistry

- 5.3.1 Photochemical synthesis in industry
- 5.3.2 Environmental photochemistry (e.g., ozone formation and depletion)
- 5.3.3 Biological photochemistry (e.g., photosynthesis, vision)

Part 4: Chemical Warfare Agents

- 5.4.1 Definition and classification of chemical warfare agents
- 5.4.2 Mechanisms of toxicity and reaction pathways
- 5.4.3 Case studies of chemical warfare agents in history



Part 5: Control and Mitigation Strategies

- 5.5.1 Detection and monitoring of chemical warfare agents
- 5.5.2 Neutralisation and decontamination methods
- 5.5.3 International conventions and ethical considerations

Introduction

Light is not only a source of energy but also a powerful driver of chemical change. Many reactions in nature and industry depend on the interaction between light and matter, from photosynthesis in plants to the degradation of pollutants in the atmosphere. At the same time, chemistry has been harnessed in darker ways through the development of chemical warfare agents, which pose serious threats to human health and global security. This Series brings these two contrasting themes together, helping you appreciate both the constructive and destructive potential of chemical reactions.

The aim of this Series is to introduce you to the principles and mechanisms of photochemical reactions, while also examining the chemistry of chemical warfare agents and strategies for their control. By the end, you will be able to explain how light initiates chemical change, analyse reaction pathways, and evaluate the societal implications of chemical warfare.

We shall commence this Series by exploring the fundamentals of photochemical reactions, focusing on their definition, principles, and simple examples. Next, we will move on to the mechanisms of photochemical reactions, including excited states, photodissociation, and photosensitisation. Following that, we will consider applications of photochemistry in industry, the environment, and biological systems. Afterwards, we will examine chemical warfare agents, their classification, mechanisms of toxicity, and historical case studies. Finally, we will wrap up by discussing control and mitigation strategies, including detection, neutralisation, and international conventions, thereby connecting scientific knowledge with ethical responsibility.

Series Learning Outcomes

Upon completing this Series, you should be able to:

- **SLO 5.1** define photochemical reactions and explain the role of light in initiating chemical change,
- **SLO 5.2** describe the principles of photochemistry and provide examples of simple photochemical processes,
- **SLO 5.3** analyse the mechanisms of photochemical reactions, including excited states, photodissociation, and radical formation,
- **SLO 5.4** explain the concepts of photosensitisation and quenching in photochemical pathways,
- **SLO 5.5** apply knowledge of photochemistry to industrial, environmental, and biological contexts,
- **SLO 5.6** define chemical warfare agents and classify them according to type and mode of action,



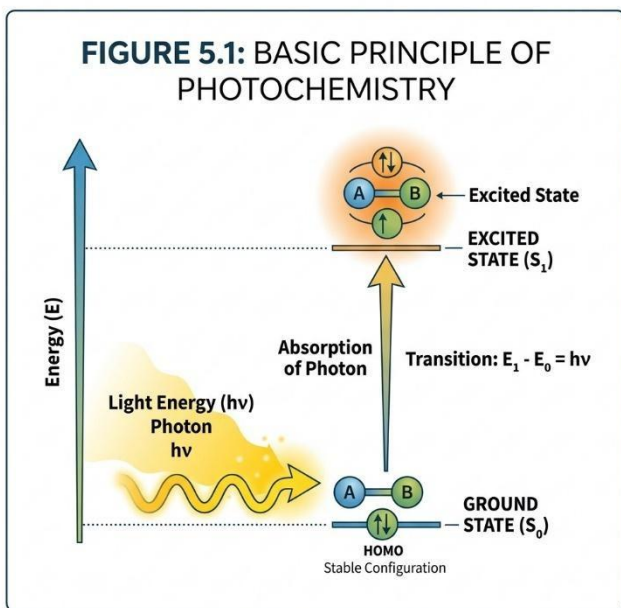
- **SLO 5.7** explain the mechanisms of toxicity and reaction pathways of selected chemical warfare agents,
- **SLO 5.8** evaluate historical case studies of chemical warfare agents and their impact on society,
- **SLO 5.9** describe methods for detecting and monitoring chemical warfare agents,
- **SLO 5.10** explain neutralisation and decontamination strategies for chemical warfare agents, and
- **SLO 5.11** assess international conventions and ethical considerations related to the control of chemical warfare agents.

5.1 Fundamentals of Photochemical Reactions

5.1.1 Definition and principles of photochemistry

Photochemistry is the branch of chemistry concerned with chemical reactions that are initiated by the absorption of light energy. When molecules absorb photons, they are promoted to higher energy states, which can lead to new reaction pathways that are not accessible under normal thermal conditions. This principle explains why light can drive processes such as photosynthesis, polymerisation, and atmospheric reactions.

Fill in the blank: Photochemistry is the branch of chemistry concerned with reactions initiated by the absorption of _____.



Source: Open Educational Resource (OER)

Diagram showing a molecule absorbing a photon and being promoted to an excited state.

Figure 5.1: Basic principle of photochemistry.

5.1.2 Role of light in chemical reactions

Light acts as a source of energy that excites electrons in molecules, enabling them to undergo transformations. The energy of light is quantised, meaning only photons of certain wavelengths



can be absorbed by a given molecule. This selectivity explains why some substances are sensitive to ultraviolet light while others respond to visible light. The absorbed energy can result in bond breaking, bond formation, or electron transfer.

Fill in the blank: The energy of light is _____, meaning only photons of certain wavelengths can be absorbed by a molecule.

Plate 5.1: Absorption of light at specific wavelengths

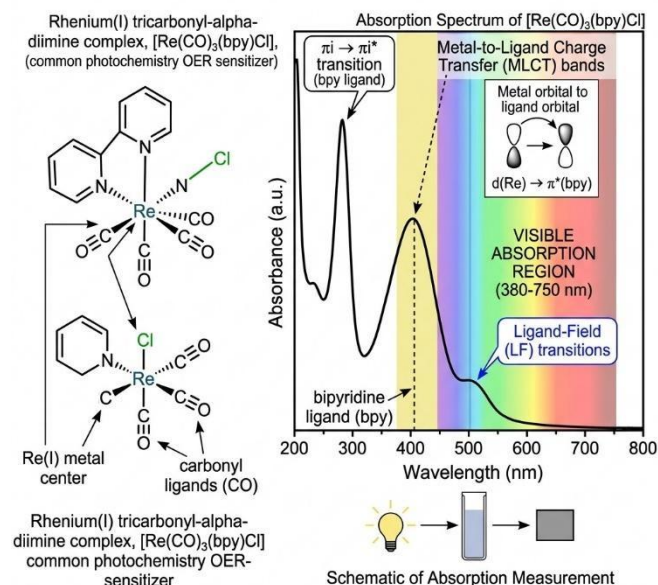


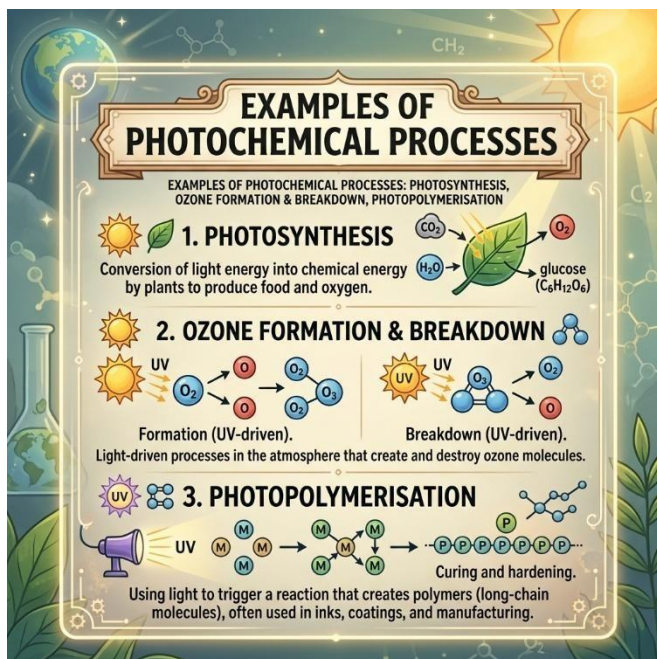
Image showing absorption spectrum of a molecule with highlighted wavelengths.
Plate 5.1: Absorption of light at specific wavelengths.

5.1.3 Examples of simple photochemical processes

Several everyday processes illustrate photochemistry. **Photosynthesis** is a biological example where plants use light energy to convert carbon dioxide and water into glucose and oxygen. In atmospheric chemistry, ultraviolet light drives the **formation and breakdown of ozone**, which protects life from harmful radiation. In industry, photochemical reactions are used in **photopolymerisation**, where light initiates the formation of polymers in coatings and adhesives.

Fill in the blank: The biological process where plants use light energy to convert carbon dioxide and water into glucose is called _____.





Box 5.1: Examples of photochemical processes

Box listing photosynthesis, ozone formation and breakdown, and photopolymerisation as examples of photochemical reactions.

Pilot questions 5.1

- Photochemistry is the branch of chemistry concerned with reactions initiated by the absorption of:
 - Heat
 - Light
 - Sound
 - Pressure
 (Linked to SLO 5.1)
- The energy of light is:
 - Continuous
 - Quantised
 - Random
 - Infinite
 (Linked to SLO 5.1)
- Which biological process is driven by photochemistry?
 - Respiration
 - Photosynthesis
 - Fermentation
 - Digestion
 (Linked to SLO 5.2)
- Ultraviolet light in the atmosphere is responsible for:
 - Ozone formation and breakdown



- B. Nitrogen fixation
 - C. Combustion reactions
 - D. Electrolysis of water
- (Linked to SLO 5.2)

5. Which industrial process uses photochemistry to initiate polymer formation?
- A. Distillation
 - B. Photopolymerisation
 - C. Cracking
 - D. Electroplating
- (Linked to SLO 5.5)

5.2 Mechanisms of Photochemical Reactions

5.2.1 Excited states and energy transfer

When a molecule absorbs light, it is promoted from its **ground state** (lowest energy level) to an **excited state** (higher energy level). Excited states are unstable and can undergo various processes such as fluorescence, phosphorescence, or chemical reactions. The energy absorbed can also be transferred to another molecule, initiating further reactions. This principle explains why photochemical reactions often involve complex energy pathways.

Fill in the blank: When a molecule absorbs light, it is promoted from the ground state to an _____ state.

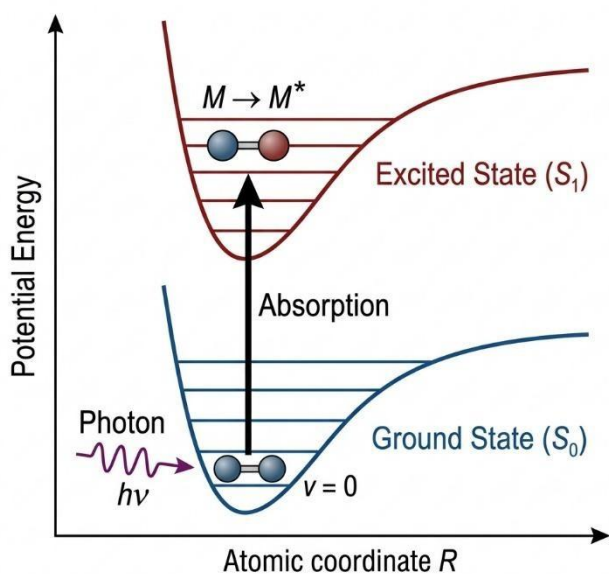


Figure 5.2: Promotion of a molecule to an excited state.

Diagram showing a molecule moving from ground state to excited state after absorbing a photon.
Figure 5.2: Promotion of a molecule to an excited state.

5.2.2 Photodissociation and radical formation



Photodissociation occurs when light energy breaks chemical bonds, producing smaller fragments. These fragments are often highly reactive **radicals**, which are species with unpaired electrons. Radicals can initiate chain reactions, making photodissociation important in atmospheric chemistry, such as the breakdown of ozone or pollutants.

Fill in the blank: Photodissociation often produces highly reactive species with unpaired electrons called _____.

Plate 5.2: Photodissociation Leading to Radical Formation.

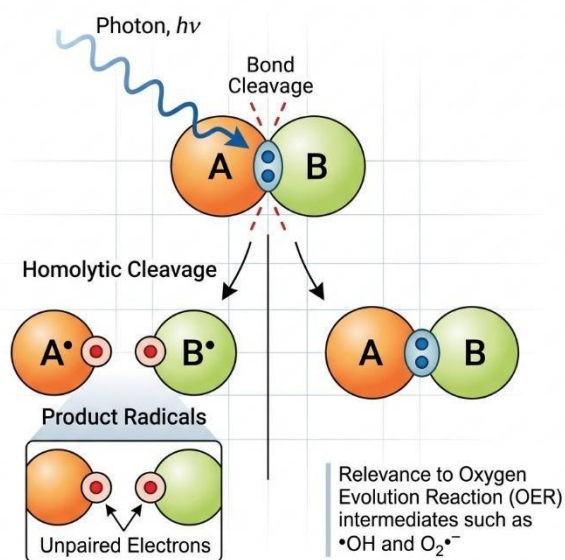


Image showing photodissociation of a molecule into radicals.

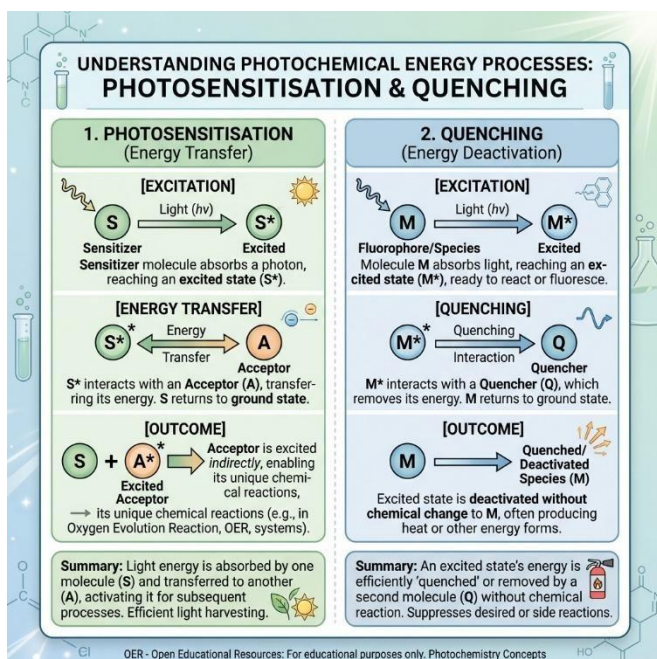
Plate 5.2: Photodissociation leading to radical formation.

5.2.3 Photosensitisation and quenching

Photosensitisation is a process where one molecule absorbs light and transfers the energy to another molecule, enabling the second molecule to react. This is common in biological systems, such as chlorophyll transferring energy during photosynthesis. **Quenching** is the opposite process, where an excited state is deactivated by another molecule, preventing further reaction. Both processes are crucial for controlling photochemical pathways.

Fill in the blank: The process where one molecule absorbs light and transfers energy to another molecule is called _____.





Box 5.2: Photosensitisation and quenching

Box summarising photosensitisation as energy transfer and quenching as energy deactivation.

Pilot questions 5.2

- When a molecule absorbs light, it is promoted from the ground state to an:
 - Neutral state
 - Excited state
 - Radical state
 - Stable state
 (Linked to SLO 5.3)
- Photodissociation often produces reactive species known as:
 - Catalysts
 - Radicals
 - Substrates
 - Products
 (Linked to SLO 5.3)
- The process where one molecule absorbs light and transfers energy to another is called:
 - Quenching
 - Photosensitisation
 - Photodissociation
 - Fluorescence
 (Linked to SLO 5.4)
- Quenching in photochemistry refers to:
 - Energy transfer to another molecule
 - Deactivation of an excited state
 - Bond breaking by light



D. Radical formation
(Linked to SLO 5.4)

5. Which of the following processes is essential in photosynthesis?
- A. Photodissociation
 - B. Photosensitisation
 - C. Quenching
 - D. Radical formation
- (Linked to SLO 5.5)

5.3 Applications of Photochemistry

5.3.1 Photochemical synthesis in industry

Photochemical synthesis refers to the use of light to drive chemical reactions that produce useful compounds. In industry, this approach is applied in the manufacture of polymers, pharmaceuticals, and fine chemicals. For example, photopolymerisation is used in coatings, adhesives, and 3D printing, where light initiates the formation of long-chain molecules. The advantage of photochemical synthesis is that it often requires milder conditions compared to thermal methods, reducing energy costs and improving efficiency.

Fill in the blank: The industrial process where light initiates the formation of long-chain molecules is called _____.

Figure 5.3: Photochemical Synthesis through Photopolymerisation.
Diagram showing light-initiated curing of industrial coatings or adhesives.

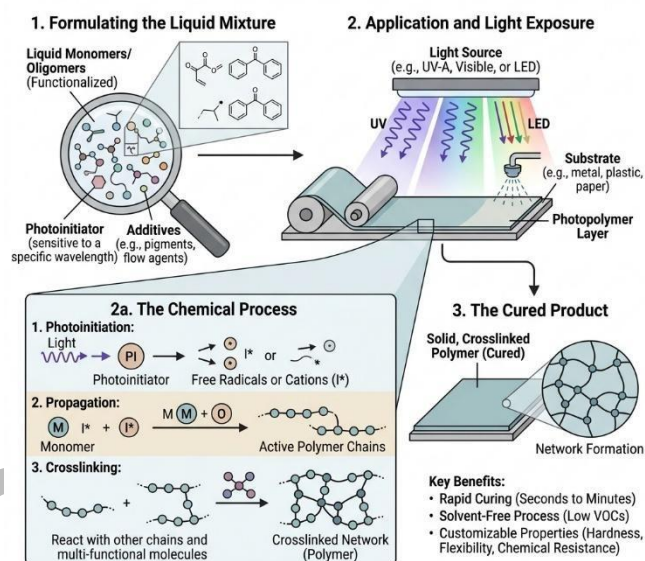


Diagram showing photopolymerisation initiated by light in industrial applications.
Figure 5.3: Photochemical synthesis through photopolymerisation.



5.3.2 Environmental photochemistry

Environmental photochemistry examines how light-driven reactions affect the atmosphere and ecosystems. A key example is the **formation and breakdown of ozone** in the stratosphere. Ultraviolet light splits oxygen molecules into atoms, which then combine to form ozone. At the same time, ozone can be broken down by light and pollutants such as chlorofluorocarbons (CFCs). These processes are crucial for protecting life from harmful UV radiation but also highlight the dangers of human activity disrupting natural cycles.

Fill in the blank: Ultraviolet light splits oxygen molecules into atoms, which then combine to form _____.

Plate 5.3: Environmental photochemistry of ozone

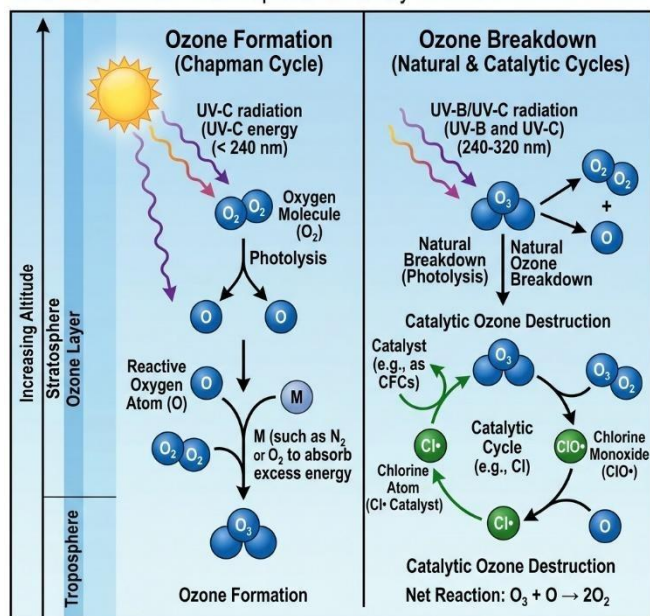


Image showing ozone formation and breakdown in the atmosphere.

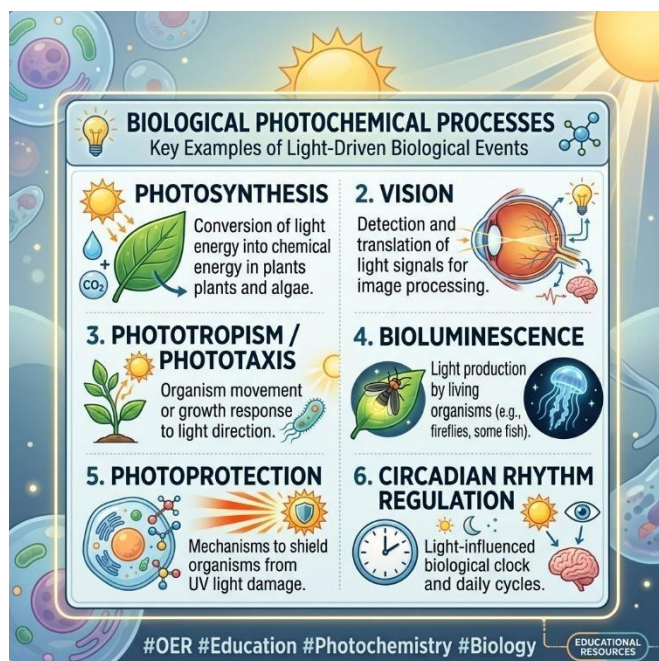
Plate 5.3: Environmental photochemistry of ozone.

5.3.3 Biological photochemistry

Biological photochemistry focuses on light-driven reactions in living organisms. The most important example is **photosynthesis**, where plants use light energy to convert carbon dioxide and water into glucose and oxygen. Another example is the photochemical process involved in **vision**, where light triggers chemical changes in retinal molecules in the eye. These processes demonstrate how photochemistry underpins essential life functions.

Fill in the blank: The photochemical process that allows plants to convert carbon dioxide and water into glucose is called _____.





Box 5.3: Examples of biological photochemistry

Box listing photosynthesis and vision as examples of biological photochemical processes.

Pilot questions 5.3

- The industrial process where light initiates polymer formation is called:
 - Cracking
 - Photopolymerisation
 - Distillation
 - Electrolysis
 (Linked to SLO 5.5)
- Ultraviolet light splits oxygen molecules into atoms, which then combine to form:
 - Nitrogen
 - Ozone
 - Carbon dioxide
 - Hydrogen
 (Linked to SLO 5.5)
- Which pollutant contributes to the breakdown of ozone in the atmosphere?
 - Carbon monoxide
 - Chlorofluorocarbons (CFCs)
 - Methane
 - Sulphur dioxide
 (Linked to SLO 5.5)
- The biological process where plants use light energy to produce glucose is:
 - Respiration
 - Photosynthesis
 - Fermentation



D. Digestion
(Linked to SLO 5.5)

5. Which photochemical process is essential for human vision?
- A. Photodissociation
 - B. Radical formation
 - C. Chemical changes in retinal molecules
 - D. Photosensitisation
- (Linked to SLO 5.5)

5.4 Chemical Warfare Agents

5.4.1 Definition and classification of chemical warfare agents

Chemical warfare agents are toxic chemicals deliberately used to harm or kill humans, animals, or plants during conflict. They are classified based on their physiological effects, such as **nerve agents** (which disrupt the nervous system), **blister agents** (which cause severe skin and lung damage), **blood agents** (which interfere with oxygen transport), and **choking agents** (which damage the respiratory system). This classification helps in understanding their mechanisms and planning protective measures.

Fill in the blank: Chemical warfare agents are classified based on their _____ effects.

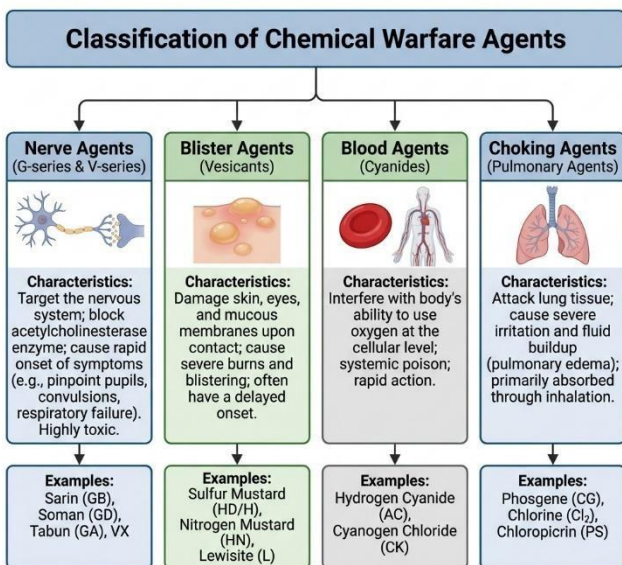


Figure 5.4: Classification of chemical warfare agents

Diagram showing classification of chemical warfare agents by physiological effect.

Figure 5.4: Classification of chemical warfare agents.



5.4.2 Mechanisms of toxicity and reaction pathways

The toxicity of chemical warfare agents arises from their ability to disrupt vital biological processes. For example, **nerve agents** inhibit the enzyme acetylcholinesterase, leading to overstimulation of nerves and muscle paralysis. **Blister agents** react with cellular components, causing tissue damage and blister formation. **Blood agents** interfere with haemoglobin, preventing oxygen transport, while **choking agents** damage lung tissue, leading to suffocation. Understanding these pathways is essential for developing antidotes and protective strategies.

Fill in the blank: Nerve agents inhibit the enzyme _____, leading to overstimulation of nerves.

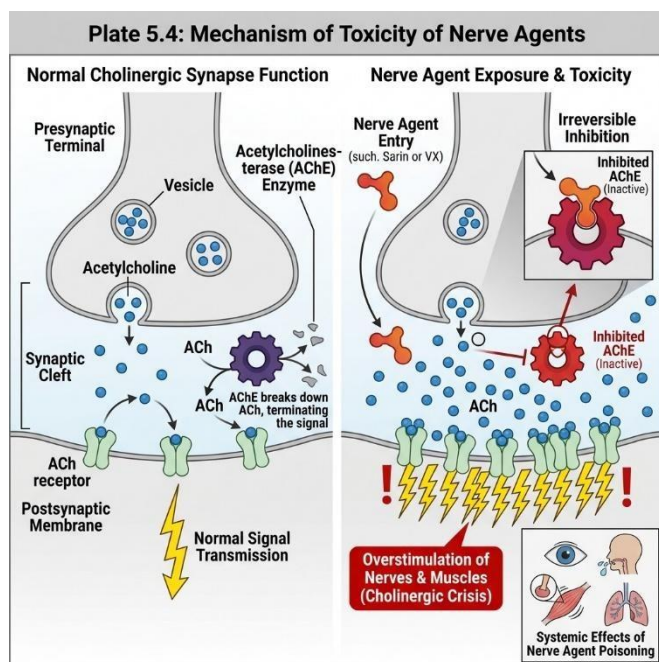


Image showing how nerve agents inhibit acetylcholinesterase, leading to paralysis.

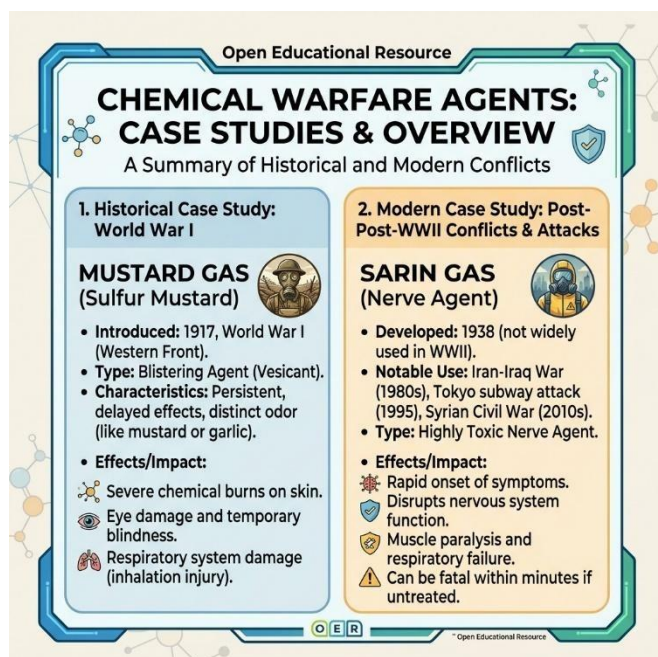
Plate 5.4: Mechanism of toxicity of nerve agents.

5.4.3 Case studies of chemical warfare agents in history

Historical case studies illustrate the devastating impact of chemical warfare agents. During World War I, **mustard gas** was used as a blister agent, causing severe injuries and long-term health effects. In more recent times, **sarin gas** has been deployed in conflicts and terrorist attacks, highlighting the ongoing threat posed by these substances. These examples underscore the importance of international conventions and scientific research aimed at preventing their use.

Fill in the blank: The blister agent used during World War I that caused severe injuries was _____ gas.





Box 5.4: Case studies of chemical warfare agents

Box summarising mustard gas in World War I and sarin gas in modern conflicts as case studies.

Pilot questions 5.4

- Chemical warfare agents are classified based on their:
 - Colour
 - Physiological effects
 - Source material
 - Physical state
 (Linked to SLO 5.6)
- Nerve agents cause paralysis by inhibiting:
 - Haemoglobin
 - Acetylcholinesterase
 - DNA polymerase
 - Photosystem II
 (Linked to SLO 5.7)
- Which type of agent interferes with oxygen transport in the blood?
 - Blister agent
 - Blood agent
 - Choking agent
 - Nerve agent
 (Linked to SLO 5.7)
- The blister agent used during World War I was:
 - Sarin
 - Mustard gas



C. Cyanide
D. Chlorine
(Linked to SLO 5.8)

5. Which chemical warfare agent has been used in modern conflicts and terrorist attacks?
- A. Mustard gas
 - B. Sarin gas
 - C. Chlorine gas
 - D. Phosgene
- (Linked to SLO 5.8)

5.5 Control and Mitigation Strategies

5.5.1 Detection and monitoring of chemical warfare agents

Detection refers to the identification of chemical warfare agents in the environment, while **monitoring** involves continuous observation to track their presence and concentration. Modern detection methods include portable sensors, chemical test kits, and advanced spectroscopic techniques. These tools are crucial for early warning systems, enabling rapid protective measures to be taken.

Fill in the blank: Continuous observation to track the presence and concentration of chemical warfare agents is called _____.

Figure 5.5: Detection and monitoring of chemical warfare agents

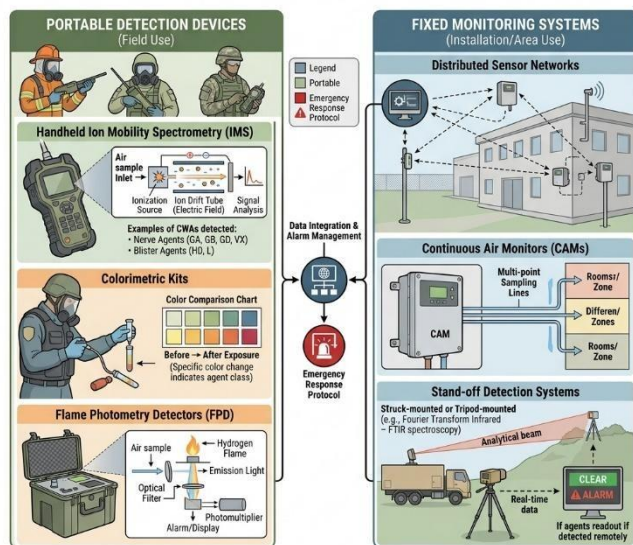


Diagram showing portable detection devices and monitoring systems for chemical warfare agents.

Figure 5.5: Detection and monitoring of chemical warfare agents.



5.5.2 Neutralisation and decontamination methods

Neutralisation is the process of chemically rendering warfare agents harmless, often by converting them into less toxic compounds. **Decontamination** involves removing or destroying agents from surfaces, equipment, or the environment. Common methods include chemical neutralisers, absorbent powders, and specialised cleaning agents. These strategies are essential for protecting both military personnel and civilians after exposure.

Fill in the blank: The process of chemically rendering warfare agents harmless is called _____.

PLATE 5.5: NEUTRALISATION AND DECONTAMINATION METHODS



METHODS FOR DECONTAMINATING EQUIPMENT USING CHEMICAL NEUTRALISERS AND ABSORBENT POWDERS

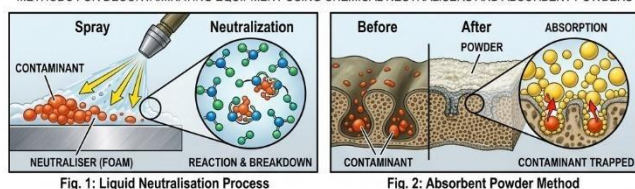


Image showing decontamination of equipment using neutralising agents.

Plate 5.5: Neutralisation and decontamination methods.

5.5.3 International conventions and ethical considerations

The use of chemical warfare agents is prohibited under international law. The **Chemical Weapons Convention (CWC)** is a treaty that bans the development, production, and stockpiling of chemical weapons, requiring member states to destroy existing stockpiles. Ethical considerations emphasise the responsibility of scientists and governments to prevent misuse of chemical knowledge. This highlights the importance of combining scientific expertise with global cooperation to ensure safety and peace.

Fill in the blank: The international treaty that bans the development and stockpiling of chemical weapons is called the _____.





Box 5.5: International conventions on chemical warfare agents
Box summarising the Chemical Weapons Convention and ethical responsibilities of scientists.

Pilot questions 5.5

- Continuous observation to track the presence and concentration of chemical warfare agents is called:
A. Neutralisation
B. Monitoring
C. Decontamination
D. Detection
(Linked to SLO 5.9)
- The process of chemically rendering warfare agents harmless is called:
A. Neutralisation
B. Monitoring
C. Detection
D. Decontamination
(Linked to SLO 5.10)
- Removing or destroying agents from surfaces or equipment is known as:
A. Neutralisation
B. Decontamination
C. Monitoring
D. Detection
(Linked to SLO 5.10)
- The international treaty that bans the development and stockpiling of chemical weapons is the:
A. Geneva Protocol



- B. Paris Agreement
 - C. Chemical Weapons Convention
 - D. Kyoto Protocol
- (Linked to SLO 5.11)

5. Ethical considerations in chemical warfare emphasise the responsibility of:
- A. Engineers only
 - B. Scientists and governments
 - C. Military personnel only
 - D. Environmental activists only
- (Linked to SLO 5.11)

Series Summary

This Series has explored the constructive and destructive potential of light-driven chemistry and toxic agents, highlighting both scientific innovation and ethical responsibility. We began with the fundamentals of photochemical reactions, defining their principles and examining how light initiates chemical change. We then studied mechanisms such as excited states, photodissociation, radical formation, photosensitisation, and quenching. Following that, we considered applications of photochemistry in industry, environmental systems, and biological processes. Afterwards, we examined chemical warfare agents, their classification, mechanisms of toxicity, and historical case studies. Finally, we concluded with control and mitigation strategies, including detection, neutralisation, decontamination, and international conventions.

By completing this Series, you should now be able to define and explain photochemical reactions (SLOs 5.1–5.2), analyse their mechanisms (SLOs 5.3–5.4), apply knowledge of photochemistry to real-world contexts (SLO 5.5), classify and explain chemical warfare agents and their toxicity (SLOs 5.6–5.8), and evaluate strategies for control and mitigation (SLOs 5.9–5.11). These outcomes ensure that you can connect scientific principles with practical applications and ethical considerations, equipping you to interpret, apply, and critically assess photochemical processes and chemical warfare agents in diverse contexts.

Glossary of Terms

- **Acetylcholinesterase:** An enzyme that breaks down the neurotransmitter acetylcholine; inhibition of this enzyme by nerve agents leads to paralysis.
- **Blood agents:** Chemical warfare agents that interfere with the body's ability to transport oxygen, often by affecting haemoglobin.
- **Chemical Weapons Convention (CWC):** An international treaty that bans the development, production, and stockpiling of chemical weapons, requiring destruction of existing stockpiles.
- **Chemical warfare agents:** Toxic chemicals deliberately used in conflict to harm or kill humans, animals, or plants.
- **Choking agents:** Chemical warfare agents that damage the respiratory system, leading to suffocation.
- **Decontamination:** The process of removing or destroying chemical warfare agents from surfaces, equipment, or the environment.



- **Detection:** The identification of chemical warfare agents in the environment using sensors or test kits.
- **Excited state:** A higher energy level that a molecule reaches after absorbing light, often leading to chemical reactions.
- **Ground state:** The lowest energy level of a molecule before it absorbs light.
- **Monitoring:** Continuous observation to track the presence and concentration of chemical warfare agents.
- **Mustard gas:** A blister agent used during World War I that caused severe injuries and long-term health effects.
- **Neutralisation:** The process of chemically rendering warfare agents harmless by converting them into less toxic compounds.
- **Nerve agents:** Chemical warfare agents that disrupt the nervous system by inhibiting acetylcholinesterase.
- **Ozone:** A molecule formed in the atmosphere when oxygen atoms combine; it protects life from harmful ultraviolet radiation but can also be broken down by pollutants.
- **Photochemistry:** The branch of chemistry concerned with chemical reactions initiated by the absorption of light energy.
- **Photodissociation:** A process where light energy breaks chemical bonds, often producing reactive radicals.
- **Photopolymerisation:** An industrial process where light initiates the formation of polymers, used in coatings, adhesives, and 3D printing.
- **Photosensitisation:** A process where one molecule absorbs light and transfers the energy to another molecule, enabling the second molecule to react.
- **Quenching:** The deactivation of an excited state by another molecule, preventing further reaction.
- **Radicals:** Highly reactive species with unpaired electrons, often formed during photodissociation.
- **Sarin gas:** A nerve agent used in modern conflicts and terrorist attacks, known for its extreme toxicity.

Concept Check Questions [Series 5]

Objective Questions

1. Photochemistry is the branch of chemistry concerned with reactions initiated by the absorption of:
 - A. Heat
 - B. Light
 - C. Sound



D. Pressure
(Linked to SLO 5.1)

2. Which process involves breaking chemical bonds using light energy?

- A. Photosensitisation
- B. Photodissociation
- C. Quenching
- D. Neutralisation

(Linked to SLO 5.3)

3. The industrial process where light initiates polymer formation is called:

- A. Cracking
- B. Photopolymerisation
- C. Distillation
- D. Electrolysis

(Linked to SLO 5.5)

4. Nerve agents cause paralysis by inhibiting:

- A. Haemoglobin
- B. Acetylcholinesterase
- C. DNA polymerase
- D. Photosystem II

(Linked to SLO 5.7)

5. The international treaty that bans the development and stockpiling of chemical weapons is the:

- A. Geneva Protocol
- B. Paris Agreement
- C. Chemical Weapons Convention
- D. Kyoto Protocol

(Linked to SLO 5.11)

Short-Answer Questions

6. Define photochemistry.

(Linked to SLO 5.1)

7. Explain what is meant by an excited state in photochemical reactions.

(Linked to SLO 5.3)

8. State one example of environmental photochemistry.

(Linked to SLO 5.5)

9. Give one historical example of a chemical warfare agent used in conflict.

(Linked to SLO 5.8)

10. What is meant by neutralisation in the context of chemical warfare agents?

(Linked to SLO 5.10)



Long-Answer Questions

11. Analyse the role of photodissociation and radical formation in atmospheric chemistry.
(Linked to SLO 5.3)

- **Basic response:** Describe how photodissociation breaks bonds and produces radicals that drive chain reactions.
- **Value-added response:** Extend by discussing ozone formation and breakdown, highlighting the balance between protective and harmful effects in the atmosphere.

12. Evaluate the applications of photochemistry in industry, environment, and biology.
(Linked to SLO 5.5)

- **Basic response:** Explain examples such as photopolymerisation, ozone chemistry, and photosynthesis.
- **Value-added response:** Critically assess the benefits and challenges, including sustainability, pollution control, and the importance of light-driven processes in life.

13. Discuss the classification and mechanisms of toxicity of chemical warfare agents.
(Linked to SLOs 5.6–5.7)

- **Basic response:** Define chemical warfare agents and describe categories such as nerve, blister, blood, and choking agents.
- **Value-added response:** Provide detailed mechanisms, such as enzyme inhibition or tissue damage, and link these to case studies like mustard gas or sarin.

14. Assess international conventions and ethical considerations in controlling chemical warfare agents.
(Linked to SLO 5.11)

- **Basic response:** State that the Chemical Weapons Convention bans development and stockpiling of chemical weapons.
- **Value-added response:** Discuss the importance of global cooperation, ethical responsibility of scientists, and challenges in enforcement.

Answers to Concept Check Questions [Series 5]

Objective Questions

1. B. Light
2. B. Photodissociation
3. B. Photopolymerisation
4. B. Acetylcholinesterase
5. C. Chemical Weapons Convention

Short-Answer Questions



6. Photochemistry is the branch of chemistry concerned with chemical reactions initiated by the absorption of light energy.
7. An excited state is a higher energy level that a molecule reaches after absorbing light.
8. Ozone formation and breakdown in the atmosphere.
9. Mustard gas used during World War I.
10. Neutralisation is the process of chemically rendering warfare agents harmless.

Long-Answer Questions

11. **Basic response:** Photodissociation breaks bonds and produces radicals that sustain chain reactions.

Value-added response: In the atmosphere, radicals drive ozone formation and breakdown, balancing protection against harmful UV radiation with risks of depletion.

12. **Basic response:** Applications include photopolymerisation in industry, ozone chemistry in the environment, and photosynthesis in biology.

Value-added response: These processes support sustainability, pollution control, and essential life functions, though they also present challenges such as managing pollutants.

13. **Basic response:** Chemical warfare agents are classified as nerve, blister, blood, and choking agents, each with distinct toxic effects.

Value-added response: Nerve agents inhibit enzymes, blister agents damage tissues, blood agents block oxygen transport, and choking agents harm lungs. Case studies include mustard gas and sarin.

14. **Basic response:** The Chemical Weapons Convention bans chemical weapons development and stockpiling.

Value-added response: Ethical responsibility and international cooperation are vital, though enforcement remains challenging in global security contexts.

Answers to Pilot Questions [Series 5]

Part 1: Fundamentals of Photochemical Reactions

1. Light
2. Quantised
3. Photosynthesis
4. Ozone formation and breakdown
5. Photopolymerisation

Part 2: Mechanisms of Photochemical Reactions

1. Excited state
2. Radicals
3. Photosensitisation
4. Deactivation of an excited state
5. Photosensitisation

Part 3: Applications of Photochemistry



1. Photopolymerisation
2. Ozone
3. Chlorofluorocarbons (CFCs)
4. Photosynthesis
5. Chemical changes in retinal molecules

Part 4: Chemical Warfare Agents

1. Physiological effects
2. Acetylcholinesterase
3. Blood agent
4. Mustard gas
5. Sarin gas

Part 5: Control and Mitigation Strategies

1. Monitoring
2. Neutralisation
3. Decontamination
4. Chemical Weapons Convention
5. Scientists and governments

References and Attributions [Series 5]

This section compiles all references, attributions, and illustration sources used or suggested in **Series 5: Photochemical Reactions and Chemical Warfare Agents**. Entries are presented in APA style for clarity and consistency.

Textual References

- Atkins, P., & de Paula, J. (2018). *Physical Chemistry* (11th ed.). Oxford University Press.
- Housecroft, C. E., & Constable, E. C. (2010). *Chemistry: An Introduction to Organic, Inorganic and Physical Chemistry* (4th ed.). Pearson.
- Laidler, K. J. (1997). *Chemical Kinetics* (3rd ed.). Pearson.
- Organisation for the Prohibition of Chemical Weapons (OPCW). (1993). *Chemical Weapons Convention*. Retrieved from <https://www.opcw.org>

Illustrations (Figures, Plates, Boxes)

- *Figure 5.1: Basic principle of photochemistry*
AI-generated using prompt: “Generate a diagram showing a molecule absorbing light energy and moving to an excited state.”
Suggested OER search string: “photochemistry excited state diagram OER”.
- *Plate 5.1: Absorption of light at specific wavelengths*
AI-generated using prompt: “Create an image showing a molecule’s absorption spectrum with highlighted wavelengths absorbed.”
Suggested OER search string: “molecule absorption spectrum photochemistry OER”.



- *Box 5.1: Examples of photochemical processes*
AI-generated using prompt: "Create a text box listing examples of photochemical processes: photosynthesis, ozone formation and breakdown, photopolymerisation."
Suggested OER search string: "examples of photochemical reactions OER".
- *Figure 5.2: Promotion of a molecule to an excited state*
AI-generated using prompt: "Generate a diagram showing a molecule absorbing a photon and moving from ground state to excited state."
Suggested OER search string: "excited state photochemistry diagram OER".
- *Plate 5.2: Photodissociation leading to radical formation*
AI-generated using prompt: "Create an image showing a molecule absorbing light and breaking into radicals with unpaired electrons."
Suggested OER search string: "photodissociation radicals diagram OER".
- *Box 5.2: Photosensitisation and quenching*
AI-generated using prompt: "Create a text box summarising photosensitisation (energy transfer) and quenching (energy deactivation)."
Suggested OER search string: "photosensitisation quenching photochemistry OER".
- *Figure 5.3: Photochemical synthesis through photopolymerisation*
AI-generated using prompt: "Generate a diagram showing photopolymerisation initiated by light in industrial coatings or adhesives."
Suggested OER search string: "photopolymerisation industrial photochemistry diagram OER".
- *Plate 5.3: Environmental photochemistry of ozone*
AI-generated using prompt: "Create an image showing ozone formation and breakdown in the stratosphere driven by ultraviolet light."
Suggested OER search string: "ozone formation breakdown photochemistry OER".
- *Box 5.3: Examples of biological photochemistry*
AI-generated using prompt: "Create a text box listing biological photochemical processes such as photosynthesis and vision."
Suggested OER search string: "biological photochemistry photosynthesis vision OER".
- *Figure 5.4: Classification of chemical warfare agents*
AI-generated using prompt: "Generate a diagram showing classification of chemical warfare agents into nerve, blister, blood, and choking agents."
Suggested OER search string: "classification of chemical warfare agents diagram OER".
- *Plate 5.4: Mechanism of toxicity of nerve agents*
AI-generated using prompt: "Create an image showing nerve agents inhibiting acetylcholinesterase and causing overstimulation of nerves."
Suggested OER search string: "nerve agents acetylcholinesterase inhibition diagram OER".
- *Box 5.4: Case studies of chemical warfare agents*
AI-generated using prompt: "Create a text box summarising case studies of chemical



warfare agents, including mustard gas in WWI and sarin gas in modern conflicts.”
Suggested OER search string: “chemical warfare agents case studies OER”.

- *Figure 5.5: Detection and monitoring of chemical warfare agents*
AI-generated using prompt: “Generate a diagram showing portable detection devices and monitoring systems for chemical warfare agents.”
Suggested OER search string: “chemical warfare agents detection monitoring diagram OER”.
- *Plate 5.5: Neutralisation and decontamination methods*
AI-generated using prompt: “Create an image showing decontamination of equipment using chemical neutralisers and absorbent powders.”
Suggested OER search string: “neutralisation decontamination chemical warfare agents OER”.
- *Box 5.5: International conventions on chemical warfare agents*
AI-generated using prompt: “Create a text box summarising the Chemical Weapons Convention and ethical responsibilities in preventing misuse of chemical knowledge.”
Suggested OER search string: “Chemical Weapons Convention summary OER”.

