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Based on National Curriculum of Pakistan 2022-23

Textbook of
CHEMISTRY
Grade 12

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National Curriculum Council
Ministry of Federal Education and Professional Training

National Book Foundation
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A Textbook of Chemistry for Grade 12
based on National Curriculum of Pakistan (NCP) 2022-23

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PREFACE

In a historic footstep, the national curriculum of Pakistan 2022-2023 has introduced a new era for schooling in the country, This is the first-ever core curriculum in the 75-year history of Pakistan. It is in line with the protected right to school education by Article 25-A.

Chemistry might be a difficult subject for someone, but it holds significance for those who embrace a systematic approach to understanding its concepts.

This new Textbook has been developed as a model Textbook for Pakistan. The book consolidates critical thinking methodologies, guiding scientific reasoning, and thinking abilities. The book incorporates problem-solving strategies, which will guide students toward analytical thinking and skills. These skills would be invaluable for both academic as well as practical life.

The book also inspires concept assessment exercises in every unit, which have been designed to evaluate acquired knowledge and promote critical thinking and analysing data.

One of the book`s distinctive features is the key points at the end of each unit, which serve as a quick reference to reinforce the salient features of each unit.

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UTILITY OF CHEMISTRY IN EVERYDAY LIFE

Chemistry plays a vital role in our daily activities, from the food we eat to the medicines we use. Understanding how different chemical processes work helps us make sense of the world around us. From powering our phones with electrochemical cells to understanding the balance of acids and bases in our digestive systems, chemistry shapes every aspect of life. Electrochemistry studies chemical reactions involving the movement of electrons. These reactions help power our modern devices.

- Oxidizing and Reducing Agents are substances that either gain or lose electrons in chemical reactions, such as in batteries or rusting metals.
- Electrochemical Series ranks elements based on their ability to gain or lose electrons, crucial for predicting reaction behaviour.
- Cell Potential measures how much electrical energy is produced by a reaction, used in devices like smartphones.
- Electrochemical Cells are devices that convert chemical energy into electrical energy. Batteries are common examples, including dry cells and rechargeable cells.
- In many reactions, products and reactants exist in a balance, known as equilibrium. Buffers are solutions that resist changes in pH, essential in maintaining the pH balance of our blood. Partition Coefficient is used in separating compounds, it helps in designing effective drugs and understanding how they distribute in the body. Solubility Product concept is used in purifying water, removing unwanted salts, and forming precipitates in laboratory tests.

Acids and Bases are substances which interact with water to form ions. Acids, like vinegar, are sour, while bases, like baking soda, are slippery. They are used in household cleaning, digestion, and even in the environment.

Transition metals have lot of daily life applications from constructing strong materials (e.g., steel) to enhancing electrical efficiency. They play key roles in environmental protection, agriculture, and water treatment by reducing pollution and improving crop production. Additionally, transition metals are essential in advanced technologies, powering batteries, electronics, and space exploration equipment.

Organic compounds have potential use in the fields of agriculture and the chemical industry. They are used in the manufacture of fertilizers, pesticides, and herbicides, improving crop yields. They are also essential in producing pharmaceuticals, cosmetics, shampoos, lotions and cleaning agents. This highlights the vast applications of hydrocarbons in energy, manufacturing, agriculture, and healthcare, making them integral to modern life.

Hydrocarbons have significant contributions in serving our daily lives. They are excellent fuels for powering our houses, vehicles and industries. Pharmaceutical industries use hydrocarbons to synthesis medicines and vitamins to protect and improve our health. Halogenated hydrocarbons are used in making medicines like anesthetics (halothane) and propellant for inhalers. Freon is fluorinated hydrocarbon used as refrigerant.

Alcohols are used in disinfectants and perfumes, while carboxylic acids like vinegar are common in food. Naphthols and Phenols are used in making dyes and antiseptics, they are key ingredients in cleaning agents. Azo-compounds are used to create vivid dyes for fabrics and plastics.

Polymers (Nylon, Kevlar) are long chains of molecules, forming everyday items like clothing and bulletproof vests. Nylon is used in textiles, while Kevlar provides strength in protective gear.

Biochemistry involves studying living organisms at the molecular level. Amines and Amides are found in proteins, amines are essential for life, and amides form the backbone of synthetic fibers like nylon. Lipids, Carbohydrates, and Proteins are macromolecules are the building blocks of life, providing energy, structure, and function to our bodies. Enzymes are proteins that speed up chemical reactions, playing critical roles in digestion and metabolism. Cholesterol is a key component of cell membranes, while insulin regulates blood sugar. DNA and RNA store genetic information, guiding the development of every living thing.

Chromatography ensures drug safety, detects food additives, and monitors water and air quality. It's vital in forensic science for identifying substances at crime scenes. It also ensures the safety of cosmetics and beverages by detecting contaminants.

Materials science impacts daily life through alloys for strength, plastics for durability, and ceramics for heat resistance. Concrete is essential for infrastructure, while catalysts speed up industrial reactions. X-ray crystallography aids drug design by revealing molecular structures.

Qualitative Analysis helps in identifying contaminants, additives, and adulterants in food products, such as checking for harmful heavy metals in water or verifying the purity of food ingredients. Collecting and analyzing data on nutrients like proteins, carbohydrates, and fats in food to provide accurate nutritional information on packaging. Tracking pollutant levels in air, soil, and water to assess environmental quality and comply with safety standards.

Understanding errors like systematic and random errors helps improve accuracy in measuring ingredients or temperatures in cooking and laboratory experiments. Minimizing errors in production lines, for instance, by ensuring precise amounts of chemicals are used in pharmaceutical or food products.

Spectroscopy Techniques like infrared (IR) Spectroscopy is used in identifying organic compounds in essential oils and fragrances by analyzing their IR absorption patterns. Visible Spectroscopy is applied in determining the colour intensity of food dyes and beverages, helping to control colour consistency in food products. Nuclear Magnetic Resonance (NMR) is utilized in pharmaceuticals to determine molecular structure and verify the purity of synthesized drugs.

Industrial Chemistry deals with synthesizing preservatives like sodium benzoate to extend the shelf life of food products. Using organic chemistry to create artificial flavours that mimic natural tastes for beverages, snacks, and desserts.

Drugs like aspirin, penicillin, and antiviral drugs help combat pain and infections.

Chemicals like fertilizers help plants grow, while pesticides protect crops from pests. These substances improve food production, ensuring a steady food supply.

The study of these processes not only enhances our knowledge but also enables us to solve real-world problems. Through this textbook, we will explore everyday applications, helping you connect the science of chemistry with the world around you.

Managing Author

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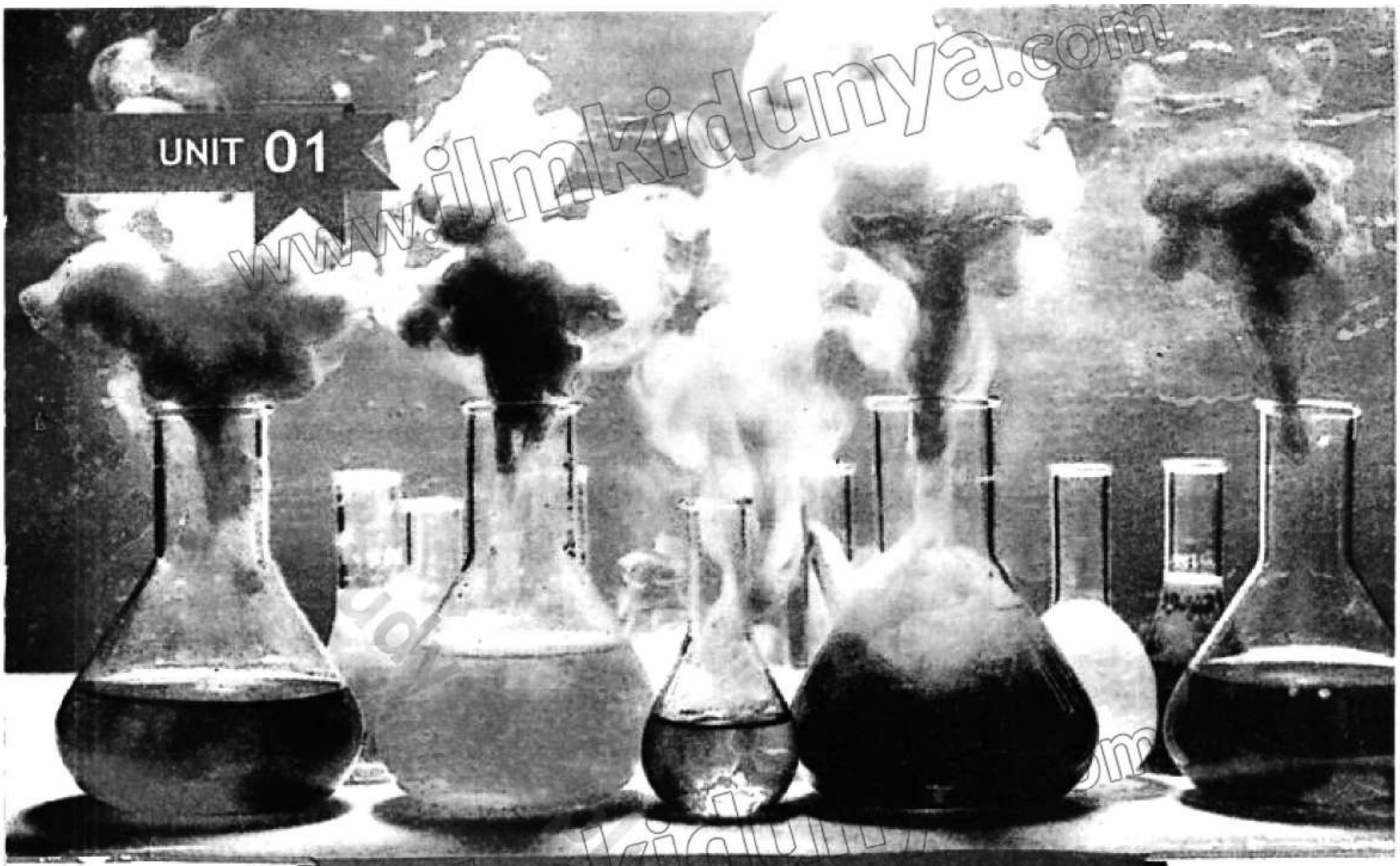
UNIT 01



ETHICS AND VALUES IN CHEMISTRY

Student Learning [illegible]

- Identify common cognitive biases/fallacies that can hinder sound scientific reasoning in physical sciences(some examples include: a. The conformation bias, b. Hasty generalizations, c. Post hoc ergo propter hoc(false cause), d. the straw man fallacy, e. Redefinition(moving the goalposts), f. The appeal to tradition, g. False authority, h. Falling Occam`s Razor, i. Argument from non-testable hypothesis, j. Begging the question, k. Fallacy of exclusion, l. Faulty analogy.
- Explain the pros and cons of ethical considerations involved in the production and use of chemical substances and the processes(some examples include: the impact on human health and the environment; the responsibility of scientists and companies; the role of regulations and laws).
- Explain and apply the following terms to deconstruct the structure of a scientific argument in a variety of formats such as speeches, written articles and advertisement brochures: a. Claims, b. Counterclaims, c. Rebuttals, d. premises, d. conclusions, e.assumptions.

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Morals and beliefs in the field of chemistry are essential for guaranteeing the ethical and positive progress of the discipline. Researchers in chemistry need to follow the rules of truthfulness and openness in their work and writings. They should make sure that their results are precise and can be replicated.

1.1 Cognitive Biases and Fallacies

Cognitive bias is the tendency to make decisions or behave illogically because of our values, memory, socialization and other personal characteristics. In other words, it refers to a certain pattern of thinking based on how our brain works.

Logical fallacies refer to the way we currently make claims and construct our arguments. These are claims that sound convincing at first but can be refuted by logical reasoning.

Some common ones are as follows:

1. Confirmation Bias:

Confirmation bias is the tendency of people to process information by searching for or interpreting information that is consistent with their existing beliefs. This biased approach to decision-making is largely unintentional and results in the individual ignoring information that contradicts their beliefs.

2. Hasty Generalizations:

A hasty generalization fallacy is a claim made on the basis of insufficient evidence. Instead of examining examples and evidence that are much more representative of a typical or average situation, you are using a small, unrepresentative sample to draw a conclusion about a large population.

3. Post Hoc Ergo Propter Hoc (False Cause):

A false cause fallacy happens when an individual wrongly believes that there's a cause-and-effect connection between two objects or happenings. This is an incorrect inference since either there's no such connection or the proof for it is not enough.

This fallacy assumes that if one event occurs after another, the first must be the cause of the second. In the physical sciences, it can mislead scientists into false causal relationships.

4. The Straw Man Fallacy:

The straw man fallacy occurs when someone distorts or exaggerates another's claim and then attacks the distorted version of the claim instead of refuting the original claim.

5. Redefinition (Shifting the Standards):

Altering the criteria for success or acceptance of a theory once it has been achieved. This can hinder scientific advancement by establishing unrealistic expectations for proof.

6. The Appeal to Tradition

Believing something is true or superior just because it's a traditional practice or has been done that manner for a long time. In the realm of physical sciences, this mindset can hinder the acceptance of fresh approaches or concepts that might be more precise or effective.

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7. False Authority:

An informal logical error or a convincing method where it's taken for granted that the views of a well-known authority in one field should be followed in another field. In physical sciences, this could lead to the acceptance of incorrect theories based on an expert's general prestige rather than their specific knowledge.

8. Falling Occam's Razor:

The principle of Occam's razor is frequently mentioned. A 14th-century monk named William of Ockham suggested that if there are two possible explanations for the same event, you should choose the more straightforward one.

9. Argument from Non-Testable Hypothesis:

Proposing a hypothesis that cannot be verified or disproven. This is a major problem in the physical sciences because it weakens the foundation of scientific investigation based on evidence.

10. Begging the Question:

Asking a question that begs an answer is referred to as "begging the question," and is frequently substituted with "a question that seems to require an answer." On the other hand, a less common but more precise definition is "to overlook a question, presuming it has been previously addressed." The term originates from a rendering of an Aristotelian expression translated as "beg the question," but with the actual meaning being "assume the conclusion. In scientific reasoning, this fallacy can result in circular arguments that do not advance understanding.

11. The Fallacy of Exclusion:

Excluding evidence that could disprove a hypothesis. This can severely skew scientific research by ignoring contradictory data.

12. Faulty Analogy:

This error is based on the idea that if two objects share similarities in one or more aspects, they must also share similarities in another aspect. In the realm of physical sciences, this can result in wrong deductions if the comparison doesn't prove valid when examined closely.

1.2 Ethical Considerations in the Production and Use of Chemical Substances

The production and use of chemical substances involve various ethical considerations. These impact human health, the environment, the responsibilities of scientists and companies, and the role of regulations and laws. There are many pros and cons associated with these ethical considerations:

1. Impact on Human Health and the Environment

Chemical substances contribute to numerous benefits, including medical advancements, agricultural improvements, and the creation of everyday products that enhance the quality of life.

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Pros:

Chemicals can solve pressing issues, such as pharmaceuticals treating diseases, fertilizers increasing food production, and clean energy technologies reducing carbon footprints.

Cons:

Exposure to harmful chemicals can cause health problems, such as cancer, respiratory issues etc. This risk is significant for both workers in the chemical industry and the general public. Improper disposal and accidental releases of chemicals can lead to environmental, water and soil pollution.

2. Responsibility of Scientists and Companies

Scientists and companies have the opportunity to lead by example in ethical practices, prioritizing safety and sustainability in their operations and research.

Pros:

Companies can enhance their reputation and consumer trust by adopting corporate social responsibility, practices that focus on reducing their environmental impact and promoting community health.

Cons:

The financial incentives might lead companies to prioritize profits over safety and ethical considerations, potentially resulting in harmful practices and cover-ups of negative effects. Determining who is responsible for chemical-related incidents can be challenging, especially in cases of long-term or diffuse pollution.

3. Role of Regulations and Laws

Regulations and laws are designed to protect public health and the environment by setting safety standards, controlling emissions, and ensuring proper handling and disposal of chemicals.

Pros:

Regulations encourage the development of industry standards and best practices, fostering innovation in safer and more sustainable chemical processes.

Cons:

In some regions, weak or outdated regulations may fail to address current risks, leaving populations and ecosystems vulnerable.

Strict regulations can impose significant compliance costs on companies, potentially stifling innovation and making it difficult for smaller enterprises to compete.

Examples of Ethical Considerations

Pesticides: The use of pesticides in agriculture improves crop yields but poses risks to human health (e.g., exposure to toxic chemicals) and the environment (e.g., contamination of water bodies, harm to non-target species).

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Pharmaceuticals: The development of life-saving drugs benefits society, but the ethical dilemma arises with issues like drug pricing, access to medication, and potential side effects.

Industrial Chemicals: Chemicals used in manufacturing processes can lead to pollution if not managed properly, raising ethical concerns about environmental justice, particularly in low-income communities disproportionately affected by industrial activities.

1.3 Deconstructing the Structure of a Scientific Argument

To break down the framework of a scientific argument presented in different forms like oral presentations, written pieces, and promotional pamphlets, it's important to grasp and pinpoint the main elements of the argument. These components include claims, counterclaims, rebuttals, premises, conclusions, and assumptions.

1. Claims

A claim is a declaration or proposition that represents the central idea or stance of a debate. It's the evidence the speaker or author is attempting to demonstrate.

For instance, in a presentation supporting the use of green energy, a claim could be, "Green energy options like solar and wind are important for minimizing carbon dioxide emissions."

2. Counterclaims

A counterclaim is a statement that opposes the main claim. It represents an opposing viewpoint or objection.

For example, an article discussing renewable energy might include a counterclaim such as, "Renewable energy sources are unreliable and cannot provide a stable energy supply."

3. Rebuttals

A rebuttal challenges and opposes an opposing viewpoint, offering proof or logic to undermine or disprove it.

For instance, when countering the argument that renewable energy is not dependable, a counterargument might be, "Innovations in technology and enhanced methods of energy storage have greatly enhanced the dependability of renewable energy sources."

4. Premises

Premises are the statements or reasons that provide the foundation for the claim. These are the supporting points that lead to the conclusion.

For example, premises for the claim about renewable energy might include:

"Burning fossil fuels releases large amounts of carbon dioxide into the atmosphere."

"Solar and wind power do not produce carbon emissions during operation."

5. Conclusions

The conclusion is the final statement that naturally follows from the initial statements. It represents the ultimate goal of the argument.

For instance, considering the initial statements given, the conclusion could be, "Hence, it is essential to invest in renewable energy to fight against climate change.

6. Assumptions

Assumptions are the basic convictions or declarations accepted without evidence. They lay the groundwork for the reasoning, yet they are not directly mentioned.

For instance, in the case of the renewable energy debate, some assumptions could be:

"Cutting down on carbon emissions is an essential objective."

"The listeners agree that climate change is a significant issue."

"Innovations in technology will keep enhancing the effectiveness of renewable energy technologies."

Application for Various Formats

1. Speeches

Claim: Investing in renewable energy is very important for our future.

Premises: Fossil fuels are limited. They pollute the environment. Renewable energy reduces dependence on foreign oil, so it can boost the economy.

Counterclaim: Renewable energy is insufficient and too expensive.

Rebuttal or Objections: New technologies have improved efficiency and have reduced costs.

Conclusion: We must prioritize investments in renewable energy. This can ensure a sustainable future,

2. Written Articles

Claim: We should switch over to electric vehicles to significantly reduce air pollution in cities.

Premises: Electric cars do not produce emissions. Urban areas suffer from high air pollution.

Counterclaim or Objection: Electric cars still have high costs due to battery production.

Rebuttal: Recycling and advances in battery technology have reduced these environmental impacts.

Conclusion: "Therefore, promoting the use of electric cars is the best strategy to improve air quality.

3. Brochures

Claim: Our new eco-friendly product is the best choice for environmentally conscious consumers.

Premises: It is made from 100% recycled materials. It reduces waste and pollution. Hence, it supports sustainable practices.

Counterclaim: It is eco-friendly products but tends to be more expensive and less durable.

Objections: Our product is competitively priced. It has undergone rigorous durability testing.

Conclusion: Choosing our products ensure a greener and more sustainable lifestyle.

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KEY POINTS

- Sound scientific reasoning is essential for accurate results and meaningful discoveries.
- Drawing broad conclusions from a small or unrepresentative sample can lead to erroneous results.
- Drawing an analogy between two unrelated things and assuming they share a particular property is called faulty analogy.
- Chemical substances contribute to numerous benefits, including medical advancements, agricultural improvements, and the creation of everyday products that enhance quality of life.
- Regulations and laws are designed to protect public health and the environment.
- The use of pesticides in agriculture improves crop yields but poses risks to human health.
- A claim is a statement or assertion that is the main point or position of an argument. It is what the speaker or writer is trying to prove.
- A counterclaim is a statement that opposes the main claim. It represents an opposing viewpoint or objection.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. What is cognitive bias?

a) The process of making decisions based on logical reasoning.

b) The tendency to make decisions based on personal characteristics and beliefs.

c) The evaluation of arguments using empirical evidence.

d) The method of constructing arguments using logical fallacies.

ii. What is a hasty generalization fallacy?

a) Drawing a conclusion based on a large, representative sample

b) Drawing a conclusion based on insufficient evidence

c) Drawing a conclusion by misrepresenting an opponent's argument

d) Drawing a conclusion based on a false cause-and-effect relationship

iii. What does the post hoc ergo propter hoc fallacy assume?

a) One event is caused by another simply because it follows it

b) One event is unrelated to another

c) One event is the result of a thorough investigation

d) One event is part of a larger series of events

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iv. Which fallacy involves attacking a distorted version of an opponent's claim?

a) Confirmation Bias b) Hasty Generalizations

c) The Straw Man Fallacy d) Redefinition

v. What does the principle of Occam's Razor advocate?

a) Choosing the most complex explanation for an event
b) Choosing the simplest explanation for an event
c) Choosing an explanation based on tradition
d) Choosing an explanation based on authority

vi. What is an example of the appeal to tradition fallacy?

a) Believing a theory is valid because an expert supports it
b) Believing a practice is correct because it has always been done that way
c) Believing an argument because it cannot be tested
d) Believing a hypothesis because it is the simplest explanation

vii. Which of the following is a pro of chemical substances?

a) They always have a negative impact on health
b) They reduce carbon footprints through clean energy technologies
c) They are always safe for workers
d) They never cause environmental pollution

viii. What is a con of weak or outdated regulations regarding chemicals?

a) They protect public health effectively
b) They foster innovation in chemical processes
c) They fail to address current risks
d) They reduce compliance costs for companies

ix. What role do premises play in a scientific argument?

a) They oppose the main claim
b) They provide the foundation for the claim
c) They represent the conclusion
d) They are unsupported assumption

x. In the context of written articles, what would be a counterclaim for promoting electric vehicles?

a) Electric cars produce no emissions
b) Urban areas suffer from high air pollution
c) Electric cars still have high environmental costs due to battery production

3. Short Answer Questions

i. Define cognitive bias.
ii. What is a false cause fallacy?
iii. Describe the straw man fallacy.
iv. What does the fallacy of exclusion involve?
v. Give an example of a faulty analogy.
vi. List one pro and one con of chemical substances in terms of human health and the environment.
vii. What is the responsibility of scientists and companies in the production and use of chemical substances?
viii. Why are regulations and laws important in the chemical industry?
ix. What is a claim in the context of a scientific argument?
x. Provide an example of an assumption in a debate about renewable energy.

4. Long Answer Questions

i. Explain confirmation bias and its potential impact on scientific research.
ii. Discuss the ethical considerations in the production and use of chemical substances, highlighting the balance between benefits and risks.
iii. Deconstruct the structure of a scientific argument using the example of promoting electric vehicles to reduce air pollution.
iv. Analyse the role of regulations and laws in ensuring ethical practices in the chemical industry, citing specific examples.
v. Evaluate the pros and cons of using pesticides in agriculture, considering both human health and environmental impacts.

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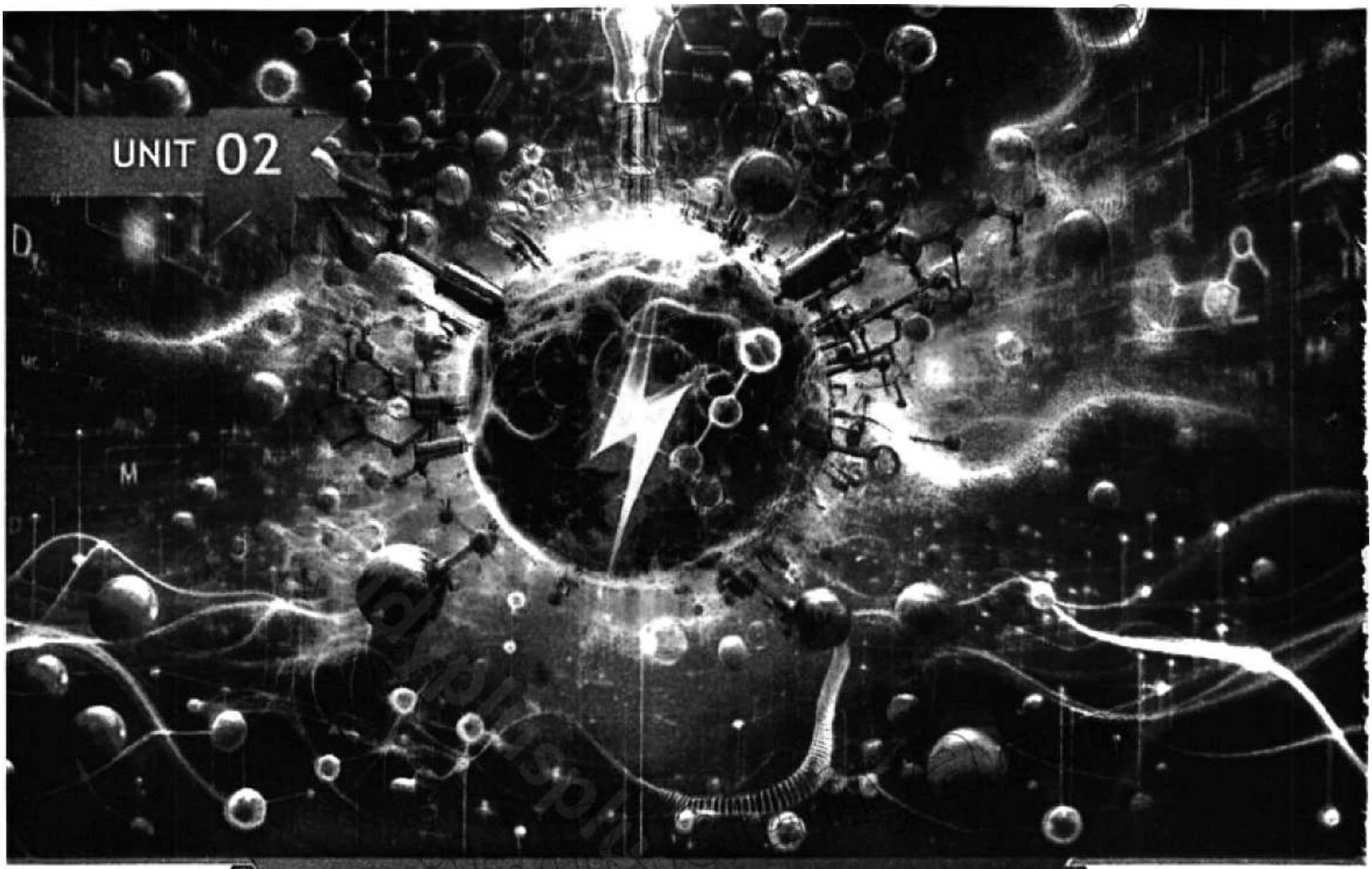
UNIT 02



ELECTROCHEMISTRY

Student Learning Outcomes (SLOs)

- Apply the concept of oxidation numbers in identifying oxidation and reduction reactions.
- Apply the concept of changes in oxidation numbers to balance chemical equations.
- Define the terms redox, oxidation, reduction, and disproportionation (in terms of electron transfer and changes in oxidation number).
- Identifying the oxidizing and reducing agents in a redox reaction.
- Describe the role of oxidizing and reducing agents in the redox reaction.
- Explain the concept of the activity series of metals and how it relates to the ease of oxidation.
- Deduce the feasibility of redox reactions from activity series or reaction data.
- Explain the use of the Winkler Method to measure biochemical oxygen demand(BOD) and its use as a measure of water pollution.
- Explain how electrolytic cells convert electrical energy to chemical energy, with oxidation at the anode and reduction at the cathode.

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- Predict the identities of substances liberated during electrolysis based on the electrolyte, position in the redox series, and concentration.
- Apply the relationship between the Faraday constant, Avogadro constant, and the charge on the electron to solve problems.
- Calculate the quantity of charge passed during electrolysis and the mass or volume of substance liberated during electrolysis.
- Deduce the Avogadro constant by an electrolytic method.
- Define the terms standard electrode potential and standard cell potential.
- Describe the standard hydrogen electrode and methods used to measure standard electrode potential.
- Calculate the standard cell potentials by combining the potentials of two standard electrodes and then use these to predict the feasibility of a reaction and the direction of electron flow in a simple cell.
- Deduce the relative reactivity of elements, compounds, and ions as oxidizing agents or reducing agents from their electrode potential values.
- Construct redox equations using relevant half-equations.
- Explain how electrode potential varies with the concentrations of aqueous ions and use the Nernst equation to predict this quantitatively.
- Explain how voltaic (galvanic) cells convert energy from spontaneous, exothermic chemical processes to electrical energy, with oxidation at the anode and reduction at the cathode.
- Explain how voltaic cells convert chemical energy from redox reactions to electrical energy using Cu-Zn galvanic cells as an example.

Electrochemistry is concerned with a wide range of significant processes, many of which are dependent on the exchange of electrons from one chemical to another. Electrochemical processes include redox (oxidation-reduction) reactions, where the energy released during spontaneous reactions is converted into electricity, or in which the electricity is used to induce a non-spontaneous reaction. Redox reactions involve the transfer of electrons between two or more substances. Electrochemistry deals with energy sources that are highly efficient, such as batteries, and fuel cells. The chemistry of these devices is discussed here.

2.1 Oxidation - Reduction Concepts

Recall the definition of oxidation and reduction in terms of transfer of oxygen or hydrogen or electrons. Here we will discuss oxidation and reduction in terms of loss or gain of electrons by a chemical reaction.

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Example 2.1

When a piece of zinc metal is dipped in an aqueous solution of $CuSO_4$, it is observed that a dark brown layer of copper begins to form at the zinc surface. At the same time, the blue colour of the solution is discharged. If we analyse this solution we find that Zn^{++} ions are present in the solution. The change can be described by the following chemical equation.

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

This reaction can be described in terms of two-half reactions.

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

In this reaction, zinc metal loses two electrons and changes into Zn^{2+} ions while Cu^{2+} ions gain two electrons and give copper metal. The two processes taking place simultaneously are called oxidation-reduction reactions.

"A reaction in which a substance loses electrons is called oxidation. The reaction in which a substance gains electrons is called reduction. Oxidation-reduction reactions are also known as redox reactions. In a redox reaction, elements undergo a change in their oxidation number.

2.1.1 Oxidation Number

The oxidation number (oxidation state) is defined as the apparent charge, positive or negative, which an element would have in a compound.

2.1.2 Oxidation-Reduction in Terms of Change in Oxidation Number

We have already defined oxidation and reduction in terms of the transfer of one or more electrons. We can also define oxidation and reduction in terms of change in oxidation number. An increase in oxidation number is called oxidation and a decrease in oxidation number is called reduction. For example;

$$2Na_{(g)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$$

Assign oxidation numbers to all the atoms involved in this reaction and write it over their symbols.

$$2\overset{0}{Na}_{(g)} + \overset{0}{Cl}_{2(g)} \longrightarrow 2Na^{1+}Cl^{1-}_{(s)}$$

Note that the oxidation number of Na is zero because it is in its elemental form. In this reaction, the oxidation number of Na changes from zero to +1 when it loses one electron, which is called oxidation.

$$2\overset{0}{Na}_{(g)} \longrightarrow 2\overset{1+}{Na}_{(g)} + 2e^-$$

On the other hand, each Cl atom in the Cl_2 molecule changes its oxidation number from zero to -1, gains one electron, and is called reduction.

$$\overset{0}{Cl}_{2(g)} + 2e^- \longrightarrow 2Cl^{1-}_{(g)}$$

So we can also define oxidation and reduction in terms of change in oxidation number.

Oxidation is an increase in oxidation number (loss of electrons).

Reduction is a decrease in oxidation number (gain of electrons).

Example 2.2

Identify the elements undergoing oxidation or reduction in terms of change in oxidation number in the following reaction which takes place in the combustion of natural gas.

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$$

Solution

Assign oxidation number to all the atoms involved in this reaction.

$$\overset{4-}{C}\overset{(1+)4}{H}_{4(g)} + 2\overset{0}{O}_{2(g)} \longrightarrow \overset{+4}{C}\overset{(2-)2}{O}_{2(g)} + 2\overset{2(1+)}{H}_2\overset{2-}{O}_{(l)}$$

The C changes its oxidation number from -4 in CH_4 to +4 in CO_2 whereas oxygen changes its oxidation number from 0 to -2. This means C undergoes an increase in oxidation number. On the other hand, O changes its oxidation number from zero in O_2 to -2 in H_2O and CO_2. Each oxygen atom gains two electrons and therefore it is reduced.

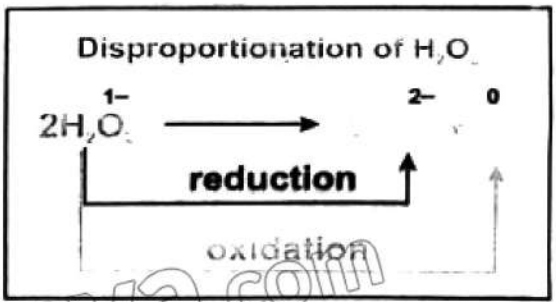
We can say that,

i) C is oxidized because there has been an increase in its oxidation number.

ii) O is reduced because there has been a decrease in its oxidation number.

2.1.3 Disproportionation Reaction

In some redox reactions, the same element is oxidised and reduced simultaneously. Such reactions are called self-oxidation-reduction reactions or disproportionation reactions. For example, consider the decomposition of hydrogen peroxide. In this reaction, oxygen is oxidized to 0 in O_2 and reduced to 2- in H_2O.



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CONCEPT ASSESSMENT EXERCISE 2.1

Use the oxidation number change method to identify the atoms undergoing oxidation or reduction in the following redox reactions.

$$Cl_{2(g)} + 2NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + NaClO_{(aq)} + H_2O_{(l)}$$

$$4Fe_{(s)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}$$

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(l)}$$

2.2 Balancing of Equations

i. Redox Method (Oxidation Number Method)

ii. Ion Electron Method

i. Redox Method (Oxidation Number Method)

It is based on the principle that in any redox reaction, the total number of electrons lost by one element must be equal to the total number of electrons gained by another element. This method can be understood by the following example.

Example 2.3

Balance the following equation by the oxidation number method.

$$P + HNO_3 + H_2O \longrightarrow H_3PO_4 + NO$$

Solution

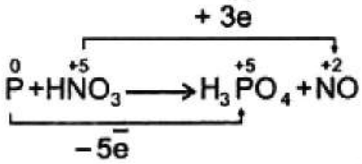
Step 1: **Assign oxidation numbers to all the atoms involved in the equation.**

$$\overset{0}{P} + \overset{+1\,+5\,(-2)3}{HNO_3} + \overset{(+1)2\,-2}{H_2O} \longrightarrow \overset{3(+1)+5(-2)4}{H_3PO_4} + \overset{+2\,-2}{NO}$$

Step 2: **Identify the elements changing oxidation number.**

The P goes from zero to +5 oxidation state in H_3PO_4. This is 5 electrons change. N in HNO_3 goes from +5 to +2 oxidation state in NO. This is 3 electron change.

Step 3: **Draw a bridge between the same atoms whose oxidation numbers have changed, Indicate this change by the number of electrons gained or lost by each element.**



Step 4: **Equalize the number of electrons lost and gained by multiplying the two numbers, by a small whole number which produces a common number. Use these multiples as coefficients of the respective substance.**

To balance a $3e^-$ gain against a $5e^-$ loss, we need to multiply $3e^-$ gain by 5 and $5e^-$ loss by 3. This will equalize the number of electrons gained and lost.

$$+3\bar{e}\times 5 = +15\bar{e}$$

$$\overset{0}{P} + H\overset{+5}{N}O_3 \longrightarrow H_3\overset{+5}{P}O_4 + \overset{+2}{N}O$$

$$-5\bar{e}\times 3 = -15\bar{e}$$

Multiply the coefficients of P and that of H_3PO_4 by 3. Whereas multiply the coefficients of HNO_3 and NO by 5.

$$3P + 5HNO_3 + H_2O \longrightarrow 3H_3PO_4 + 5NO$$

Now the coefficient of H_3PO_4 and NO should not be changed hereafter it.

Step 5: **Balance the rest of the equation by inspection method. Balance the atoms other than oxygen and hydrogen first, then oxygen atoms and finally hydrogen atoms.**

To balance oxygen atoms, multiply coefficient of H_2O by 2.

$$3P + 5HNO_3 + 2H_2O \longrightarrow 3H_3PO_4 + 5NO$$

Inspect the equation, it is balanced.

CONCEPT ASSESSMENT EXERCISE 2.2

Using the oxidation number method balance the following equation.

1. $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$
2. $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

2.2.1 Construction of Redox Equations

There are two half-reactions in any given oxidation and reduction reaction: the oxidation-half reaction and the reduction-half reaction. The oxidation and reduction reaction is the sum of the two half-reactions.

We can balance the half-reaction by the ion-electron method. Equalise the number of electrons lost and gained in the two half-reactions and combine them. The rest of the equation is balanced by the inspection method. The steps involved in this method can be understood by considering the following example.

Example 2.4

Construct a redox equation using the following half-equations.

Reduction half-reaction:

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$

Oxidation half-reaction:

$$H_2SO_3 \longrightarrow HSO_4^-$$

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Step 1:

Balance each half-reaction. First, consider reduction half-reaction. Two Cr atoms on the left require 2 before Cr^{+3}

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

There are seven O atoms on the left and none on the right. We will add 7 H_2O on the right side.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

There are 14 H atoms on the right and none on the left, so we will add 14 H^+ on the left side.

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

Now balance charges. The left side has one di-negative and 14 mono-positive charges, corresponding to -2 +14 = +12. The right side has two tri-positive charges corresponding to +3 × 2 = +6. Thus left side needs $6e^-$.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \qquad ---(1)$$

In the other half-reaction (Oxidation half-reaction), S atoms are already balanced.

$$H_2SO_3 \longrightarrow HSO_4^-$$

Balance O - atoms. As there are three O - atoms on the left and four on the right, we will add one H_2O to the left.

$$H_2SO_3 + H_2O \longrightarrow HSO_4^-$$

There are four H-atoms on the left and one on the right. We will add $3H^+$ to the right.

$$H_2SO_3 + H_2O \longrightarrow HSO_4^- + 3H^+$$

For charge, the left side is neutral, but the right side has a net charge of (-1) + (+3) = +2.

Thus, we will add $2e^-$ to the right side.

$$H_2SO_3 + H_2O \longrightarrow HSO_4^- + 3H^+ + 2e^- \qquad -----(2)$$

Step 2:

Equalize the number of electrons transferred in the two half-reactions and add half-reactions. Reduction half-reaction uses up $6e^-$ and oxidation half-reaction produces $2e^-$. Therefore, multiplying equation (1) by one and equation (2) by three and adding two equations we get.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$3H_2SO_3 + 3H_2O \longrightarrow 3HSO_4^- + 9H^+ + 6e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 3H_2SO_3 + 3H_2O + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O + 3HSO_4^- + 9H^+ + 6e^-$$

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Step 3:

Cancel the duplication. Duplications are $6e^-$, $3H_2O$ and $9H^+$. Strike these out from both sides.

$$Cr_2O_7^{2-} + 5H^+ + 3H_2SO_3 \longrightarrow 2Cr^{3+} + 4H_2O + 3HSO_4^-$$

(-2) (+5) (+6) (-3)

= +3 = +3

Result:

Since LHS charges are equal to RHS charges, therefore the equation is balanced.

CONCEPT ASSESSMENT EXERCISE 2.3

Use the half-reaction method to balance the following redox reactions.

(i) $Co + Cr^{3+} \longrightarrow Co^{2+} + Cr^{2+}$ (ii) $Au^{3+} + H_2 \longrightarrow H^+ + Au$

(iii) $Cl_2 + I^- \longrightarrow I_2 + Cl^-$

CONCEPT ASSESSMENT EXERCISE 2.4

Construct a redox equation from the following half-equations.

1. $MnO_4^- \rightarrow Mn^{2+}$ and $H_2O_2 \rightarrow O_2$
2. $NO_3^- \rightarrow NO$ and $Br^- \rightarrow Br_2$
3. $MnO_4^- \rightarrow Mn^{2+}$ and $C_2O_4^{2-} \rightarrow CO_2$

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2.3 Oxidizing and Reducing Agents

An oxidizing agent is a substance that accepts electrons and causes oxidation, therefore, its oxidation state decreases. A reducing agent is a substance that causes reduction through the loss of electrons; therefore, its oxidation state increases. This means an oxidizing agent is a substance that causes the oxidation of another substance. On the other hand, a reducing agent is the substance that causes another substance to reduce.

An oxidizing agent contains an element that is being reduced (gaining electrons). The reducing agent contains an element that is being oxidized (losing electrons). Consider the following reaction.

$$3\overset{0}{P} + 5\overset{+1}{H}\overset{+5}{N}\overset{(-2)3}{O_3} + 2\overset{(+1)2}{H_2}\overset{-2}{O} \longrightarrow 3\overset{3(+1)}{H_3}\overset{+5}{P}\overset{(-2)4}{O_4} + 5\overset{+2}{N}\overset{-2}{O}$$

P is undergoing oxidation, so it is reducing agent. Whereas N present in HNO_3 is undergoing reduction HNO_3 is an oxidising agent. Similarly,

$$\overset{+4}{Mn}O_2 + 4H\overset{-1}{Cl} \longrightarrow \overset{+2}{Mn}Cl_2 + 2H_2O + \overset{0}{Cl_2}$$

Mn present in MnO_2 is undergoing reduction, therefore MnO_2 is an oxidising agent. Cl of HCl is oxidised, so HCl is a reducing agent.

How can you identify oxidising and reducing agents in a chemical reaction?

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CONCEPT ASSESSMENT EXERCISE 2.5

Identify the oxidising and reducing agents in the following reaction.

$$CuO + H_2 \rightarrow Cu + H_2O$$

Activity 2.1: Identifying Oxidizing and Reducing Agents

Prepare solutions of ferrous sluphate ($FeSO_4$) and potassium permanganate ($KMnO_4$) in separate beakers. Transfer about 10cm^3 of ferrous sulphate solution in a test tube. Add about 10cm^3 of dil. H_2SO_4 in it. Now add a few drops of $KMnO_4$ the solution in the test tube. What happens?

$FeSO_4$ reduces $KMnO_4$, so its purple colour is discharged. $KMnO_4$ oxidizes $FeSO_4$ in this reaction. $FeSO_4$ is a reducing agent whereas $KMnO_4$ is an oxidizing agent.

How can you identify oxidizing and reducing agents in a chemical reaction?

Consider the following reaction that takes place in the manufacture of steel.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

To identify the oxidizing and reducing agents, work out the oxidation states of all the elements involved in the reaction.

$$\overset{2(+3)\ (-2)3}{Fe_2O_3} + \overset{+2\ -2}{3CO} \longrightarrow \overset{0}{2Fe} + \overset{+4(-2)2}{3CO_2}$$

(i) Carbon is being oxidized because there is an increase in its oxidation state.

(ii) Fe is being reduced because there is a decrease in its oxidation state.

(iii) The reactant CO contains the C that is being oxidized, so CO is a reducing agent.

(iv) The reactant Fe_2O_3 contains the Fe that is being reduced. So Fe_2O_3 is an oxidizing agent.

Oxidizing or reducing agent is the whole molecule or formula unit and not the atom that has undergone a change in oxidation number. The oxidizing agent facilitates oxidation by accepting electrons, while the reducing agent promotes reduction by donating electrons.

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2.4 Electrode, Electrode Potential and Electrochemical Series

2.4.1 The Galvanic Cell (Daniel Cell)

When a Zn rod is dipped into a copper(II) sulphate solution, zinc atoms are oxidized to zinc ions, and copper (II)ions are reduced to copper metal, which deposits on the zinc rod. The following reaction occurs:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

In this reaction, electrons flow directly from the zinc rod to Cu^{2+} ions in solution. However, if the electrons transfer from the zinc rod to the copper ions in solution could be directed through an external circuit, the spontaneous redox reaction could be used to generate an electric current. But when a zinc rod dipped in zinc sulphate solution in one container is connected by a copper wire to the copper rod dipped in copper (II) sulphate solution in a separate container, no current flows through the external circuit. However, when the two solutions are connected with a tube (**salt bridge**) filled with a solution of an electrolyte such as KCl, KNO_3 or Na_2SO_4, the current flows through the external circuit.

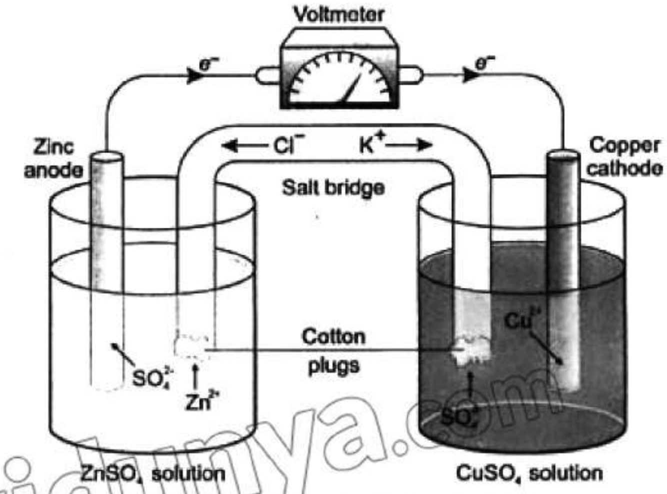

Fig 2.1: A simple Galvanic Cell

The salt bridge allows the movement of ions from one solution to the other without mixing the two solutions. It maintains electrical neutrality within the internal circuit of the cell by allowing ions to flow between the two half-cells. This flow of ions prevents the buildup of charge in either half-cell, which would otherwise stop the reaction and the flow of electricity. (See Fig. 2.1)

Half-cell, in which oxidation occurs is called an oxidation half-cell or anode half-cell. The other half-cell, in which reduction occurs is called a reduction half-cell or cathode half-cell. The reaction taking place in the oxidation half-cell is called the oxidation half reaction and the reaction taking place in the reduction half-cell is called the reduction half reaction. The electrode at which oxidation occurs is called the anode. The electrode at which reduction occurs is called the cathode.

Zn has a greater tendency to lose electrons than Cu. Therefore, the Zn electrode acquires a negative charge relative to the Cu electrode. The electrons flow from the Zn electrode through the external circuit to the Cu electrode. The following half-cell reactions occur at the two electrodes.

At anode: $Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^-$ (Oxidation half-reaction)

At cathode: $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ (Reduction half-reaction)

Overall cell reaction

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

An electrochemical cell in which a spontaneous redox reaction produces an electric current is known as a galvanic or voltaic cell.

2.4.2 Cell Potential

The cell potential for a galvanic cell is literally the potential of the cell to do work on its surroundings by driving an electric current through a wire. The work that can be accomplished when electrons are transferred through a wire depends upon the push or force behind the electrons.

The force with which electrons are pushed to flow through the wire from the anode to the cathode is called the electromotive force or emf. It is measured in **volts (V).**

The emf produced by the galvanic cell is called cell potential (E^0 cell). It depends upon the difference in the electrode potentials of the two half-cells joined in series. Thus the electrode with a more negative reduction potential acts as the anode and the electrode with a more positive reduction potential acts as the cathode. Thus under standard conditions (1 mol dm^{-3} concentration at 25 °C and 1 atm pressure), the reaction with a more negative E° value occurs as oxidation (anode reaction). The reaction with a more positive E° value occurs as reduction (cathode reaction). The voltage of any cell under standard conditions can be calculated using tabulated standard reduction potentials (see Table 2.1).

The combination of two half-cells will produce a complete cell. The overall cell reaction is obtained by suitably combining the equations for the two half-reactions. Standard cell potential E°_{cell} or emf of the cell is the algebraic difference between the respective standard reduction potentials of the two half-cells.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

The cell potential has a positive value for any spontaneous redox reaction. The potential of a galvanic cell can be measured with a voltmeter. However, a single half-cell potential or the **electrode potential** cannot be measured directly. This is because one half-cell reaction cannot occur without a simultaneous reaction in another half-cell. However, the relative half-cell potential (electrode potential) can be determined by coupling it with the **standard hydrogen electrode (SHE)** as a reference electrode, with a standard potential of 0.00 volt.

The standard electrode potential is defined as the tendency of a half-cell reaction to undergo reduction relative to the standard hydrogen electrode. Its potential difference developed when an electrode of an element is placed in a solution containing ions of that element when all the components are in their standard state i.e. 1 atm. for gases, 1M for solutions, pure solid for electrode, and at 25 °C.

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2.4.3 Standard Hydrogen Electrode

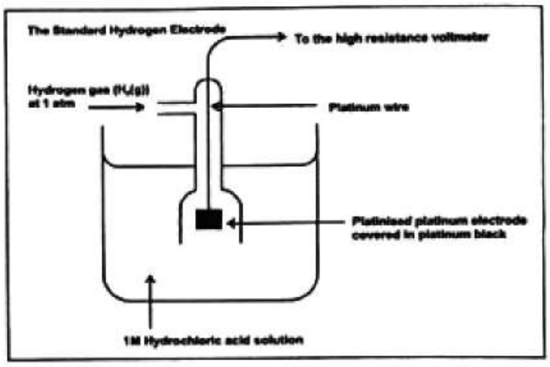

Fig 2.2: Standard Hydrogen Electrode

A standard hydrogen electrode (SHE) consists of a platinum foil coated with finely divided platinum, surrounded by hydrogen gas at 1atm pressure in contact with 1M HCl solution at 298K, as shown in Fig. 2.2. Its electrode potential is arbitrarily chosen as zero at all temperatures.

By convention, the half-cell potential for reduction of $H^+_{(aq)}$ to H_2 gas or the potential for the oxidation of H_2 to $H^+_{(aq)}$ in standard hydrogen, a half-cell is defined as exactly 0.00V.

Reduction: (act as cathode)

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)} \qquad E^o_{H^+/H_2} = 0.00V$$

Oxidation: (act as anode)

$$H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^- \qquad E^o_{H_2/H^+} = 0.00V$$

S.H.E. can act as a cathode or anode depending upon the nature of the electrode with which it is connected to complete an electrochemical cell.

The symbol E^o designates a standard potential i.e., the potential measured under standard conditions (1M concentration, 1 atm pressure, and 25 °C).

2.4.4 Method to measure the electrode potentials

The Standard Hydrogen Electrode (SHE) is the primary reference electrode used to measure the standard electrode potentials of other half-cells, such as copper and zinc. It has a standard electrode potential of 0 V by definition.

Determination of Standard Electrode Potential of Zn^{2+}/Zn Electrode

An Electrochemical Cell is Setup in which a zinc rod is dipped in 1 M zinc Sulphate solution. This half-cell is combined with a standard hydrogen electrode through a salt bridge. The deflection of the voltmeter indicates that current is flowing from the zinc electrode to the hydrogen electrode or the electrons are moving from the zinc rod to the hydrogen electrode. Hence the zinc electrode acts as an anode and the SHE acts as a cathode. In this case, the reading (E^o) by the voltmeter is 0.76 V. The cell can be represented as

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$$

Calculations

The E^o_{Cell} is 0.76 volt

$E^o_{Cell} = E^o_{Anode} + E^o_{Cathode}$

$0.76 = E^o_{Anode} + 0$ or $E^o_{Anode} = +0.76\ V$

Hence oxidation potential of zinc is 0.76 V and the reduction potential of zinc will be - 0.76 V.

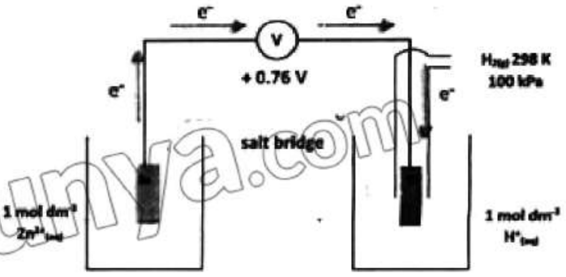

Fig 2.3: Measurement of Standard Electrode Potential of Zn/Zn^{2+} Electrode

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Determination of Standard Electrode Potential of Cu^{2+}/Cu Electrode

An Electrochemical Cell is set up in which a copper rod is dipped in 1 M copper sulphate solution. This half-cell is combined with a standard hydrogen electrode through a salt bridge. The deflection of the voltmeter indicates that current is flowing from the hydrogen electrode to the copper electrode or the electrons are moving from the hydrogen rod to the copper electrode. Hence the copper electrode acts as a cathode and the hydrogen electrode acts as an anode. In this case, the reading (EMF) by the voltmeter is 0.34 V. The cell can be represented as

$$Cu^{2+}_{(aq)} + H_{2(g)} \rightarrow 2H^+_{(aq)} + Cu_{(s)}$$

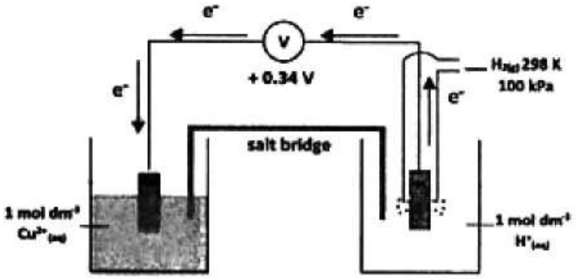

Fig 2.4: Measurement of Standard Electrode Potential of Cu^{2+}/Cu Electrode

Calculations

The E^o of the cell is 0.34 volt

$E^o_{Cell} = E^o_{Anode} + E^o_{Cathode}$

$0.34 = 0.0 + E^o_{Cathode}$ or $E^o_{Cu2+/Cu} = +0.34$ V

Hence reduction potential of copper is 0.34 V and the oxidation potential of copper will be -0.34V.

Table 2.1: Reduction potentials of some elements, ions and compounds

Reduction Half-reaction	E^0 (Volts)
$Li^+ + \bar{e} \rightleftharpoons Li$	-3.05
$K^+ + \bar{e} \rightleftharpoons K$	-2. 92
$Ba^{2+} + 2\bar{e} \rightleftharpoons Ba$	-2.90
$Ca^{2+} + 2\bar{e} \rightleftharpoons Ca$	-2.76
$Na^{1+} + 1\bar{e} \rightleftharpoons Na$	-2.71
$Mg^{2+} + 2\bar{e} \rightleftharpoons Mg$	-2.38
$Al^{3+} + 3\bar{e} \rightleftharpoons Al$	-1.67
$Mn^{2+} + 2\bar{e} \rightleftharpoons Mn$	-1.03
$2H_2O + 2\bar{e} \rightleftharpoons H_2 + 2OH^-$	-0.83
$Zn^{2+} + 2\bar{e} \rightleftharpoons Zn$	-0.76
$Cr^{3+} + 3\bar{e} \rightleftharpoons Cr$	-0.74
$Fe^{2+} + 2\bar{e} \rightleftharpoons Fe$	-0.44
$PbSO_4 + 2\bar{e} \rightleftharpoons Pb + SO_4^{2-}$	-0.36
$Ni^{2+} + 2\bar{e} \rightleftharpoons Ni$	-0.25
$Sn^{2+} + 2\bar{e} \rightleftharpoons Sn$	-0.14

$Pb^{2+} + 2\bar{e} \rightleftharpoons Pb$	-0.13
$Fe^{3+} + 3\bar{e} \rightleftharpoons Fe$	-0.04
$2H^+ + 2\bar{e} \rightleftharpoons H_2$	0.00
$AgCl + \bar{e} \rightleftharpoons Ag + Cl^-$	+0.22
$Hg_2Cl_2 + 2\bar{e} \rightleftharpoons 2Hg + 2Cl^-$	+0.27
$Cu^{2+} + 2\bar{e} \rightleftharpoons Cu$	+0.34
$Cu^+ + 1\bar{e} \rightleftharpoons Cu$	+0.52
$I_{2(aq)} + 2\bar{e} \rightleftharpoons 2I^-$	+0.54
$Fe^{3+} + \bar{e} \rightleftharpoons Fe^{2+}$	+0.77
$Ag^+ + \bar{e} \rightleftharpoons Ag$	+0.80
$Br_{2(aq)} + 2\bar{e} \rightleftharpoons 2Br^-$	+1.09
$O_2 + 4H^+ + 4\bar{e} \rightleftharpoons 2H_2O$	+1.23
$MnO_2 + 4H^+ + 2\bar{e} \rightleftharpoons Mn^{2+} + 2H_2O$	+1.28
$Cr_2O_7^{2-} + 14H^+ + 6\bar{e} \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cl_{2(g)} + 2\bar{e} \rightleftharpoons 2Cl^-$	+1.36
$2ClO_3^{-1} + 12H^+ + 10\bar{e} \rightleftharpoons Cl_2 + 6H_2O$	+1.47
$8H^+ + MnO_4^- + 5\bar{e} \rightleftharpoons Mn^{2+} + 4H_2O$	+1.49
$PbO_2 + SO_4^{-2} + 4H^+ + 4\bar{e} \rightleftharpoons PbSO_4 + 2H_2O$	+1.69
$H_2O_2 + 2H^+ + 2\bar{e} \rightleftharpoons 2H_2O$	+1.7
$S_2O_3^{-2} + 2\bar{e} \rightleftharpoons 2SO_4^{-2}$	+2.00
$F_2 + 2\bar{e} \rightleftharpoons 2F^-$	+2.87

2.4.4 Determination of Cell Potential

A cell reaction consists of two half-reactions. Reduction takes place in the half-cell having greater value of reduction potential. Oxidation takes place in the half-cell having the smaller value of reduction potential. The equation of the half-cell reaction having a smaller value of reduction potential is reversed and added to the equation of the half-cell having a greater value of reduction potential. The sum of these two equations represents cell reaction.

Standard cell potential E^o_{cell} or emf of the cell is the algebraic difference between the respective standard reduction potentials of the two half-cells.

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

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Example 2.5

Calculate E° cell for the Zn-Cu cell and write cell reactions. Predict the direction of electron flow.

Solution

	Half Cell-reaction	Reduction potential
i)	$Zn^{++}_{(aq)} + 2\bar{e} \longrightarrow Zn_{(s)}$	- 0.76V
ii)	$Cu^{++}_{(aq)} + 2\bar{e} \longrightarrow Cu_{(s)}$	+ 0.34V

Data indicates that the reduction potential of the second half-cell is greater than the first. Hence reduction reaction will occur in the second half-cell and oxidation in the first half-cell. Reverse the first equation and add it to the second equation to get the cell reaction.

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2\bar{e} \quad \text{(Oxidation half-reaction)}$$

$$Cu^{2+}_{(aq)} + 2\bar{e} \longrightarrow Cu_{(s)} \quad \text{(Reduction half-reaction)}$$

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)} \quad \text{(Cell reaction)}$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = E^0_{Cu} - E^0_{Zn}$$

$$E^0_{cell} = +0.34 - (-0.76)$$

$$E^0_{cell} = +1.10V\ s$$

Since E^0_{cell} is positive, the electrons will flow from the anode to the cathode i.e., from the Zn electrode to the Cu electrode.

Example 2.6

The standard reduction potentials for the following half-reactions are:

$Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$ $\quad E^0 = -0.25V$

$Mg^{2+}_{(aq)} + 2e^- \longrightarrow Mg_{(s)}$ $\quad E^0 = -2.38V$

Calculate E^0_{cell} for Ni-Mg cell, write cell reaction, and direction of electron flow, and identify the anode of the cell.

Solution:

Data indicates that the reduction potential of the first reaction is greater than that of the second reaction. Hence reduction will occur in the first reaction and oxidation in the second reaction. Reverse the second reaction and add it to the first reaction to get the cell reaction.

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$$Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2e^- \quad \text{(Anode reaction)}$$

$$Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)} \quad \text{(Cathode reaction)}$$

$$Mg_{(s)} + Ni^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Ni_{(s)} \quad \text{(Cell reaction)}$$

Thus Mg will act as the anode and Ni as the cathode. Electrons will flow from Mg to Ni.

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = E^0_{Ni} - E^0_{Mg}$$

$$= -0.25 \quad -(-2.38)$$

$$= 2.13\ V$$

Since E^0_{cell} is positive, the Electrons will flow from the anode to the cathode i.e., from the Mg electrode to the Ni electrode.

CONCEPT ASSESSMENT EXERCISE 2.6

The standard reduction potentials for the following half-reactions are:

$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ E = +0.34V

$F_2(g) + 2e^- \rightarrow 2F^-$ E = +2.87V

Estimate E^0_{cell} for Cu-F_2 cell, write cell reactions, choose cathode and show the direction of electron flow.

2.4.5 Feasibility of a Chemical Reaction

Whether a chemical reaction is feasible or occurs spontaneously or not, can be inferred from the sign of the sum of E^o values of the two half-cell reactions. If this value is positive, a reaction occurs spontaneously or will be feasible. The negative value indicates that the reaction is not feasible.

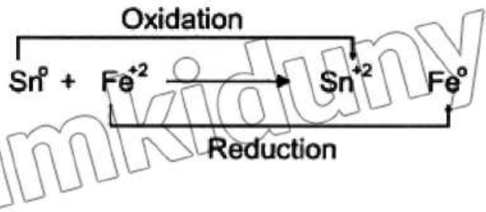
Example 2.7

Is the following reaction feasible?

$$Sn + Fe^{2+} \longrightarrow Sn^{2+} + Fe$$

The standard reduction potential values are $E^0_{Sn} = -0.14V$, $E^0_{Fe} = -0.44V$

Solution



It is clear from the above equation that oxidation of Sn and reduction of Fe is taking place. Sn is acts as an anode and Fe as the cathode. The above reaction consists of the following two half-cell reactions.

$$Sn \longrightarrow Sn^{2+} + 2\bar{e} \qquad \text{(oxidation half-reaction)}$$

$$Fe^{2+} + 2\bar{e} \longrightarrow Fe \qquad \text{(reduction half-reaction)}$$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E^0_{cell} = -0.44V - (-0.14V)$$

$$= -0.30V$$

As E^0_{cell} is negative, therefore the given reaction is not feasible. However reverse reaction would be spontaneous.

CONCEPT ASSESSMENT EXERCISE 2.7

1. Using emf data, argue on the following:
   (i) Can Mg displace Cu from a solution of Copper(II) sulphate.?
   (ii) Can Iodine displace chlorine from an aqueous solution of Potassium chloride?
2. Is the following reaction feasible?

$$Al + Mn^{2+} \rightarrow Al^{3+} Mn$$

The standard reduction potential values are $E^0_{Al} = -1.66V$, $E^0_{Mn} = -1.18V$

2.5 Nernst Equation

The relationship between concentration and electrode potential is given by the Nernst equation.

The electrode potential is influenced by the concentrations of the ions involved in the redox reaction. The Nernst equation is a mathematical expression that relates the standard electrode potential (E°) to the actual electrode potential (E) under non-standard conditions, considering the concentrations of the reactants and products.

Mathematically Nernst equation is:

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

Where n = No. of electron transferred from the reduced species to oxidised species.

R = the universal gas constant. Its value is 8.314J/mol.

T = Kelvin temperature

F = Charge of a mol of electron and the charge of 1 mol of electron is 9.648×10^4 $Cmol^{-1}$)

[oxidized species] = Conc. of species with higher oxidation state.

[reduced species] = Conc. of species with lower oxidation state.

$$E = E^0 + \frac{2.303\ RT}{nF} \log \frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

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Remember that $lnx = 2.303logx$

$$E = E^0 + \frac{0.059}{n}\log\frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

$$\frac{2.303RT}{F} = \frac{2.303 \times 8.314JK^{-1}mol^{-1} \times 298K}{9.648x10^4 Cmol^{-1}}$$

$= 0.059JC^{-1} = 0.059V$ since $1J/C = 1V$

2.5.1 Electrode potentials and concentration

We have already discussed copper half-equation; it has the following standard electrode potential.

$$Cu^{2+} + 2e^- \rightarrow Cu \quad +0.34V$$

For this value of E^o the Cu^{2+} ions should have a concentration of 1 mol/dm^3. What will happen if the concentration of Cu^{2+} ions is decreased by adding water? If you decrease the concentration of any species in an equilibrium reaction, then according to Le Chatelier`s Principle the position of equilibrium shifts in such a way as to counter-act or nullify the change. The position of equilibrium will shift to the left, increasing the concentration of Cu^{2+} ions again. Since E^o measures the position of the equilibrium. The electrode potential would become less positive. So, it will no longer be a standard potential.

Electrode potential measures how easily a species gains or losses electrons. It depends on the concentration of the ions in the redox reaction.

When the concentration of ions changes:

1. An increase in the concentration of ions (e.g., Cu^{2+} ions for copper electrodes) makes reduction easier because more ions are available to gain electrons. This increases electrode potential.
2. A decrease in the concentration of ions makes reduction harder because fewer ions are available to accept electrons. This decreases the electrode potential.

The Nernst equation quantitatively predicts these changes.

Example: The standard electrode potential of the Cu^{2+}/Cu system is +0.34V. What is the electrode potential of a solution containing 0.5M Cu^{2+} ions?

Solution:

$$E = E^0 + \frac{0.059}{n}\log\frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

Nernst equation for Cu^{2+}/ Cu system is:

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} + \frac{0.059}{n}\log\frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

$$E_{Cu^{2+}/Cu} = 0.34 + \frac{0.059}{2}\log\frac{0.5}{1}$$

$$= 0.34 + 0.0295 \times (-0.301)$$

$$= 0.34 - 0.0089$$

$$= 0.331V$$

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CONCEPT ASSESSMENT EXERCISE 2.8

The standard electrode potential of Fe^{3+}/Fe^{2+} is 0.77V. What is the electrode potential of the system containing 1.0 mol/dm^3 of Fe^{3+} and 0.2 mol/dm^3 of Fe^{2+} ions? **Ans: 0.811V**

2.6 Electrochemical Series

Under the recommendation of the International Union of Pure and Applied Chemistry (IUPAC) the half-cell reactions are given in the reduction reactions (Table 2.2) therefore E° values are known as reduction potentials. However, the value of oxidation potential for an electrode can be obtained by reversing the sign of reduction potential for that electrode. Note that the given reduction potential values relate to standard conditions only. i.e.,1M solution of ions, 25 °C (298K) and 1 atm. pressure. Changes in conditions will alter these values.

Such a list of arrangement of elements in the order of their standard electrode potential with reference to standard hydrogen electrode is called an electrochemical series (Table 2.1).

2.6.1 Activity Series of Metals

A displacement or replacement reaction occurs when an element displaces another element that is a part of a compound. The general equation,

$$A + XY \longrightarrow X + AY$$

In this reaction, atom A replaces atom X in the compound XY. When Zn metal is placed in a blue solution of copper (II) sulphate, the blue colour slowly fades away and grey metal is replaced by red-orange Cu metal. In this reaction Cu ions in the solution are reduced to Cu metal and Zn atoms are oxidized to Zn ions (for details see section 2.1).

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

However, when copper metal is placed in a zinc sulphate solution, no replacement reaction occurs. Table 12.1 shows that the standard reduction potential of copper is greater than that of zinc. This means that it is easy to oxidize Zn to its ions and reduce Cu^{2+} ions to its atoms. Thus, Zn can replace Cu^{2+} ions from its solution. For the same reason Mg and Al can also displace Cu^{2+} ions, but Ag cannot displace Cu^{2+} ions.

Similarly, it is observed that metals like Na, and K can displace H_2 from water but metals like Cu, and Ag cannot displace H_2 from water. Metals are, therefore, ranked according to their ability to replace other metals and hydrogen from their compounds. In this ranking **metals and hydrogen are arranged in order of decreasing ease of oxidation to their respective ions in aqueous solution.** This arrangement is called **activity series** (see Table 2.2).

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Table 2.2 Activity series of common metals

Increase in Reactivity ↑	Li K Ba Sr Ca Na	Very Active metals; React with cold water with the liberation of hydrogen gas; (K and Na react violently with water), They also react violently with acids
	Mg Al Mn Zn Cr Fe Cd	Metals of intermediate activity: React with steam or with acids such as HCl with the liberation of H_2
	Co Ni Sn Pb	Moderately active metals React slowly with HCl Do not react with water
	H_2	
	Cu Ag Hg	Moderately noble metal; Do not react with water, or HCl but react with oxidizing acids such as HNO_3
	Pt Au	Very noble metals; React only with aqua regia

1. Metals higher on the list transfer electrons to metal cations lower on the list. The greater the separation between the species the more vigorous will be the reaction. For example, when powdered barium is heated with lead (II) oxide, a replacement reaction occurs. This is because Ba is more active than Pb. Barium is oxidized to form barium oxide and lead is reduced to elemental lead.

$$Ba_{(s)} + PbO_{(s)} \longrightarrow BaO_{(s)} + Pb_{(s)}$$

On the other hand, when iron pellets are added to a solution of $MgCl_2$ no reaction will occur. This is because Fe is below Mg in the activity series.

CONCEPT ASSESSMENT EXERCISE 2.8

Predict whether a replacement reaction will occur in the following instances. Defend your conclusion.

a) Magnesium ribbon is in a solution of silver nitrate.
b) A copper plate is dipped in iron(II) sulphate ($FeSO_4$) solution.
c) Lead(II) oxide is heated with powdered zinc.
d) Nickel wire is placed into a solution of silver nitrate.

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2.7 The Relative Reactivity of Species as Oxidizing Agents or Reducing Agents

Electrode potential values, also known as reduction potentials, provide insight into the relative reactivity of elements, compounds, and ions as oxidizing or reducing agents. By comparing reduction potentials, you can determine the relative reactivity of species as oxidizing or reducing agents. Those with higher reduction potentials are stronger oxidizing agents, while those with lower reduction potentials are stronger reducing agents.

For Example

Consider the reaction reduction potentials for the following half-reactions.

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad E^0 = +0.34V$$

$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad E^0 = -0.76V$$

Note that Cu^{2+} ions have a higher reduction potential compared to Zn^{2+} ions. So, Cu^{2+} ions have a greater tendency to gain electrons and thus act as a stronger oxidizing agent than Zn^{2+} ions.

For Example

Consider the reaction between potassium permanganate ($KMnO_4$) and iron(II) sulphate ($FeSO_4$) in an acidic solution.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \qquad E^0 = +1.52V$$

$$Fe^{2+} \longrightarrow Fe^{3+} + 1e^- \qquad E^0 = +0.77V$$

Here, MnO_4^- ions have a higher value of reduction potential than Fe^{2+} ions. So, MnO_4^- ions act as a strong oxidizing agent and Fe^{2+} ions act as a strong reducing agent in this reaction.

2.8 Types of Electro-Chemical Cells

Devices, that convert electrical energy into chemical energy and vice versa, are known as electrochemical cells. There are two types of electrochemical cells.

1) Electrolytic cells.
2) Galvanic or voltaic cells. (see section)

2.8.1 Electrolytic Cells

An electrolytic cell is a device that converts electrical energy to chemical energy by electrolysis. Electrolysis is the process by which chemical reactions are stimulated by an external electrical current. In electrolytic cells, oxidation takes place at the anode (positive electrode) where electrons are lost. At the cathode (negative electrode), electrons are gained. The oxidation process results in the conversion of electrical energy into chemical energy by stimulation of a non-spontaneous reaction.

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Electrolysis

Electrolysis is a process in which a chemical reaction occurs by means of an electric current in a molten state or in an aqueous state. The apparatus for electrolysis consists of an electrolytic cell containing the electrolyte either in a molten state or in an aqueous state. Two electrodes are placed in the solution. The electrodes are connected to a battery. The current is carried from the battery through the wires by means of electrons (metallic conduction). Within the cell, the current is carried by the anions and cations of the electrolyte (Electrolytic conduction). The electrodes serve as a point where conduction changes from metallic to electrolytic or vice versa. At each electrode, a chemical reaction takes place in which electrons are gained by the ions in solution at one electrode. Simultaneously electrons are released by some substance at the other electrode. These electrons are returned to the battery through the connecting wire. Thus, oxidation-reduction reactions occur at the electrodes. The electrode at which oxidation occurs is called an **anode**. The electrode at which reduction occurs is called as **cathode**. The changes, that occur at the electrodes, depend on the relative oxidation-reduction tendencies of the substances involved.

Units

The SI unit of charge is the **coulomb (C)**. It is the charge on 6.25×10^{18} electrons. Although the coulomb is the usual unit for measuring charge, the chemist finds that a more convenient unit is the **Faraday (F)**. It corresponds to the charge carried by one mole of electrons and amounts to 96487 C. The SI Unit of current is the ampere, which is the amount of current flowing when one coulomb passes a specific point in one second. Frequently, an ampere is referred to as "a coulomb per second".

2.8.2 Factors Influencing the Products of Electrolysis

Electrolysis involves the use of an electric current to drive a non-spontaneous redox reaction. The substances liberated during electrolysis depend on the following factors.

- The state of electrolyte
- Position in the electrochemical or redox series
- Concentration of the electrolyte

1. The state of electrolyte:

Electrolytes are substances that conduct electricity when dissolved in water or in their molten state. When molten electrolyte is used, its cations and anions are discharged at the electrodes. But aqueous solutions of electrolytes contain both ions from dissolved electrolytes and that of water. In this case, water molecules may produce H_2 at the cathode.

2. Position in the Electrochemical or Redox Series:

The position of substances in the electrochemical series can give an indication of their tendency to be reduced or oxidized during electrolysis. Generally, substances higher in the series tend to be reduced, while those lower in the series tend to be oxidized. In aqueous solutions, cations less reactive than hydrogen are preferentially discharged at the cathode e.g., Cu^{2+} ions. But cations more reactive than hydrogen do not discharge and remain in solution e.g., Na^+, Mg^{2+} etc. In this case, water molecules are discharged at the cathode to liberate hydrogen.

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3. **Concentration of Electrolyte:**

The concentration of ions in the electrolyte solutions also affects the ease with which they are liberated during electrolysis. Higher concentrations can favour the liberation of certain ions. The ions with lower concentrations are not discharged, instead, water molecules are *discharged.*

The following examples show how the identities of substances liberated in electrolysis depend on specific electrolytes, their constituent ions as well as their position in the electrochemical series.

1. Electrolysis of fused NaCl

   At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

   At cathode: $2Na^+ + 2e^- \rightarrow 2Na$

   Net reaction: $2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2$

2. Electrolysis of concentrated aqueous NaCl (brine)

   Since the solution contains a higher concentration of Cl^- ions. So, they are discharged at the anode instead of OH^- ions. Na^+ ions being more reactive than hydrogen remain in solution and are not discharged. Instead water molecules are discharged at the cathode.

   At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

   At cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

   Net reaction: $2H_2O + 2Cl^- \rightarrow H_2 + Cl_2 + 2OH^-$

3. Electrolysis of dilute aqueous NaCl

   In dilute aqueous NaCl solution, Cl^- ions have a lower concentration. So, chloride ions are not discharged at the anode. Instead, OH^- ions are discharged at the anode. Here again, Na^+ ions being more reactive than hydrogen remain in the solution and water molecules are discharged at the cathode.

   At anode: $4OH^- \rightarrow O_2 + 4e^- + 2H_2O$

   At cathode $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

   Net reaction: $4H_2O \rightarrow 2H_2 + O_2$

2.9 Relation Between the Faraday Constant, Avogadro Constant, and the Change on the Electron

The amount of a substance produced at an electrode during electrolysis depends on the period of time for which a constant current is passed and the quantity of charge in coulombs that passes through the electrolyte. The relation between current and time is:

$$Q = I \times t$$

Where, Q = Quantity of charge in coulombs (C)

I = Current in Ampere (A)

t = time of electrolysis in seconds(s)

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The quantity of electricity can be expressed by Faraday constant (F). One faraday is the amount of electric charge carried by one mole of electrons.

Charge on one electron = $1.60217662 \times 10^{-19}$ C

Charge on one mole of electrons = $1.60217662 \times 10^{-19}$ C x 6.022×10^{23} per mol

= 96485.332 C/ mol

It is therefore concluded that 96485.332 C is the charge on one mole of electrons. This quantity of charge is referred to as one Faraday. Thus, the quantity of the change in electrolysis can be determined from the number of Faraday's of charge, which passes. For most calculations, the value of the Faraday will be taken as 96500 C.

The relationship between the Faraday constant (F), Avogadro constant (N_A), and the charge on the electron (e) can be expressed by the equation:

$$F = N_A \cdot e$$

where:

F = the Faraday constant (charge per mole of electrons),

N_A = the Avogadro constant (number of entities per mole) = 6.022141×10^{23} per mol

e = the elementary charge (charge on a single electron) = $1.60217662 \times 10^{-19}$ C

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For example

$$Na^+ + e^- \rightarrow Na$$

To deposit one mole of Na, the amount of electricity needed is 1F (96500 C).

$$Cu^{2+} + 2e^- \rightarrow Cu$$

But to deposit one mole of Cu, 2 mole of electrons are required. So, the amount of electricity needed is 2F.

Example 2.8

In the electrolysis of molten $ZnCl_2$, how much Zn can be deposited at the cathode by the passage of 0.01-ampere current for one hour?

Solution

0.01 Amp. for one hour carries charge = $0.01 \times 1 \times 60 \times 60$

= 36 C

Since 1F = 96500 C

Therefore, 36 C = 3.7×10^{-4} Faraday

In molten Zinc chloride, the cathode reaction is

$$Zn^{+2} + 2e^- \longrightarrow Zn$$

2F current = 1 mol of Zn

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1F current = $\frac{1}{2}$ mol of Zn

3.7 x 10^{-4}F current = $\frac{1}{2}$ x 3.7 x 10^{-4}

= 1.85 x 10^{-4} mol of Zn

Mass of zinc = n x molar mass

= 1.85 x 10^{-4} x 63.37

= 0.012gm

Example 2.9

A constant current was passed through a solution of $AuCl_4^-$ ions between gold electrodes. After a period of 10.0 minutes, the cathode increased in weight by 1.314 grams.

i) How much charge was passed?
ii) What was the amount of current?
iii) What volume of Cl_2 was collected at the anode at 1 atm and 25 °C?

Solution

The reaction at the cathode is the reduction of Au (III) to Au metal

$$AuCl_4^- + 3e^- \longrightarrow Au + 4Cl^-$$

It means that for every 3 Faraday of electricity used up, 1 mole of Au is produced.

Moles of Au = $\frac{1.314 gAu}{197 g/\text{mole of Au}}$ = 6.67×10^{-3}

i) Charge = 6.67×10^{-3} mole Au $\times \frac{3\text{ Faraday}}{\text{mole of Au}}$

= 2×10^{-2} Faraday

ii) Current = $\frac{\text{Charge}}{\text{Time(s)}}$

Time = 10 mins = 10×60 = 600s

Current = $\frac{(2\times10^{-2}F)(96500C/F)}{600s}$ = 3.22 A.

iii) The reaction at the anode is the oxidation of Cl^- ions.

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

For every 2 Faraday of electricity, 1 mole of Cl_2 was produced.

For 1 Faraday of electricity = 1/2 moles of Cl_2 was produced.

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For 2×10^{-2} Faraday of electricity = $1/2 \times 2\times10^{-2}$ moles of Cl_2 was produced.

= 1×10^{-2} moles of Cl_2 was produced.

$n = 1 \times 10^{-2}$ mol

$P = 1$atm

$T = 25 + 273 = 298K$

$R = 0.0821 atm.dm^3mol^{-1}$

$V = ?$

Volume of Cl_2 produced can be calculate by the following formula

$$V = \frac{nRT}{P}$$

$$= \frac{1\times10^{-2} \times 0.0821 \times 298}{1} \quad = 0.245 dm^3$$

2.10 Experimental Determination of Avogadro Constant By Electrolytic Method

Electrolysis provides a concrete way to measure the Avogadro Constant experimentally. In this experiment, a known electrolyte is electrolysed. The mass of metal deposited at the cathode is determined by passing known amperes of current for a known time. Suppose you electrolysed $AgNO_3$ using Ag electrodes. The experimental data shows that when 0.1 amperes is passed for exactly 30 minutes through the aqueous solution of silver nitrate solution, the amount of Ag deposited on the cathode is 0.201g. From this data, you can calculate the Avogadro Constant as follows;

I = 0.1amp

t = 30 min.= 30x 60= 1800s

Q = I x t

Q = 0.1 x 1800

Q = 180 Coulombs

Mass of Cu produced = 0.201g

This means 0.201g of Ag is produced by 180C of electricity.

So, 1 mol or 107.868g Ag would require = 180/0.201 x 107.868

= 96598.209 Coulombs

This charge must be present on electrons producing 1 mol of Ag

Cathode Reaction: $Ag^+_{(aq)} + 1e^- \rightarrow Ag_{(s)}$

This equation shows that 1 mole of electrons gives 1 mole of Ag.

So, the charge on 1 mole of electrons = 96598.209 C

As the charge on one electron is = 1.602×10^{-19}C

Therefore the number of electrons in one mole = $96598.209\ C/1.602 \times 10^{-19}C$

$= 6.0298 \times 10^{23}$

This value is very close to the accepted value of 6.02214×10^{23}

CONCEPT ASSESSMENT EXERCISE 2.10

1. An electrolytic cell is connected to a power source for two hours. If the current flowing through the cell is 0.5A during this time. Find the mass of the substance liberated during this time interval. (the molar mass of the substance is 107.9g/mol.)
2. Calculate the charge in coulombs when 3 moles of electrons flow through a circuit.
3. Calculate the mass of silver deposited at the cathode during electrolysis of $AgNO_3$ solution, if you use a current of 0.1A for 20 minutes.

2.11 Winkler Method for Biological Oxygen Demand

The biological oxygen demand (BOD) is the amount of oxygen used to decompose the organic matter in a sample of water over a specified time period, usually 5 days, at a specified temperature. A high BOD indicates a greater quantity of organic waste in the water, which means a lower level of dissolved oxygen. Dissolved oxygen is used as an indicator of the health of a water body, where higher dissolved oxygen concentrations are correlated with high productivity and little pollution.

The Winkler Method

The Winkler Method is a widely used redox technique to measure dissolved oxygen in freshwater systems.

The principle of the Winkler method

Oxygen present in a water sample is used to oxidize iodide ions into iodine. The amount of iodine produced is determined by titrating with a standard sodium thiosulphate solution. The amount of oxygen present in the original sample of water is determined from the titer.

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ACTIVITY 2.2: DETERMINING OXYGEN PRESENT IN A WATER SAMPLE

Materials Required

- 300 BOD bottle
- Manganese(II) sulphate solution 2 cm^3
- Alkali iodide azide 2 cm^3
- Conc. H_2SO_4 2 cm^3
- Potassium iodide solution 2 cm^3.
- Sodium thiosulphate solution 0.1M
- Starch solution 2 cm^3

Procedure

- Collect sample water in a 300 cm^3 BOD bottle. To do this, the BOD bottle is immersed in water, remove the cap under water, fill the bottle with water and, put the cap under water.
- Add 2 cm^3 of alkaline iodide azide solution (an aqueous solution of 32.7% NaOH + 15% KI + 1% NaN_3) and close it with the cap. Then add 2 cm^3 of manganese(II) sulphate solution. Swirl the sample bottle a few times. Oxygen dissolved in the alkaline solution oxidizes the manganese(II) ions to manganese(IV) oxide, which appears as a brown precipitate.

$$2Mn^{2+}_{(aq)} + 4OH^-_{(aq)} + O_{2\,(aq)} \rightarrow 2MnO_{2\,(s)} + 2H_2O_{(l)}$$

- Add.2 cm^3 of conc. H_2SO_4 and then 2 cm^3 solution of potassium iodide, KI, to the solution. The precipitate will dissolve into a solution, so Mn(IV) is reduced back to Mn(II) liberating iodine in the process.

$$MnO_{2\,(s)} + 2I^-_{(aq)} + 4H^+_{(aq)} \rightarrow Mn^{2+}_{(aq)} + I_{2(aq)} + 2H_2O_{(l)}$$

- Start the titration process. Titrate 201 cm^3 of above water against standard sodium thiosulphate solution until the solution turns pale yellow. Now add 2 cm^3 starch solution as an indicator. The solution will turn blue. Continue to add sodium thiosulphate solution till the blue colour just disappears.

$$2S_2O_3^{2-}{}_{(aq)} + I_{2\,(aq)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-_{(aq)}$$

- The above stoichiometric equations show that:

  1 mole of $O_2 \rightarrow$ 2 moles of $MnO_2 \rightarrow$ 2 moles of $I_2 \rightarrow$ 4 moles of $S_2O_3^{2-}$

- Therefore, after determining the number of moles of iodine produced, you can work out the number of moles of oxygen molecules present in the original water sample.
- The oxygen content is usually presented as mg/dm^3 or ppm

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KEY POINTS

1. Redox reactions i.e., oxidation and reduction reactions involve the transfer of electrons or change in oxidation numbers.
2. Redox equations can be balanced by using the oxidation number method and ion-electron method.
3. The driving force behind the spontaneous redox reaction is called the cell potential.
4. The magnitude of cell potential depends upon the conditions under which the measurement is made. Under standard conditions, all solutions have 1M concentration; all gases have a partial pressure of 1 atm. The standard potential for the reduction of H^+ to hydrogen gas is arbitrarily taken as zero volts.
5. In a galvanic cell, oxidation and reduction reactions take place at separate electrodes and electrons flow through the external circuit. These separate parts of the galvanic cell are half cells. The reactions which occur at these half cells are the half-cell reactions. A salt bridge allows the ions to flow between the half cells.
6. In a galvanic cell, oxidation occurs at the node, reduction occurs at cathode and the electrons flow in the external circuit from the anode to the cathode.
7. Voltaic cells use a spontaneous redox reaction to drive an electric current through a wire. Whereas, the electrolytic cells use an electric current to drive a redox reaction.
8. The quantity of electricity carried by 1mole of electrons is called a Faraday. It is equal to 96,500 coulombs.
9. In electrolysis, electric current from an external source drives a non-spontaneous chemical reaction. The amount of chemical reaction that takes place in electrolysis is directly proportional to the quantity of charge transferred at the electrode.
10. A battery is a galvanic cell or a group of galvanic cells connected in series. Some of the well-known batteries are the dry cell, the nickel-cadmium battery, the lead-storage battery used in automobiles, fuel cells, etc.
11. The corrosion of metals is an electrochemical phenomenon.

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EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which of the following elements is reduced in the reaction? $2Na+Cl_2 \rightarrow 2NaCl$

a) Na b) Cl c) Both Na and Cl d) Neither Na nor Cl

ii. In the reaction $Fe+CuSO_4 \rightarrow FeSO_4.Cu$, what is the reducing agent?

a) Fe b) Cu c) SO_4^{2-} d) $CuSO_4$

iii. What is the oxidation number of sulphur in H_2SO_4?

a) -2 b) 0 c) +2 d) +6

iv. Which of the following best describes the process of oxidation?

a) Gain of electrons b) Loss of electrons
c) Gain of protons d) Loss of protons

v. In the electrolysis of water, which substance is liberated at the cathode?

a) H_2 b) O_2 c) H_2O d) OH^-

vi. Which of the following metals would not react with HCl to produce H_2 gas?

a) Zn b) Fe c) Cu d) Mg

vii. The Winkler method measures the concentration of which substance to determine BOD

a) O_2 b) CO_2 c) N_2 d) H_2

viii. In a redox reaction, the oxidizing agent:

a) Loses electrons b) Gains electrons
c) Loses protons d) Gains protons

ix. The standard electrode potential of the hydrogen electrode is defined as:

a) 0 V b) 1 V c) -1 V d) 0.5 V

x. What is the relationship between the Faraday constant (F), Avogadro's number (NA), and the charge of an electron (e)?

a) $F=N_A \times e$ b) $F=e/N_A$ c) $F=N_A/e$ d) $F=e2 \times N_A$

2. Short Answer Questions

Explain the following with reasons.

i. The oxidation potential of Zn is +0.76V and its reduction potential is -0.76V

ii. A salt bridge maintains the electrical neutrality in the cell.

iii. Na and K can displace hydrogen from acids but Cu and Pt cannot.

iv. Define oxidation in terms of electron transfer.

v. What is the oxidation number of oxygen in H_2O_2?

vi. Identify the reducing agent in the reaction
$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

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vii. State the purpose of the Winkler method.

viii. Explain what happens at the anode during the electrolysis of aqueous sodium chloride.

ix. What does a positive standard electrode potential indicate about a substance's tendency to gain electrons?

x. Calculate the oxidation number of chromium in $K_2Cr_2O_7$

xi. Describe the role of the standard hydrogen electrode in electrochemistry.

xii. What is the significance of the activity series of metals?

xiii. How can you deduce the feasibility of a redox reaction using electrode potentials?

xiv. Bauxite ore is used for the commercial preparation of Al. For this purpose, bauxite ore is first purified to produce pure alumina, Al_2O_3. Alumina is then electrolyzed. The following reaction occurs:

$$2Al_2O_{3(s)} \longrightarrow 4Al_{(s)} + 3O_{2(g)}$$

Calculate the mass of Al, that collects at the cathode and the volume of oxygen that collects at the anode when Al_2O_3 is electrolyzed for 10 hours with a 15 ampere current at 1 atm and 25°C.

(Ans: mass of Al=50.36g, volume of oxygen=34.20dm^3)

xv. Which of the following compounds will give more mass of metal, when 15 ampere current is passed through a molten mass of these salts for 1 hr.

(a) NaCl (b) $CaCl_2$.

(Ans: NaCl will give more Na)

xvi. How many hours would electroplating have to be continued at the rate of 5 amperes if 75g of copper is to be deposited from $CuSO_4$ solution?

xvii. Differentiate between the following

(a) A galvanic and electrolytic cell

(b) Oxidation half-reaction and reduction half-reaction

xviii. An electroplating apparatus is used to coat jewellery with gold. What mass of gold can be deposited from a solution that contains $[Au(CN)_4]^{-1}$ ion if a current of 5.0 amperes flows for 30 minutes? The following half-reaction occurs;

$$[Au(CN)_4]^{-1}_{(aq)} + 3e^- \longrightarrow Au_{(s)} + 4CN^-_{(aq)}$$

(Ans: mass of gold =6.12g)

xix. Construct redox equations using the following half equations.

(a) $SO_2 \rightarrow HSO_4^-$

$MnO_4^- \rightarrow Mn^{2+}$

(b) $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

$Cl^- \rightarrow Cl_2$
(c) $H_2O_2 \rightarrow O_2$
$MnO_4^- \rightarrow Mn^{2+}$
(d) $Sn^{2+} \rightarrow Sn^{4+}$
$Fe^{3+} \rightarrow Fe^{2+}$
(e) $IO_3^- \rightarrow I^-$
$AsO_3^{3-} \rightarrow AsO_4^{3-}$

xx. In the reaction between potassium permanganate and iron(II) sulphate in an acidic solution:

$$MnO_4^- + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}$$

a) Identify the oxidation states of manganese and iron before and after the reaction.

b) Explain which species is oxidized and which is reduced.

c) Balance the redox reaction using changes in oxidation numbers.

d) Identify oxidising and reducing agents.

xxi. Explain why magnesium can displace zinc from zinc sulphate solution but copper cannot.

Predict the outcome of placing a zinc strip in a copper(II) sulphate solution, including the balanced chemical equation.

3. Long Answer Questions

i. Explain the process of balancing a redox equation using the oxidation number method. Include an example.

ii. Describe the Winkler method for measuring biochemical oxygen demand (BOD) and its importance in assessing water quality.

iii. Explain how the activity series of metals can be used to predict the outcome of displacement reactions.

iv. Describe the construction and function of an electrolytic cell.

v. Calculate the mass of copper deposited at the cathode during the electrolysis of CuSO4 solution when a current of 2 A flows for 30 minutes. (Faraday's constant = 96500 C/mol, Molar mass of Cu = 63.5 g/mol). **Ans: 1.18g**

vi. Balance the following equations by the oxidation number method.

a. $MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$

b. $HNO_3 + HI \longrightarrow NO + I_2 + H_2O$

c. $Ag + H_2S + O_2 \longrightarrow Ag_2S + H_2O$

d. $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$

e. $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

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vii. During the electrolysis of molten sodium chloride:

  a) Describe the process occurring at the anode and the cathode.

  b) Calculate the total charge passed through the cell if a current of 3 A is applied for 2 hours. **Ans: 21600 C**

viii. Consider the following half-reactions and their standard electrode potentials:

$$Ag^+ + e^- \rightarrow Ag \qquad E^\circ = +0.80\,V$$
$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E^\circ = -0.76\,V$$

  a) Calculate the standard cell potential for the galvanic cell constructed with these half-cells. **Ans: 1.56V**

  b) Predict the direction of electron flow in the cell.

  c) Using the calculated cell potential, discuss the feasibility of the redox reaction in this cell.

ix. A current of 1.0 A is passed through a solution of $AgNO_3$ for 965 seconds.

  (a) How many Faradays of charge were passed? **Ans: 0.01F**

  (b) How many moles of silver would be deposited? **Ans: .01 moles**

THINK TANK

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1. Predict the outcome of mixing aqueous solutions of $FeSO_4$ and $AgNO_3$ with Cu based on their standard electrode potentials. Explain your reasoning.
2. Using the Nernst equation, calculate the cell potential of a galvanic cell with the following half-reactions: $Zn^{2+} + 2e^- \rightarrow Zn$ ($E^\circ = -0.76$ V) and $Cu^{2+} + 2e^- \rightarrow Cu$ ($E^\circ = +0.34$ V) if the concentration of Zn^{2+} is 0.1 M and Cu^{2+} is 1.0 M. **Ans: 1.39V**
3. A voltaic cell is constructed using a copper electrode in a 1 M copper(II) sulphate solution and a zinc electrode in a 1 M zinc sulphate solution:
   a) Calculate the cell potential under standard conditions using the given standard reduction potentials:

   $E^\circ(Cu^{2+}/Cu) = +0.34\,V$

   $E^\circ(Zn^{2+}/Zn) = -0.76\,V$ **Ans: 1.10V**

   b) Discuss how the Nernst equation can be used to predict the effect of changing the concentration of Cu^{2+} ions on the cell potential.

PROJECT

Discuss the environmental implications of high BOD levels in water bodies and the potential sources of this pollution.

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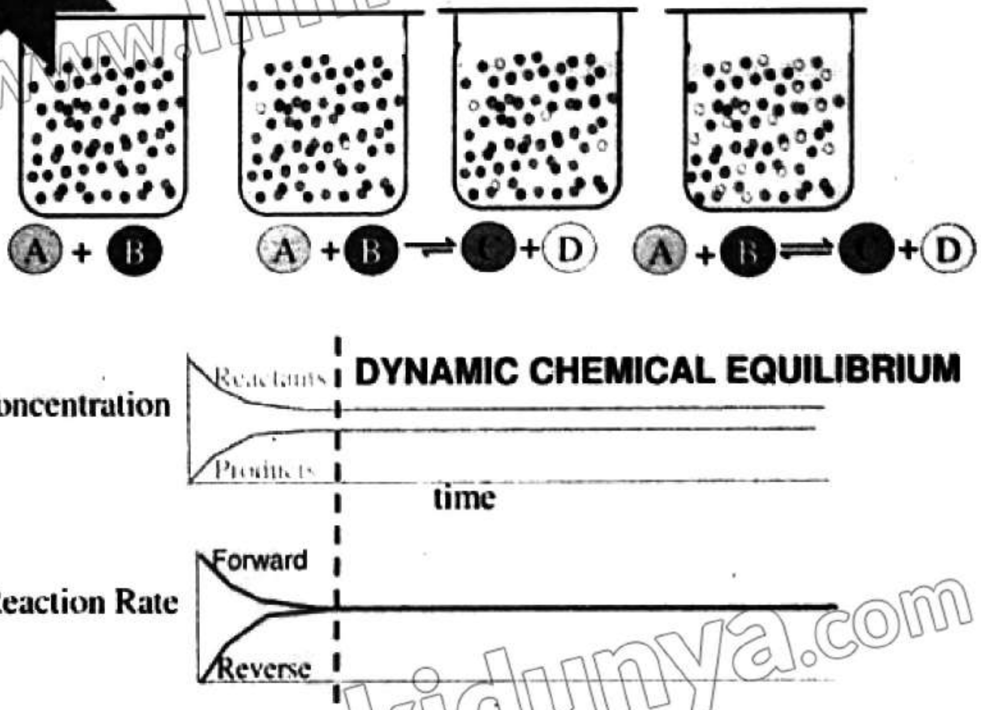
UNIT 03



CHEMICAL EQUILIBRIA

Student Learning Outcomes (SLOs)

- Explain common ion effects giving suitable examples.
- Use the extent of ionization and the acid dissociation constant, K_a, to distinguish between strong and weak acids.
- Use the extent of ionization and the base dissociation constant, K_b, to distinguish between strong and weak bases.
- Explain what is meant by a chemical buffer and how a buffer system works. (For context this should include: a. defining what is a buffer solution. b. Explain how a buffer solution can be made. c. explaining how buffer solutions control pH: use chemical equations in these explanations. d. Describe and explain the uses of buffer solutions, including the role of HCO_3^- in controlling pH in blood.
- Calculate concentration of slightly soluble salts.
- State what is meant by the term partition coefficient, K_{pc}.
- Calculate a partition coefficient for a system in which the solute is in the same physical state in the two solvents.
- Explain the factors affecting the value of a partition coefficient in terms of the polarities of the solute and the solvent used.

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How do substances behave in various environments? This requires an understanding of chemical reactions and equilibrium. When an additional ion is added, the common ion effect predicts solution reactions. The strength of acids and bases can be estimated from their dissociation constants, which differentiate strong acids from weak ones. Buffer solutions maintain pH equilibrium and regulate blood pH. This you will understand in this chapter. The distribution of solutes among solvents is predicted by the partition coefficient, which is useful in estimating the distribution of drugs within the body. So it is very important for drug design. These concepts play a key role in industrial and environmental science

3.1 Strength of Acids and Bases

The degree to which different Bronsted acids give off protons is called "acid strength". A relatively strong acid is an acid that can give off more protons than another acid. Hydrochloric acid, for example, is relatively strong compared to acetic acid, which is relatively strong relative to water. Bases differ in the degree to which they accept protons as well. A strong base can accept protons to a greater extent than another base, so ammonia is relatively stronger relative to water because it can accept protons to a higher degree than water.

3.1.1 Strong and Weak Acids

The extent of ionization and the acid dissociation constant K_a can be used to distinguish between strong and weak acids.

The strength of an acid is generally expressed in terms of the acid ionization constant, K_a of the acid. Consider the case of ionization of a general acid HX in water. In this aqueous solution, the established equilibrium may be represented as follows:

$$HX + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + X^-_{(aq)}$$

The equilibrium constant K for this ionization process may be written as follows:

$$K = \frac{[H_3O^+][X^-]}{[HX][H_2O]}$$

or $$K[H_2O] = \frac{[H_3O^+][X^-]}{[HX]}$$

Since water is a solvent, it is present in excess and therefore its concentration may be regarded as constant. Thus, $K[H_2O]$ is another constant and is designated as K_a.

$$K[H_2O] = K_a = \frac{[H_3O^+][X^-]}{[HX]}$$

K_a is termed as the acid dissociation constant. It is a measure of the extent to which an acid is ionized or dissociated at the equilibrium state. It must be kept in mind that the acid dissociation constant, K_a, is dependent on temperature. Therefore, the value of K_a should be mentioned along with the temperature at which K_a was determined. The dissociation constant, K_a, of acetic acid in water at 25°C is 1.8×10^{-5}. The comparison of K_a Values of different acids provides a method to compare their strengths.

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"The greater the value of K_a, the stronger the acid".

The values of K_a are usually inconvenient numbers, therefore, for convenience, these values are converted to pK_a values. The relationship between K_a and pK_a is as follows:

$$pK_a = -\log K_a$$

Since pK_a refers to the negative logarithm of K_a, the lower the pK_a value, the stronger the acid, since a lower pK_a value corresponds to a higher K_a value. Table 3.1 lists the ionization constants and pK_a values of some common acids in water at 25 °C. Which acid is the strongest? Which acid is the weakest?

Table 3.1: Ionisation constants and pK_a of Acids

Name of Acid	Formula	K_a	pK_a
Perchloric acid	$HClO_4$	1.0×10^{10}	-10.0
Hydroiodic acid	HI	1.0×10^{10}	-10.0
Hydrobromic acid	HBr	1.0×10^{9}	-9.0
Hydrochloric acid	HCl	1.0×10^{6}	-6.0
Sulphuric acid	H_2SO_4	1.0×10^{3}	-3.0
Hydrofluoric acid	HF	7.2×10^{-4}	+3.1
Formic acid	$HCOOH$	1.8×10^{-4}	+3.75
Benzoic acid	C_6H_5COOH	6.3×10^{-5}	+4.2
Acetic acid	CH_3COOH	1.8×10^{-5}	+4.7
Phenol	C_6H_5OH	1.3×10^{-10}	+8.9
Water	H_2O	1.8×10^{-16}	+15.7

Which acid is stronger HCl or HF?

Example 3.1

Calculate the concentration of H^+ ions of a solution that contains

1.0M HF ($K_a = 7.2 \times 10^{-4}$)

Solution:

	$HF_{(aq)}$	$\rightleftharpoons$	$H^+_{(aq)}$	+	$F^-_{(aq)}$
Initial conc.	1.0M		0		0
Eq. conc. (mole dm^{-3})	1.0−x		x		x

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

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$$7.2\times10^{-4} = \frac{x\,.\,x}{1.0-x}$$

Since x is very small as compared to 1.0, the term in the denominator can be approximated as follows:

$$1.0-x = 1.0$$

$$7.2\times10^{-4} = \frac{x^2}{1}$$

$$x = 0.268\text{M}$$

$$[H^+] = 0.268\text{M}$$

3.1.2 Strong and Weak Bases

The strength of a base is the ability to accept a proton from a solvent. Hydroxides of alkali metals such as sodium hydroxide and potassium hydroxide are strong bases and ionize completely in aqueous solution.

$$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

$$KOH_{(aq)} \longrightarrow K^+_{(aq)} + OH^-_{(aq)}$$

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The OH^- ion thus formed is a Bronsted base because it can accept proton H^+.

$$OH^- + H^+ \longrightarrow H_2O$$

The ability of a base to accept a proton from an acid, usually water, is termed as the strength of the base. For a base B, an equilibrium reaction with water can be represented by the following equation:

$$B + H_2O_{(aq)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant K_b is called the base ionization constant and can be derived. As;

$$K_b = \frac{[BH^+]\,[OH^-]}{[B]}$$

K_b value will be large if the degree of ionization of the base B is high i.e. if the base B is strong. The Value of K_b will be small for a weak base B. Again, for convenience, a parameter pK_b has been devised to express the K_b value in convenient numbers. Thus, pK_b is defined as the negative logarithm of K_b.

$$pK_b = -\log K_b$$

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Table 3.2: K_b and pK_b Values of Some Common Bases

Name of Base	Formula	K_b	pK_b
Diethlyamine	$(C_2H_5)_2NH$	9.6×10^{-4}	3.02
Ethylamine	$C_2H_5NH_2$	5.6×10^{-4}	3.25
Methylamine	$CH_3\ NH_2$	4.5×10^{-4}	3.34
Ammonia	NH_3	1.7×10^{-5}	4.76
Pyridine	C_5H_5N	5.6×10^{-9}	8.25
Aniline	$C_6H_5\ NH_2$	4.3×10^{-10}	9.37

According to these values, ammonia is a stronger base than pyridine and aniline but weaker than methylamine and ethylamine. Also, diethyl amine is the strongest base among all those listed in Table 3.2.

3.2 Buffer Solutions and their Applications

A buffer solution is a solution, the pH of which does not change significantly when a small amount of acid or base is added to it. Such a solution has a constant pH which does not change keeping it constant for a long time.

Types of buffer solutions

A buffer solution can be made in two ways:

(1) By mixing a weak acid and a salt of it with a strong base. Such solutions give acidic buffers with pH less than 7. e.g. $CH_3COOH + CH_3COONa$.

(2) By mixing a weak base and a salt of it with a strong acid. Such solutions will give basic buffers with a pH of more than 7. e.g. $NH_4OH + NH_4Cl$.

Buffer Action:

Consider a buffer solution of CH_3COOH and CH_3COONa. The common ion effect helps us to understand how the buffer will work. CH_3COOH being a weak electrolyte undergoes very little dissociation. When CH_3COONa, a strong electrolyte is added to the CH_3COOH solution, the dissociation of CH_3COOH is suppressed due to the common ion effect of CH_3COO^-.

$$CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

$$CH_3COONa_{(s)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

(i) Suppose we add a few drops of HCl to it. Its H^+ ions are used up by CH_3COO^- ions.

Thus the addition of HCl will not change the pH of the buffer solution.

$$CH_3COOH_{(l)} \xrightleftharpoons{H_2O} CH_3COO^-_{(aq)} + H^+_{(aq)}$$

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

$$CH_3COO^-_{(aq)} + H^+_{(aq)} \rightleftharpoons CH_3COOH_{(aq)}$$

(ii) In the same buffer solution, if a strong base is added, it is neutralised by the acid.

$$CH_3COOH_{(l)} \xrightleftharpoons{H_2O} CH_3COO^-_{(aq)} + H^+_{(aq)}$$

$$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)}$$

Thus the addition of NaOH will not change the value of pH.

3.2.1 Calculation of pH of Buffer Solution

The concentration of conjugate base in the reaction mixture is predominately supplied by the salt which is a strong electrolyte. Therefore, assuming the concentration of conjugate base is equal to that of salt and the original concentration of acid as equilibrium concentrations, the pH of a buffer can be calculated.

The following example explains the calculations associated with buffer solutions.

Example 3.2

(a) Calculate the pH of an acetic acid-sodium acetate buffer solution containing 1.0 moles of each component.

(b) What will be the pH of this solution after the addition of 0.01 mole of hydrochloric acid to 1dm^3 of the solution? Assume that the volume of the solution remains unchanged with the addition of hydrochloric acid. (K_a for acetic acid is 1.8×10^{-5}).

Solution

(a) The pH of the buffer solutions can be calculated by assuming the equilibrium concentration of both the acid and its conjugate base as the starting concentration.

Thus $[CH_3CO_2H] = 1.0M$ $\quad [CH_3COO^-] = 1.0M$

For acetic acid dissociation;

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$

$$1.8 \times 10^{-5} = \frac{[1.0][H^+]}{[1.0]}$$

Thus, the pH of the buffer solution is 4.745.

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(b) After HCl addition:

$$\underset{0.01\ \text{mole}}{HCl_{(aq)}} \longrightarrow \underset{0.01\ \text{mole}}{H^{+}_{(aq)}} + \underset{0.01\ \text{mole}}{Cl^{-1}_{(aq)}}$$

Initially, there were 1.0 mole of CH_3COOH and 1.0 mole of CH_3COO^- present per dm^3 of the solution. After the addition of hydrochloric acid 0.01 mole of CH_3COO^- ions is combined with the H^+ ions formed from the dissociation of 0.01 mole of added hydrochloric acid. This can be written as:

$$\underset{0.01\ \text{mole}}{CH_3COO^-_{(aq)}} + \underset{0.01\ \text{mole}}{H^+_{(aq)}} \longrightarrow \underset{0.01\ \text{mole}}{CH_3CO_2H_{(aq)}}$$

Thus, the numbers of moles of acetic acid and acetate ions, after the addition of hydrochloric acid are:

$$CH_3CO_2H = (1.0+0.01)\ \text{mole} = 1.01\text{mole}$$

$$CH_3COO^- = (1.0-0.01)\ \text{mole} = 0.99\text{mole}$$

The equilibrium equation for this new situation can be written as;

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3CO_2H]}$$

$$\text{or} \quad [H^+] = \frac{Ka[CH_3CO_2H]}{[CH_3.COO^-]}$$

$$[H^+] = \frac{1.8\times10^{-5}(1.01)}{0.99}$$

$$\text{pH} = -\log(1.83\times10^{-5})$$

$$= 4.736$$

Notice there is a slight change in pH from 4.745 to 4.736 which is only a difference of 0.009. Thus, a buffer does a very good job in limiting the change in pH to a very small amount.

3.2.2 Applications of Buffer Solutions

Buffers play a crucial role in various everyday applications, helping to maintain stability and prevent abrupt changes in different systems. Here are some important applications of buffers in everyday life.

1. The buffer system in blood plasma

The bicarbonate ion (HCO_3^-) plays a crucial role in maintaining blood pH through the bicarbonate buffer system. Blood pH is a measure of its acidity or alkalinity, and it must be tightly regulated for various physiological processes to function properly. The normal pH range of blood is approximately 7.35 —7.45, a value higher than 7.8 or lower than 6.8 can lead to death.

In the bicarbonate buffer system, there is a reversible exchange of carbon dioxide (CO_2) and bicarbonate ions in the blood. The reaction can be summarized as follows:

(a) Formation of carbonic acid (H_2CO_3):

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$

(b) Decomposition of carbonic acid into bicarbonate (HCO_3^-) and hydrogen ion (H^+):

$$H_2CO_{3(aq)} \qquad HCO^-_{3(aq)} + H^+_{(aq)}$$

This system is catalyzed by an enzyme found in red blood cells called carbonic anhydrase. CO_2, H_2CO_3, HCO_3^- and H^+ levels are related, and any imbalance can affect the pH of the blood. Thus HCO_3^- helps regulate blood pH:

Neutralization of acids:

When there are many acids (H^+ ions) in the blood, bicarbonate acts as a base, binding to these hydrogen ions and forming carbonic acid. This reaction helps to neutralize and eliminate excess acidity:

$$HCO^-_{3(aq)} + H^+_{(aq)} \rightleftharpoons H_2CO_{3(aq)}$$

Neutralization of bases:

Conversely, if there are many bases in the blood, such as hydroxide ions (OH^-), the carbonic acid dissociates, releasing hydrogen ions that can combine with excess bases:

$$OH^-_{(aq)} + H_2CO_{3(aq)} \rightleftharpoons HCO^-_{3(aq)} + H_2O_{(l)}$$

Participating in these reversible reactions, bicarbonate ions help maintain the acid-base balance in the blood. This buffer system is crucial in preventing rapid changes in blood pH and provides a stable environment for enzymes and other biochemical processes to function optimally. The respiratory and renal systems also play an important role in regulating CO_2 and bicarbonate levels to maintain blood pH in a normal range.

2. Household Cleaning Products:

Detergents: Many cleaning agents and detergents contain buffers to maintain a stable pH, ensuring effective cleaning without causing harm to the surface or skin.

3. Personal Care Products:

Shampoos and Soaps: Buffers are often used to maintain the pH of shampoos and soaps, preventing skin irritation and ensuring the products are gentle.

4. Swimming Pools:

Water Treatment: Buffers are employed in swimming pools to help maintain a stable pH level, preventing corrosion of pool equipment and ensuring a comfortable environment for swimmers.

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5. Food and Beverage Industry:

Food Preservation: Buffers are used in food processing to control acidity, preserve flavours, and maintain the stability of certain food products.

Beverage Production: Buffers help control the pH in beverages, ensuring consistency in taste and preventing spoilage.

6. Photography:

Developer Solutions: Buffers are used in photographic developer solutions to maintain a stable pH, allowing for controlled and consistent film or print development.

3.3 Solubility Product and **Precipitation Reactions**

Now we will discuss some of the important equilibria which have some analytical importance.

3.3.1 Solubility Product

When an excess of slightly soluble ionic compound is mixed with water. Some of it dissolves and the remaining compound settles at the bottom. Dynamic equilibrium is established between an undissolved solid compound and its ions in the saturated solution. For example, when CaF_2 is mixed with water. The following equilibrium is established.

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^{-}_{(aq)}$$

K_c for this equilibrium can be written as

$$K_c = \frac{[Ca^{+2}][F^-]^2}{[CaF_2]}$$

DO YOU KNOW

K_{sp} is used for solutes which are only slightly soluble and do not completely dissolve in solution. The higher the K_{sp} value of a compound, the more it is soluble in water.

Since CaF_2 is a slightly soluble salt its concentration almost remains constant.

Therefore,

$$K_c[CaF_2] = [Ca^{+2}]\,[F^-]^2$$

$$K_{sp} = [Ca^{+2}]\,[F^-]^2$$

Where K_{sp} is a constant known as **the solubility product constant. It is defined as the product of the molar concentrations of ions, each raised to a power which is equal to the coefficient of the ion in the balanced chemical equation.**

In general, K_{sp} expression of any slightly soluble ionic compound, A_mB_n can be written as

$$A_mB_{n(s)} \rightleftharpoons mA^{+n}{}_{(aq)} + nB^{-m}{}_{(aq)}$$

$$K_{SP} = [A^{+n}]^m [B^{-m}]^n$$

This means that the solubility product constant is equal to the product of the equilibrium concentration of ions each raised to a power equal to the number of such ions in the formula unit of the compound.

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CONCEPT ASSESSMENT EXERCISE 3.1

Write the dissociation reaction and the solubility product constant expression for each of the following solids.

1. $PbSO_4$
2. $Al(OH)_3$
3. $BaSO_4$

3.3.2 Calculating Concentrations of ions

Given the K_{sp} for AgBr ($K_{sp} = 1.60\times10^{-10}$), we can use the K_{sp} expression to calculate the concentrations of each ion in the solution.

If we represent the x moles of AgBr dissolved in one dm^3 of water

$$AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$$

$$x \qquad\qquad x \qquad\qquad x$$

$$K_{sp} = [Ag+][Br-]$$

$$1.60\times10^{-10} = x.x$$

$$X^2 = 1.6\times10^{-10}$$

$$X = 1.26 \times 10^{-5}M$$

So, $[Ag^+] = [Br^-] = 1.26 \times 10^{-5}M$

Slightly soluble salts dissociate only to a small extent in water, leading to low ion concentrations. To calculate the concentration of these salts in solution, we use their solubility product constant (K_{sp}).

The K_{sp} expression relates the concentrations of the ions in equilibrium with the undissolved salt.

Steps to calculate the concentration:

1. Write the dissociation equation for the salt.
2. Set up the K_{sp} expression.
3. Solve for ion concentrations based on stoichiometry.

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Example 3.3

Calculate the concentration of Silver chloride (AgCl) in its aqueous solution.

1. **Dissociation:**

   $$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

2. **Ksp expression:**

   $K_{sp} = [Ag^{+}][Cl^{-}]$

   For AgCl, $K_{sp} = 1.8\times10^{-10}$ at 25°C.

3. **Concentration Calculation:**

   Since each mole of AgCl gives one mole of Ag^{+} and Cl^{-} ions, let the solubility of AgCl be x mol/dm³. Then,

   $$Ksp = [x][x]$$
   $$1.8\times10^{-10} = x^2$$
   $$x^2 = 1.8 \times 10^{-10}$$
   $$x = 1.34\times10^{-5}\ mol/dm^3$$

   Thus, the solubility (or concentration of Ag^{+} and Cl^{-}) in water is approximately 1.34×10^{-5} mol/dm³

CONCEPT ASSESSMENT EXERCISE 3.2

1. K_{sp} for PbF_2 is 4×10^{-8}. Calculate the concentration Pb^{2+} and F^{-} ions in solution.

   Ans : 2.5×10^{-3} mol dm^{-3}, 4.3×10^{-3} mol dm^{-3}

2. K_{sp} for $BaSO_4$ is 1×10^{-10}. Write the equation and the equilibrium expression for the dissolving of barium sulphate. Also calculate the concentration of each ion.

   Ans: 1×10^{-5} mol dm^{-3} each.

3.4 Common Ion Effect

An interesting situation arises when a weak electrolyte and a salt containing a common ion are present simultaneously in an aqueous solution. For example, in a solution of weak acid, hydrofluoric acid $K_a = 7.2 \times 10^{-4}$, its salt sodium fluoride produces the common ion.

$$HF_{(aq)} \xrightleftharpoons{H_2O} H^{+}_{(aq)} + F^{-}_{(aq)}$$

$$NaF_{(s)} \xrightarrow{H_2O} Na^{+}_{(aq)} + F^{-}_{(aq)}$$

Since HF is a weak electrolyte, it slightly dissociates. NaF being a strong electrolyte breaks up completely into its ions. The common ion F^{-} produced by NaF will upset its equilibrium. This will increase the concentration of F^{-} ions. According, to Le Chatelier's principle, the equilibrium will shift to the left to use some of the F^{-} ions. This will decrease the dissociation of HF. Thus dissociation of HF will decrease in the presence of dissolved NaF. This means as a result of the equilibrium shift, the concentration of HF will increase.

Similarly, when a highly soluble salt is added to the saturated solution of a less soluble salt containing a common ion. *The degree of dissociation* of the less soluble salt decreases. Therefore, it causes a decrease in its solubility.

DO YOU KNOW

The separation and identification of cations into analytical groups is based on solubility product principle and common ion effect. In general, any procedure that involves precipitation follows these principles.

The term common ion effect is used to describe the behaviour of a solution in which the same ion is produced by two different compounds. **"The phenomenon in which the degree of ionization or solubility of an electrolyte is suppressed by the addition of highly soluble electrolyte containing a common ion is called common ion effect".**

Examples

i. Potassium per chlorate $KClO_4$ is moderately soluble in water. When highly soluble KCl is added to the saturated solution of $KClO_4$. It causes an increase in the concentration of K^+ ion.

$$KClO_{4(s)} \rightleftharpoons K^+_{(aq)} + ClO^-_{4(aq)}$$

$$KCl_{(s)} \longrightarrow K^+_{(aq)}\ Cl^-_{(aq)}$$

According to Le Chatelier's principle K^+ ions will react with ClO_4 ions to form $KClO_{4(s)}$ This will suppress, the ionization of $KClO_4$. Thus it will precipitate out.

ii. When HCl gas is passed through the saturated solution of NaCl (Brine), it increases the concentration of Cl^- ion.

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^{-1}_{(aq)}$$

According to Le Chatelier's principle Cl^- ions will combine with Na^+ ions to form precipitate of a pure NaCl.

Self Check Exercise 3.3

i. Ammonium Chloride, NH_4Cl is a water-soluble salt. What will happen if this salt is added to a solution containing ammonium hydroxide?

$$NH_4OH_{(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

ii. Carbonic acid is a weak acid. It ionizes in water as follows

$$H_2CO_{3(aq)} \rightleftharpoons 2H^+_{(aq)} + CO^{-2}_{3(aq)}$$

What will happen if a strong electrolyte such as Na_2CO_3 is added to a solution containing carbonic acid?

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3.5 The Partition Coefficient

If you put two immiscible liquids like ether and water in a separatory funnel and shake. On standing, you can see two layers. Ether is less dense, so it forms the upper layer. Assume that solute X dissolves in both liquids. If you prepare a solution of known concentration of X in water and mix it with ether in a separatory funnel and shake well. On standing, the two layers separate again. Now determine the concentration of the water layer. You will notice a decrease in concentration. Why? Where did the solute go? Analysis of the ether layer shows that there is also a solute in the ether layer. This means that the solute is distributed between the two solvents. A dynamic equilibrium is created between these two solutions. At equilibrium, the concentration of X becomes constant in both layers.

$$X(\text{in water}) \rightleftharpoons X(\text{in ether})$$

$$K_{PC} = \frac{[X \text{ in ether}]}{[X \text{ in water}]}$$

This equilibrium constant is called the partition coefficient and is represented by the symbol K_{pc}. It has a constant value at a constant temperature.

The distribution law, or Nernst distribution law, gives a generalization that governs the distribution of a solute between two immiscible solvents. This law was first given by Nernst, who studied the partitioning of several solutes between various suitable pairs of solvents.

The partition coefficient (K_{pc}) is defined as the ratio of the concentrations of a solute in two different immiscible solvents in contact with each other when equilibrium has been established at a particular temperature. The partition coefficient is a ratio of two concentrations, so it has no units.

3.5.1 Calculation of Partition Coefficient

The **partition coefficient** (K_{pc}) for a system in which the solute is in the same physical state in the two solvents can be calculated using the equilibrium expression.

ACTIVITY 3.1: Calculating the partition coefficient

Procedure

- Measure 100 cm^3 of a 0.150M solution of aqueous methylamine and add it into a separatory funnel.
- Add 75 cm^3 of an organic solvent in the separatory funnel.
- Shake the separatory funnel gently but thoroughly to allow the solute to distribute between the two solvents. Allow the system to reach equilibrium (about 5-10 minutes).
- Let the layers settle and separate the two solvents into different beakers.
- Measure the concentration of the solute in each solvent.

Calculations

When100 cm^3 of a 0.150 mol dm^{-3} solution of aqueous methylamine (CH_3NH_2) is shaken with 75.0 cm^3 of an organic solvent in the separating funnel to allowed to come to equilibrium. Only 25 cm^3 of the aqueous layer is run off and titrated against 0.225MHCl 7.05 cm^3 of HCl was used.

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Data for calculations

1. **Volume of aqueous methylamine solution: 100 cm^3**
2. **Initial concentration of methylamine: 0.150 mol dm^{-3}**
3. **Volume of organic solvent: 75.0 cm^3**
4. **Volume of aqueous layer titrated: 25.0 cm^3**
5. **Volume of HCl used for titration: 7.05 cm^3**
6. **Concentration of HCl: 0.225 mol dm^{-3}**

Calculate the partition coefficient of methylamine in the organic solvent and water.

Solution

Step 1: **Write down the equilibrium equation:**

$$CH_3NH_{2(aq)} \rightleftharpoons CH_3NH_2\ \text{(organic solvent)}$$

Step 2: **Write down the K_{pc} expression:**

$$K_{PC} = \frac{[CH_3NH_2\ \text{(organic layer)}]}{[CH_3NH_{2(aq)}]}$$

Step 3: **Determine the total moles of methylamine in the original solution.**

Determine the total moles of CH_3NH_2 in the original solution.

$$\text{Total moles } CH_3NH_2 = \frac{0.100 \times 150}{1000}$$

$$= 0.015\ \text{mol}$$

These moles were distributed between the two layers.

Step 4: **Determine the no. of moles methylamine in the aqueous layer.**

$$CH_3NH_{2(aq)} + HCl_{(aq)} \rightarrow CH_3NH_3Cl_{(aq)}$$

25 cm^3 of aqueous layer reacted with 7.05 cm^3 of 0.225 MHCl

$$1\ \text{mol of } CH_3NH_2 \text{ is: } 1\ \text{mol of } HCl$$

$$n = M \times V dm^3$$

moles of CH_3NH_2 reacted with HCl solution = moles of HCl solution

$$= 0.225 \times \frac{7.05}{1000}$$

$$= 0.001586 \text{ mol}$$

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As 25cm^3 of the aqueous layer was titrated, the 0.001586 mol of methylamine was present in 25cm^3 of the aqueous layer.

So, the moles of methylamine present in 100 cm^3 of aqueous layer = $\frac{0.001586 \times 100}{25}$

$$= 0.00634 \text{ mol}$$

Step 5: **Determine the number of moles of CH_3NH_2 present in the organic layer.**

Mol CH_3NH_2 (organic layer) = mol CH_3NH_2 (total) - mol CH_3NH_2(aqueous layer)

$$= 0.015 - 0.00634$$

$$= 0.00867 \text{ mol}$$

Step 6: **Change the number of moles into concentrations:**

Concentration (CH_3NH_2 in aqueous layer) = $0.0063 \times \frac{1000}{100}$

$$= 0.063 \text{ mol dm}^{-3}$$

Concentration (CH_3NH_2 in organic layer) = $0.0866 \times \frac{1000}{75}$

$$= 0.116 \text{ mol dm}^{-3}$$

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Step 7: **Substitute the values into the K_{pc} expression:**

$$K_{PC} = \frac{0.116}{0.0364}$$

$$K_{pc} = 1.83$$

Since the value of K_{pc} is **larger than** 1, methylamine is more soluble in the organic solvent than in water.

CONCEPT ASSESSMENT EXERCISE 3.3

When 2 grams of a solute is shaken with a mixture of 150 cm^3 of water and 20 cm^3 of chloroform. After shaking, 1.5 grams of the solute is found in the chloroform layer. Calculate the partition coefficient.

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3.5.2 Factors Affecting the Numerical value of Partition coefficient

The partition coefficient (K_{pc}) indicates how a solute distributes itself between two immiscible phases, usually a non-polar solvent and a polar solvent.

Factors that affect the numerical value of the partition coefficient are:

1. The Polarity of the solute:

A polar solute has a greater affinity for a polar phase (eg, water). This is because polar solutes interact with polar solvents through dipole-dipole or hydrogen bonding interactions.

For example;

A polar solute like ethanol (a polar molecule because of the hydroxyl group) between octanol and water. Ethanol is more soluble in water than octanol, resulting in a higher partition coefficient in favour of the polar phase.

2. The Solvent Polarity:

The nature of the solvents used in the partition plays a decisive role. Non-polar solvents promote the partitioning of non-polar solutes, while polar solvents promote the partitioning of polar solutes. For example;

When a non-polar solute such as benzene is added, its partition coefficient is higher in octanol than in water, because benzene is non-polar and interacts more with non-polar octanol.

3. Temperature:

Temperature can affect the partition coefficient by affecting the solubility and kinetic energy of the solute in both solvents. In general, an increase in temperature can increase the solubility of solutes in polar solvents. For instant;

The partitioning of a polar solute such as aspirin between octanol and water can show different values at different temperatures. At higher temperatures, aspirin is more soluble in water than in octanol.

4. Molecular structure and size

Large solute molecules can interact with solvents differently than smaller molecules. Molecular structure, including functional groups, can also affect the distribution coefficient.

Consider the partitioning of octanol and water between two molecules of similar structure but different sizes, such as ethyl acetate and butyl acetate. A larger butyl acetate molecule may have a lower partition coefficient in favour of the non-polar phase due to increased steric hindrance.

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KEY POINTS

- The degree to which different Bronsted acids give off protons is called "acid strength"
- The greater the value of Ka, the stronger the acid".
- The strength of a base is the ability to accept a proton from a solvent
- A buffer solution is a solution, the pH of which does not change significantly when a small amount of acid or base is added to it.
- The bicarbonate ion (HCO_3^-) plays a crucial role in maintaining blood pH through the bicarbonate buffer system.
- The normal pH range of blood is approximately 7.35 —7.45.
- The solubility product is defined as the product of the equilibrium concentrations of ions, each raised to a power which is the coefficient of the ion in the balance chemical equation.
- The phenomenon in which the degree of ionization or solubility of an electrolyte is suppressed by the addition of a highly soluble electrolyte containing a common ion is called the common ion effect.
- The partition coefficient (K_{pc}) is defined as the ratio of the concentrations of a solute in two different immiscible solvents in contact with each other when equilibrium has been established at a particular temperature.
- Nernst`s law states that a solute is distributed between two layers of immiscible solvents so that the ratio of its concentration in each solvent is equal to its solubility.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which phenomenon describes a shift in equilibrium due to the addition of an ion already involved in the equilibrium?

a) Le Chatelier's Principle
b) Common Ion Effect
c) Nernst's Law
d) Avogadro's Principle

ii. What property is used to distinguish between strong and weak acids?

a) Molar mass
b) Extent of ionization
c) Density
d) Melting point

iii. Which factor is considered when distinguishing between strong and weak bases?

a) Colour
b) Odor
c) Extent of ionization
d) Solubility

iv. What defines a buffer solution?

a) High concentration of ions
b) Presence of a weak acid and its conjugate base
(or a weak base and its conjugate acid)
c) Low pH
d) Absence of ions

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v. How can a buffer solution be made?

a) Mixing strong acids and bases

b) Mixing a weak acid and its conjugate base (or a weak base and its conjugate acid)

c) Diluting a strong acid d) Adding water to a strong base

vi. What role does HCO_3^- play in controlling pH in blood?

a) Neutralization of acids b) Buffering against changes in pH

c) Catalysing reactions d) Enhancing oxygen transport

vii. How is the concentration of a slightly soluble salt calculated?

a) Using the solubility product constant (K_{sp})

b) Titration with a strong base

c) Measuring density

d) Conductivity measurement

viii. Which term is used to describe the strength of an acid in terms of its ionization in water?

a) Acid Concentration b) Acid Dissociation Constant (Ka)

c) Acid Molarity d) Acid Equilibrium Constant

ix. Which type of solvent would favour the partitioning of a polar solute?

a) Non-polar solvent b) Hydrophobic solvent

c) Polar solvent d) Aprotic solvent

x. What is the partition coefficient defined as?

a) Ratio of solute concentration in one solvent to the other

b) Ratio of solute concentration in a single solvent

c) Ratio of solute mass in one solvent to the other

d) Ratio of solute mass in a single solvent

2. Short Answer Questions

i. Explain the common ion effect with a suitable example.

ii. Differentiate between strong and weak acids using the extent of ionization and K_a.

iii. Differentiate between strong and weak bases using the extent of ionization and K_b.

iv. Define a buffer solution and provide an example of how it can be made.

v. How does a buffer solution control pH? Include chemical equations in your explanation.

vi. Describe the uses of buffer solutions in various applications.

vii. Explain how HCO_3^- plays a role in controlling pH in the blood.

viii. Calculate the concentration of a slightly soluble salt given its *solubility product* constant (K_{sp}).

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3. Long Answer Questions

i. **Discuss the principles behind the common ion effect, providing two examples to illustrate its application.**

ii. **Compare and contrast strong and weak acids based on their extent of ionization and the value of Ka.**

iii. **Elaborate on the factors that distinguish strong and weak bases, incorporating the concept of ionization and the base dissociation constant (K_b).**

iv. **Provide a comprehensive explanation of buffer solutions, including how they are prepared, how they control pH, and their uses in different scenarios.**

v. **Calculate the pH of an NH_4OH and NH_4Cl buffer solution containing one mole of each. K_b of NH_4OH is 1.8×10^{-5}.** **Ans: 9.26**

vi. **A solute has a partition coefficient $K_{benzene/water} = 4$, 100 cm^3 of water is shaken with 100 cm^3 of benzene containing 0.20 mol of the solute. Find the amount of solute that remains in water at equilibrium.** **Ans: 0.04 mol**

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UNIT 04

ACID-BASE CHEMISTRY

Student Learning Outcomes (SLOs)

- State that pH =-log[H^+_{aq}] and [H^+] = 10(to the power)-pH.
- State that change of one pH unit represents a 10 -fold change in the hydrogen ion concentration [H^+].
- Use the ionic product constant, K_w=[H^+][OH^-] = 10^{-14} at 298 k to solve problems.
- Sketch the pH titration curves of titrations using combinations of strong and weak acids with strong and weak alkalis.

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Acid-base chemistry is a fundamental aspect of chemical science. It describes the concepts of acids and bases as well as their interactions in aqueous solutions. Acid-base reactions are essential in various chemical processes, from biological systems to industrial applications, and are often visualized through pH of solutions.

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4.1 The pH

The pH scale was originally introduced by the Danish biochemist S.P.L. Sorenson in 1909 and used the symbol of pH. The letter p is derived from the German word potenz meaning power or exponent of, in this case, 10. In 1909, S.P.L. Sorenson published a paper in Biochem Z in which he discussed the effect of H^+ ions on the activity of enzymes. In the paper, he invented the term pH (purported to mean pond us hydrogen ii in Latin) to describe this effect and defined it as the $-\log[H^+]$. In 1924, Sorenson realized that the pH of a solution is a function of the "activity" of the H^+ ion and not the concentration. Thus, he published a second paper on the subject. A better definition would be.

$$\text{pH} = -\log\,[H^+]$$

where a{H^+} denotes the activity(an effective concentration) of the H^+ ions. The activity of an ion is a function of many variables of which concentration is one. Concentration is abbreviated by using square brackets, e.g., [H_3O^+]is the concentration of hydronium ion in solution. Activity is abbreviated by using "a" with curly brackets.

The concentration of Hydrogen ions in aqueous solution can be expressed in terms of the pH scale. The pH of a solution is the logarithm to base 10 of the reciprocals of the numerical value of the hydrogen ion concentration.

$$\text{pH} = \log \frac{1}{[H_3O^+]}$$

$$= -\log\,[H_3O^+] \qquad \text{OR} \qquad = -\log\,[H^+]$$

pH values of bases

The concentration of hydroxide ions in a solution can be expressed in terms of pOH. This is given by:

$$\text{pOH} = -\log[OH^-]$$

It is possible to write an expression relating pH and pOH as $pK_w = pH + pOH$

At 25°C: $\text{pH} + \text{pOH} = 14$

4.2 The pH Scale

The pH scale is a numerical scale that shows acidic or alkaline strength of solution. The values on the pH scale go from 0-14 (extremely acidic substances have values of below 1). All acids have pH values less than 7. The lower the pH, the more acidic the solution is. The higher the pH, the more alkaline the solution is.

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pH is an indication of concentration of H^+. For example, at a pH of zero the hydronium ion concentration is one molar, while at pH 14 the hydroxide ion concentration is one molar. Typically, the concentrations of H^+ in water in most solutions fall between a range of 1 M (pH=0) and 10^{-14} M (pH=14). Figure 1.1 depicts the pH scale with common solutions and where they are on the scale.

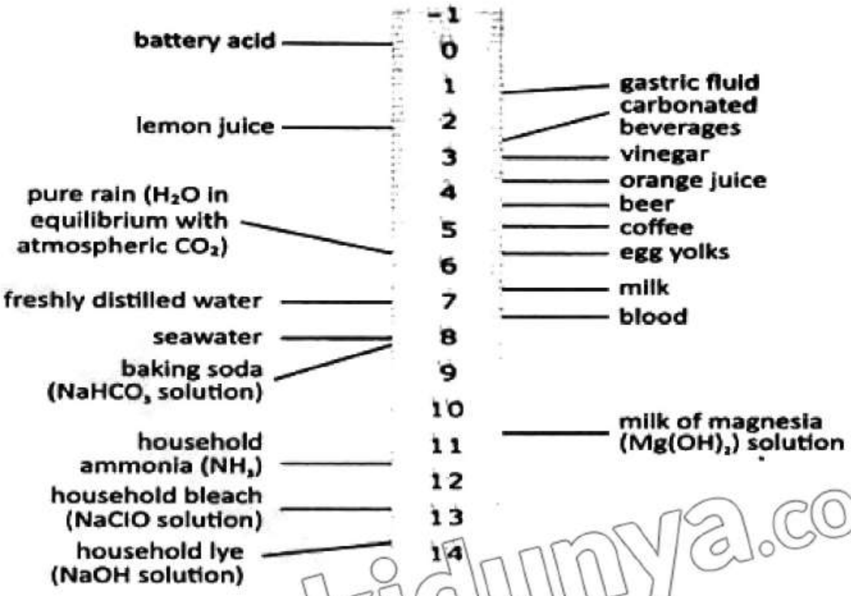

Fig 4.1: Solutions and the placement of them on pH scale

Example: 4.1

Find the pH of a solution of 0.002 M of HCl.

Solution

The equation for pH is -log $[H^+]$

$$[H^+] = 2.0\times 10^{-3}M$$

$$pH = -\log[2.0\times 10^{-3}] = 2.70$$

Example: 4.2

If moist soil has a pH of 7.84, what is the H^+ concentration of the soil solution?

Solution

$$pH = -\log[H^+]$$

$$7.84 = -\log[H^+]$$

$$[H^+] = 1.45\times 10^{-8}M$$

Hint

Place −7.84 in your calculator and take the antilog (often inverse log or 10^x) = 1.45×10^{-8}M

Concept Assessment Exercise 4.1

1. What is the pH of a solution of 2g pure H_3PO_4 per dm^3 of solution?
2. Calculate the concentration of hydrogen ion(H^+) in a solution of sulphuric acid having pH of 1.5.

4.3 Ionic Product of Water and Calculation of pH and pOH

Recall that the product of the concentration of H^+ and OH^- ions in pure water at room temperature (298 k).

$$K_w = [H_3O^+][OH^-]$$

Where K_w is the ionic product or dissociation constant of water.

Unit of K_w is mol^2dm^{-6}.

In pure water, the concentration of H^+ and OH^- ions are equal i.e 1.0×10^{-7}. So, value of K_w at room temperature is 1.0×10^{-14}.

$$pK_w = -\log K_w$$

As value of K_w is 1.0×10^{-14} so $\quad pK_w = -\log 1.0 \times 10^{-14} = 14$

The ionic product of water is related to the dissociation constants pKa and pKb of an acid and its conjugate base respectively.

$$pK_a + pK_b = pK_w = 14 \text{ (at 298 K)}$$

OR

$$pH + pOH = pK_w = 14 \text{ (at 298 K)}$$

Thus, if the pK_a value of an acid is known, the pK_b value of its conjugate base can be found.

Example: 4.3

If the concentration of NaOH in a solution is 2.5×10^{-4} M, what is the concentration of H_3O^+ ion at 25 °C?

Solution

Data:

$$[OH^-] = 2.5 \times 10^{-4}\ M$$

We can assume room temperature, so

$$1.0 \times 10^{-14} = [H_3O^+][OH^-]$$

to find the concentration of H_3O^+, solve for the $[H_3O^+]$.

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-4}}$$

$$= 4.0 \times 10^{-11} M$$

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Example: 4.4

Calculate the pH value of 0.001 moldm^{-3} solution of NaOH at 25°C.

Solution

Data:

$$[OH^-] = 0.001\ moldm^3$$

$$\text{As } K_w = [H_3O^+][OH^-]$$

value of K_w at 298 k is $1.0 \times 10^{-14} mol^2 dm^{-6}$

$$1.0 \times 10^{-14} = [H_3O^+][0.001]$$

$$[H_3O^+] = \frac{1.0\times10^{-14}}{0.001} = 1.0 \times 10^{-11} \text{mol dm}^{-3}$$

$$pH = -\log[H_3O^+]$$

$$pH = -\log[1 \times 10^{-11}] = 11$$

Example: 4.5

Calculate the pH of $5.0\times 10^{-5} M$ solution of sodium hydroxide.

Solution

The equation for pOH is

$$pOH = -\log[OH^-]$$

$$[OH^-] = 5.0\times 10^{-5} M$$

$$pOH = -\log[5.0\times 10^{-5}] = 4.30$$

$$14 = PH + pOH$$

$$pH = 14 - pOH$$

$$pH = 14 - 4.30 = 9.70$$

Concept Assessment Exercise 4.2

1. The concentration of hydroxide ion in given solution of slaked lime ($Ca(OH)_2$) is 0.001M. Calculate the concentartion of hydrogen ion in it.
2. An aqueous solution contain 2×10^{-3} M of hydrogen ions (H^+). Calculate pOH of this solution.

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4.4 pH Titration Curves

In order to determine the concentration of the unknown solution, the technique of titration is used in neutralisation reactions between acids and alkalis. It involves adding a titrant of known concentration from a burette into a conical flask containing the analyte of unknown concentration. An indicator is added which will change colour at the endpoint of the titration. The endpoint is the point at which equal number of moles of titrant and analyte reacts with each other. The equivalence point is halfway the vertical region of the curve.

Equivalence point → moles of alkali = moles of acid

This is also known as the equivalence point, and this is the point at which neutralisation takes place. There are different types of titration curves depending on the strength of acid or alkalis used.

a. Strong acid and strong alkali pH titration curve

In this case hydrochloric acid is taken in the conical flask. Initially, there are only H^+ ions present in the conical flask (initial pH about 1-2). As the volume of strong alkali (NaOH) added from the burette increases, the pH of the HCl solution slightly increases too as more and more H^+ ions react with the OH^- ions from the NaOH to form water. The change in pH is not that much until the volume added gets close to the equivalence point. The pH surges upwards very steeply. The equivalence point is the point at which all H^+ ions have been neutralised (therefore pH is 7 at equivalence point). Adding more NaOH will increase the pH as now there is an excess in OH^- ions (final pH about 13-14). Figure 4.2 represents the titration curve 1.0 mol dm^{-3} HCl with NaOH. Hence 25 cm^3 of titrant (NaOH) is used to neutralise 25 cm^3 of HCl.

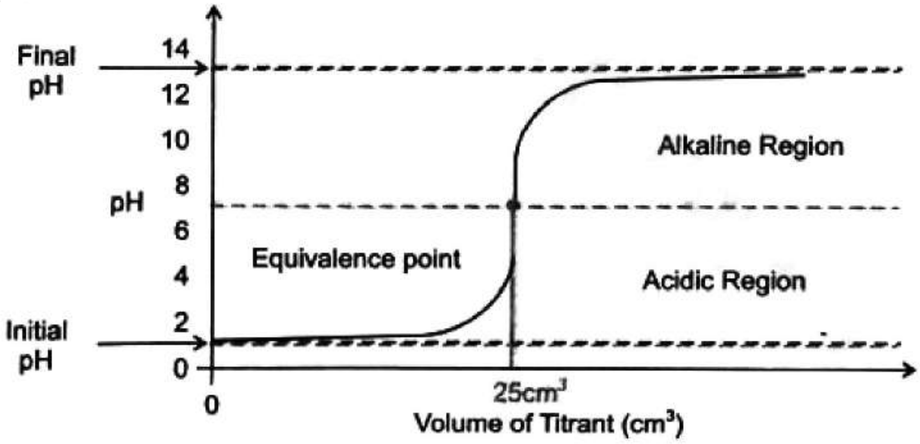

Fig 4.2: The diagram shows a pH titration curve of 1.0 mol dm^{-3} HCl (25 cm^3) with NaOH

The pH titration curve for HCl added to a NaOH has the same shape. The initial pH and final pH are the other way around. The equivalence point is still 7. Following figure represents a pH titration curve when HCl is added from a burette into the conical flask containing aqueous solution of NaOH.

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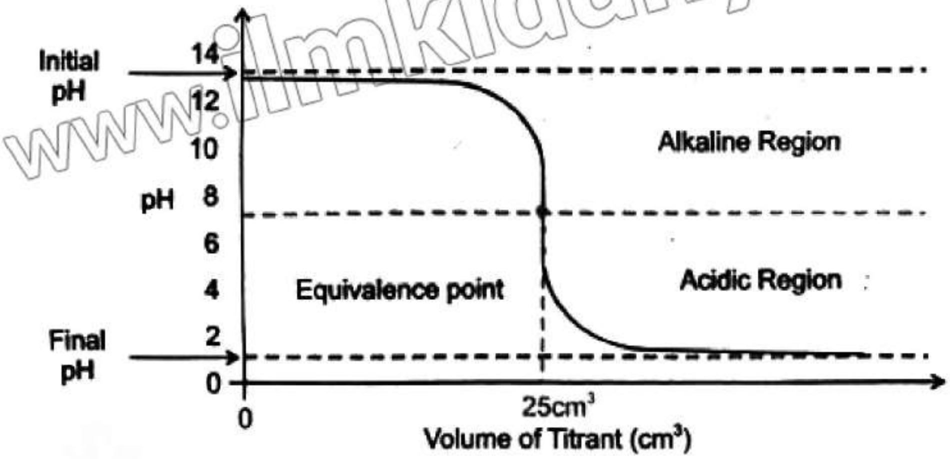

Fig 4.3: The diagram shows a pH titration curve of 1.0 mol dm^{-3} NaOH (25 cm^3) with HCl

b. Strong acid and weak alkali pH titration curve

Initially, there are only H^+ ions present in the conical flask (initial pH about 1-2). As the volume of weak alkali (NH_3) added form the burette increases, the pH of the analyte solution slightly increases too as more and more H^+ ions react with the NH_3. The change in pH is not that much until the volume added gets close to the equivalence point.

The equivalence point is not neutral, but the solution is still acidic (pH about 5.5). This is because all H^+ have reacted with NH_3 to form NH_4^+ which is a relatively strong acid, causing the solution to be acidic. As more of the NH_3 is added, the pH increases to above 7 but below that of a strong alkali as NH_3 is a weak alkali. Following figure represents the pH titration curve of this reaction.

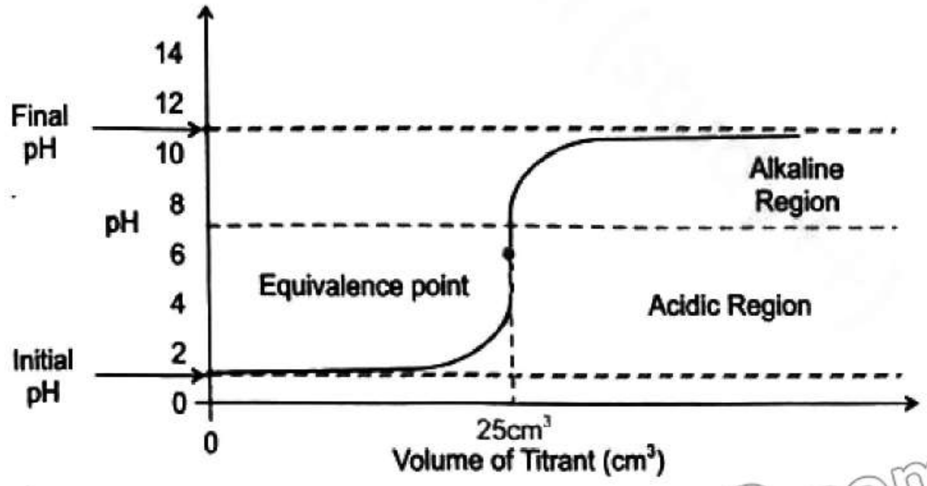

Fig 4.4: The diagram shows a pH titration curve of 1.0 mol dm^{-3} HCl (25 cm^3) with NH_3

The pH titration curve for strong acid added to a weak alkali has the same shape. The initial and final pH are the other way around. The equivalence point is still about 5.5.

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c. Weak acid and strong alkali pH titration curve

Initially ethanoic acid (CH_3COOH), having initial pH of about 2-3 is taken in the conical flask. As the volume of strong alkali (NaOH) added from the burette increases, the pH of the ethanoic acid solution slightly increases too as more and more H^+ ions react with the OH^- from the NaOH to form water. The change in pH is not that much until the volume added gets close to the equivalence point. The pH surges upwards very steeply. The equivalence point is not neutral, but the solution is slightly basic (pH about 9). This is because all H^+ in CH_3COOH have reacted with OH^- however, CH_3COO^- is a relatively strong base, causing the solution to be basic. As more of the NaOH is added, the pH increases to about 13-14. Following figure represents the pH titration curve of this reaction.

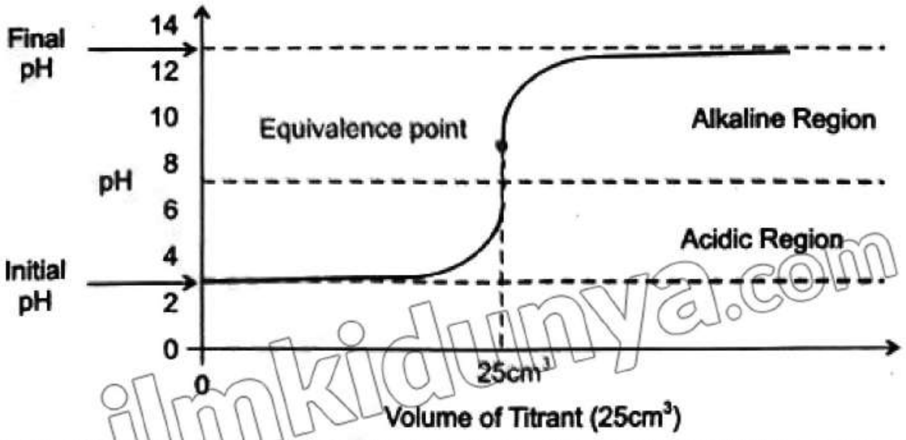

Fig 4.5: The diagram shows a pH titration curve of a weak acid with a strong base

The pH titration curve for weak acid added to a strong alkali has the same shape. The initial and final pH are the other way around. The equivalence point is still about 9.

d. Weak acid and weak alkali pH titration curve

Initially there are only H^+ ions present in solution from the dissociation of the weak acid (CH_3COOH, ethanoic acid) (initial pH about 2-3). In these pH titration curves, there is no vertical region. There is a 'point of inflexion' at the equivalence point. The curve does not provide much other information.

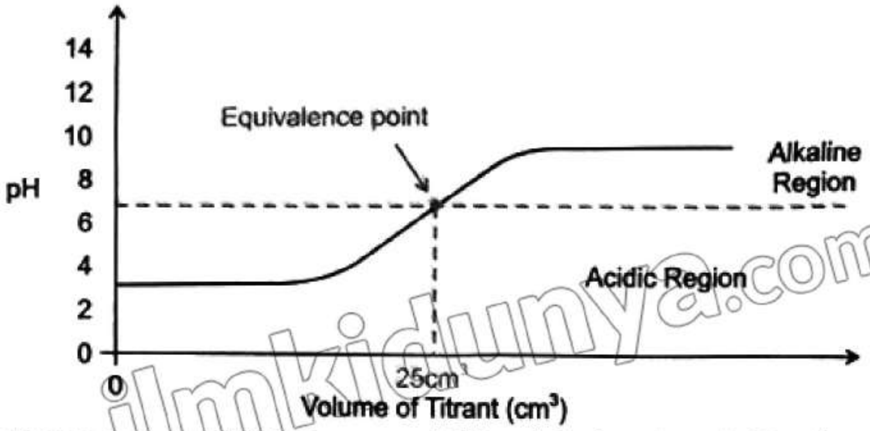

Fig 4.6: The diagram shows a pH titration curve of 1.0 mol dm^{-3} weak acid (25 cm^3) with weak alkali

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Concept Assessment Exercise 4.3

1. In a titration it is found that 25 cm^3 of 0.1 M solution of NaOH is neutralised with 19 cm^3 of HCl of unknown concentration. Calculate concentration of a given HCl solution.

   $$HCl + NaOH \rightarrow NaCl + H_2O$$

2. Draw the pH titration curve when 20 cm^3 of HCl from the burette is added to 20 cm^3 of aqueous solution of ammonia present in the conical flask.

KEY POINTS

- The pH of a solution is the logarithm to base 10 of the reciprocals of the numerical value of the hydrogen ion concentration.
- pH is used to find the relative strength of acidity and alkalinity of the solution.
- The pH scale ranges from 0–14. As the pH of a given solution increases basic character increases and vice versa
- The ionic product of water is the product of the concentration of hydrogen ion and hydroxide ion.
- Value of Kw at 25 °C is 1×10^{-14} .
- Titration is a technique used in neutralisation reactions between acids and alkalis to determine the concentration of the unknown solution.
- Equivalence point is the point at which indicator changes its colour and the point at which neutralisation takes place. $H^+ + OH^- \rightarrow H_2O$

References for additional information.

- George M. Bodner and harry L. Pardue, Chemistry an Experimantal Science.
- Disha Expert- Disha NCERT Xtract errorless objective Chemistry
- Chemistry for A level by Francesca

EXERCISE

1. Multiple Choice Questions (MCQs)

i. The value of the ionic product of water

a) depends on volume of water
b) depends on temperature
c) changes by adding acid or alkali
d) always remains constant

ii. A base when dissolved in water yields a solution with a hydroxyl ion concentration of 0.05 mol dm^{-3}. The solution is

a) Basic
b) Acidic
c) Neutral
d) either b or c

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iii. pH scale was introduced by.

a) Arrhenius b) Sorensen

d) Lewis d) Lowry

iv. pH of solution is defined by expression

a) $\log[H^+]$ b) $\log\left[\frac{1}{H^+}\right]$

c) $\frac{1}{log[H^+]}$ d) $\frac{1}{-log[H^+]}$

v. The pH of a 10^{-3} M HCl solution at 25°C if it is diluted 1000 times, will be

a) 3 b) zero

c) 5.98 d) 6.02

vi. How many dm^3 of water must be added to 1 dm^3 an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2?

a) 0.1 dm^3 b) 0.9 dm^3

c) 2.0 dm^3 d) 9.0 dm^3

vii. What is the approximate pH of a 1×10^{-3} M NaOH solution?

a) 3 b) 11

c) 7 d) 1×10^{-11}

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viii. Calculate the pOH of a solution at 25°C that contains1×10^{-10} M of hydronium ions, i.e. H_3O^+

a) 4.0 b) 9.0

c) 1.0 d) 7.0

ix. The pH value of a 10 M solution of HCl is

a) less than 0 b) equal to 0

c) equal to 1 d) equal to 2

x. Which of the following has the highest pH?

a) $\frac{M}{4}\ KOH$ b) $\frac{M}{4}\ NaOH$

c) $\frac{M}{4}\ NH_4OH$ d) $\frac{M}{4}\ Ca(OH)_2$

xi. Which of the following statements are correct?

(i) $K_w = [H^+][OH^-] = 10^{-14}\ mol^2dm^{-6}$ at 298K

(ii) At 298K $[H^+] = [OH^-] = 10^{-7}$

(iii) Kw does not depend upon temperature

(iv) Molarity of pure water = 55.55 M

a) (i), (ii) and (iii) b) (i), (ii) and (iv)

c) (i) and (iv) d) (ii) and (iii)

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2. Short Answer Questions

i. Calculate H^+ ion concentration of a solution prepared by dissolving 4 g of NaOH (Atomic weight of Na = 23 amu) in1000 cm^3 of solution?

ii. Calulate the pH of 0.005 molar solution of H_2SO_4

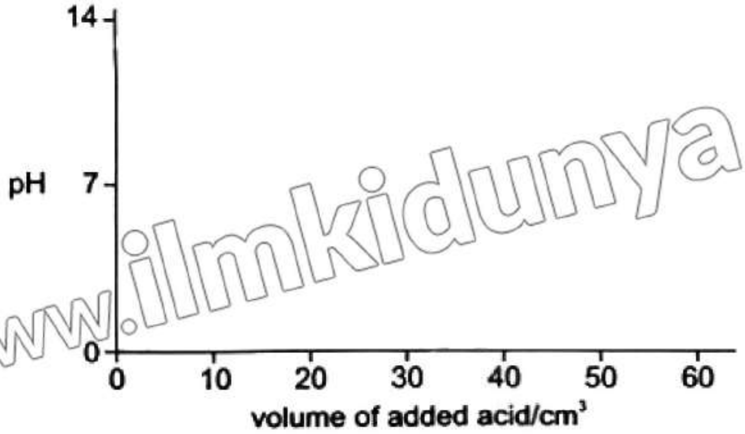
iii. Calculate the pH of the following compounds

(i) 10^{-4} M KOH (ii) 10^{-10} M HCl (iii) 10^{-10} M KOH (iv) 10^{-4} M HCl

iv. 100 cm^3 of 0.04 M HCl aqueous solution is mixed with 100 cm^3 of 0.02 M NaOH solution. Calculate the pH of the resulting solution.

v. Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture?

vi. A 20.0 cm^3 sample of 0.200 mol dm^{-3} $NH_3(aq)$ was titrated with 0.100 mol dm^{-3} HCl. On the following axes, sketch how the pH changes during this titration. Mark clearly where the end point occurs.



3. Long Answer Questions

i. Explain the concept of pH and its significance in acid-base chemistry. How does the pH scale relate to the concentration of hydrogen ions in a solution?

ii. Compare and contrast the titration curves for a strong acid with a strong base, a weak acid with a strong base, a strong acid with a weak base, and a weak acid with a weak base.

iii. A 50 cm^3 solution of 0.1 M acetic acid is titrated with 0.1 M sodium hydroxide. The K_a of acetic acid at 25 °C is 1.8×10^{-5} mol dm^{-3}. Calculate the pH of the solution at the equivalence point and explain the shape of the titration curve for this reaction.

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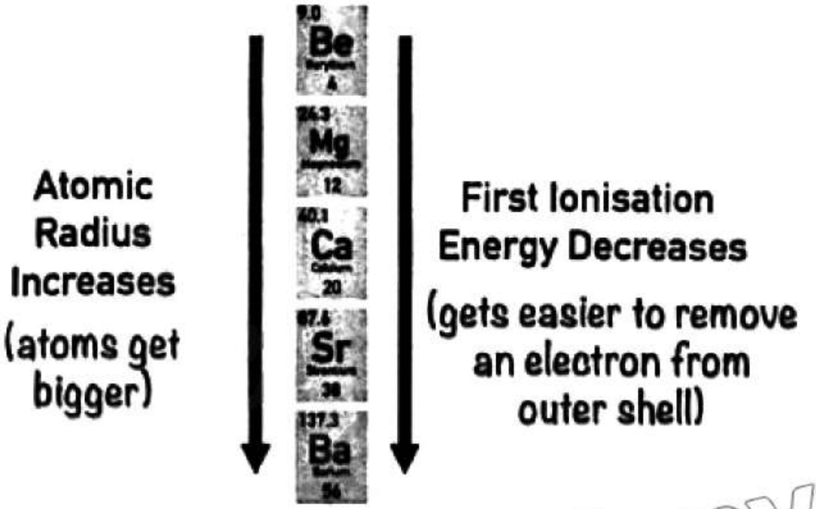
UNIT 05



GROUP 2 ELEMENTS

Student Learning Outcomes (SLOs)

- **Describe the properties and trends of group 2 elements, including their electron configuration, reactivity, and common compounds such as oxides, hydroxides and carbonates.**
- **Explain the chemical reactivity of Group 2 elements, including their reactions with oxygen, water and acids (Be, Mg, Ca).**
- **Explain the reactivity of group 2 elements in terms of their electron configuration and valence electrons.**
- **Describe the industrial and everyday use of group 2 compounds, including their role in medicine and agriculture.**
- **Explain the term reactivity series and its application in predicting the outcome of chemical reactions.**
- **Use the term reactivity series and its application in predicting the outcome of chemical reactions.**

- Explain the extraction and purification process of group II elements and their compounds.
- Understand the term thermal decomposition and its application in the analysis of group 2 compounds, especially carbonates and nitrates.
- Use the term thermal decomposition and its application in the analysis of group 2 compounds, especially carbonates and nitrates.
- Explain the trend in solubility of group II sulphates and hydroxides using the terms enthalpy of hydration and enthalpy of solution.
- Compare the properties and reactivity of group 2 elements with group 1 in the periodic table.
- Explain the term complex ion and its application in the formation of group 2 compounds.
- Explain the term basic oxide and its application in the formation of group 2 compounds.
- Describe qualitatively the trend in the thermal stability of nitrates and carbonates including the effect of ionic radius on the polarization of the large anion.
- Describe qualitatively the variation in solubility and enthalpy change of solution, ΔH sol, of hydroxides and sulphates in terms of relative magnitudes of the enthalpy change of hydration and the lattice energy.

Elements from Group 2 are used in a wide range of applications. For example, Group 2 metals produce coloured flames when heated, leading to their use in flares and fireworks. Magnesium in powdered form is used in flares.

The elements in Group 2 of the Periodic Table are referred to as alkaline earth metals because their oxides and hydroxides are water-soluble (alkaline) in nature and oxides are found in the earth's crust. As they are in Group 2, these elements have two electrons in their outermost shell. These two outer electrons occupy s subshell. Their general electronic configuration is ns^2. Electronic configurations of the first three elements in Group 2 are:

Beryllium (Be)	$1s^2 2s^2$
Magnesium (Mg)	$1s^2 2s^2 2p^6 3s^2$
Calcium (Ca)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

5.1 General Trends of Physical Properties and Chemical Reactivity of Group 2 Elements

All Group 2 metals can form ionic compounds in which they donate two outermost electrons to become an ion with +2 charge. So, they act as reducing agents as they get oxidised. When going down the group, the metals become more reactive. This can be explained by looking at the Group 2 ionisation energies in the figure 5.1.

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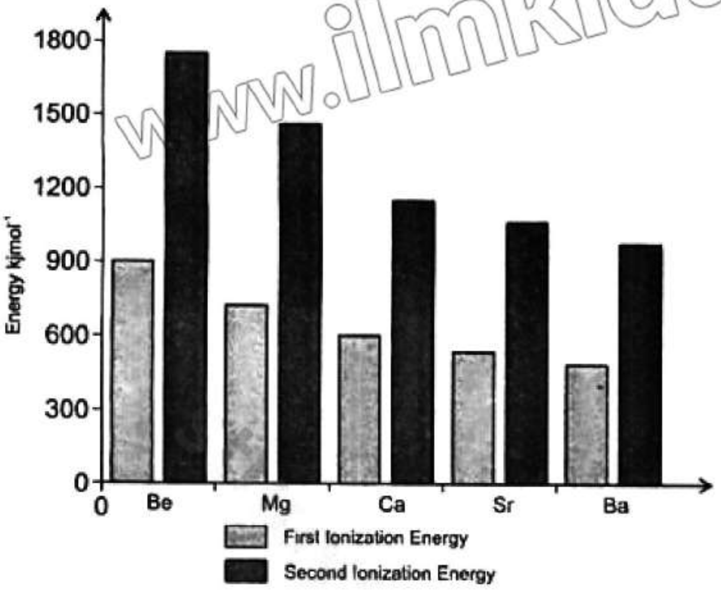

Decreasing order of 1st ionization energy of group 2 elements is

Be > Mg > Ca > Sr > Ba

Fig 5.1: Trend of first and second ionization energies of group 2 elements

5.1.1 Trends in ionization energy and chemical reactivity

Ionization energy is the minimum amount of energy required to remove one mole of electron from the isolated gaseous atom or ion. This graph shows that both the first and second ionization energies decrease going down the group. The graph above shows that going down the group, it becomes easier to remove the outer two electrons of the metals. This is due to the increased shielding effect and a larger distance between the outermost electrons and nucleus. As a result of this, the elements become more reactive going down the group as it gets easier for the atoms to lose two electrons and become 2+ ions. This trend is shown by looking at the reactions of the Group 2 metals:

With dilute hydrochloric acid: bubbles of hydrogen gas are given off much faster indicating that the reactions become more vigorous. For example:

$$Mg_{(s)} + 2HCl_{(aq)} \quad MgCl_{2(aq)} + H_{2(g)}$$

With oxygen: the metals get more reactive with oxygen down the group (Ba is so reactive that it must be stored in oil to prevent it from reacting with oxygen in air.

5.1.2 Trends in atomic radius

Look at the atomic radii of the Group 2 elements, shown in Table 5.1. The atoms of Group 2 elements get larger going down the group. This is because of the increase in extra shell and shielding effect, attraction between the nucleus and valence electrons decreases. Hence, size of atom increases. Figure 5.2 represents the atomic radius of group 2 elements.

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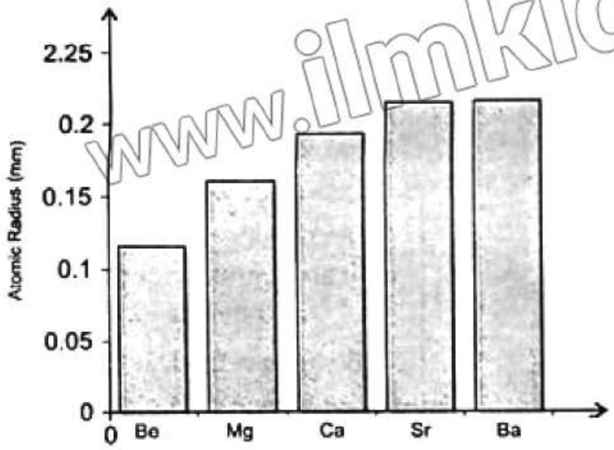

Increasing order of atomic radius of group 2 elements is

Be < Mg < Ca < Sr < Ba

Fig 5.2: Trend of Atomic radius of group 2 elements

5.1.3 Trends in melting point

The melting point of the elements decreases going down the group as the outer electrons get further away from the nucleus. This means that the attraction between the nucleus and the delocalised electrons decreases hence strength of metallic bond decreases causing a decrease in melting point. Figure 5.3 represents the melting points of group 2 elements.

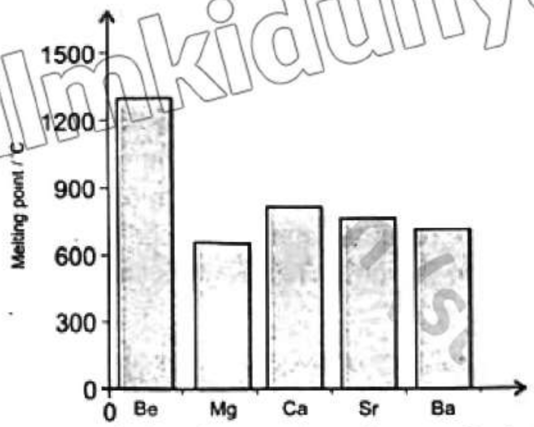

Fig 5.3: Trend of melting point of group 2 elements

Following table 5.1 represents the general trends in physical properties, such as atomic radius, melting point and density.

Table 5.1: Physical properties of alkaline earth metals

Group 2 Element	Metallic radius/nm	Atomic number	Melting point/°C	Density/gcm^{-3}
beryllium (Be)	0.122	4	1280	1.85
magnesium (Mg)	0.160	12	650	1.74
calcium (Ca)	0.197	20	838	1.55
strontium (Sr)	0.215	38	768	2.66
barium (Ba)	0.217	56	714	3.56

5.2 Trends in Chemical Reactivity with Oxygen, Water and Dilute Acids

(a) Reaction with Oxygen/ Formation of Basic oxide

The Group 2 metals burn in air, and more rapidly in oxygen, forming white solid oxides. Strontium and Barium also form peroxides (MO_2). For example, magnesium ribbon burns with a bright white flame once ignited in a Bunsen flame.

$$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$$

Beryllium and magnesium oxides are insoluble in water while the solubility of remaining oxides increases down the group, as they form soluble hydroxides.

All oxides of group 2 elements are basic in character except BeO which is amphoteric in nature as it reacts both with acid and base. Basic character increases on moving down the group.

$$BeO_{(s)} + 2HCl_{(aq)} \rightarrow BeCl_{2(aq)} + H_2O_{(l)}$$

$$BeO_{(s)} + 2NaOH_{(aq)} \rightarrow Na_2BeO_{2(aq)} + H_2O_{(l)}$$

The Group 2 metals get more reactive with oxygen going down the group. The larger atoms lose their outer two electrons more readily than the smaller atoms in the group. The greater reactivity of barium metal is illustrated by the fact that it must be stored under oil to keep it out of contact with air.

BeO is covalent in character while remaining oxides are basic in nature. This is due to the small size of Be^{2+} ion. Polarizing power of Be^{2+} is greater because of which oxide ion can easily be polarised. Hence electrons are shared by the nuclei of both atoms. That is why BeO is covalent in character.

Flame test

Some of the Group 2 metals burn with characteristic flame colours. It is the 2+ ions formed in the reaction that cause the colours. We can test for calcium, strontium and barium in compounds using flame tests. A nichrome wire, cleaned with concentrated hydrochloric acid, is dipped into a sample of the salt to be tested and heated in a non-luminous Bunsen flame:

- calcium compounds give a brick-red colour.
- strontium compounds give a scarlet/red colour
- barium compounds give an apple-green colour

(b) Reaction with water

Beryllium does not react with water because of the protective layer of BeO on its surface.

Magnesium does not react with cold water. However, it burns in steam to forms magnesium oxide and hydrogen.

$$Mg_{(s)} + H_2O_{(g)} \rightarrow MgO_{(s)} + H_{2(g)}$$

Calcium reacts more readily than magnesium, with water.

$$Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$

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This reaction forms a cloudy white suspension of slightly soluble calcium hydroxide. The calcium hydroxide dissolves make the solution weakly alkaline. The hydrogen gas is given off at a steady rate. Going down the group, reactivity of group II elements with water increases as hydrogen gas is released more and more rapidly.

General reaction of all group 2 metals except Be and Mg with water follows the following general equation.

$$M_{(s)} + 2H_2O_{(l)} \rightarrow M(OH)_{2(s)} + H_{2(g)}$$

(c) Reaction with Dilute Acids

The Group 2 metals undergo redox reaction with dilute acids to form salts and hydrogen gas. The reactions become more vigorous and exothermic down the group. The reaction of all group 2 metals with dilute HCl follows the following general equation.

$$M_{(s)} + 2HCl_{(aq)} \rightarrow MCl_{2(aq)} + H_{2(g)}$$

(d) Reaction of group 2 oxides with acid

Group 2 oxides are basic oxides, these oxides are used in making useful compounds by their reaction with acid.

$$MgO_{(s)} + H_2SO_{4(aq)} \rightarrow MgSO_{4(aq)} + H_2O_{(l)}$$
$$CaO_{(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + H_2O_{(l)}$$

Magnesium sulfate is used for short-term relief of constipation. It is also used as a soaking solution to relieve minor sprains, bruises, muscle aches or discomfort and joint stiffness. Calcium chloride is used as a solidifying agent in paint production, coagulant in the manufacture of rubber.

Concept Assessment Exercise 5.1

1. What is the general trend in the melting points going down Group 2?
2. Explain why the atoms in Group 2, as in any other group, get larger with increasing atomic number.
3. Write a balanced chemical equation, including state symbols, for the reaction of:
   i. strontium with oxygen
   ii. strontium oxide with hydrochloric acid.
4. Barium reacts vigorously when added to water.
   i. Write a balanced chemical equation, including state symbols, for the reaction of barium with water.
   ii. State two observations that could be made during this reaction.
   iii. Suggest the approximate pH of the resulting solution.
   iv. Will the reaction be more or less vigorous than the reaction of barium with water? Explain your answer.
5. Describe what you would see when magnesium reacts with cold water and steam. Also write an equation for the reaction with steam.

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5.3 Comparison of Reactivity of Group 1 and Group 2 Element

Reactivity of an element depends upon the ionization energy. Smaller the value of ionization energy, greater is the reactivity. Alkaline earth metals have higher ionization energy as compared to alkali metals. It is because of their smaller size and greater attraction of electrons towards nucleus. Group II elements are less reactive than Group I elements in the same period because of low ionization energy of group I elements as compared to group II.

Alkali metals react vigorously with water. The reaction is so vigorous that the evolved hydrogen catches fire. While alkaline earth metal reacts slowly with water.

$$Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(l)}$$

$$Ca_{(s)} + 2H_2O \rightarrow Ca(OH)_{2(aq)} + H_{2(l)}$$

Alkali metals are good reducing agents compared to alkaline earth metals because they possess smaller value of I.E.

5.4 Uses of Group 2 Compounds

Use of Limestone in industry

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Limestone is made up mainly of calcium carbonate. There are many types of limestone, which provide useful rocks for building. They can be shaped into blocks that can be stuck to each other using mortar. Previously, this mortar was made using lime and sand.

Now it is more usual to use cement and sand, although the cement is made from lime. Marble is another form of calcium carbonate used as a building material, for example in making of expensive tiles. However, most calcium carbonate is used to make cement. The first stage in the manufacture of cement is the roasting of limestone in a lime kiln. At high temperatures in the kiln, calcium carbonate decomposes to form calcium oxide also called lime or quick lime.

$$CaCO_{3(s)} \xrightarrow{\text{Heat}} \underset{\text{lime}}{CaO_{(s)}} + CO_{2(g)}$$

The calcium oxide made in the lime kiln goes on to be roasted with clay to make cement. Cement can be mixed with sand and small pieces of rock to make concrete, the most widely used building material in the world. Its tensile strength can be improved by letting the concrete set with iron rods running through it.

Use of slaked lime in agriculture

Calcium hydroxide (slaked lime) is used in agriculture to increase the pH of acidic soils.
Calcium hydroxide is basic, so it will react with and neutralise acid, raising the pH of the soil.

$$Ca(OH)_{2(s)} + 2H^{+}_{(aq)} \rightarrow Ca^{2+}_{(aq)} + 2H_2O_{(l)}$$

Use of Group 2 compounds in medical

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Barium sulphate ($BaSO_4$) is used in medicine because it absorbs X-rays strongly and is used to diagnose disorders of the intestines and stomach. As it is insoluble, and not absorbed into the blood stream from the gut.

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Group 2 hydroxides and carbonates are bases and are often used as antacids to treat acid indigestion (an excess of hydrochloric acid in the stomach) by neutralisation. Gaviscon and Rennies use calcium carbonate and magnesium carbonate, while Milk of Magnesia is a suspension of magnesium hydroxide in water.

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$$

$$Mg(OH)_{2(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + 2H_2O_{(l)}$$

5.4 Thermal Decomposition of Group 2 Carbonates and Nitrates

Thermal decomposition is the breakdown of a compound into two or more different substances by the application of heat.

The carbonates and nitrates of group 2 elements decompose, when heated. The carbonates break down to form the metal oxide and give off carbon dioxide gas. For example:

$$MgCO_{3(s)} \xrightarrow{Heat} MgO_{(s)} + CO_{2(g)}$$

The temperature at which thermal decomposition takes place increases going down Group 2 carbonate.

The Group 2 nitrates also undergo thermal decomposition. For example:

$$2Ca(NO_3)_{2(s)} \xrightarrow{Heat} 2CaO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

A brown gas is observed when a Group 2 nitrate is heated. This is toxic nitrogen dioxide, NO_2 (nitrogen dioxide). Like carbonates, a higher temperature is needed to thermally decompose the nitrates as group 2 is descended.

5.4.1 Trend in thermal stabilities

Thermal stability of group 2 carbonates or nitrates increases down the group. The relative ease of thermal decomposition is shown by the values of the enthalpy changes of reaction. The more positive the enthalpy change, the more energy will be needed to decompose the metal carbonates.

Table 5.2: Enthalpy change of reaction values for the decomposition of some Group 2 carbonates.

Group 2 carbonate	Decomposition temperature (°C)	Enthalpy change of reaction (KJmol^{-1})
Magnesium carbonate	540	+117
Calcium carbonate	900	+176
Strontium carbonate	1280	+238
Barium carbonate	1360	+268

We can explain this trend using ideas about ion polarisation:

The carbonate ion has a relatively large ionic radius, so it is easily polarised by a small highly charged cation. Size of Group 2 cations increases down the group:

$$Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$$

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The smaller the ionic radius of the cation, the better it is at polarising the carbonate ion. A small highly charged cation such as Mg^{2+} can attract electrons and distort a larger carbonate anion to such an extent that the bond formed has a considerable amount of covalent character. This is shown in figure 5.4.

Fig 5.4 Magnesium ions are better polarisers of carbonate ions than calcium ions.

So, the degree of polarisation of the carbonate ion by the group 2 cation follows the order

$$Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

the greater the polarisation of the carbonate ion, the easier it is to weaken a carbon-oxygen bond in the carbonate and form carbon dioxide and the metal oxide on heating. The order of stability of carbonates is

$$BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$$

A similar pattern is observed with the thermal decomposition of Group 2 nitrates. The order of stability with respect to the products is in the order:

$$Ba(NO_3)_2 > Sr(NO_3)_2 > Ca(NO_3)_2 > Mg(NO_3)_2$$

Concept Assessment Exercise 5.2

1. Which one of the three compounds listed will decompose at the lowest temperature?
   i. Calcium carbonate, strontium carbonate, barium carbonate
   ii. Barium nitrate, calcium nitrate, magnesium nitrate
2. Write a balanced chemical equation, including state symbols, for the thermal decomposition of:
   i. Strontium carbonate ii. Barium nitrate.

5.5 Trends in Solubility of the Group 2 Hydroxides and Sulphate

(a) Solubility of hydroxides of group II elements

The solubility of hydroxides increases as we move down the group, with barium hydroxide being highly soluble in water. The order of solubility is

$$Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$

Table 5.3 shows the solubility in water of some Group 2 hydroxides. We can explain this variation in solubility in terms of the relative values of enthalpy change of hydration and the corresponding lattice energy.

Table 5.3 Solubilities in water of some group 2 hydroxides.

Group 2 hydroxide	Solubility at 298 k (mol/100 g of water)
$Mg(OH)_2$	2×10^{-5}
$Ca(OH)_2$	1.5×10^{-3}
$Sr(OH)_2$	3.4×10^{-3}
$Ba(OH)_2$	1.5×10^{-2}

(b) Change in hydration enthalpy down the group

Hydration enthalpy is directly proportional to the charge on ion and inversely proportional to the size of ion. Smaller ions (with the same charge) have greater enthalpy changes of hydration. So, the enthalpy change of hydration decreases (gets lessexothermic) in the order.

$$Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

this decrease is relatively small down the group and it depends entirely on the increase in the size of the cation, as the anion is unchanged (it is the hydroxide ion in every case).

(c) Change in lattice energy down the group

Lattice energy is greater if the ions (with the same charge) forming the lattice are small so the lattice energy decreases in the order.

$$Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

The lattice energy is also inversely proportional to the sum of the radii of the anion and cation. So, the decrease in lattice energy is relatively large down the group and it is determined more by the size of the large cation ion than the size of the hydroxide.

(d) Difference in enthalpy change of solution of Group 2 hydroxide

Substances that have a very high solubility in water are likely to have enthalpy of solution with a high negative (exothermic) value. As a rough guide, the higher the negative value of enthalpy of solution the more soluble is the salt.

Conclusion:

The lattice energy of the hydroxides decreases by relatively higher values down the group. The enthalpy changes of hydration decreases (gets less exothermic) by relatively lower values down the group. The value of enthalpy of solution gets more exothermic down the group. so, the solubility of the Group 2 hydroxides increases down the group. Compound is likely to be soluble in water only if enthalpy of solution is negative or has a small positive value.

(e) Solubility of sulfates of group II elements

The solubility of sulphates decreases as we move down the group, with barium sulphate being insoluble in water. Table 5.4 shows the solubility in water of some Group 2 sulfates. The solubility decreases as the radius of the metal ion increases.

$$MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$$

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Table 5.4 Solubilities in water of some group 2 sulphates.

Group 2 Sulphates	Solubility at 298 k (mol/dm^3)
$MgSO_4$	1.83
$CaSO_4$	4.66×10^{-2}
$SrSO_4$	7.11×10^{-4}
$BaSO_4$	9.43×10^{-6}

When we move down the group, both the lattice dissociation enthalpy and hydration enthalpy decrease. The hydration enthalpy decreases more than the lattice dissociation enthalpy. So, the enthalpy of the solution becomes more endothermic.

Concept Assessment Exercise 5.3

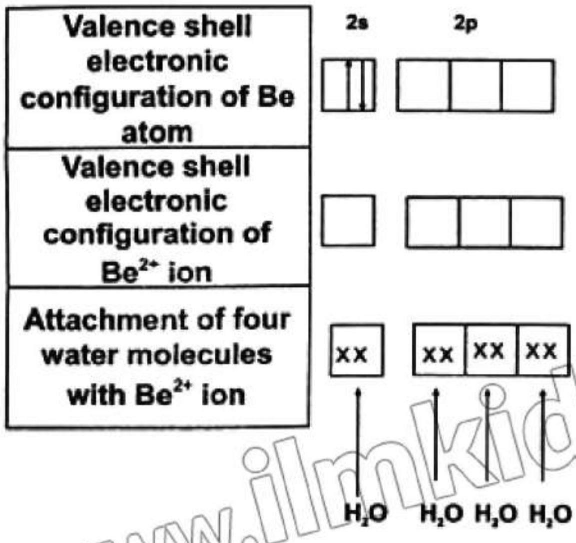
Explain why magnesium sulphates is more soluble than barium sulfate by referring to the relative values of the lattice energies and enthalpy changes of hydration.

5.6 Complexes of The Alkaline Earth Metals

Group 2 elements almost exclusively form ionic compounds containing the M^{2+} ion, They are more reactive towards group 5 elements, and they have a greater tendency to form complexes with Lewis bases than do the alkali metals.

Because of their higher positive charge (+2) and smaller ionic radii, the alkaline earth metals have a much greater tendency to form complexes with Lewis bases than do the alkali metals. This tendency is most important for the lightest cation (Be^{2+}) and decreases rapidly with the increasing radius of the metal ion.

The chemistry of Be^{2+} is dominated by its behaviour as a Lewis acid, forming complexes with Lewis bases that produce an octet of electrons around beryllium. For example, Be^{2+} salts dissolve in water to form acidic solutions that contain the tetrahedral $[Be(H_2O)_4]^{2+}$ ion. Because of its high charge-to-radius ratio, the Be^{2+} ion polarizes coordinated water molecules, thereby increasing their acidity.



$$[Be(H_2O)_4]^{2+} \longrightarrow [Be(H_2O)_3(OH)]^{1+} + H^+$$

Similarly, in the presence of a strong base, beryllium and its salts form the tetrahedral hydroxo complex $[Be(OH)_4]^{2-}$. Hence beryllium oxide is amphoteric. Beryllium also forms a very stable tetrahedral fluoride complex $[BeF_4]^{2-}$, $[BeF_3]^{1-}$. This is all because of small size and high charge density of Be^{2+} ion. Recall that beryllium halides behave like Lewis acids by forming adducts with Lewis bases.

The heavier alkaline earth metals also form few complexes, but usually with a coordination number of 6 or higher. Complex formation is most important for the smaller cations (Mg^{2+} and Ca^{2+}). Thus aqueous solutions of Mg^{2+} contain the octahedral $[Mg(H_2O)_6]^{2+}$ ion. In this complex Mg can extend their coordination number to six by using one 3s, three 3p and two 3d orbitals which are present in its outer most shell.

5.7 Extraction and Purification Process of Group 2 Elements and their Compounds

Group 2 elements, also known as alkaline earth metals, include beryllium, magnesium, calcium, strontium, barium, and radium.The extraction and purification processes of Group 2 elements and their compounds involve several steps tailored to the specific properties of each element.

1. Extraction:

a. Ore Preparation: Group 2 elements are typically found in minerals such as carbonates, sulfates, oxides, and silicates. The ore containing the desired metal is first mined and then crushed to obtain a fine powder in order to extract the elemental metal.

b. Roasting: Group 2 Carbonates are unstable towards heat. They thermally decompose to form metal oxide and carbon dioxide. For example, to extract magnesium from its carbonate first it is roasted to form magnesium oxide and CO_2.

$$MgCO_{3(s)} \xrightarrow{\text{Heat}} MgO_{(s)} + CO_{2(g)}$$

c. Reduction: Depending on the ore, reduction is often carried out to extract the metal. For example, magnesium can be extracted by the electrolysis of molten magnesium oxide, while calcium and strontium can be obtained by reducing their halides with sodium or magnesium.

2. Electrolysis (Purification):

Pure samples of most of the alkaline earth metals can be obtained by electrolysis of the chlorides or oxides. In some cases, electrolysis is used to further purify the extracted metal. Beryllium was first obtained by the reduction of its chloride; radium chloride, which is radioactive, was obtained through a series of reactions and separations.

Examples

Here is an overview of the extraction and purification methods for some key Group 2 elements:

1. Beryllium:

Extraction: Beryllium is usually extracted from beryl ore ($Be_3Al_2(SiO_3)_6$) through a chemical process involving acid digestion and solvent extraction.

Purification: It is purified by converting beryllium hydroxide into beryllium *fluoride*, which is then reduced by magnesium to obtain high-purity beryllium metal.

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2. Magnesium:

Extraction: Magnesium is commonly produced by the electrolysis of molten magnesium chloride (from sea water or brines).

Purification: The magnesium obtained is further purified by fractional distillation or vacuum distillation processes.

Concept Assessment Exercise 5.4

1. Why beryllium form complex compounds?
2. Starting from calcium carbonate how would you extract pure calcium metal.

KEY POINTS

- The Group 2 elements magnesium to barium are typical metals with high melting points and they are good conductors of heat and electricity.
- Progressing down Group 2 from magnesium to barium, the atomic radius increases. This is due to the addition of an extra shell of electrons for each element as the group is descended.
- The Group 2 elements magnesium to barium react with water to produce hydrogen gas and the metal hydroxide, which may be only slightly soluble.
- The Group 2 elements magnesium to barium burn in air to form white solid oxides. These oxides form hydroxides with water. The hydroxides get more soluble in water going down the group so their solutions can become more alkaline.
- The sulfates of Group 2 elements get less soluble in water going down the group.
- Reactivity of the elements with oxygen or water increases down Group 2 as the first and second ionisation energies decrease.
- The Group 2 carbonates and nitrates get more resistant to thermal decomposition descending the group.
- Many of the compounds of Group 2 elements have important uses. Limestone, which contains mainly calcium carbonate, is used as a building material and is used to make cement, which is a component in the mixtures that make concrete and mortar. Slaked lime (calcium hydroxide) is used to neutralise acids in acidic soil.
- Pure samples of most of the alkaline earth metals can be obtained by electrolysis of the chlorides or oxides.

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EXERCISE

1. Multiple Choice Questions (MCQs)

i. The oxidation state shown by alkaline earth metals is

a) +2 b) -2 c) +1,+2 d) -1, -2

ii. Which one of the following is the most soluble in water?

a) $Mg(OH)_2$ b) $Ca(OH)_2$ c) $Sr(OH)_2$ d) $Ba(OH)_2$

iii. Which of the following alkaline earth metal hydroxides is amphoteric in character

a) $Be(OH)_2$ b) $Sr(OH)_2$ c) $Ca(OH)_2$ d) $Ba(OH)_2$

iv. Of the metals Be, Mg, Ca and Sr of group 2 A. In the periodic table the least ionic chloride would be formed by

a) Be b) Ca c) Mg d) Sr

v. The order of solubility of sulphates of alkaline earth metals in water is

a) Be > Mg > Ca > Sr > Ba b) Mg > Be > Ba > Ca > Sr
c) Be > Ca > Mg > Ba > Sr d) Mg > Ca > Ba > Be > Sr

vi. The solubilities of carbonates decrease down the magnesium group due to a decrease in

a) hydration energies of cations b) inter-ionic attraction
c) entropy of solution formation d) lattice energies of solids

vii. In which of the following the hydration energy is higher than the lattice energy?

a) $MgSO_4$ b) $SrSO_4$ c) $RaSO_4$ d) $BaSO_4$

viii. Which of the following alkaline earth metal sulphates has hydration enthalpy higher than the lattice enthalpy?

a) $CaSO_4$ b) $BaSO_4$ c) $BeSO_4$ d) $SrSO_4$

ix. Which gas is released when $CaCO_3$ reacts with dilute HCl?

a) H_2 b) O_2 c) CO_2 d) Cl_2

x. Brick red is characteristics flame colour of

a) Beryllium b) Magnesium c) Calcium d) Barium

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2. Short Answer Questions

i. Describe and explain the trend observed in the thermal stabilities of the carbonates of Group II.

ii. Describe the use of Group II elements or its compounds in agriculture.

iii. Write an equation to represent the thermal decomposition of calcium nitrate,

iv. Why are the elements of Group 2 called alkaline earth metals?

v. How do group 1 metals differ from Group 2 metals?

vi. Explain with the help of an equation the amphoteric nature of beryllium oxide.

vii. Explain qualitatively the variation in solubility of the hydroxides of the elements in Group II down the Group from magnesium to barium.

3. Long Answer Questions

i. Explain the reactivity of group II elements with water and dilute HCl with chemical reactions.

ii. Analyse the trends in the thermal stability of nitrates and carbonates of alkaline earth metals.

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UNIT 06

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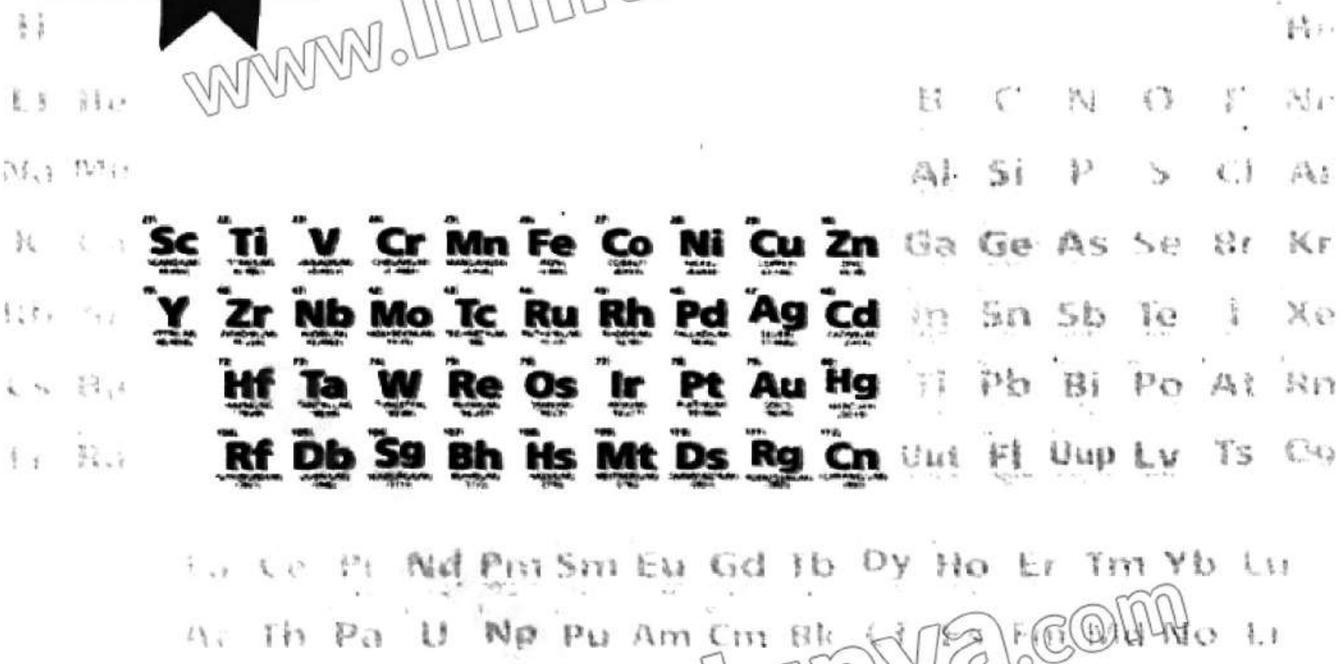

THE TRANSITION METALS

Student Learning Outcomes (SLOs)

- Identify the general physical and chemical properties of the first row of transition elements, titanium to copper.
- Define a transition element as a d-block element which forms one or more stable ions with incomplete d orbitals
- Sketch the shape of $3d_{xy}$ and 3_{dz^2} orbitals
- Identify the properties of transition elements, some examples including

  a. They have variable oxidation states
  b. They behave as catalysts
  c. They form complex ions
  d. They form coloured compounds
- Explain why transition elements have variable oxidation states in terms of similarity in energy of the 3d and 4s sub-shells.
- Explain why transition elements behave as catalysts in terms of having more than one stable oxidation states, and vacant d-orbitals that are energetically accessible and can form dative bonds with ligands.

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- Explain why transition elements form complex ions in terms of vacant d-orbitals that are energetically accessible.
- Explain the reaction of transition elements with ligands to form complexes, including complexes of copper (II) and cobalt (II) ions with water and ammonia molecules and hydroxides and chloride ions.
- Define the term ligand as a species that contains a lone pair of electrons that forms a dative covalent bonds to a central metal atom/ion.
- Use the term monodentate ligand including examples water, ammonia, chloride and cyanide.
- Use the term bidentate ligand including 1,2-diaminoethane and ethanedioate ion, polydentate ligand including EDTA.
- Define the term complex as a molecule or ion formed by a central metal atom/ion surrounded by one or more ligands.
- Describe the geometry (shape and bond angles) of transition elements complexes which are linear, square planar, tetrahedral or octahedral.
- State what is meant by coordination number.
- Predict the formula and charge of a complex ion, given the metal ion, its charge or oxidation state, the ligand and its coordination number or geometry.
- Explain qualitatively that ligand exchange can occur, including the complexes of copper (II) ions and cobalt (II) ions with water and ammonia molecules and hydroxide and chloride ions.
- Predict, using E° values, the feasibility of redox reactions, involving transition elements and their ions.
- Analyse reactions involving $MnO_4^-/C_2O_4^{2-}$ in acid solution given suitable data (including describing the reaction and doing calculations).
- Analyse reactions involving MnO_4^-/Fe^{2+} in acid solution given suitable data (including describing the reaction and doing calculations).
- Analyse reactions involving Cu^{2+}/I^- given suitable data (including describing the reaction and doing calculations).
- Perform calculations involving other colour of complexes.
- Use the terms degenerate and non-degenerate d-orbitals
- Describe the splitting of degenerate d-orbitals into two non-degenerate sets of d-orbitals of higher energy, and use ΔE in (a) octahedral complexes, two higher and three lower d-orbitals (b) tetrahedral complexes, three higher and two lower d-orbitals.
- Explain why transition elements form coloured compounds in terms of the frequency of light absorbed as an electron is promoted between two non-degenerate d-orbitals.
- Describe, in qualitative terms, the effects of different ligands on ΔE°, frequency of light absorbed, and hence the complementary colour that is observed.
- Use the complexes of copper (II) ions and cobalt (II) ions with water and ammonia molecules and hydroxide, chloride ions as examples of ligand exchange affecting the colour observed.
- Describe the types of stereoisomerism shown by complexes, including those associated with bidentate ligands:

- geometrical isomerism, e.g square planar such as $[Pt(NH_3)_2Cl_2]$ and octahedral such as $[Co(NH_3)_4(H_2O)_2]^{2+}$ and $[Ni(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+}$
- Optical isomerism, e.g $[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}$ and $[Ni(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^2$
- Deduce the overall polarity of complexes.
- Define stability constant (K_{stab}) of a complex as the equilibrium constant for the formation of the complex ion in a solvent (from its constituent ions or molecules).
- Write an expression for a K_{stab} of a complex, $[H_2O]$ should not be included.
- Write an expression for a K_{stab} of a complex, $[H_2O]$ should not be included.
- Use K_{stab} expressions to perform calculations.
- Explain ligand exchanges in terms of K_{stab} values and understand that a large K_{stab} is due to formation of a stable complex ion.

When we come across the periodic table, we find a very important block at the centre, call transition elements. They possess unique chemical and physical properties, making them vital for daily use. Copper is used in wiring, coins, and plumbing, while iron is essential for bridges, vehicle parts, and construction. Chromium enhances plumbing fixtures; gold and silver are valuable for jewelry and electronics; platinum aids in catalytic converters; titanium is used in bicycles, aircraft, and artificial joints; and nickel, vanadium, molybdenum, and tantalum serve various industrial and medical purposes. Transition metals also form alloys, such as brass (copper and zinc) and bronze (copper and tin). In this chapter, transition metals are explored in detail.

Transition elements are those which have incomplete d-subshell in their most stable ionic states are called transition elements. They have been given the name 'transition' (which means change) because they show gradual change from much reactive group 2 elements (calcium) to much less reactive group 13 elements (gallium).

The first period of transition elements starts from scandium to zinc. However, zinc does not qualify the definition of transition elements because it forms only one colourless ion, Zn^{2+}, with a complete 3d sub-shell. Although, zinc can form complexes like transition metals, but this is not sufficient for it to be included in the transition elements block.

Remember!
Zinc is d-block element, but not transition element.

Scandium was initially controversial, as its common +3 oxidation state (Sc^{3+}) has an empty d sub-shell. However, it was later included in the transition metals by IUPAC system when compounds with +1 and +2 oxidation states, such as $CsScCl_3$, were synthesized.

In this chapter we will be mainly focused on the first row, the elements from titanium through to copper. To have full understanding of different properties of transition metals, we need to study their electronic configuration in detail.

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6.1 Electron Configurations of the d-block elements

The electronic configuration of transition metals follows Aufbau principle. However, there are some exceptions to this rule. For example, chromium and copper break Aufbau principle. The reason is that atoms or ions with a half-filled 3d sub-level ($3d^5$) or a filled 3d sub-level ($3d^{10}$) are relatively stable, avoiding the inter-electronic repulsion in 4s orbital that occurs with the $4s^2$ configuration. Moreover, in both the cases, the 3d electron cloud is symmetrical which shields the nucleus relatively in a more effective way.

The electron configurations of some of the first-row d-block elements and their ions with orbital diagrams are given:

Key Information
When forming cations, electrons are always removed from the higher energy sub-shell, i.e 4s in first row of d block elements.

Element	Electronic configuration	Ion	Electronic configuration
Sc	$[Ar]3d^14s^2$	Sc^{1+}	$[Ar]\ 3d^14s^1$
		Sc^{2+}	$[Ar]\ 3d^1$
Ti	$[Ar]3d^24s^2$	Ti^{2+}	$[Ar]\ 3d^2$
V	$[Ar]3d^34s^2$	V^{4+}	$[Ar]\ 3d^1$
Cr	$[Ar]\ 3d^54s^1$	Cr^{2+}	$[Ar]\ 3d^4$
		Cr^{3+}	$[Ar]\ 3d^3$
Mn	$[Ar]\ 3d^54s^2$	Mn^{2+}	$[Ar]\ 3d^5$
Fe	$[Ar]\ 3d^64s^2$	Fe^{2+}	$[Ar]\ 3d^6$
		Fe^{3+}	$[Ar]\ 3d^5$
Co	$Ar]\ 3d^74s^2$	Co^{2+}	$[Ar]\ 3d^7$
Ni	$Ar]\ 3d^84s^2$	Ni^{2+}	$[Ar]\ 3d^8$
Cu	$Ar]\ 3d^{10}4s^1$	Cu^{1+}	$[Ar]\ 3d^{10}$
		Cu^{2+}	$[Ar]\ 3d^9$
Zinc	$[Ar]\ 3d^{10}\ 4s^2$	Zn^{2+}	$[Ar]\ 3d^{10}$

Relative Energies of 4s and 3d Sub-shells

The energy difference between 3d and 4s orbitals changes across the period of transition metals. In calcium, the 4s orbital has lower energy than the 3d orbital because the 4s electron experience full attraction of the unscreened nucleus. This makes the 4s electrons more penetrating than the 3d electrons.

Along 3d period, after calcium, the 4s electrons are shielded by the 3d electrons, slightly decreasing their energy causing small rise in the first and second ionization energies. On the contrary, the 3d electrons faces higher effective nuclear charge due to less shielding, strongly attracted by the nucleus. This results in potential increase of 3d electrons, reflected in higher rise of third ionization energy.

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6.2 Properties of Transition Elements

The transition elements are much more like each other than the elements across period 3. For instance, they are all metals rather *than showing* a change from metal to metalloids and non-metal. On the other hand, when we move along period 3, there come metals, then metalloids, non-metals and then noble gases. Similarly, there is not that decrease in atomic radii as in period 3 elements. Due to such similarities, transition metals show the following physical and chemical properties.

Interesting Information

The atomic radii of vanadium (23) and zinc (30) is same because the shielding offered by addition of 3d electrons counter the effect of increasing nuclear charge.

6.2.1 Physical properties

Transition metals show the following physical properties.

- They have high melting points because of strong metallic bonding in them.
- They have high density due to close packing of atoms in their lattices.
- They are good conductors of electricity because they have free electrons.
- They are good thermal conductors.
- They have a shiny metallic luster.
- They are malleable and ductile.
- They are hard and strong which makes them suitable for construction and manufacturing.
- They show magnetic properties, like paramagnetism and ferromagnetism and this property is exploited in various application, including magnetic resonance imaging (MRI).

6.2.2 Physical Characteristics

Some of their physical properties of first row of transition metals are given in detail.

1. Density

Density of metals is the mass per unit volume expressed in the unit gram per cubic centimetre (g/cm^3). It is an important physical property of metals which shows how closely the metal atoms are packed in metallic lattice.

Moving through first period of transition metals, from scandium to copper, the density of transition metals generally increases. This is because of the two factors:

- The atomic mass of the metals increases, making their nuclei progressively heavier as we move to the right across the period.
- The atomic radius decreases across the period due to the increasing nuclear charge, which pulls the electron cloud closer, thereby reducing the size (volume) of the atoms.

Since density is directly related to mass and inversely related to volume, the increase in mass and decrease in volume across the period generally lead to an increase in the density of the metals.

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However, there are some exceptions to the general trend. The density of manganese and copper is different from what is generally expected. The atomic radius of zinc is larger than that of copper because its full 3d sub-shell ($3d^{10}$) leads to less tight packing of zinc atoms in its metallic lattice, resulting in reduced density.

2. Atomic Radii

Transition metals show specific trends of atomic radii across the period. Understanding these trends require consideration of both shielding effect and electronic configuration.

In the first-row transition elements, the atomic radii decrease across the period because the nuclear charge increases, pulling electron closer to the nucleus. However, unlike main group elements, this decrease is less steep because electrons being added in 3d sub-shell do not shield one another sufficiently from the nuclear charge.

In the beginning, the atomic radii decrease because of increasing nuclear charge which overcomes the shielding effect.

Important Information
While discussing covalent and ionic radii, two factors are taken into consideration simultaneously, electron-electron repulsion and electron-nucleus attraction.

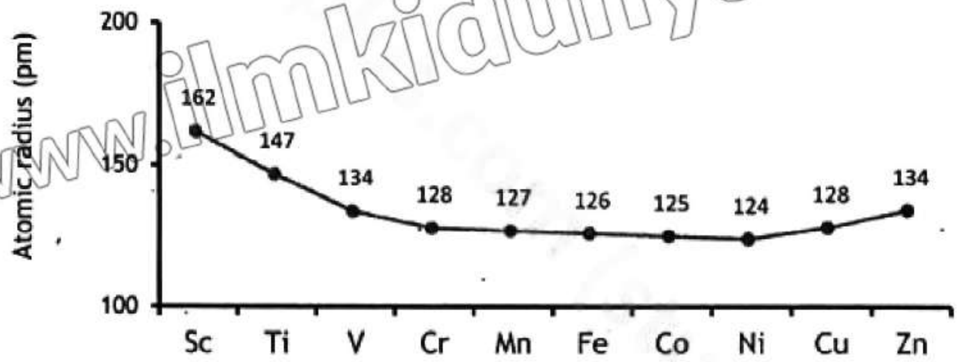

Fig 6.1: Atomic radii of first row transition metals

The decrease in atomic radii is not that pronounced while going through the middle of the period because of the two factors, i.e increasing nuclear charge and shielding effect, counterbalance each other. In this way, the atomic radii remain almost constant at the centre of the period.

Moving towards the end, atomic radii increase from nickel to copper and zinc. The reason is that the 3d sub-shell becomes full which causes shielding effect, pushing 4s sub-shell away from the nucleus.

Similarly, when moving from copper to zinc, we see an unexpected increase in atomic radius. The atomic radius of zinc is larger than that of copper because the additional electron in the 4s sub-shell in zinc increases the shielding effect, which outweighs the effect of the higher nuclear charge.

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The melting and boiling points of the transition elements are generally much higher than those of the s- and p-block elements. They have strong metallic bonding because of involvement of electrons of both 3d and 4s sub-shells. When we plot melting and boiling points against atomic number, both graphs have some irregular behaviour. In the beginning, melting and boiling points increases as atomic number increases. Then we get two minima at manganese which reflect that the full 4s and half 3d sub-shells are much stable and not readily available for metallic bonding.

Zinc has lowest melting and boiling points because of full 3d and 4s sub-shells which cannot participate in metallic bonding. This is why mercury is liquid at room temperature as it belongs to zinc family (with full 3d and 4s sub-shells).

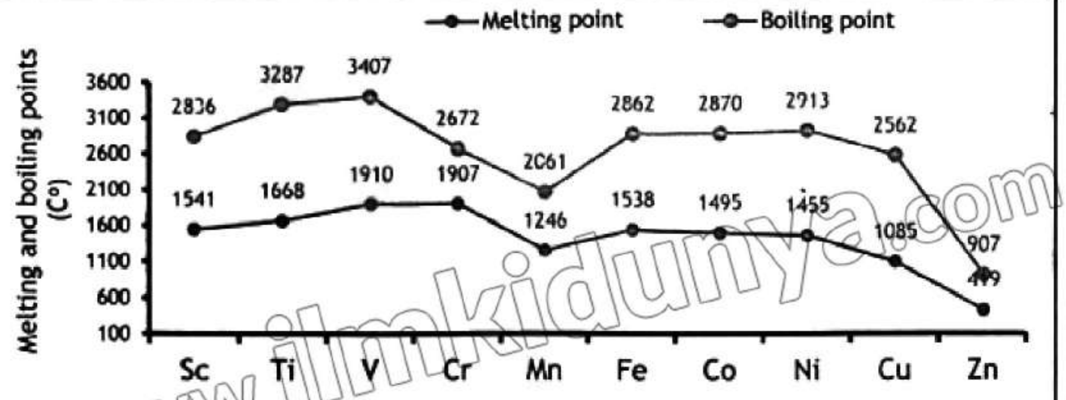

Fig 6.2: Melting and boiling points of transition metals

Key Information
Metallic bonding is directly related tp the number of unpaired electrons in outermost shells. However, the stability of sub-shells is also counted in this regard.

Magnetic Properties

Transition metals and their compounds show magnetic properties which provide us information about chemical bonding in them and important uses in modern technology. An electron spinning around its own axis generates magnetic field just like electric current flowing through a wire does. It means that a single unpaired electron acts like a small magnet. Based on unpaired and paired electrons in outermost shells, transition metals and their compounds show different magnetic properties.

Paramagnetic substances are weakly attracted in magnetic field. For example, aluminium and sodium etc. The reason is that they have unpaired electron(s) in valence shells. The unpaired electrons on atoms or ions are not influenced by the electrons on surrounding atoms so they are directed randomly. When a paramagnetic solid is placed in magnetic field, the magnetic moments are aligned parallel to one another and a net weak attraction is observed. However, when the magnet is removed, the solid loses its paramagnetic properties.

Ferromagnetic substances are strongly attracted in magnetic field, for example iron, cobalt and nickel. They have also unpaired electrons in the valence shells of their atoms and ions in solid states. Their unpaired electrons are influenced by the electrons of surrounding atoms and ions and align in same direction. When a ferromagnetic substance is placed under magnet, a very strong attraction is observed-nearly million times more than a paramagnetic substance. Ferromagnetic substances maintain their magnetic moment even after removal of magnetic field, so they are permanent magnets.

Diamagnetic substances are those which are weakly repelled by magnet because they have paired electrons in outermost shells. For example, copper and iron etc. The paired electrons in an orbital cancel out their individual magnetic moments making net magnetic moment zero.

Alloys are the mixtures of metals which carry useful properties. Transition metals can form alloys because of their similar atomic size. They can substitute one another in their metallic lattices. Steel is an alloy of iron, chromium, nickel and manganese possessing more useful properties, like hardness; corrosion resistance and shiny. Other examples of alloys are brass (copper and zinc) and bronze (copper and tin).

6.2.3 Chemical Properties

While crossing first row transition metals, there is no such similarity in chemical properties as we found in physical properties. Some important chemical properties of transition metals are given here.

1. Variable Oxidation States

The common oxidation state for the first row of the d-block elements is +2 obtained by loss of two 4s electrons to form an M^{2+} ion. The maximum stable oxidation state frequently corresponds to the maximum number of electrons (3d and 4s) available for bonding. For example, manganese, with electronic configuration, $[Ar]3d^5 4s^2$, can have a maximum oxidation state of +7.

Do You Know?
The simple ions of transition metal exist in low oxidation states (Mn^{2+}) while their complex ions (MnO_4^{1-}) are stable in high oxidation states.

The oxidation states of first row transition metals is shown:

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Co	Ni	Cu	Zn
								+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3			
	+4	+4		+4					
		+5							
			+6	+6					
				+7					

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The stability of +2 oxidation state compared to +3 oxidation state increases with atomic number from left to right across the first row of the d-block as it becomes increasingly difficult to remove 3d electrons. On the other hand, the stability of the higher oxidation states decrease with atomic number from left to right across the series.

The greater stability of +2 oxidation state of manganese compared to its +3 oxidation state and +3 oxidation state of iron relative to its +2 oxidation state can be explained on the basis of stability of half-filled 3d sub-shell.

2. Catalytic Activity

Transition elements or their compounds can be used as catalysts in various chemical reactions. They show two unique properties responsible for their catalytic activity:

- They can exist in more than one stable oxidation state.
- They have vacant d orbitals capable of forming temporary dative bonds with ligands.

First row transition metals have a unique property to change between different oxidation state, like Fe^{2+} and Fe^{3+} or Cu^{+} to Cu^{2+}. They temporarily change their oxidation states by gaining or losing electrons during chemical reactions and help reactants convert to products. At the end of reaction, they regain their original oxidation state and become ready to play their role as catalysts again.

These metals possess incomplete 3d-orbitals in their valence shells. These vacant orbitals can accept electrons pairs from ligands (molecules or ions) forming temporary dative bonds between the transition metals and ligands. These dative bonds are responsible for holding reactants on the surface of transition metal and bring them closer. Resultantly, the bonds within reactant particles weaken and ultimately break. The product formation takes place on the surface of transition metal. In this way transition metals speed up the reaction to occur. After completion of reaction, the transition metal releases the products and becomes ready to bind to new reactants, continuing its role as catalyst.

In the Haber process of ammonia synthesis, iron is used as catalyst which adsorbs hydrogen and nitrogen gas on its surface and make them react faster. Similarly, in the Contact process, the vanadium pentoxide (V_2O_5) is used as catalyst involving reversible change in oxidation state of vanadium from +5 to +4. Both these examples involve reactants and catalysts with different physical states, so they are heterogeneous catalysis.

On the other hand, we may have homogeneous catalysis where reactants and catalysts are in same physical states. For example, oxidation of iodide ion (I^-) by peroxodisulphate (VI) ion ($S_2O_8^{2-}$).

$$2I^-_{(aq)} + S_2O_8^{2-}{}_{(aq)} \longrightarrow 2SO_4^{2-}{}_{(aq)} + I_{2(aq)}$$

The reaction is slow because the negatively charged ions of reactants repel each other. It can be catalyzed by the addition of d-block metal ions like Fe^{2+} (aq) which change its oxidation states reversibly between +2 and +3 as shown.

$$2Fe^{2+}{}_{(aq)} + S_2O_8^{2-}{}_{(aq)} \longrightarrow 2Fe^{3+}{}_{(aq)} + 2SO_4^{2-}{}_{(aq)}$$

$$2Fe^{3+}{}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}{}_{(aq)} + I_{2(aq)}$$

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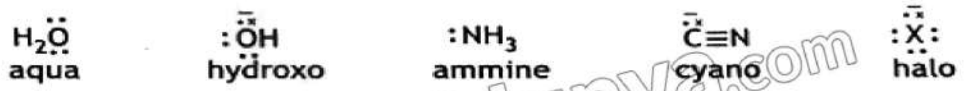
Both the steps of this mechanism involve a reaction between two oppositely charged ions making the reactions faster than the previous uncatalyzed case.

Ligands

A ligand is an atom or group of atoms which is electron rich and can donate lone pairs of electrons to the transition metal ions, making dative covalent bonds with them. Ligands may be molecules or ions made of non-metal atoms. They are also called Lewis bases or nucleophiles because they can donate electrons. Based on the number of lone pair they can contribute to coordinate covalent bond formation, ligands have the following classes.

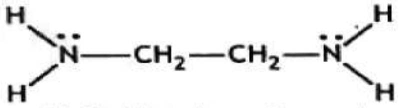
Key Information
The d sub-shell splitting is caused when ligands approach the central metal ion.

Monodentate Ligands: The ligand which can form one dative covalent bond with transition metal atom/ion is called monodentate (Latin word-meaning 'one-toothed'). They may have more than one lone pair of electrons but can donate only one. For example, aqua (H_2O), halo (X^-), hydroxo (OH^-), ammine (NH_3), and cyano (CN^-) etc.



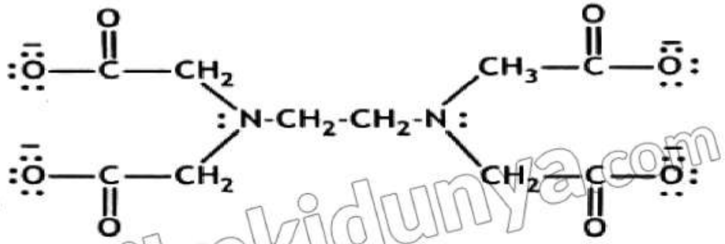
The ligand that can donate more than one lone pair of electrons are called polydentate ligands (many-toothed). For example, 1,2-diamminoethane ($NH_2CH_2CH_2NH_2$) and ethanedioate $(COO^-)_2$ are bidentate ligands as they can form two coordinate covalent bonds at a time with central transition metal ions.

(ethanedioate)
oxalato



(1,2-diaminoethane)
ethylenediammine (en)

Similarly, ethanediaminetetraethanoic acid (EDTA) is hexadentate ligand because it can donate six lone pairs of electrons to the central metal atom.



ethylenediaminetetraacetate acid (EDTA)

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6.3 Formation of Complex Compounds

A complex compound or coordination compound is formed between transition metals and ligand*(s)*. *Ligands* donate lone pair of electrons in the vacant orbitals of transition metals while transition metals accept the electron pair making coordinate covalent bonds. Ligand is electron pair donor, so it is called Lewis base. while transition metal accepts electron pair and is called Lewis acid. Transition metal complexes may be positive, negative or neutral. Transition metals form complex ions due to the following two reasons:

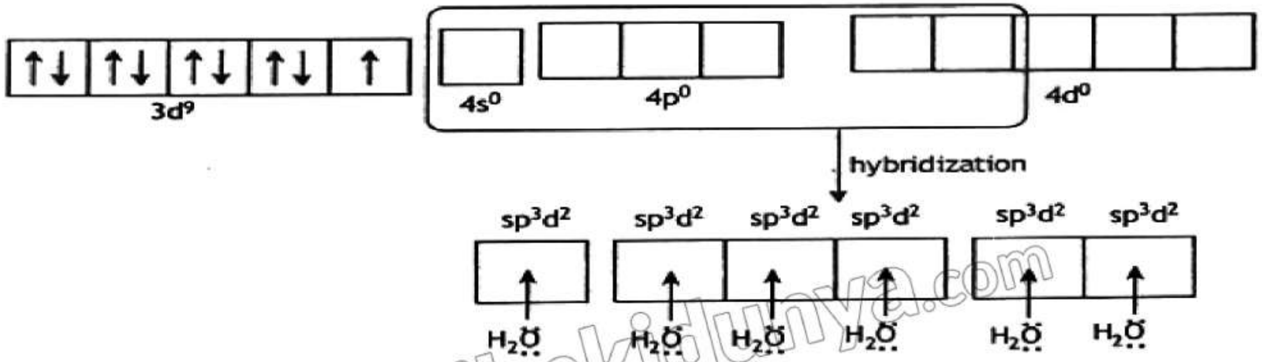
- They have a small size and high charge density, enabling them to strongly attract ligands.
- They have 3d sub-shell which has low energy and can bond to p-orbitals of ligands easily.

Transition metals lose electrons and become cations. They have vacant d orbitals that undergo hybridization to produce same number of new orbitals with equal energy. This process is followed by reaction of ligands with transition metal ion to form complex. The ligands donate electron pair to the hybridized vacant 3d orbitals of central metal ion. The vacant 3d orbitals of first row transition metals are energetically accessible because they have low energy, and ligands can easily donate lone pairs of electrons to them making dative bond with them. After this process, ligands come and donate electron pairs to those hybridized orbitals forming complex ion.

I. Complexes of Copper (II) with Water and Chloride Ligands

Copper (II) ion ($Cu^{2+}_{(aq)}$) has electronic configuration [Ar] $3d^9$. Six water ligands approach to copper(II) ions and form six coordinate covalent bonds with copper (II) ion. However, before making bonds, the six vacant orbitals of copper (II) ion undergo hybridization, generating six sp^3d^2 hybrid orbitals. These orbitals are then available for six water molecules to coordinatively bond and form the given complex as reflected from the 'electrons-in-box diagram.

Do You Know?
The transition metal ions have high charge density, so they are highly polarizing compared to s-block metals. This is why they have higher tendency to form complexes.



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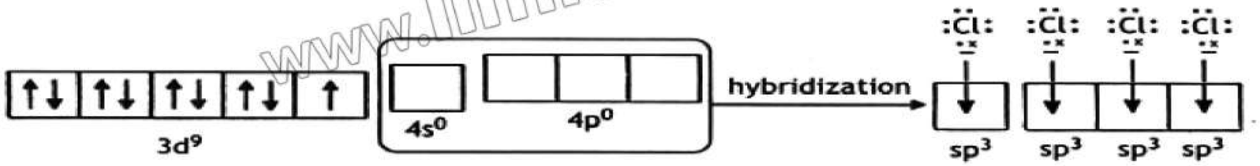
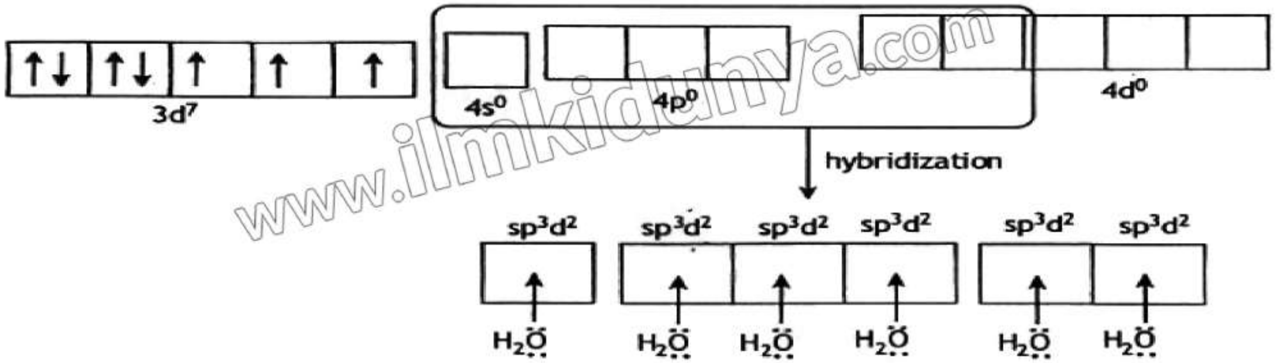
Similarly, copper (II) ions intermix four vacant orbitals (4s and 4p) giving four sp^3 hybrid orbitals. Then four chloride ligand coordinatively bond with those four hybrid orbitals as shown:



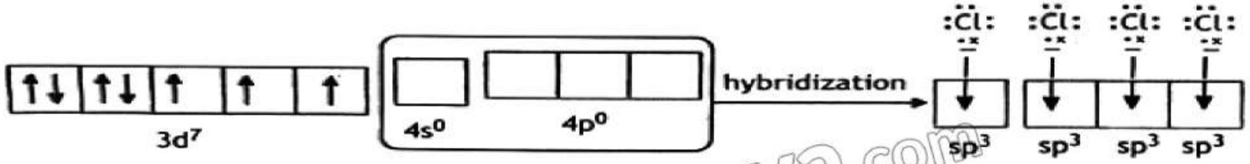
With chloride ligands, copper(II) forms tetrahedral complex, tetrachlorocuprate(II) ion, because chloride is a big ligands and six chloride ligands cannot surround a small copper(II) ion.

ii. Complexes of Cobalt(II) ion with Water and Chloride Ligands

The condensed electronic configuration of cobalt(II) ion is $[Ar]3d^7$. It forms octahedral complex where six water ligands form dative bonds with the empty orbitals available with cobalt(II) ion. The following diagram shows the formation of octahedral complex of hexaaquacobalt(II) ion with six water ligands making six coordinate bonds with six sp^3d^2 hybrid orbitals.



Similarly, cobalt(II) ion reacts with four chloride ligands, making four dative bonds and give tetrahedral complex, tetrachlorocobaltate(II) ion. Before making bonds, the four vacant orbitals of cobalt (II) ions undergo hybridization as shown.



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Terminology of complex compounds

- **Coordination Number**
  The number of coordinate covalent bonds formed by metals ions with ligands is called coordination number. The most common coordination number are 4 and 6, however, complexes with coordination number 2 can also exist. For example, the coordination number of compounds $[Cu(NH_3)_4]^{2+}$, $[Ni(CO)_4]$, $Na_4[Fe(CN)_6]$ and $[Co(NO_2)_3(NH_3)_3]$ are four, four, six and six respectively.
- **Coordination Sphere**
  The central atom or ion with ligand(s) is called coordination sphere enclosed by square bracket. The coordination sphere may be neutral, anionic and cationic. For example, $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$ and $[Ni(CO)_4]$ have anionic, cationic and neutral coordination sphere respectively.

- **Charge on Coordination Sphere**
  It is the sum of total charges on transition metal ion and ligands (if any). Examples:
  i. $Na_4[Fe(CN)_6]$
  Oxidation state of iron = +2
  Total charge on six cyanide ligands = -6
  Charge on coordination sphere = +2+(-6) = -4
  ii. $[Cu(NH_3)_4]SO_4$
  Oxidation state of copper= +2
  Total charge on four ammonia ligands = 0
  Charge on coordination sphere= +2+0 = +2

> The charge on coordination sphere is equal but opposite to the charge on the ions outside the coordination sphere.

6.3.1 Naming Complex Compounds

IUPAC nomenclature of complex compounds recommends the following rules:

i. Name cation before anion, whether it is simple ion or complex ion.
ii. While naming coordination sphere, the ligands are named first in alphabetical order, then the transition metal ion.
iii. The suffix "ate" is added to the name of the central metal atom if the coordination sphere is anionic. For example ferrate for iron, cuperate for copper and argentate for silver. Otherwise, the name of metal remains unchanged.
iv. We use the prefixes di, tri and tetra etc for ligands to show their number. For polydentate ligands, prefixes bis (two), tris (three), tetrakis (four) ligands and pentakis (five) etc are usded.
v. Naming anionic ligands, we use suffix "o", e.gchloro (Cl^-), hydroxo (OH^-) and carbonato (CO_3^{2-}) etc. Neutral ligands usually retain their names, like aqua/aqua (H_2O), ammine (NH_3) and carbonyl (CO) etc.
vi. The oxidation state of the central ion is represented by Roman numerals and put in parenthesis after the name of metal atom.

Examples of Complex Compounds

$[Pt(NH_3)_4BrCl]Cl_2$	tetraaminebromochloroplatinium(IV) chloride
$[Cu(NH_3)_2]^{2+}$	Diamminecopper(II) ion
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$[Cr(H_2O)_6]Cl_3$	Hexaaquachromium(III) chloride
$[Ni(CO)_4]$	Tetracarbonylnickel (0)
$[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrocobalt (III)
$[Cr(en)_2Cl_2]Cl$	Dichlorobis(1,2-diaminoethane)chromium(III) chloride [en=ethylenediamine]
$K_2[PtCl_6]$	Potassium hexachloroplatinate(IV)

While naming complex compounds, the number of counter ions is not counted.

6.3.2 Working Out the Charge on Complexes and Their Formulae

The total charge on a complex ion depends upon the oxidation state of metal ion and the number and nature of ligands. The oxidation state of metal ion can be calculated from the charge on the complex ion. Remember that oxidation state on transition metal ion equals to charge on the complex minus sum of charges on the ligands.

The ions outside the coordination sphere neutralizing complex ion are called counter ions.

Worked Examples

- Deduce the charge on the tetraamminedichlorocobalt(III) complex ion. What is its formula?
- The formula has two chloride ions and four ammonia molecules, so the ligands contribute two negative charges (−2). The central cobalt cation has an oxidation number of +3, so it contributes three positive charges (+3). Hence the total or net charge on the complex ion is +1. The formula is therefore $[CoCl_2(NH_3)_4]^+$.
- Deduce the oxidation state of copper in the $[CuCl_4]^{2-}$ complex ion. What is its name?
- The complex ion is an anion with a total or net charge of −2. The formula has four chloride ions acting as ligands which contribute a total of four negative charges (−4). Hence the central copper ion must contribute two positive charge so its oxidation state is +2. This ion is the tetrachlorocuprate(II) ion.

Concept-Assessment Exercise 6.1

1. Determine the oxidation states of transition metals in the following complexes.
   i. $[Co(NH_3)_6]Cl_3$. ii. $Na_2[MnCl_5]$ iii. $[Co(en)_2(H_2O)_2]$
   iv. $[CuCl_4]^{2-}$ v. $Na_4[Fe(CN)_2(OH)_4]$
2. Name the following complex ions.
   i. $[Co(NH_3)_4Cl_2]Cl$ ii. $[Zn(OH)_4]^{2-}$ iii. $[CrCl_2(NH_3)_4]^+$

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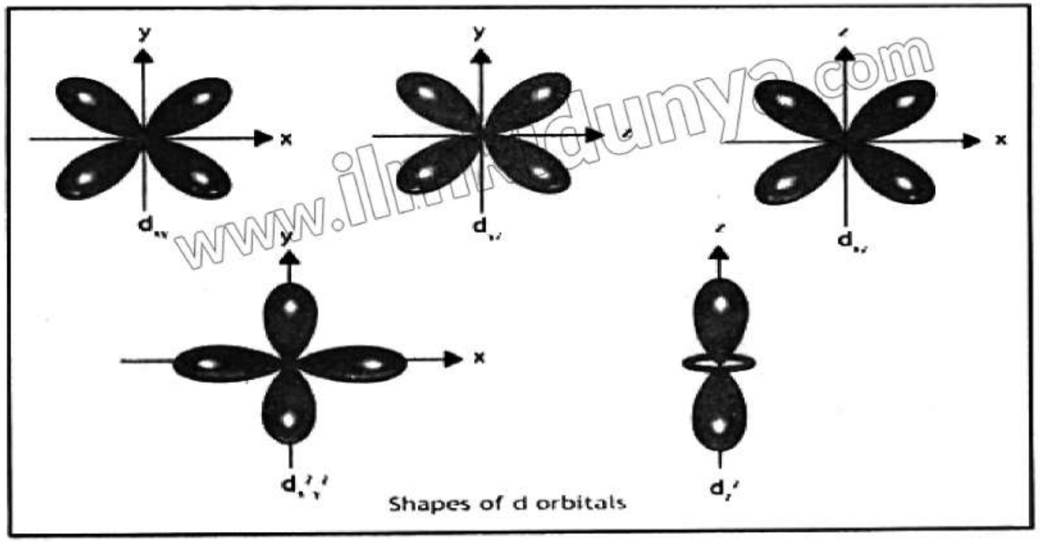
6.3.3 Coloured Complexes

If white light is passed on a transition metal complex, either in solid form or solution form, some light is *absorbed and some* is transmitted. There are three possibilities.

- **If all the light is absorbed, the compound appears 'black'.**
- **If some light is absorbed, the compound will appear coloured.**
- **If all the light is reflected, the colour of the complex compound will appear 'white'.**

Transition metal ion, in solution or solid form, are coloured because it absorbs a part of visible light and the remaining part is transmitted. Light is absorbed by those transition metal complexes which have incomplete 3d sub-shells. For example, copper (II), ([Ar]$3d^9$), complex has incomplete d sub-shell so it has coloured compounds. On the other hand, zinc (II), [Ar]$3d^{10}$) is colouless compound because it has complete d sub-shell. Before digging in the topic in detail, we must know about d orbitals.

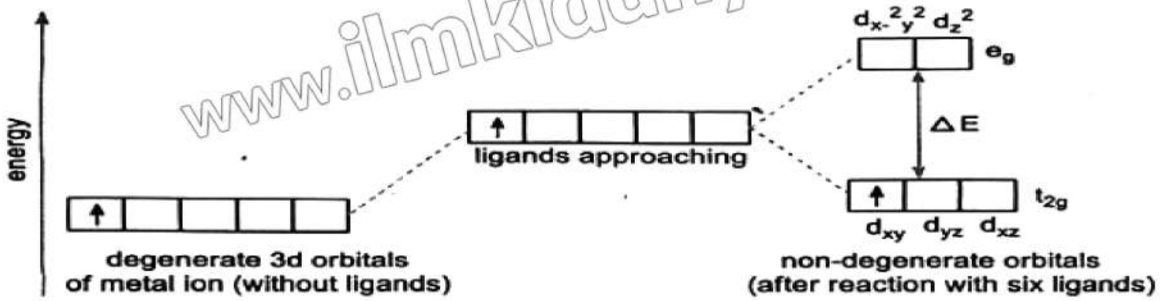
All d orbitals in d sub-shell have same energy so they are called degenerate orbitals. However, they are oriented in different directions along x, y and z axes as shown.



Shapes of d orbitals

Consider octahedral complex where six ligands approach the central metal ion along x, y and z axes. Almost all transition metals have octahedral complexes. The interaction between ligands and central metal ion caused splitting of d sub-shell into two set of orbitals. Ligands interacting with the two d orbitals lying along x, y and z axes ($d_{x^2-y^2}$ and d_{z^2}) experience greater repulsion than that with the d orbitals orienting in between the axes (d_{xy}, d_{yz} and d_{xz}). The higher repulsion results in higher energy set of orbitals called e_g whereas the lesser repulsion give rise to lower energy set of orbitals called t_{2g}. The overall energy of both e_g and t_{2g} orbitals of complex is higher than the degenerate 3d orbitals of metal ions without ligand.

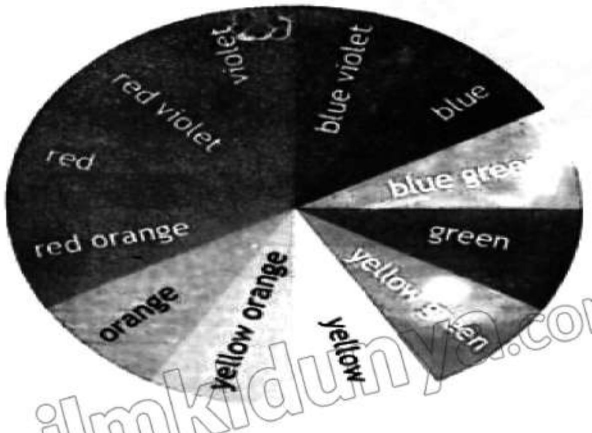
The d-d splitting pattern is shown.



The energy difference (ΔE) between the two sets of d orbitals in a complex ion is equal to the energy of a photon of characteristic light in visible spectrum. When white light is passed through a complex ion, whether in solution or solid form, photon of a particular energy and frequency is absorbed which will excite electron from lower energy set of d orbitals (t_{2g}) to higher energy set of d orbitals (e_g). This shift of electron between the two sets of orbitals is called d-d electronic transition.

Key Information
The terms e_g and t_{2g} stands for "doubly gerade" and "triply gerade" respectively. The subscript "g" stands for "gerade" which is a German word meaning even (degenerate).

As a result of this electronic transition, a colour from the white light is removed and the solution gives a complementary colour to the absorbed light. Different complexes give different colours depending upon the colour absorbed from white light. Each colour absorbed gives its own complementary colour as shown from the colour wheel.



The colour wheel

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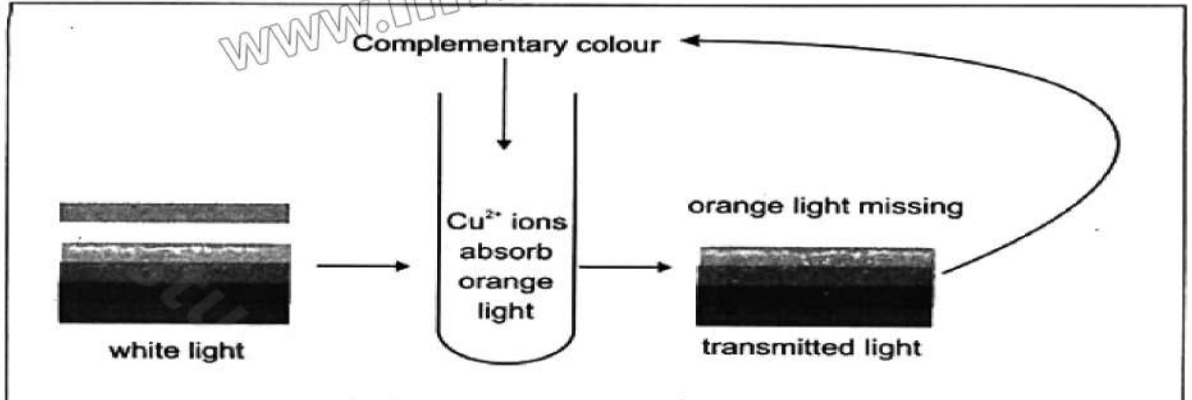
The nickel complex, $[Ni(H_2O)_6]^{2+}$, absorbs red light from white light and appears green, which is complementary colour to red. Similarly, the copper complex, $[Cu(H_2O)_6]^{3+}$, absorbs orange colour and appears blue (a complementary colour to orange) as shown in the diagram.



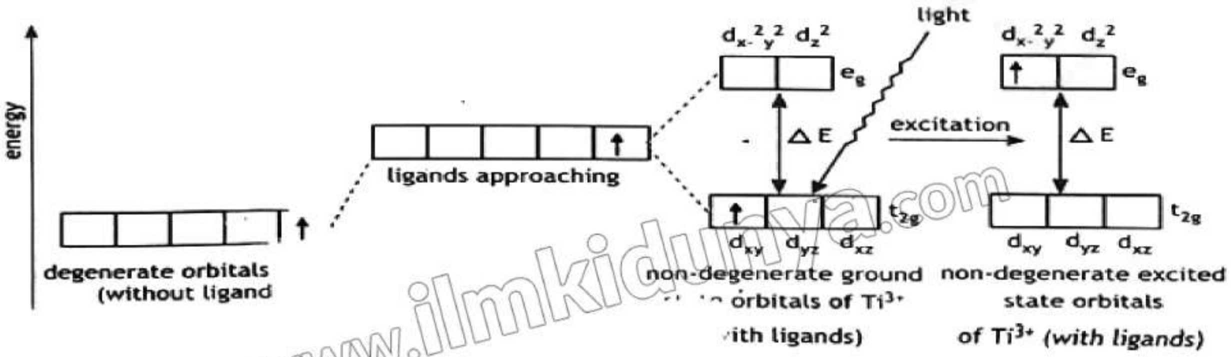
How complexes Get Colours?

6.3.4 The d-d Splitting Pattern in Octahedral and Tetrahedral Complexes

Let's consider the example of the aqua complex of titanium (III). This complex has an octahedral shape, with six water molecules acting as ligands around the titanium ion. In octahedral complexes, the three t_{2g} orbitals (dxy, dyz, and dxz) lie between the six ligands, so they experience less repulsion from the ligands' lone pairs. In contrast, the two e_g orbitals are aligned directly toward the ligands, which causes them to experience more repulsion.

Octahederal Complexes

Based on the extent of repulsion between the orbitals and ligands, t_{2g} set of orbitals has lower energy while e_g set has higher energy. When white light strikes $[Ti(H_2O)_6]^{3+}$ complex ion, in solid form or solution form, it absorbs yellow green light for excitation of electron and gives red-violet colour.



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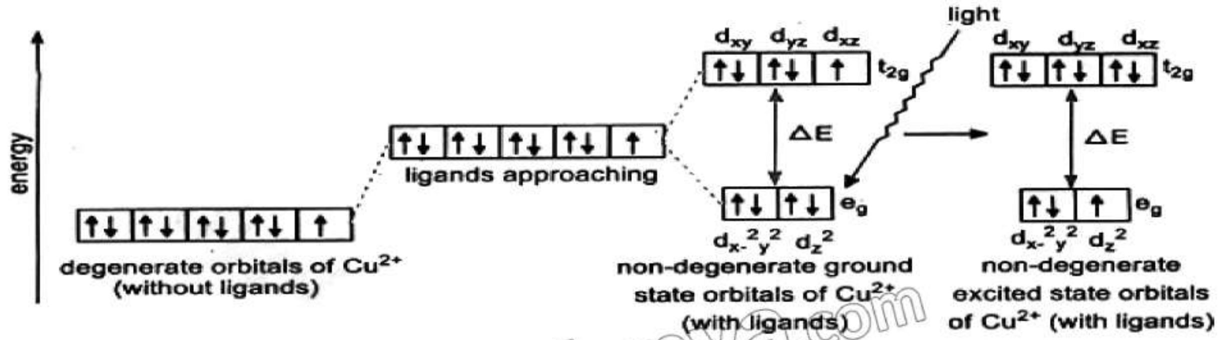
Tetrahedral Complexes

In tetrahedral complexes, the three t2g orbitals are oriented toward the ligands, leading to more repulsion and higher energy. In contrast, the two e_g orbitals are positioned between the ligands, so they experience less repulsion and have relatively lower energy. Based on the degree of repulsion between 3d orbital electrons and ligands, t_{2g} set of orbitals have higher energy whereas e_g has lower energy. For example, consider the tetrachlorocuprate(II) complex, $[CuCl_4]^{2-}$.

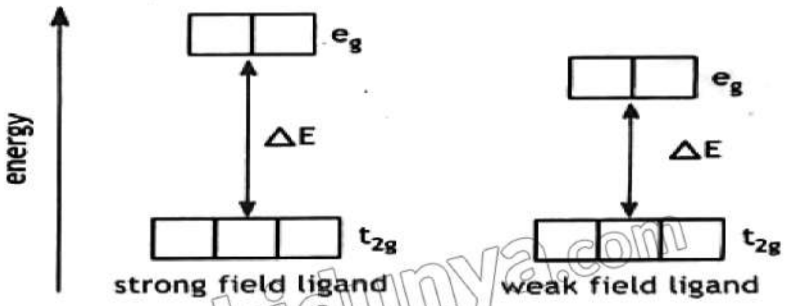


6.3.5 Effect of Ligands on Colour of Complexes

When ligands approach transition metal ions, their electric fields interact with the d orbitals of metal ions resulting in splitting of d orbitals into two different energy levels. On the basis of their different abilities to split d orbitals, ligands show different field strengths and follow the order:

$$CN^- > NH_3 > H_2O > OH^- > Cl^- > Br^-$$

A strong field ligand splits d orbitals to greater extent hence causes higher splitting energy (ΔE) than a weak field ligand as shown.



Consider the addition of ammonia solution to the aqueous solution of copper (II) ions and subsequent change in colour of the given complex. We know that ammonia is a strong field ligand whereas water is a weak field ligand so ammonia will replace water in the complex.

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In this reactions, four ammonia molecules replace four water molecules, shifting absorption from blue to violet-blue.

$$\underset{\text{blue}}{[Cu(H_2O)_6]^{2+}(aq)} + 4NH_3(aq) \longrightarrow \underset{\text{violet-blue}}{[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)} + 4H_2O(l)$$

Concept Assessment Exercise 6.2

- What are degenerate and non-degenerate 3d orbitals?
- Why degenerate 3d orbital split into two sets of orbitals in some complexes while not in others?
- Which different ligands cause different splitting energy (ΔE) ? Give one example.

6.3.6 Geometries of Complexes

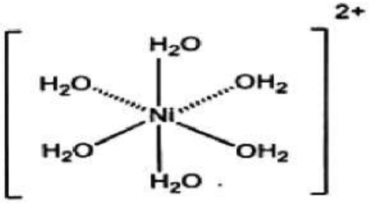
In previous class, we applied valence shell electron pair repulsion (VSEPR) theory on simple molecules to determine geometries of molecules. Similarly, we can use this theory on transition metal complexes to ensure maximum distances and minimum repulsion among dative bond pairs.

Copper (II) ion can bond to four chloride ligands, six water and six ammonia ligands. This is because the chloride ligand is bigger than water and ammonia, as chlorine belongs to period 3 while oxygen in water and nitrogen in ammonia belong to period 2. The space around copper (II) ion is not enough to surround six Cl^- ions.

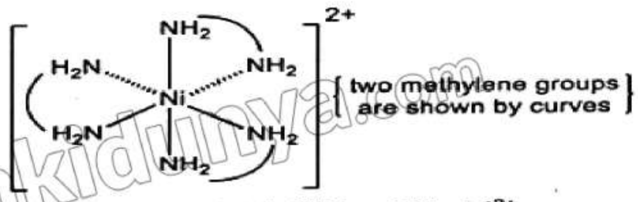
1. Complexes with Coordination Number 6

The complexes with coordination number 6 adopts octahedral shapes in which six donor atoms of ligands (both monodentate and polydentate) are positioned at the vertices of octahedron (oct means eight and hedron means faces). According to valence shell electron pair repulsion (VSEPR) theory, this three-dimensional arrangement of ligands experiences minimum ligand-ligand repulsion.

Octahedral complexes are the most common and stable complexes and almost all transition metals can form octahedral complexes. The octahedral complexes can have both monodentate and polydentate ligands. The angles between all ligands is 90°.



Hexaaquanickel(II) ion, $[Ni(H_2O)_6]^{2+}$



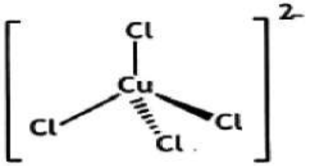
Tris(1,2-diaminoethane)nickel(II) ion, $[Ni(en)_3]^{2+}$

2. Complexes with Coordination Number 4

There are two possible arrangements of ligands or dative bond pairs around central metal ions in complexes with four coordination number structures. One is tetrahedral arrangement of dative bonds following VSEPR argument and the other is square planar geometry which violates VSEPR theory. We discuss the two geometries separately.

i. Tetrahedral Complexes

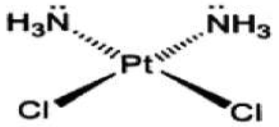
They are less common than octahedral complexes and you will often see them with chloride ligands, like tetrachlorocuprate(II), $[CuCl_4]^{2-}$. The tetrahedral geometry of $[CuCl_4]^{2-}$ complex is supported by VSEPR theory and the four chloride ligands are at maximum distances, making 109.5° angles.



Tetrahedral complexes are mostly formed by metal ions with d^{10} electron configuration such as Cu^+ and Zn^{2+}. Some other examples are $[Cu(CN)_4]^{3-}$ and $[Zn(NH_3)_4]^{2+}$ etc.

ii. Square Planar Complexes

Square planar complexes have four ligands directed at the four corners of a square making 90° angles with one another. This arrangement of ligands in this type of complexes is against VSEPR theory. They are less common than tetrahedral complexes. Most square complexes are made by platinum, like diamminedichloroplatinum(II) complex.



cis-diaaminedichloroplatinum(II)

They are mostly formed by metal ions with d^8 electronic configuration such as Ni^{2+} and Pt^{2+} and Au^{3+}. Examples are $[Ni(CN)_4]^{2-}$, $[AuCl_4]^-$ and $[Pt(NH_3)_4]^{2+}$ etc.

3. Complexes with Coordination Number 2

Linear complexes are less stable. They have two monodentate ligands lying at 180° angle as shown.

$$[H_3\ddot{N}-Ag-\ddot{N}H_3]^+$$

Diamminesilver(I) ion

Some other examples are $[CuCl_2]^-$ and $[Au(CN)_2]^-$ etc.

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6.4 Ligand Substitution Reactions

Transition metals undergo many types of reactions, such as redox reactions, deprotonation reactions, and ligand substitution reactions, but we shall discuss only ligand exchange reactions in this section.

The reaction in which one ligand is substituted by another ligand is called ligand exchange reaction, also called ligand substitution reactions. The reactions take place if the complex formed is more stable than the reacting complex. They involve either complete or partial exchange of ligands.

We will restrict ourselves to the reactions of copper(II) complexes and cobalt(II) complexes only. The ligands participating in the reactions will be water, ammonia, hydroxide and chloride ions.

i. Copper(II) Complexes

We add strong base, like sodium hydroxide (NaOH), to the blue solution of copper sulphate ($CuSO_4$), we observe a pale blue precipitate. In this reaction, two hydroxide ligands (OH^-) replaced two water ligands.

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}{}_{(aq)}} + 2OH^-{}_{(aq)} \longrightarrow \underset{\text{pale blue precipitate}}{[Cu(H_2O)_4(OH)_2]_{(s)}} + 2H_2O_{(l)}$$

The hydroxide ions do not substitute water ligands directly. They act as a base and take protons from water molecules forming water and leaving hydroxide ions behind. The hydroxide ions thus made act as a ligands and exchange with water molecules.

Do You Know?
A solution of copper(II) sulphate in water is shown by formula $[Cu(H_2O)_6]^{2+}$ or $Cu^{2+}{}_{(aq)}$.

Adding excess of ammonia solution dissolves pale blue precipitate giving deep blue solution.

$$\underset{\text{pale blue precipitate}}{[Cu(H_2O)_4(OH)_2]_{(s)}} + 4NH_{3(aq)} \longrightarrow \underset{\text{blue solution}}{[Cu(NH_3)_4(H_2O)_2]^{2+}{}_{(aq)}} + 2H_2O_{(l)} + 2OH^-{}_{(aq)}$$

If we add aqueous ammonia, instead of aqueous sodium hydroxide, we get the same observation. In this reaction, ammonia acts as a base and removes protons from water, leaving behind hydroxide ions which substitutes water as ligand. This reaction is specifically called deprotonation reaction.

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}{}_{(aq)}} + 2NH_{3(aq)} \longrightarrow \underset{\text{pale blue precipitate}}{[Cu(H_2O)_4(OH)_2]_{(s)}} + 2NH_4^+{}_{(aq)}$$

This is a ligand exchange reaction in which four ammonia molecules replaced two water ligands and two hydroxide ligands.

Similarly, the water ligands in hexaaquacopper(II) ion can also be exchanged for chloride ligands if we add concentrated hydrochloric acid dropwise. This reaction gives yellow solution tetrachlorocuprate(II).

$$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)} \rightleftharpoons [CuCl_4]^{2-}{}_{(aq)} + 6H_2O_{(l)}$$

blue solution yellow solution

The reaction is reversible and the m. e has green colour because it contains both blue and yellow solutions.

ii. Cobalt Complexes

If we add strong base, like sodium hydroxide (NaOH), to the pink aqueous solution of cobalt(II) chloride, we see blue precipitate of cobalt(II) hydroxide.

$$[Co(H_2O)_6]^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \longrightarrow [Co(H_2O)_4(OH)_2]_{(s)} + 2H_2O_{(l)}$$

pink solution blue precipitate

Adding concentrate aqueous ammonia slowly can also exchange for water in aqua complex of cobalt(II) ion.

$$[Co(H_2O)_6]^{2+}{}_{(aq)} + 6NH_3{}_{(aq)} \longrightarrow [Co(NH_3)_6]^{2+}{}_{(aq)} + 6H_2O_{(l)}$$

pink solution brown solution

Addition of concentrated hydrochloric acid to aqueous solution of cobalt(II) ions gives blue solution of tetrachlorocobaltate(II) complex.

$$[Co(H_2O)_6]^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)} \longrightarrow [CoCl_4]^{2-}{}_{(aq)} + 6H_2O_{(l)}$$

pink solution blue solution

6.4.1 Stability of Complexes and Stability Constant (K_{stab}).

The equilibrium constant obtained from ligand exchange reactions in a solvent is called stability constant (K_{stab}). The stability of a complex is expressed in terms of equilibrium constant for ligand exchange reactions. The ligand exchange reactions are reversible so we can derive equilibrium constant expression for such a reaction. Deriving stability constant is similar to equilibrium constant (K_c) we studied in chemical equilibrium.

Consider the chemical reaction:

$$[Co(H_2O)_6]^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)} \rightleftharpoons [CoCl_4]^{2-}{}_{(aq)} + 6H_2O_{(l)}$$

pink solution blue solution

The position of equilibrium lies in the direction of more stable complex. The strong field ligand always substitutes the weak field ligand in the complex.

If we add water to this reaction mixture, reverse reaction takes place and pink colour of hexaaquacobalt(II) appears. Similarly, when we add concentrated hydrochloric acid to the system, forward reaction is favoured and blue colour of the tetrachlorocobaltate(II) is observed. In both these observation, the chloride and water ligands compete with one another for bond to cobalt(II) ion.

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Applying equilibrium constant expression:

$$K_c = \frac{[[CoCl_4]^{2-}]\,[H_2O]^6}{[[Co(H_2O)_6]^{2+}]\,[Cl^-]^4}$$

Water is solvent so it is in large excess. It is treated as constant and not shown in stability constant.

$$K_{stab} = \frac{[CoCl_4]^{2-}}{[Co(H_2O)_6]^{2+}\,[Cl^-]^4}$$

Where K_{stab} is called stability constant. The units of stability constant are calculated as those of equilibrium constant (K_c). The values of stability constants show how firmly a ligand is bonded to the central metal ion. Generally, the ligand atoms with lower electronegativity bond firmly with central metal ion than those with higher electronegativity values. This is why ammonia form strong bond with metal ion and has higher stability constant value while water binds weakly to the metal ion and has lower value of stability constant.

The stability constant values (K_{stab}) of some copper(II) complexes are given.

	[illegible]
$[CuCl_4]^{2-}$	5.6
$[Cu(NH_3)_6]^{2+}$	13.1
$[Cu(EDTA)]^{2-}$	18.8

The values of stability constants are so large that they are shown on $\log_{10}$ scale so they have no units.

The data show that complexes with polydentate ligands have higher stability constant values than those with monodentate ligands.

$$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 3en \longrightarrow [Cu(en)_3]^{2+} + 6H_2O_{(l)}$$

The values of stability constants guide us which ligands can replace one another. For example, adding excess of ammonia to tetrachlorocuprate(II) complex gives dark blue solution of hexaamminecopper(II) complex because the stability constant value of ammonia complex is more than chloride complex and position of equilibrium shifts in the direction of more stable complex (right side).

$$[CuCl_4]^{2-}{}_{(aq)} + 6NH_{3(aq)} \longrightarrow [Cu(NH_3)_6]^{2+} + 4Cl^-{}_{(aq)}$$

Worked Example 1: We get a mixture of aqueous solutions tetrachlorocuprate(II) and hexaaquacopper(II) ion after adding concentrated hydrochloric acid to an aqueous solution of copper(II) sulphate.

i. Write expression for the stability constant for aqueous solution of tetrachlorocuprate(II).

ii. What are the units of stability constant?

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Concept Assessment Exercise 6.3

- Arrange the following ligands in increasing order of stability constants in ligand substitution reactions of iron (II) complexes.

  CN^-, OH^-, NH_3, H_2O, Br^-
- Given the stability constant, why can ammonia exchange for water in copper(II) complex? Give reason.

6.5 Redox Reactions

The transition elements can exist in various oxidation states. In redox reactions, the oxidation states of transition elements are changed when they undergo chemical reaction under suitable conditions. In redox reactions, transfer of electrons takes place from one atom to the other. The decrease in oxidation state is reduction (gain of electron/s) while increase in oxidation state is called oxidation (loss of electron/s).

Oxidizing agent is the species which accepts electron/s and undergoing reduction while reducing agent undergoes oxidation by losing electron/s. Here we will discuss three redox reactions with their feasibility supported by their standard electrode potential data.

i. Reaction of Acidified Manganate(VII) ions with Ethanedioate ions

The reaction between ethanedioate ions and acidified manganate(VII) ion is analysed to find which way it will take place. The standard electrode potentials of individual reactions are taken into consideration to check feasibility of overall reaction. Both reactions are taken in reduction mode according to IUPAC recommendations and then we compare their standard reduction potentials.

$$2CO_{2(g)} + 2e^- \longrightarrow C_2O_4{}^{2-}{}_{(aq)} \qquad E^\circ = +0.49V$$

$$MnO_4{}^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \longrightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} \qquad E = +1.52V$$

Now the question arises whether manganate(VII) oxidizes ethanedioate to carbon dioxide or carbon dioxide oxidizes manganese(II) ion to manganate(VII)? Which one should be oxidizing agent and which one reducing agent?

This problem can be resolved by comparing the standard reduction potentials of the two reactions. The reaction with higher positive value of standard reduction potential is more likely to occur and proceed to the right and vice versa.

The given reduction potential values indicate that manganate(VII) ion must reduce to manganese(II) ion and should act oxidizing agent while oxalate should oxidize to carbon dioxide and act as reducing agent.

For writing the overall chemical equation, the reaction with lower standard electrode potential must be reversed and be taken in oxidation mode because it is oxidation reaction. The sign of its standard electrode potential is reversed while its magnitude remains the same.

The standard reduction potential values of reactions do not change with changing the co-efficients.

$$C_2O_4{}^{2-}{}_{(aq)} \longrightarrow 2CO_{2(g)} + 2e^- \qquad E = -0.49V$$

Before combining the two half reactions, the number of electrons lost must equals the number of electrons gained. This can be done by multiplying the two half equations with different multipliers (coefficients). In this case, oxidation half equation is multiplied by 2 and reduction half equation by 5.

$$2MnO_4{}^-{}_{(aq)} + 16H^+{}_{(aq)} + 10e^- \longrightarrow 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} \qquad E = +1.52V$$

$$5C_2O_4{}^{2-}{}_{(aq)} \longrightarrow 10CO_{2(g)} + 10e^- \qquad E = -0.49V$$

$$2MnO_4{}^-{}_{(aq)} + 5C_2O_4{}^{2-}{}_{(aq)} + 16H^+{}_{(aq)} \longrightarrow 2Mn^{2+}{}_{(aq)} + 10CO_{2(g)} + 8H_2O_{(l)} \qquad E = +1.03V$$

This large positive value of standard electrode potential (+1.03V) supports the forward reaction to occur so this redox reaction is feasible. Remember that the negative value of standard electrode potential means that the reaction will not take place.

ii. Reaction of Manganate(VII) ion with Iron(II) ion

In this redox reaction we consider two half equations, one is reduction of maganate (VII) whereas the other is reduction of iron (III).

$$MnO_4{}^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \longrightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} \qquad E = +1.52V$$

$$Fe^{3+}{}_{(aq)} + e^- \longrightarrow Fe^{2+}{}_{(aq)} \qquad E = +0.77V$$

To write the net redox reaction, we need to reverse the second reaction, treat it as an oxidation reaction by reversing it, and change the sign of its standard reduction potential to negative.

$$Fe^{2+}{}_{(aq)} \longrightarrow Fe^{3+}{}_{(aq)} + e^- \qquad E = -0.77V$$

Combine and balance the two equations and sum up their standard electrode potentials so that we can check the feasibility of overall equation.

$$MnO_4{}^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \longrightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)} \qquad E = +1.52V$$

$$5Fe^{2+}{}_{(aq)} \longrightarrow 5Fe^{3+}{}_{(aq)} + 5e^- \qquad E = -0.77V$$

$$MnO_4{}^-{}_{(aq)} + 5Fe^{2+}{}_{(aq)} + 8H^+{}_{(aq)} \longrightarrow Mn^{2+}{}_{(aq)} + 5Fe^{3+}{}_{(aq)} + 4H_2O_{(l)} \qquad E = +0.75V$$

The positive value of the standard electrode potential indicates that this reaction will proceed to the right, making this reaction feasible.

iii. Reaction Between Copper(II) ion and Iodide ion

Take an aqueous solution of copper(II) sulphate in a flask and add an excess of potassium iodide to it. The following reaction takes place.

$$2Cu^{2+}{}_{(aq)} + 4I^-{}_{(aq)} \longrightarrow \underset{\text{white ppt}}{2CuI_{(s)}} + \underset{\text{red-brown solution}}{I_{2(aq)}}$$

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Split the redox reaction in two half-equations.

$$\frac{1}{2} I_{2(aq)} + e^- \longrightarrow I^-_{(aq)} \qquad E^\ominus = +0.54V$$

$$Cu^{2+}_{(aq)} + 1e^- \longrightarrow Cu^+_{(aq)} \qquad E^\ominus = +0.15V$$

The higher standard reduction potential value of I_2/I^- couple indicates that this reaction is more likely to occur.

On the contrary, the lower standard reduction potential of Cu^{2+}/Cu^{1+} reaction indicates that this reaction is less inclined to proceed in the forward direction, making copper (I) a better reducing agent. However, this reaction proceeds in the forward direction because of continuous precipitation of copper (I) iodide in the reaction, although the overall standard potential value is negative as shown.

$$\begin{array}{lll} 2I^-_{(aq)} & \longrightarrow I_{2(aq)} + 2e^- & E^\circ = -0.54V \\ 2Cu^{2+}_{(aq)} + 2e^- & \longrightarrow 2Cu^+_{(aq)} & E^\circ = +0.15V \\ \hline 2Cu^{2+}_{(aq)} + 2I^-_{(aq)} & \longrightarrow 2Cu^+_{(aq)} + I_{2(aq)} & E^\circ = -0.39V \end{array}$$

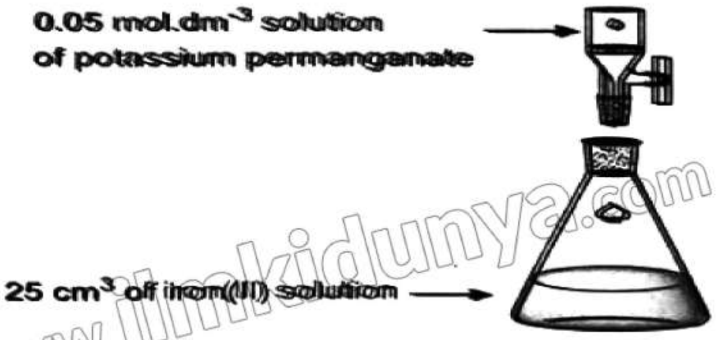
The amount of aqueous solution of iodine formed in this reaction can be determined by titrating it with sodium thiosulphate solution.

Practical Activity 6.1: Redox titration

The above reaction can be used practically to calculate the amount of iron (Fe^{2+} ions) in a sample, such as an iron tablet, by carrying out a titration. As this is redox reaction so the titration involved is called redox titration.

We take a known volume (e.g. 25 cm^3) of an unknown concentration of Fe^{2+}(aq) is placed in a conical flask. A solution of a known concentration (0.05 $mol.dm^3$) of potassium manganate(VII) solution is put in a burette.

The potassium manganate(VII) solution is titrated against the solution containing Fe^{2+}(aq) in the conical flask. During the reaction of MnO_4^- (aq) with Fe^{2+}(aq) in the flask, the purple colour of the manganate(VII) ions is diappears. The end-point is reached when the Fe^{2+}(aq) ions have all reacted and the first permanent purple colour appears in the conical flask. This is when the MnO_4^- (aq) ions become in excess in the reaction mixture



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Worked Example 6.1

An excess of potassium iodide solution was added to a 30.00 cm^3 of copper(II) sulphate solution in a flask. The solution was then titrated against 0.05 mol dm^{-3} sodium thiosulphate solution, *using starch solution* as indicator. The volume of sodium thiosulphate solution added from the burette was 10 cm^3 when the endpoint reached. Calculate the concentration of the copper(II) sulphate solution.

Solution

Volume of copper(II) sulphate solution = 30 cm^3 = 30/1000 = 0.03 dm^3
Volume of sodium thiosulphate solution = 10 cm^3 = 10/1000 = 0.01 dm^3
Concentration of sodium thiosulphate solution = 0.05 mol.dm^{-3}
Concentration of copper(II) sulphate solution = ?
For solving concentration related problems of solutions, we use the following formulae.

$$\text{concentration} = \frac{\text{moles}}{\text{volume } (dm^3)}$$

$$\text{moles} = \text{concentration} \times \text{volume } (dm^3)$$

The following two chemical equations are involved in this titration.

$$2Cu^{2+}{}_{(aq)} + 4I^{-}{}_{(aq)} \longrightarrow 2CuI_{(s)} + I_{2(aq)}$$

$$I_{2(aq)} + 2S_2O_3{}^{2-}{}_{(aq)} \longrightarrow 2I^{-}{}_{(aq)} + S_4O_6{}^{2-}{}_{(aq)}$$

First, we calculate the number of moles of thiosulphate ions used in the reaction.

$$\text{concentration} = \frac{\text{moles}}{\text{volume } (dm^3)}$$

$$\text{moles} = \text{concentration} \times \text{volume } (dm^3)$$

$$\text{moles} = 10/1000 \times 0.05 = 0.0005 \text{ mol thiosulfate ions}$$

From the above two chemical equations, we can deduce that the number of moles of copper(II) ions in the flask is equal to the number of moles of thiosulphate ions in the titre used.

Concentration of copper(II) ions = 0.0005/0.030 = 0.016 mol.dm^{-3}

6.6 Stereoisomerism in Coordination Compounds

We have already discussed isomerism in organic compounds in the previous class. In this topic we shall focus on isomerism exhibited by coordination compounds.

Stereoisomerism stems from different arrangements of atoms/ligands of complexes in the space. Stereoisomers are divided into two types, geometric isomers and optical isomers.

i. Geometric isomerism

Geometric isomerism is shown by those complexes that have ligands arranged differently in space relative to the central metal ion. Such isomers are also called cis-trans isomers or diastereomers. Take the example of diamminedichloroplatinum(II), $[Pt(NH_3)_2Cl_2]$, which is square planar complex.

Do You Know?

Tetrahedral complexes cannot show geometric isomerism because all four ligands are adjacent to each other.

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The isomer having identical ligands next to each other is called cis-isomer while the one with identical ligands opposite to each other is called trans-isomer. Remember that their biological behaviours are remarkably different from one another.

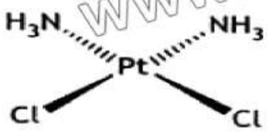
Fighting Cancer

In 1965, Barnett Rosenberg was the first who found that cis-platin had inhibiting cell division property and could be used as anticancer drug. On the other hand, trans-platin had no such medicinal properties.

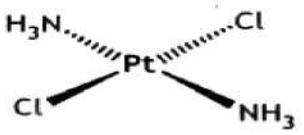
Cancer is mostly caused by abnormal DNA replication where the double helix 'unwinds' to form the template for a new strand. When replication process follows the wrong way, it either causes mutation or can grow with uncontrollable speed, resulting in cancerous tumors.

The cancer patient is administered cis-platin in solution which passes through the cell membranes into the nucleus of the cancerous cells. The cis-platin complex forms a bridge within a DNA strand of the nucleus where the donor atoms of the strands replace chloride ligands and bind themselves strongly to the platin atoms. This new platin complex disrupts the replication process of DNA and consequently the cancerous cells die. In the case of fast-growing tumor cells, the cis-platin complex shrinks the cancerous cells, leading to remission of cancer.

However, cis-platin discontinues DNA replication in both cancerous and healthy fast-growing cells, like white blood cells, leading to side effects (increased infection, hair loss and kidney damage). Despite this, it remains effective in treating many types of cancers.



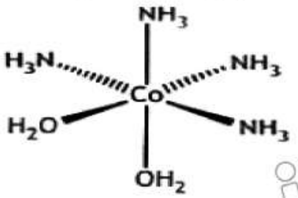
cis-diaminedichloroplatinum(II)



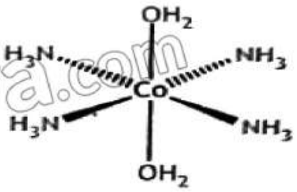
trans-diaminedichloroplatinum(II)

In cis-complex, the two chloride ligands and two ammonia ligands are next to each other whereas in trans-complex, the two chloride and two ammonia ligands are opposite to one another. These isomers of platinum have different biological behaviours.

Similarly, octahedral complexes can also show geometric isomerism. For example tetraamminediaquacobalt(II) complex has both cis and trans isomers as shown.

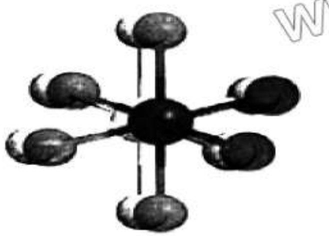


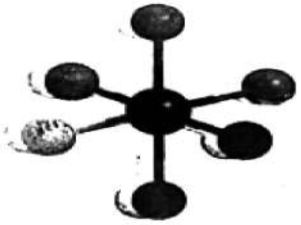
cis-tetraamminediaquacobalt(III)



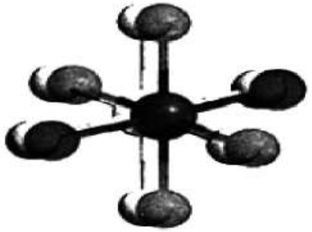
trans-tetraamminediaquacobalt(III)

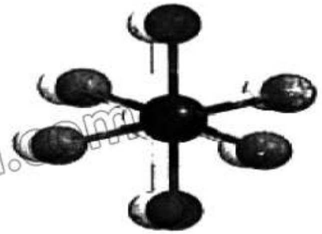
The cis-isomer of this complex has water ligands next to each other while its trans-isomer has water ligands lying on opposite side. To make cis-isomers of octahedral complexes with monodentate ligands, look the following three-dimensional diagrams.



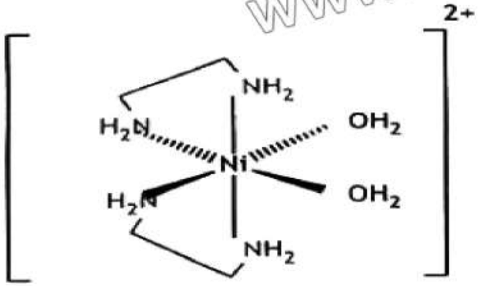


On the other hand, trans-isomers are shown below.

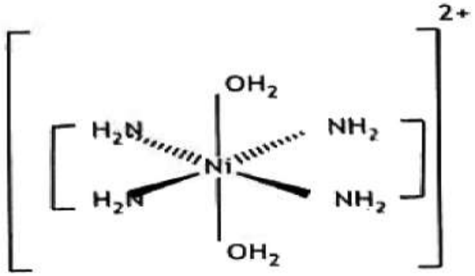




Similarly, bis(1,2-diaminoethane)diaquanickel(II) ion shows geometric isomerism.



cis-bis(1,2-diaminoethane)di-aquanickel(II) ion



trans-bis(1,2-diaminoethane)di-aquanickel(II) ion

We have already discussed that geometric isomers show different properties because of their different symmetry and polarity. The cis-isomers are polar as they have imbalance of electron cloud and lack of symmetry. The end where water is the ligand is partial negative while the other end where ammonia is bonded gets partial positive charge. The reason is that oxygen of water has higher electronegativity than nitrogen of ammonia causing electron flow towards water. The two individual dipoles created by two water ligands result into net dipole making the complex polar.

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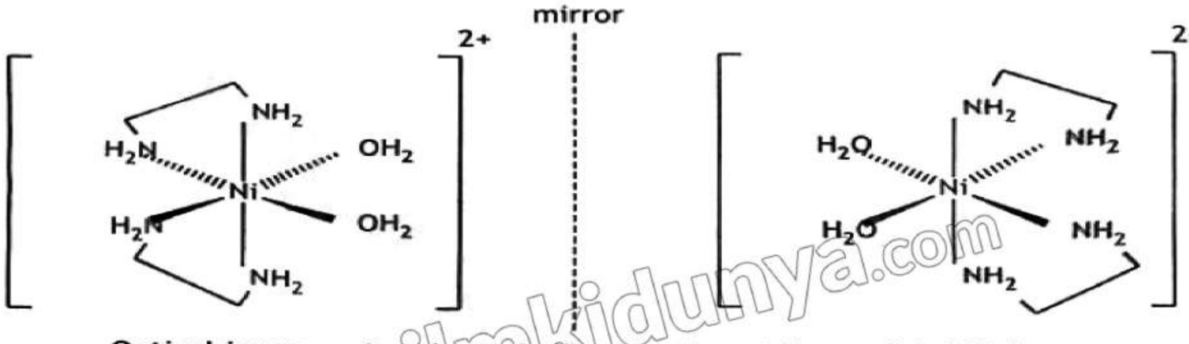
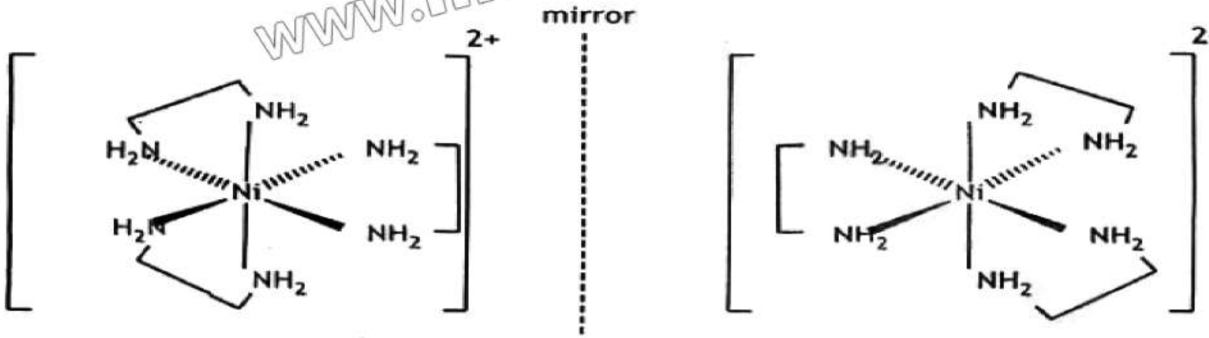
Conversely, the trans-isomers have symmetric shapes and even distribution of electron cloud making them non-polar. This is because the individual dipoles created by two water ligands work against each other cancelling the overall dipole of the complex.

ii. Optical Isomerism

Optical isomers are molecules that have non-superimposable mirror images. They are also called enantiomers. They have identical physical properties except for their ability to rotate the plane of polarized light, either clockwise or counterclockwise. Optical isomerism is exhibited by octahedral complexes. In the case of octahedral complexes with two monodentate ligands and two bidentate ligands, only the cis-isomer can show optical isomerism.



Optical isomers of cis-bis(1,2-diaminoethane)diaquanickel(II) ion



Optical isomers of tris(1,2-diaminoethane)nickel(II) ion

Similarly, octahedral complexes of three bidentate ligands can exhibit optical isomerism. They are mirror images but not superimposable on one another.

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KEY POINTS

- Transition metals are those elements that have incomplete d sub-shell.
- The elements of the 3d block have high melting points, boiling points and densities.
- The first and second ionisation energies increase only slightly across the block from scandium to zinc, as 4s electrons are being removed which are shielded from the nuclear attraction by the inner 3d electrons.
- A ligand is a molecule or ion with one or more lone pairs of electrons available to donate to a transition metal ion.
- Transition elements form complexes by combining with ligands. Ligands bond to transition metal ions by one or more dative (co-ordinate) bonds.
- Most transition elements form M^{2+} ions by loss of the 4s electrons.
- The elements vanadium, chromium and manganese have a maximum oxidation number equal to the sum of the numbers of 3d and 4s electrons.
- Transition metal ions accept electrons from ligands so metal ions act as Lewis acid while ligands as Lewis bases.
- The colours of complexes are due to d-d electronic transitions. The type of colour depends upon the nature of ligand.
- The colour of complex observed depend on the colour absorbed.
- The complexes of d block elements which have complete or empty d sub-shell are colourless.
- Transition elements can exist in several oxidation states because of the involvement of both 4s and 3d orbitals.
- Ligand exchange reactions involve exchange of ligands in a complex resulting in change in colours of complexes.
- A strong ligand can displace a weak ligand
- Ligand exchange can be described in terms of competing equilibria.
- The stability constant, Kstab, of a complex ion is the equilibrium constant for the formation of the complex ion in a solvent from its constituent ions or molecules.
- The higher the value of the stability constant, the more stable is the complex ion formed.
- The splitting pattern is different in octahedral and tetrahedral complexes. Different ligands will split the d orbitals by different amounts of ΔE, resulting in differently coloured complexes.

References for Further Information

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- Chemistry by Christopher Talbot, Richard Harwood and Christopher Coates.

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EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which one of the following species has d^{10} sub-shell?

a) Cu^{2+} b) zn^{2+} c) Mn d) Cr

ii. Which one is correct statement about zinc element?

1. It has complete 3d sub-shell
2. It is transition metal
3. It forms colourless complexes
4. It can exist in one stable oxidation state

a) 1and 2 only b) 1,3 and 4 only
c) 1 and 4 only d) all are correct

iii. The electronic configuration of iron cation in the complex, $[Fe(CN)_6]^{3-}$, is

a) $[Ar]3d^6$ b) $[Ar]3d^5$
b) $[Ar]3d^6\ 4s^1$ d) $[Ar]3d^6 4s^2$

iv. Why is the hexaaquacopper(II) ion blue in colour?

a) The d-d electronic transition absorbs blue wavelength of visible spectrum
b) The d-d electronic transition absorbs all wavelengths except blue
c) The d-d electronic transition transmits all wavelengths of white light except blue
d) The d-d electronic transition absorbs red wavelength and transmit the remaining light

v. The cyanide ligand (CN^-) can form two complexes with iron with formulae, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. What is the oxidation state of iron in them ?

a) +2 and +3 respectively b) +4 and -2 respectively
c) +2 and +4 respectively d) +3 and +2 respectively

vi. Transition metals are different from alkali metals and alkaline earth metals in many ways. Which one is incorrect statement about transition metal when compared with group 1 and group 2 metals?

a) they form coloured compounds b) they show variable oxidation states
c) they have high melting points d) they are more reactive

vii. The species that can act as ligand in transition metal complex is

a) CH_4 b) C_6H_6 c) Na d) $C_6H_4(OH)_2$

viii. Transition metals can show different oxidation states. Which one is the most common oxidation state in first row transition elements?

a) +2 b) +3 c) +4 d) +7

ix. Which one of the following properties of transition metals is held responsible for their catalytic behaviour?

a) they form coloured complexes b) they show variable oxidation states
c) they have high melting points d) they have high density

x. The coordination number of nickel in the complex $[Ni(en)_2(OH_2)_2]^{2+}$ is

a) 2 b) 4 c) 6 d) 8

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xi. Which one of the following complexes cannot show stereoisomerism?
1. $[Cu(H_2O)_6]^{2+}$ 2. $[CuCl_4]^{2-}$ 3. $[Cu(NH_3)_4(OH_2)_2]^2$ 4. $[Ni(en)_3]^{2+}$
a) 1,2 and 3 only b) 1,3 and 4 only
c) 1 and 2 only d) 1 and 4 only

xii. The weakest field ligand among the following is
a) H_2O b) CN^- c) NH_3 d) OH^-

xiii. The highest oxidation state shown by first row transition metals is shown by
a) copper b) manganese c) nickel d) cobalt

2. Short Answer Questions

i. The melting point of titanium is higher than calcium in the same period. Justify this statement?

ii. The first-row elements of d-block exist in more than one oxidation states. However, zinc shows only +2 oxidation state in its complexes. Why?

iii. Define the terms
a. ligand b. coordination number c. complex ion

iv. Explain why hydrated Ti^{4+} complexes are colourless and hydrated Ti^{3+} complexes are coloured?

v. Why do the melting points of first row transition metals increase upto the middle and then decrease? Comment

vi. Why are transition metals used as catalysts in industries for performing different reactions? Give one example.

vii. The blue cobalt chloride paper is used to test the presence of water. If water is present, the paper turns pink. This is because six water ligands exchange for four chloride ligands present in cobalt chloride, $[CoCl_4]^{2-}$. Write the equation to show the ligand substitution reaction when the test is positive.

viii. Octahedral complexes of copper(II) ion have different colours. Explain why?

3. Long Answer Questions

i. The reduction potential for Cr^{2+} ions being reduced to chromium metal is -0.91V and that for Cr^{3+} ions being reduced to Cr^{2+} ions in -0.41V as shown:

$$Cr^{2+} + e^- \rightleftharpoons Cr \qquad E^\circ = -0.91V$$

$$Cr^{3+} + e^- \rightleftharpoons Cr^{2+} \qquad E^\circ = -0.41V$$

Predict whether the chromium(II) ion will disproportionate to chromium(III) ion and chromium metal. If yes, then write the possible ionic equation.

ii. Explain the difference in the splitting pattern of the 3d atomic orbitals in the two copper(II) complexes, $[Cu(H_2O)_6]^{2+}$ and $[CuCl_4]^{2-}$.

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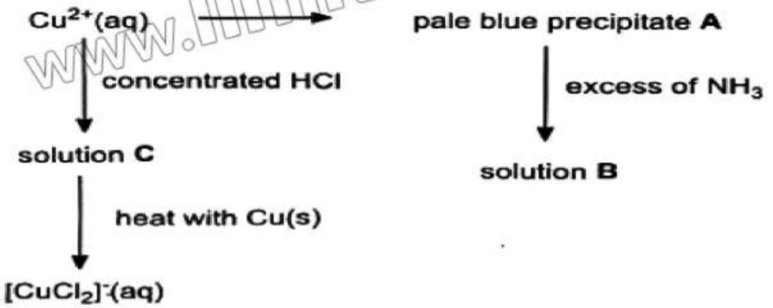
iii. The following scheme shows some reactions of copper(II) ion.



a. Suggest the formulae of A, B and C.
b. State the colours of solutions B and C.
c. Name the type of reactions occurring when C is heated with copper. Also state the role of copper in this reaction.
d. When the solution of complex $[CuCl_2]^-$ is poured into water, which colour precipitate is formed? Justify its colour.

iv. Transition metal complexes such as $[Cu(H_2O)_4(NH_3)_2]^{2+}$ and $Pt(NH_3)_2Cl_2$ show same type of stereoisomerism.
a. Name the type of isomerism.
b. Draw three-dimensional structures for the given two isomers, two for each.

v. Aqueous copper(II) ion can form complexes with the ligands, ammonia and 1,2-diaminonethane as shown.

$$[Cu(H_2O)_6]_2^{+}{}_{(aq)} + en_{(aq)} \rightleftharpoons [Cu(H_2O)_4(en)]^{2+}{}_{(aq)} + 2H_2O_{(l)} \quad K_{stab} = 3.98\times10^{10}$$

$$[Cu(H_2O)_6]_2^{+}{}_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Cu(H_2O)_4(NH_3)_2]^{2+}{}_{(aq)} + 2H_2O_{(l)} \quad K_{stab} = 5.01\times10^{7}$$

a. Write an expression for the stability constant for both equations and state their units.
b. Of the three complexes in the above two equations, state the formula of the complex that is the most stable. Give a reason also.

PROJECT

Students can research the environmental challenges associated with transition metal extraction and usage. They can create awareness campaigns or projects proposing sustainable practices.

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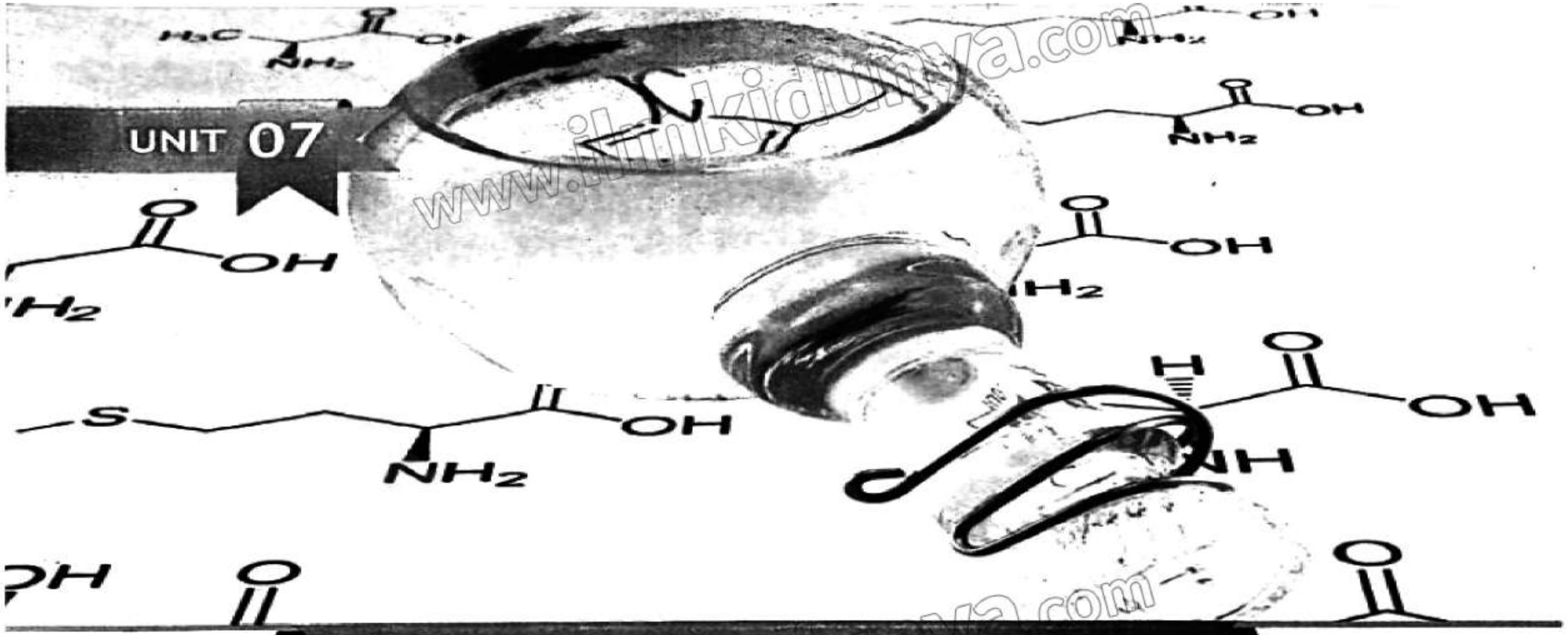

UNIT 07

ORGANIC CHEMISTRY

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Student Learning Outcomes (SLOs)

- Explain stereoisomerism and its division into geometric (cis/trans) and optical isomerism.
- Describe geometrical (cis/trans) isomerism in alkenes and explain its origin in terms of restricted rotation due to the presence of pi (π) bond.
- Describe the shape of benzene and other aromatic molecules, including sp^2 hybridisation in terms of sigma (δ) bonds and delocalized pi (π) system.
- Explain what is meant by chiral center and that such a center gives rise to two optical isomers (enantiomers).
- Describe that enantiomers have identical physical and chemical properties for their ability to rotate the plane of polarized light and potential biological activity.
- Apply the terms optically active, racemic mixture and mesocompounds on the given structure.
- Describe the effect of two optical isomers of a single substance on a plane polarized light.
- Explain the significance of chirality in synthetic reparation of drug molecules, including the potential different biological activity of enantiomers, the need to separate racemic mixtures, and the use of chiral catalysts to produce a single pure optical isomer using thalidomide as an example.

Organic chemistry is the study of preparation, properties, identification, and modifications of organic compounds. All organic compounds have carbon as an essential element. They usually contain hydrogen element and may have other elements, like oxygen, nitrogen, halogens, and sulphur etc. There are millions of organic compounds with different uses in our lives. For example, carbohydrates, proteins, food, medicines, and cloths. Many industries produce organic compounds, like polymers, insecticides, cosmetics, and dyes.

Interesting Information

In the early nineteenth century, Jakob Berzelius classified chemical compounds into two groups based on their origin, organic compounds and inorganic compounds. Organic compounds come from plants and animals while inorganic compounds have mineral origin. A striking difference is in their way of burning. Organic compounds burn on heating (undergo combustion) while inorganic chemicals melt on heating.

Recall from grade 11, that organic compounds have a vast majority in nature. Nearly 19 millions organic compounds have been discovered so far. This enormous number of organic compounds is attributed to one of the factor which is isomerism. Organic compounds show isomerism because they exhibit different structures due to the directional character of covalent bond.

Organic compounds have a unique property of showing isomerism which is one of the factors held responsible for their vast majority in nature. The phenomenon which gives different structural formulae to organic compound with same molecular formulae is called isomerism. The compounds showing such phenomenon are called isomers.

Isomerism is broadly categorized into two classes: constitutional isomerism (structural isomerism) and stereoisomerism (configurational isomerism). The constitutional isomerism arises due to different connectivity of atoms in a molecule while stereoisomerism is due to different three- dimensional arrangement of atoms or groups of atoms in the space. We can interconvert constitutional isomers simply by rotation of one part of a molecule with reference to the other about single covalent bond, without breaking bonds, whereas stereoisomers can be interconverted by breaking and making bonds.

In the previous class, we have already studied both structural and stereoisomerism. However, in this chapter we will revisit stereoisomerism and study it in more detail.

7.1.1 Stereoisomerism

Most of the chemical reactions in our body involve molecules with specific stereochemistry. Metabolic reactions are catalyzed by enzymes which can interact with those stereoisomers that can fit in their active sites. The side effects of a medical drug is caused by the wrong stereoisomer whose structure does not fit into the active site of the enzyme. Stereoisomers are those molecules which have same chemical formulae, same structural formulae but different arrangement of atoms in space. The phenomenon of existence of such molecules is called stereoisomerism. This type of isomerism is further classified into two categories.

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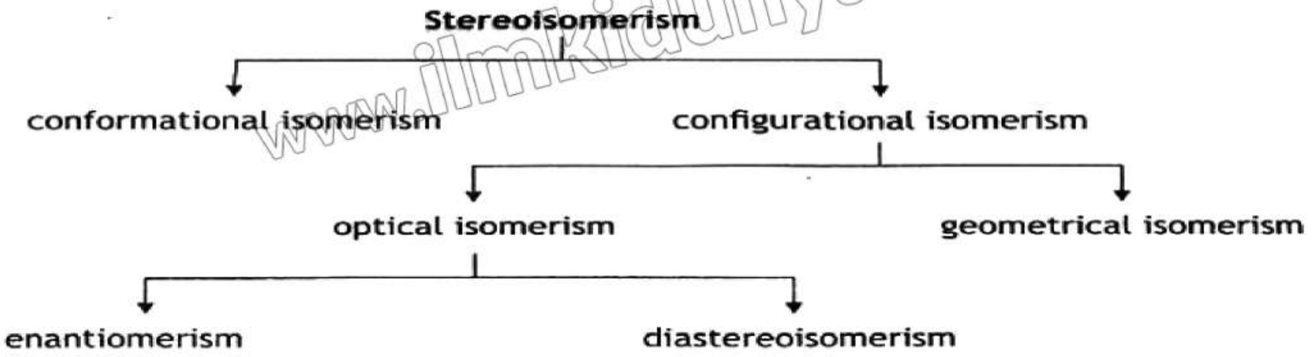

1. Geometric isomerism

Some organic compounds, like alkenes, have the same connectivity of atoms in their molecules, same structural formulae but different arrangement of atoms or groups of atoms around double bond. Such molecules are called geometric isomers, and this phenomenon is called geometric isomerism.

In alkenes, each carbon atom of double bond shows sp^2 hybridization. The double bond consists of one sigma (δ) bond and one pi (π) bond. The sigma (δ) bond is formed by head-on overlap between one of the three sp^2 hybrid orbitals on each carbon atom of double bond whereas pi (π) bond is formed by parallel overlap between unhybridized "p_z" orbitals on each carbon atom of double bond.

Since pi (π) bond between carbon atoms in alkenes restricts rotation about double bond at room temperature and does not allow free rotation of substituents around. To rotate the carbon atoms in a double bond of alkenes relative to each other, the pi (π) bond must be broken. Breaking pi (π) bond in ethene requires approximately 264 kJ/mol energy. This restricted rotation of carbon atoms of double bond is responsible for geometric isomerism in alkenes.

Alkanes, on the other hand, cannot show this type of isomerism because a single bond can easily be rotated at room temperature. For example, rotating carbon-carbon single bond in ethane requires almost 12 kJ/mol energy.

In the light of this discussion, we can say that one major difference between alkanes and alkenes is the degree of freedom of rotation about carbon-carbon single and double bonds.

Remember that alkenes molecules with same atoms or groups of atoms on same carbon atom of double bond cannot show geometric isomerism. This is because we get identical molecules even after breaking pi (π) bond and rotating the molecule across carbon-carbon double bond as shown.

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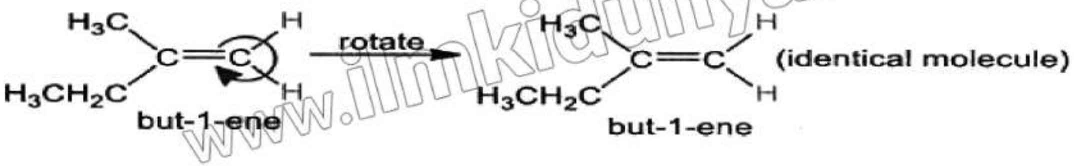
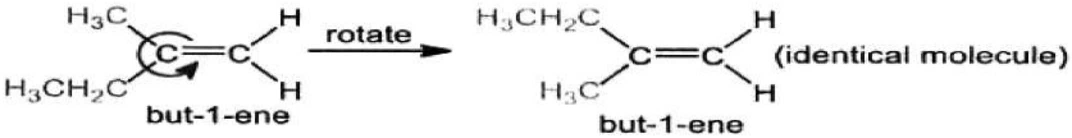
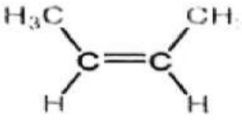
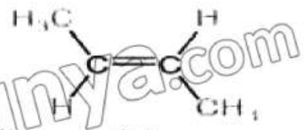




On the other hand, alkenes molecules with different substituents bonded to each carbon atom of double bond exist as two different molecules. For example, the physical properties of but-2-ene, depends on orientation of substituents around carbon-carbon double bond which means that different arrangement of substituents around double bond gives birth to different molecules as shown.

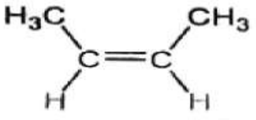

(a)

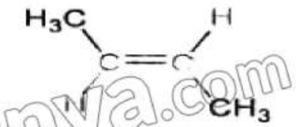

(b)

Remember that molecule (a) cannot be converted to molecule (b) simply by twisting one carbon of double bond with respect to the other due to restriction of pi (π) bond. To differentiate between such molecules based on different orientation of atoms or groups of atoms around double bond, IUPAC nomenclature recommends two types of designations for geometric isomers.

1. The cis-trans Isomerism

The cis-trans isomerism is originally used for naming disubstituted alkenes. We have some molecules that have the same substituents on the same side of double bond. Such type of molecules is called cis-isomers (Cis is a Latin word meaning "same side"). Conversely, the molecules having same atoms or groups of atoms on the opposite side of carbon-carbon double bond are called trans-isomers. In this system, the arrangement of carbon atoms of the parent chain decides whether the isomer is cis or trans. The but-2-ene molecule can show cis-trans isomerism as shown.


cis-but-2-ene


trans-but-2-ene

In cis-but-2-ene, the two methyl groups (carbon 1 and carbon 4 of the main chain) lie on the same side of carbon-carbon double bond whereas, in trans-but-2-ene, the two methyl groups stand on the opposite side of double bond.

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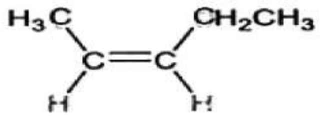
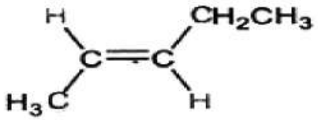
The pent-2-ene molecule becomes relatively more difficult to designate it cis and trans-isomers in the sense that it has three different substituents, ethyl, methyl and hydrogen. Chemists *decide* cis and trans-isomerism in such molecules based on carbon atoms (carbon 1 and 4 in pent-2-ene) of alkyl groups bonded to the carbon atoms of double bond and treat all alkyl groups as same substituents. Similarly, cis-trans isomerism is studied based on orientation of hydrogen atoms bonded to carbon atoms of the double bond.

In pent-2-ene, the cis-isomer has alkyl groups and hydrogen atoms on same side of double bond whereas the trans-isomer carries alkyl groups and hydrogen atoms on opposite side of double bond.

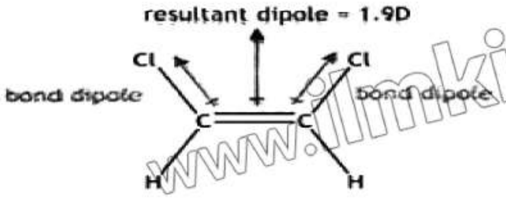


cis-pent-2-ene

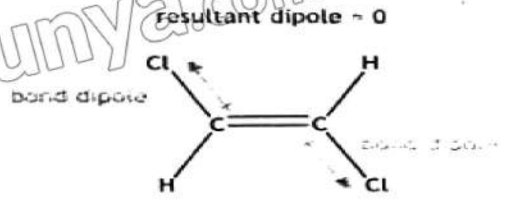


trans-pent-2-ene

The physical properties of cis-trans isomers, like melting points, boiling points, and solubility are different from one another. Cis-isomers are polar because they have dipole moment while trans-isomers are non-polar as they have zero dipole moment.



cis-1,2-dichloroethene



trans-1,2-dichloroethene

Their chemical properties are similar because they have the same functional groups, but not identical. They differ widely in biological systems due to their different shapes. Generally, cis-isomers are more reactive than trans-isomers. The closeness of bulky groups around carbo-carbon double bond causes steric hindrance, making the cis-isomer less stable compared to its trans-counterpart. Moreover, the electron cloud in cis-isomer is shifted to one side, making it more exposed to electrophilic attack compared to trans-isomer.

Interesting Information

Cis-platin has shape able to bond to the base guanine in DNA, causing DNA damage and kills cancer cells. This is why cis-platin is used in chemotherapy of different types of cancer. Tran-platin cannot play this role.

Key Information

We can also designate cis-trans isomers based on hydrogen atoms bonded to the carbon atoms of double bond.

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How Isomerism Works in Our Eye?

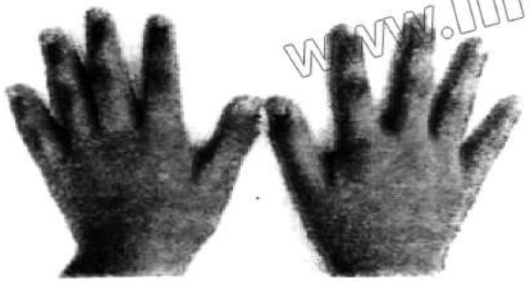
In 1950s, an American chemist, George Wald discovered that the chemistry of vision involves cis-trans isomerization. The retina of eye contains rhodopsin which consists of protein and a cis-isomer called cis-retinal. When light enters our eye, the rhodopsin absorbs energy from photons of light high enough to break the pi (π) bond in the cis-isomer. Then rotation around sigma (δ) bond takes place followed by reformation of pi (π) bond and thus the trans-isomer, called trans-retinal, is formed. The energy released during reformation of pi (π) bond is responsible for the transmittance of nerve impulse to the brain. This absorption of light changes the shape of protein, creating flow of ions into retinal cells, initiating electric impulses which are carried by nerve cells to the brain where they are interpreted.

Concept Assessment Exercise 7.1

1. Which of the following compounds can and cannot show cis-trans isomerism and why?
   i. 1-chloroprop-1-ene ii. 3-chloroprop-1-ene iii. hex-2-ene

7.1.2 Optical Isomerism

The easiest way to understand the concept of optical isomerism is to look at our hands. Our right hand is the reflection of our left hand in a mirror which means that our left-hand reflection looks just like our right hand. In nutshell, our right and left hands are mirror images of one another. Your right and left hands are nonsuperimposable mirror images, meaning they cannot align perfectly one above the other, regardless of how you orient them as shown.



Interesting Information

If our hands were superimposable we would have either two rights hands or two left hands, instead of one right and one left.

Similarly, try to put your right-handed glove on your left hand, it does not fit. All objects that are nonsuperimposable on their mirror images are called chiral (Greek word "cheir" meaning 'hand').

All chiral objects show handedness (chirality), with examples including scissors, keyboards, and cars. To understand chirality, hold your left hand outstretched (palm away) before a mirror and your right hand (palm toward you) next to it. The mirror image of your left hand will appear identical to your right hand, demonstrating chirality.

Many organic molecules exist in pairs which are non-superimposable mirror images of one another. Such molecules have carbon atom bonded to four different groups and are called

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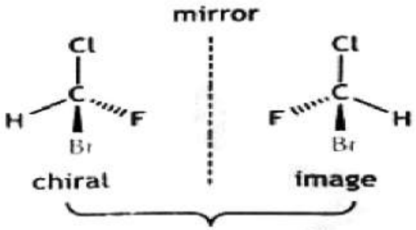
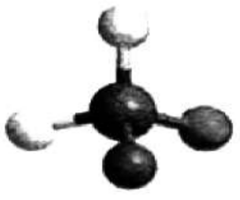
chiral molecules. The carbon which is bonded to four different atoms or groups of atoms are chiral or asymmetric carbon.

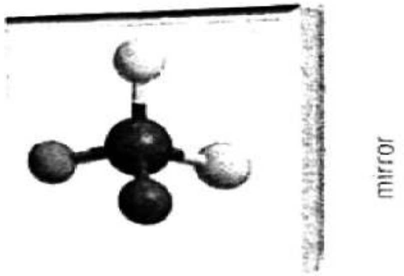
On the contrary, achiral molecules have a central carbon bonded to identical groups, making their mirror images superimposable and identical. For example, bromochlorofluoromethane has a non-superimposable mirror image.



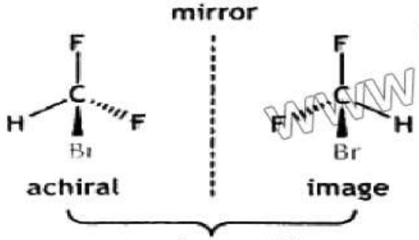
nonsuperimposable



original molecule

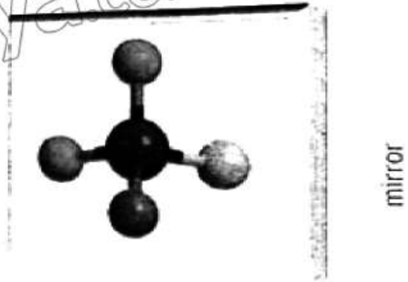


mirror image



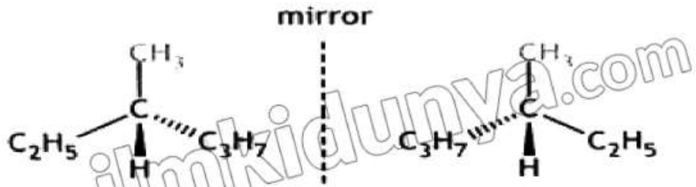
superimposable

original molecule



mirror image

The pair of stereoisomers that are nonsuperimposable mirror images of one another, just like our right hand is mirror are called enantiomers and this phenomenon is called enantiomerism. The word enantiomer comes from Greek word 'enantion' which means opposite. Consider 3-methylhexane shown.



origianl molecule mirror image

We have studied in previous class that ordinary light has waves *oscillating in all planes* perpendicular to its direction of propagation. When ordinary light is passed through a polarizing

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filter, such as calcite or Polaroid filter, only that part of light will be allowed to pass which can vibrate in parallel plane. The light vibrating in one plane is called plane polarized light.

The isomers that can rotate the plane of polarized light either in clockwise or anticlockwise direction are called optical isomers and this phenomenon is called optical isomerism. Optical isomers can exist in pairs called enantiomers or diastereomers. A solution of one enantiomer rotates the plane of polarized light in one direction whereas a solution of the other enantiomer rotates the plane of polarized light in the other direction.

Concept Assessment 7.2

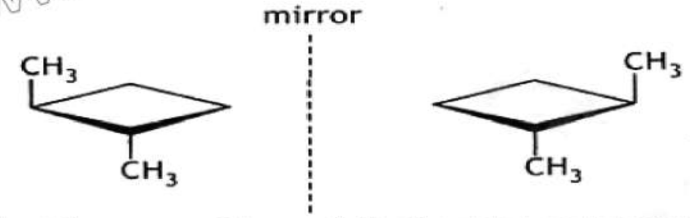
Separate chiral and achiral molecules in the following.

a.	$CF_3CH_2CCl_3$	b.	$CF_2HCHFCCl_3$	c.	$CHCl_2(CH_2)_3CH(OH)CH_3$
d.	$CH(OH)ClCH_2CH_3$	e.	$CH_2ClCH(OH)CH_3$	f.	$CF_3CH_2CCl_3$

If the mixture contains 50-50 mixture of the two types of isomers, it is called racemic mixture. It has 50% dextrorotatory (Latin 'dexter' meaning 'right') isomer which rotates the plane of polarized light in clockwise direction while the other has 50% levorotatory (a Latin word 'laevus' meaning 'left') isomer which rotates the plane of polarized light in anticlockwise direction. The symbols "l" for levo and "d" for dextro are now obsolete and IUPAC recommends symbols "+" for dextro and "-" for levo isomers. The trans-isomer of 1,2-dimthylcyclobutane shows optical isomerism as follows.

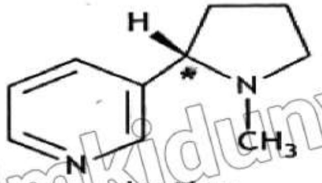
Interesting Information

Optical isomers are molecules which can have non-superimposable images while enantiomers are the pairs of molecules that are non-superimposable images of one another.



optical isomers of trans-1,2-dimethylcyclobutane

Similarly, nicotine molecules naturally synthesized by tobacco plant are chiral showing optical isomerism. Note the red star shows chiral carbon in nicotine molecule.

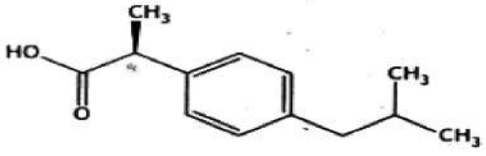


nicotine

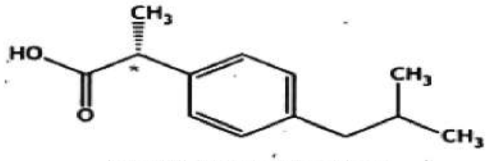
It is evident that a racemic mixture lacks the ability to rotate the plane of polarized light in either direction, making it optically inactive. The two isomers within such a mixture rotate *polarized light* equally, but in opposite directions. They cancel out their collective impact on the rotation of plane of polarized light in either direction.

Interesting Information

While administering racemic mixture of drugs, one enantiomer puts intended therapeutic effect while the other have damaging effect on the body. For example, a common painkiller, ibuprofen is chiral molecule, whose one enantiomer is active while the other is inactive as shown.



(+)-ibuprofen (active)



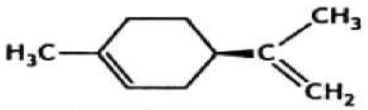
(+)-ibuprofen (inactive)

7.1.3 Properties of Optical Isomers

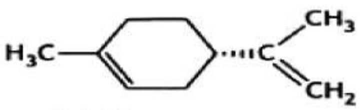
The physical and chemical properties of optical isomers are similar. For example, the optical isomers of the same compound possess the same density and melting points. Optical isomers of a compound can be differentiated based on their ability to rotate the plane of plane-polarized light in opposite directions.

However, they show different physiological effects in human body highlighting the fact that biological sensors and biochemical reactions are dependent on the shapes of molecules. For instance, one enantiomer of amino acid (asparagine) has a bitter taste whereas the other counterpart gives sweet taste.

Similarly, limonene molecule has chirality, and the body can distinguish between the taste and odour of its two enantiomers. Lemons and oranges contain the same isomer, (+)-limonene. In contrast, (-)-limonene is found in pine needles, peppermint, and spearmint and is different in smell or taste to the (+)-isomer. The (+)- and (-)-enantiomers of limonene (+)-limonene (-)-limonene.



(+)-limonene



(−)-limonene

Therapeutic drugs may also show optical isomerism as they are chiral molecules. One of the two enantiomers have desired pharmacokinetic and pharmacodynamic properties. Pharmacokinetics studies absorption, distribution, metabolism and excretion while pharmacodynamics is the study of actions administered drug on the system of the body and the way drug binds to the target site.

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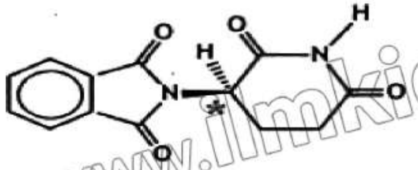
Chirality and Preparation of Drugs

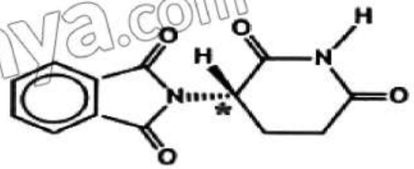
It is of high industrial concern to design, develop and supply pharmaceutical drugs globally. One cannot neglect the importance of the therapeutic effects and the heavy financial issues of the development and marketing of new drugs.

The shape of biological systems and the biological-targeted chiral molecules are deeply linked in preparation of drugs. There is a potential difference between the biological activity of a particular drug. One enantiomer of a chiral molecule has differing effects on the human body compared to the other enantiomer of the same chiral molecule. For instance, one enantiomer of propoxyphene is an analgesic (pain relieving) whereas the other has anti-coughing properties, although the commercial names are mirror images of one another.

Another example of a chiral molecule which is used is called thalidomide. It was prescribed by medical practitioners as a sedative and treating morning sickness (nausea linked with pregnancy). Later, it was found that this drug caused birth defects in babies whose mothers took it during pregnancy. Further research proved that the (+)-enantiomer of thalidomide is active and used as sedative with no side effects whereas the (-)-enantiomer is a teratogenic, causing birth defects in babies whose mothers took the drug.



(+)-thalidomide
(sedative)



(–)-thalidomide
(teratogenic)

Unfortunately, the two enantiomers of thalidomide soon interconvert, making the administration of a single intended enantiomer ineffective to prevent the harmful effects.

7.2.1 Separation of Racemic Mixture of Thalidomide

Most chiral molecules in drugs exist in the form of racemic mixture, having 50 % (+) and 50 % (-) isomers. However, such drugs are not advised by healthcare professionals in racemic mixture form because the two isomers can have different effects on human body. One enantiomer may be therapeutically active and have desired effects while the other may be inactive, less effective or even harmful. This is evident from the case of thalidomide.

To address this issue in thalidomide drug, there are two methods. One method is optical resolution which involves the separation of the racemic mixture into two enantiomers of thalidomide, removing the (—)-thalidomide enantiomer. This can be done by high-performance liquid chromatography (HPLC), crystallization or use of some enzymes. The other method is called chiral synthesis or asymmetric synthesis which ensures the formation of single desired enantiomer, like (+)-thalidomide, suppressing the formation of the other enantiomer.

Asymmetric synthesis utilizes chiral catalysts to create an environment in the chemical reaction that favours the production of desired enantiomer, suppressing the other enantiomer. A BINOL (1,1-bi-2-naphthol) catalyst has palladium or rhodium used for asymmetric synthesis of (+)-thalidomide enantiomer, making thalidomide drug safer and reliable thereby minimizing the risks of harmful effects of (—)-thalidomide enantiomer.

In asymmetric synthesis reaction thalidomide, the double bond in thalidomide, is selectively hydrogenated in the presence of a chiral catalyst. The chiral catalyst supports the addition of hydrogen to the double bond in thalidomide molecule favoring the formation of one enantiomer over the other. In this way, a single pure isomer of thalidomide is produced which can be used for intended therapeutic effects on our body.

Interesting Information
Now-a-days, different drug authorities across the globe, like US Food and Drug Authority (FDA), recommends the assessment of enantiomer activity for racemic drugs in the body to ensure the development of a single desired enantiomer.

KEY POINTS

- Organic chemistry is the study of hydrocarbons or their derivatives.
- Almost 20 million of organic compounds are known.
- Isomerism is the phenomenon stems from same molecular formulae but different structural formulae of organic molecules.
- Stereoisomers have same molecular formulae and structural formulae but different arrangement of atoms or groups of atoms in the space.
- Geometric isomerism is shown by alkenes having different atoms or groups of atoms bonded to double bonded carbon atoms.
- Geometric isomerism is also called cis-trans isomerism.
- The double bond presents restricted rotation to the two doubly bonded carbon atoms giving different configuration to the molecule.
- The E/Z designation is used specifically for those molecules having different atoms or groups bonded to double bonded carbon atoms.
- A priority rule is established by IUPAC body to decide the right configuration.
- The IUPAC nomenclature recommends E/Z system for all alkenes molecules exclusively.
- However, chemists still continue to use cis-trans designations for simple molecules.
- According to IUPAC recommendation for organic chemistry 2013, both E/Z and cis-trans systems are used for alkenes, however, the E/Z nomenclature is preferred over cis-trans nomenclature.
- Optical isomerism is shown by molecules having no symmetry. Optical isomers rotate the plane of polarized light either clockwise or anticlock-wise.
- The clock-wise rotating isomers are designated d or + sign while the ones that rotate the plane of polarized light anticlock-wise are designated l or - sign.
- The plane polarized light is the one which travels or vibrates in one plane.
- Chiral molecules are those having carbon atoms bonded to four different atoms or groups of atoms.

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- Chirality means handedness. A chiral molecule has a mirror image related to it like left hand to right hand.
- A molecule may have more than one chiral carbon atoms.
- All optical isomers have chiral carbon atoms and are asymmetric.
- All optical isomers have chiral centers but all chiral molecules are not optically active.
- A meso isomer is the one which is optically inactive, although it has chiral carbon atoms. The reason is that it is internally compensated.
- A racemic mixture is the one having 50% dextro and 50% levo rotatory isomerism making it overall optically inactive.
- Polarimeter is the instrument that determines the optical activity of organic molecules.
- Optical isomers have different properties from one another.
- Optical isomers are used as drugs. One optical isomer has the desired effect on a patient while the other counterpart has harmful effects.
- It is recommended to separate the racemic mixture of optical isomers before using them as drugs.

References for Further Information

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- Chemistry by George Facer
- Chemistry-The molecular nature of matter and change by Silberberg.
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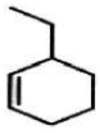
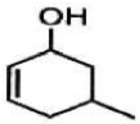
- Chemistry by Cliff Curtis, Jason Murgatroyd and Divid Scott.
- Chemistry by Christopher Talbot, Richard Harwood and Christopher Coates.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which one of the following molecules will have the ability to rotate the plane of polarized light?

I.


II


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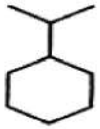
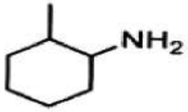


VI


a) I and II only
b) I and III only
c) I, II and IV only
d) II and IV only

ii. Which one of the following molecules shows optical isomerism/

a) $CH_2{=}CHCH_2CH_3$
b) $(CH_3)_2CHCl$
c) $CH_2{=}CHCH(Cl)CH_3$
d) $CH_3CH_2CH_2CH{=}CH_2$

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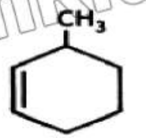
iii. How many chiral centers are present in this molecule?



a) 1 b) 2
b) 3 d) 5

iv. Geometric isomerism is shown by

a) alkenes b) alkynes
c) alkanes d) benzene

v. Which one is correct statement about cis-trans isomerism?

a) It is shown by alkenes due to restricted rotation of double bond
b) It is shown by alkenes due to free rotation of sigma bond
c) It is not shown by alkynes because it cannot have different atoms/groups
d) alkanes cannot show geometric isomerism due to free rotation of sigma bonds

vi. Which compounds need to be designated by E/Z system?

a) low substituted alkanes b) high substituted alkenes
c) highly substituted alkanes d) low substituted alkenes

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vii. Which one is the least stable compound?

a) cis-but-2-ene b) trans-but-2-ene
c) trans-hex-3-ene d) trans-pent-2-ene

viii. Which molecule is chiral and can rotate the plane of polarized light?

a) cyclohexane b) benzene
c) 2-methylbutan-2-ol d) pentan-2-ol

ix. Which one of the following is optically active?

a) racemic mixture b) meso-compounds
c) all chiral molecules d) all asymmetric molecules

x. Which one is incorrect statement about optical isomers?

a) they cause different rotation of plane polarized light
b) they have no functional groups
c) alkanes cannot show optical isomerism
d) the double bond carbon in alkenes acts chiral center

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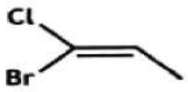
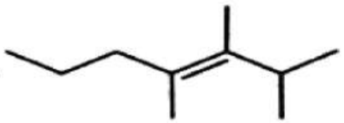
2. Short Answer Questions

i.

a 

b 

c. 

ii. Draw the cis-trans isomers of hex-3-ene.

iii. Highlight the importance of chirality in drugs. Why do we need to separate optical isomers in the preparation of drugs?

iv. What is meant by levo-rotatory and dextro-rotatory isomers? Give one example.

v. Why can't geometric isomerism occur in alkenes where identical atoms or groups are attached to the same carbon atom of the double bond?

vi. How does the presence of a π (pi) bond in alkenes restrict rotation, and what energy implication does this have for isomerism?

vii. Why are cis-isomers generally more reactive but less stable than their trans-isomer counterparts?

viii. How can a molecule be chiral yet remain optically inactive? Give the term used for such a molecule.

ix. Why is it not effective to administer only the (+)-thalidomide enantiomer to patients?

x. Why is the use of chiral catalysts preferred in the pharmaceutical industry for synthesizing optical isomers of drugs?

3. Long Answer Questions

i. Define geometric isomerism. Draw cis-trans isomers of any alkene.

ii. Why propene cannot show cis-trans isomerism?

iii. Explain the way of separating a racemic mixture of thalidomide.

iv. How a catalyst can play its role in this separation.

v. Explain why the trans-isomer of but-2-ene is more stable than the cis-isomer. What role do steric interactions play?
Given the compound 1,2-dichloroethene, identify and draw all possible geometrical isomers.

vi. Indicate which isomer would likely have a higher boiling point and why.

vii. What structural features must a molecule have to exhibit optical isomerism? Give an example and explain why it is optically active.

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UNIT 08

HYDROCARBONS

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Student Learning Outcomes (SLOs)

- Explain the shape of benzene molecule (molecular orbital aspect).
- Define resonance, resonance energy and the relative stability of benzene.
- Compare the reactivity of benzene with alkanes and alkenes.
- Describe the mechanism of substitution reactions with chlorine and bromine, including the formation of ortho, para and meta isomers, and predict the major product(s) of the reaction.
- Explain the mechanism of nitration, including the formation of a nitronium ion, and predict the major products(s) of the reaction.
- Explain the mechanism of Friedel-Craft alkylation and acylation respectively, including the role of the Lewis acid catalyst, and predict the major product(s) of the reaction.
- Explain the mechanism of side chain oxidation, including formation of a benzoic acid, and predict the major product(s) of the reaction.
- Explain the mechanism of hydrogenation, including the role of metal catalyst, and predict the major product(s) of the reaction, which is cyclohexane.
- Describe the mechanism of electrophilic aromatic substitution, including the role of electrophile and the formation of a sigma complex, and predict the major product(s) of the reaction based on the directing effects of substituents on the aromatic ring

In previous class we have discussed hydrocarbons in detail. They are compounds having hydrogen and carbon elements only. Broadly, they are classified into aliphatic and aromatic hydrocarbons. The word aliphatic comes from the Greek language "aleiphar" meaning "oil" and was given to hydrocarbons that were obtained by the chemical degradation of fats. All hydrocarbons having no benzene ring are classified as aliphatic hydrocarbons. On the other hand, hydrocarbons having at least one benzene rings are called aromatic hydrocarbons. More recently, the alternative and systematic name of arenes has been used for them. The word arene has a suffix "ar" which means aromatic and "ene" comes from the last three alphabets of benzene, reflecting unsaturation.

Michael Faraday isolated a hydrocarbon from the oily residue that was collected in the gas pipes of London and he called it "bicarburet of hydrogen". In 1834, Eilhardt Mitscherlich of the University of Berlin prepared the same substance by heating benzoic acid with lime. He found that this molecule has empirical formula "CH".

$$C_6H_5COOH + CaO \longrightarrow C_6H_6 + CaCO_3$$

Benzoic acid was obtained from gum benzoin, a resin of balsam tree (Java island of Indonesia) so it got the name benzin which, later on, became benzene.

All compounds related to benzene and toluene are called aromatic hydrocarbons. The word "aroma" is Latin word meaning fragrance. Benzene and toluene are not particularly fragrant compounds themselves; however, their origin comes from pleasant-smelling plant extracts.

Later on, it was investigated that all aromatic compounds are not pleasantsmelling, even some has harmful and unpleasant vapours. They have unusual stability because of benzene ring in them so the name aromatic was used for all those compounds that are stable. All aromatic compounds must have at least one benzene ring.

Warning !

Benzene is a chemical causing cancer (leukemia). People exposed to car exhaust or working in different factories may become victims. There are different rules in the world regarding permissible levels of concentration of benzene in the working space.

8.1 Nomenclature of Benzene

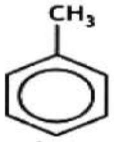
The simplest aromatic compound is benzene itself. There are many aromatic compounds with one or more different substituents. The IUPAC system still retains some common names.

Remember!

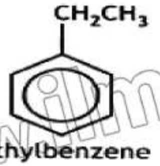
According to IUPAC conventions, all letters in the names of compounds must be written in lowercase, except when they appear at the beginning of a sentence. However, the first letter of element symbols is always uppercase.

Monosubstituted benzenes

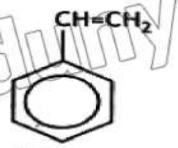
They have one substituent attached to benzene ring. The systematic or IUPAC names of some simple monosubstituted aromatic compounds are given.



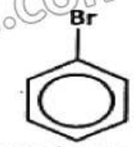
toluene



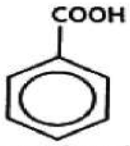
ethylbenzene



styrene



bromobenzene



benzoic acid

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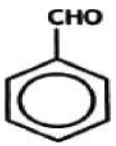
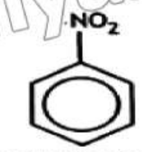


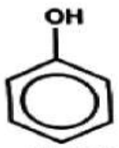
benzaldehyde

anisole

cumene



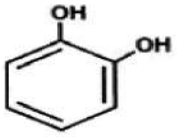
nitrobenzene



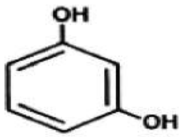
phenol

Disubstituted benzenes

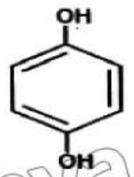
They have two substituents attached to benzene ring and can show three positional isomers. For showing positions of substituents on benzene ring, we may use numbers or Greek words ortho, meta and para. The word "ortho (o)" means straight, "meta (m)" means after and "para (p)" means beyond. The numbers 1,2 are equivalent to ortho, 1,3 equivalent to meta and 1,4 to para.



1,2-dihydroxybenzene
(Catechol)

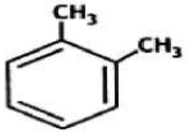


1,3-dihydroxybenzene
(Resorcinol)

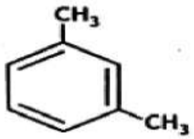


1,4-dihydroxybenzene
(Hydroquinone)

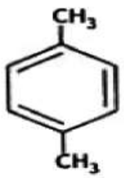
When one of the two substituents on the ring makes a special name to the compound, such as toluene, phenol and aniline, we name the compound as a derivative of that parent molecule. *In* this case, the special substituent occupies position 1 on the ring position. The IUPAC system retains the common name xylene for the three isomeric dimethylbenzenes.



1,2-dimethybenzene
(o-xylene)

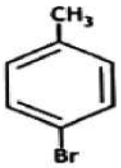


1,3-dimethylbenzene
(m-xylene)

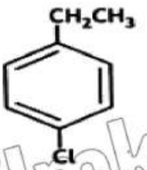


1,4-dimethylbenzene
(p-xylene)

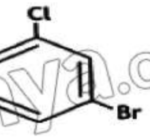
When neither group gives a special name, we treat them in alphabetical order before the word 'benzene'



4-bromotoluene
(p-bromotoluene)



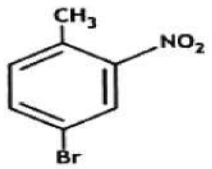
1-chloro-4-ethylbenzene
(p-ethylchlorobenzene)



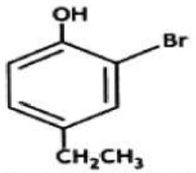
1-bromo-3-chlorobenzene
(m-chlorobromobenzene)

Polysubstituted Benzenes

When three or more substituents are present on a ring, we specify their locations by numbers. If one of the substituents imparts a special name, the molecule is named as a derivative of that parent molecule. If none of the substituents imparts a special name, we number them to give the smallest set of numbers and list them in alphabetical order before the word 'benzene'. In the following examples, the first compound is a derivative of toluene, and the second is a derivative of phenol. Because there is no special name for the third compound, we number the carbon atoms using the smallest possible set of numbers, then list its three substituents in alphabetical order, followed by the word 'benzene'.



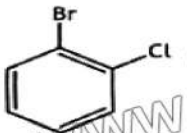
4-bromo-2-nitrotoluene

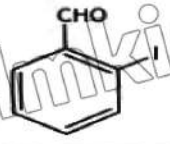


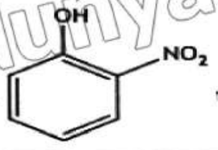
2-bromo-4-ethylphenol

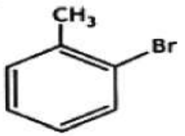
Concept Assessment Exercise 8.1

Name the following aromatic compounds.

i.


ii.


iii.


iv.


8.2 The Structure of Benzene

After the discovery of benzene in 1835, the structure of benzene molecule puzzled the nineteenth-century chemists for forty years. Elemental analysis proved that benzene has amazingly low hydrogen-to-carbon (H:C) ratio, with molecular formula "C_6H_6" and empirical formula "CH", suggesting high degree of unsaturation. Considering the unsaturated nature of benzene molecule, several chemists proposed different structures for it having carbon-carbon double and triple covalent bonds as shown below.

$$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$$

$$HC{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH$$

However, the observed properties of benzene could not align with these structures because they imagined benzene as an open molecule.

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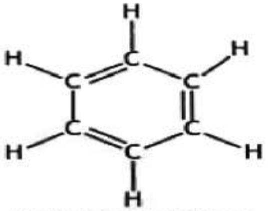
Kekul's Structure of Benzene

August Kekule
(1829-96)

In 1865, a German chemist named August Kekulé, was sitting near fire on a cold night in his laboratory. He was struggling to determine the structure of benzene molecule. Suddenly, he had a dream and saw atoms dancing *around and* making chains. Ha saw the chains changing into rings and appeared like snakes biting their tails. That image inspired Kekule and he proposed the ring (cyclic) structure of benzene molecule, having six carbon atoms for the first time. He proposed that a benzene is cyclic molecule with six carbon atoms in the ring each bonded to one hydrogen atom.

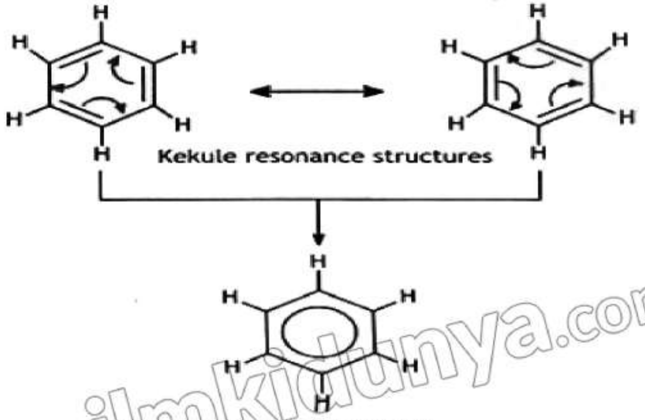


Kekule's structure

Key Information
Kekule's dream serves as an example of how imagination can lead to discoveries in the field of science.

The ring structure of benzene imagined by Kekule was an evolutionary idea in the field of chemistry. This idea led chemists to consider ring structures of different organic molecules. The cyclic structure of benzene molecule could explain the unexpectedly high stability and observed chemical properties of benzene.

Kekule further added that the benzene ring contains three carbon-carbon double bonds which alternate between their position so rapidly that the two structures he suggested cannot be distinguished. The rapid alternation of double bond is because pi (π) electrons are free to move over the six carbon atoms of entire benzene molecule. This implies that Kekule's structures cannot represent the actual structure of benzene. Instead, the real structure of benzene is resonance hybrid of the two Kekule's structures.



resonance hybrid

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Kekule's proposal survived for years as it was consistent with many experimental observations. However, his model was challenged for the following reasons:

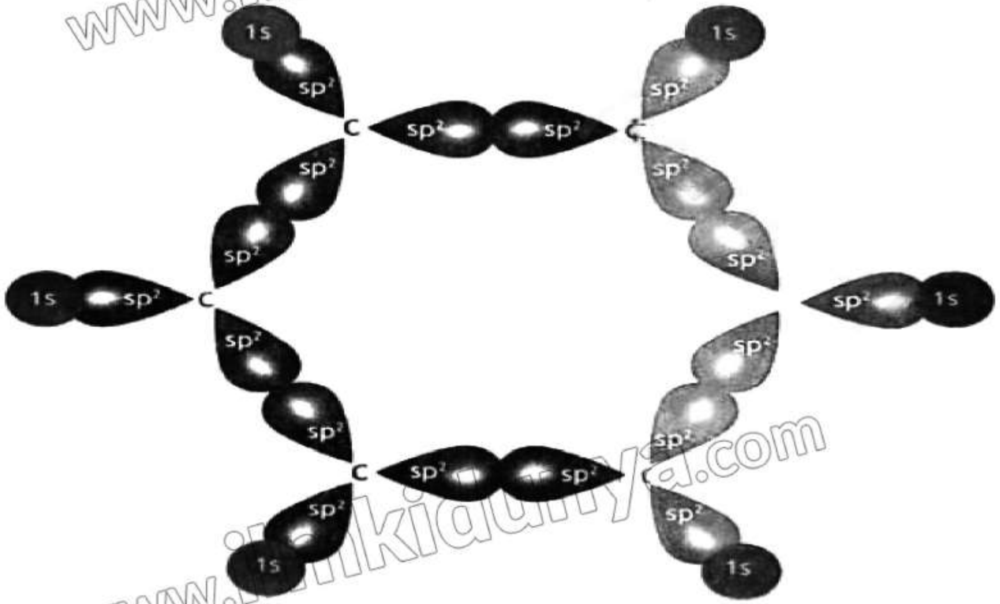
i. Why benzene does not react in a way alkenes do, if it has double bonds like alkenes?
ii. If benzene has three double bonds, why it cannot add three moles of bromine?
iii. Why benzene favours substitution reactions over addition reactions?

Taking into consideration the criticism against Kekule's structure, different models were tried in order to solve the problem of structure of benzene molecule.

Do You Know?
Resonance is the spreading of electron pairs (lone pair or pi electron pair) across several adjacent atoms in a molecule or ion. Such molecules or ions have more than one Lewis structures because a single Lewis structure cannot show the true picture of distribution of electrons among atoms. Remember that the position of atoms remains unchanged during resonance.

Atomic/Molecular Orbital Model of Benzene

In 1930s, Linus Pauling developed the concept of hybridization and theory of resonance. These two concepts gave the first adequate explanation of the structure of benzene. The carbon skeleton of benzene forms a regular hexagon with C-C-C and H-C-C bond angles of 120°. Each carbon of the ring exhibits sp^2 hybridization forming sigma (σ) bonds to two adjacent carbon atoms, by the overlap of sp^2-sp^2 hybrid orbitals, and one σ bond to hydrogen by, the overlap of sp^2–1s orbitals.



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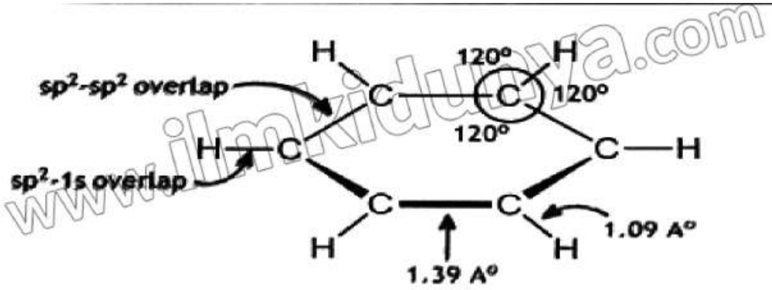
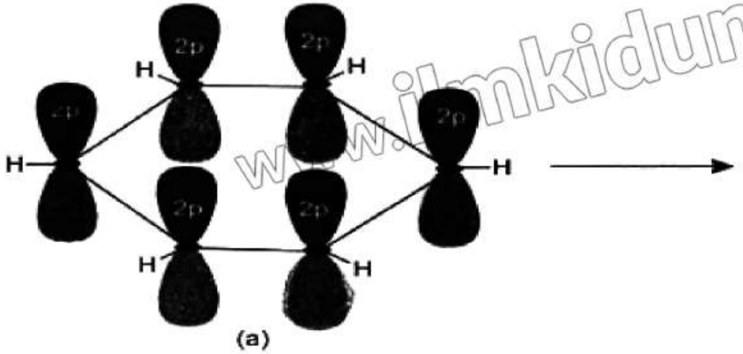
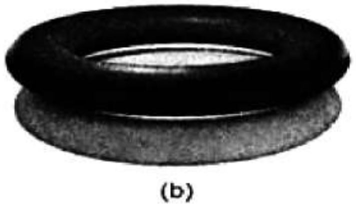


It was determined experimentally that the bond length between carbon atoms in benzene molecule is 1.39 A° which falls in between the bond lengths of a carbon-carbon single bond (1.54 A°) and carbon-carbon double bond (1.30 A°). This also shows that the carbon-carbon bonds are neither double nor single, rather partial double bonds.

Each carbon atom also has a single unhybridized 2p orbital that contains one electron. These six 2p orbitals lie perpendicular to the plane of the ring and overlap to form a continuous pi (π) electron cloud encompassing all six carbon atoms. The electron density of the pi electron (π) system of a benzene ring lies in one torus (a doughnut shaped region) above the plane of the ring and in a second torus below as shown.





(a) The carbon-hydrogen network showing six unhybrid 2p orbitals with one electron each

(b) The pi (π) electron cloud like two torus above and below the plane of the ring.

The Resonance Model of Benzene

A molecule that can be represented by more than one Lewis structure show resonance. Resonance is the delocalization of electron pairs across atoms in a molecule. The true structure for such molecule is resonance hybrid of its possible Lewis structures. The different possible Lewis structures for such molecules are called resonance contributing structures or canonical structures.

The actual structure of the benzene molecule is a resonance hybrid, representing an average of all the possible structures.

Interesting Information
The resonance structures are hypothetical so they cannot exist.

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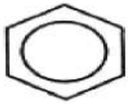
Limitations of Kekule's Structure



The resonance hybrid is shown by a circle inside the ring. The circle shows six delocalized pi (π) electrons in the six 2p-orbitals on the six carbon atoms of the ring.

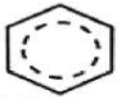
Although benzene molecule exists in more than one resonance contributing forms, but we use a single Kekule's structure because of two reasons.

i. it justifies the tetravalent nature of carbon and electron count in the benzene molecule.

ii. it easily represents the movement of electrons in reactions mechanisms.

Accurate Structure of Benzene

Johannes Thiele, in 1899, was the first chemist who proposed the concept of partial valence concept for explaining the unexpectedly high stability of benzene molecule.



Thiele structure

Werner Heisenberg described the concept of resonance by applying quantum mechanics. Finally, Linus Pauling developed resonance in 1933 and applied on all organic molecules.

Interesting Information

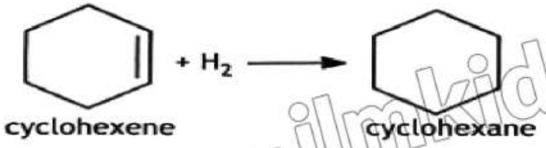
Chemists of nineteenth century faced the challenge of determination of structure of benzene molecule, but ultimately addressed with the advent of quantum mechanics. In 1931, Linus Pauling was the first chemist who explained the concept of resonance. He concluded that the benzene molecule is resonance hybrid of many Lewis structures. His findings led to a suitable explanation for high stability of benzene molecule. The concept of resonance integrated the structure of benzene molecule with its observational data.

Concept Assessment Exercise 8.2

- Draw the two Kekule structures of benzene. How did Kekule switch to closed structure of benzene molecule, although other chemists tried open structure for it?
- Define resonance in benzene. Why is benzene exceptionally stable than alkenes?

8.2.1 Resonance and Resonance Energy of Benzene

The difference in energy between the benzene molecule and hypothetical 1,3,4-cyclohexatriene is called resonance energy or delocalization energy. This energy indicated the extra stability of the benzene molecule due to the delocalization of the π-electron cloud over the six carbon atoms. To calculate the resonance energy of benzene, we compare the enthalpies of hydrogenation of cyclohexene, 1,2,3-cyclohexatriene (hypothetical) and benzene.



$\Delta H = -120$kJ/mol (experimental)

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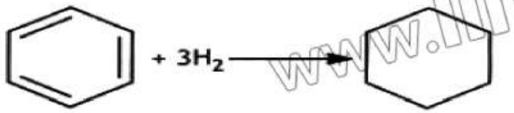
Based on the above experimental data, a molecule with three double bonds should theoretically release three times the heat of hydrogenation of cyclohexene.

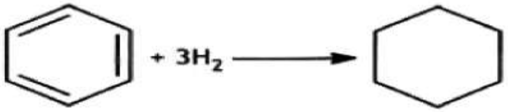


$\Delta H = 3 \times -120$ kJ/mol $= -360$ kJ/mol (calculated)

cyclohexa-1,3,5-*triene*
(hypothetical)

cyclohexane

By contrast, benzene is reduced only very slowly to cyclohexane under these conditions. It is reduced more rapidly when heated under very high pressures of hydrogen.

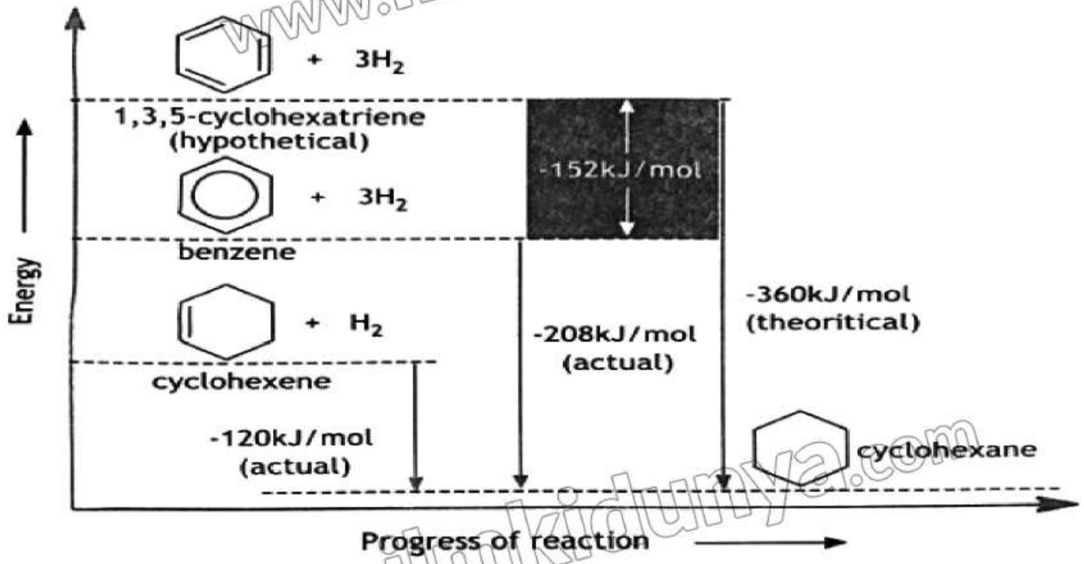


$\Delta H = -208$ kJ/mol (actual value)

benzene

cyclohexane

The enthalpy of hydrogenation per double bond varies somewhat with the degree of substitution of the double bond; for cyclohexene, $\Delta H = -120$ kJ mol^{-1}. If we consider benzene to be 1,3,5-cyclohexatriene, a hypothetical compound with alternating single and double bonds, we might expect its enthalpy of hydrogenation to be $3 \times -120 = -360$ kJ mol^{-1}. Instead, the enthalpy of hydrogenation of benzene is only -208 kJ mol^{-1}. The difference of 152 kJ mol^{-1} between the expected value and the experimentally observed value is the resonance energy of benzene.



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8.3 Reactivity of Benzene

Benzene has highly stable delocalized pi (π) electrons ring which remains intact in most reactions. Benzene shows different types of reactions such as addition reactions, oxidation reactions and electrophilic substitution reactions. We will study all these reactions one by one.

8.3.1 Electrophilic Aromatic Substitution Reactions

Electrophilic aromatic substitution reactions involve the attack of electrophile on the high electron density of the delocalized pi-(π) electron ring of benzene molecule. Electrophilic aromatic substitution reactions involve three steps:

- Attack of π-electrons of benzene ring on electrofphile, followed by partial breaking of the aromatic ring.
- Formation of an intermediate called the arenium ion.
- Elimination of hydrogen ion (H^+) from the intermediate, reforming the aromatic ring.

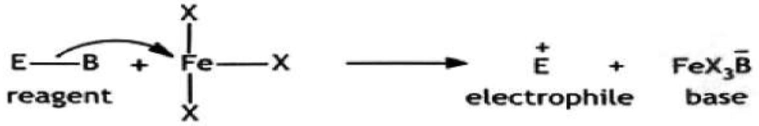
In electrophilic aromatic substitution reactions of benzene molecule, an electrophile attacks the benzene molecule and partially breaks the delocalized π-electron ring. The electrophile replaces a hydrogen atom on benzene molecule. The delocalized π-electron system restores as soon as electrophile replaces the hydrogen atom of the benzene molecule. This justifies the significant stability of benzene molecule due to delocalized π-electron ring.

Key Information
The delocalized pi (π) electron system in benzene molecule is far more stable than the localized pi (π) bonds in alkenes. This is why the benzene molecule always requires a catalyst for electrophilic substitution reactions of benzene.

The general mechanism of electrophilic aromatic substitution reactions involves three steps:

i. Generation of the electrophile.

An electrophile is generated first from a suitable reagent with the help of a Lewis acid catalyst, like FeX_3.



$$E{-}B + X{-}\underset{X}{\overset{X}{Fe}}{-}X \longrightarrow \overset{+}{E} + FeX_3\overset{-}{B}$$

ii. Reaction of electrophile with benzene.

The pi (π) electrons of benzene molecule attack on electrophile to make a cation intermediate called arenium ion. In this intermediate the aromatic ring is partially broken.

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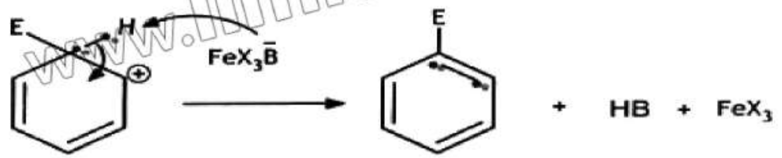
iii. Removal of hydrogen by a base.

A Lewis base takes the hydrogen from the arenium ion, resulting in the formation of a mono-substituted benzene. This restores the delocalized π-electron ring of benzene molecule.

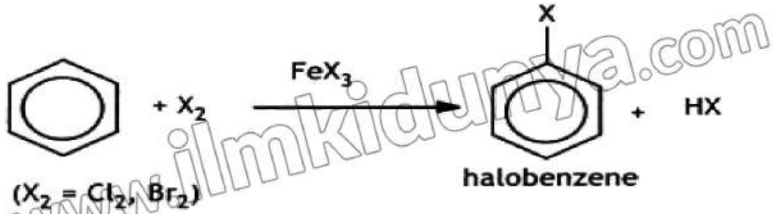


Some important electrophilic aromatic substitution reactions of benzene are given here.

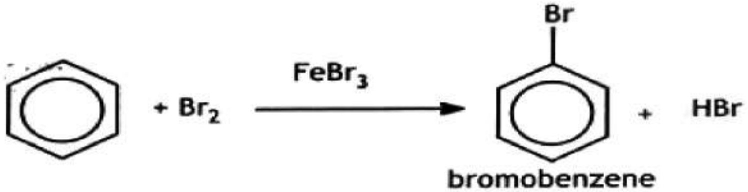
Halogenation

Halogenation is a reaction in which a halogen molecule reacts with benzene molecule, resulting in substitution of a hydrogen atom on the benzene ring with a halogen atom. This reaction takes place in the presence of a catalyst, typically iron (III) halide.

General Reaction:



For example, when a benzene molecule reacts with bromine in the presence of the catalyst iron (III) bromide ($FeBr_3$), bromobenzene is formed.



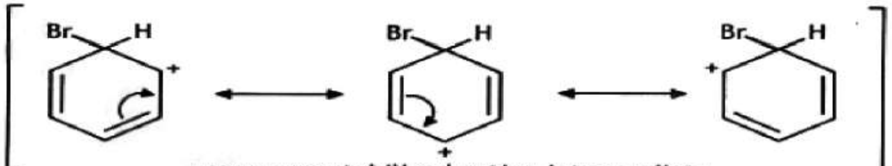
Mechanism of Bromination of Benzene:

In this reaction, the bromine molecule (Br_2) acts as a Lewis base because it donates a pair of electrons. On the other hand, iron(III) bromide ($FeBr_3$) acts as a Lewis acid as it accepts an electron pair.

Step 1: Generation of Electrophile.

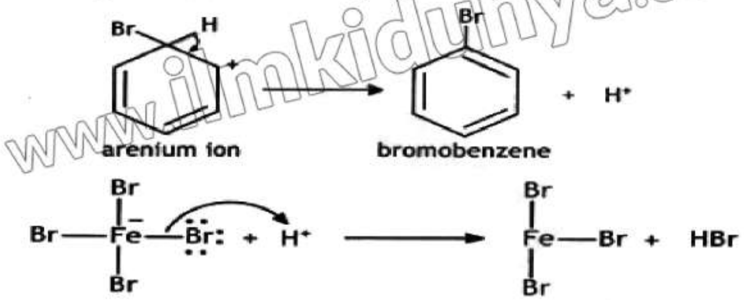
The Br^+ cation (bromonium ion) attacks on benzene ring to form an intermediate called arenium ion. Remember that the curly arrows show the movement of a pair of electrons.

Step 2: Generation of Arenium Ion/Sigma (δ) Complex.

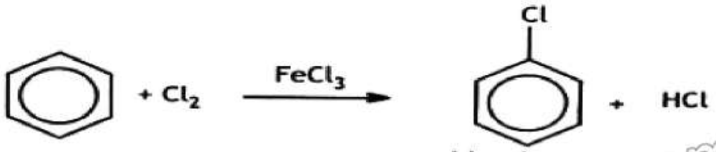


resonance-stabilized cation intermediate

Step 3: Deprotonation/Regeneration of Catalyst.



A similar reaction happens when chlorine gas is bubbled through benzene at room temperature in the presence of a catalyst, such as aluminium chloride. The products of this electrophilic substitution are chlorobenzene and hydrogen chloride.



chlorobenzene

Mechanism of Chlorination of Benzene.

It follows the same pattern as bromination of benzene as shown.

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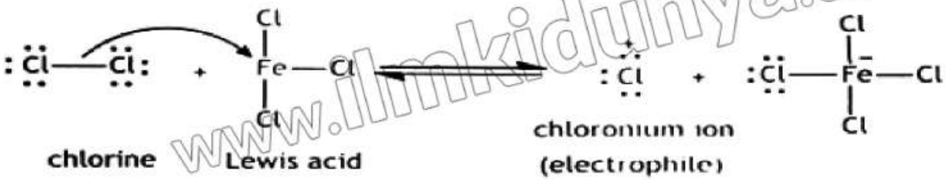
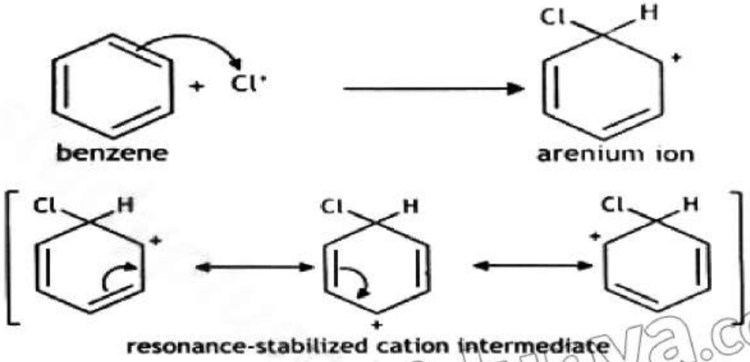
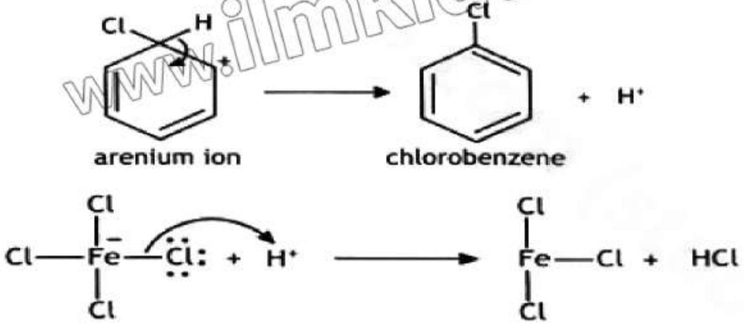
Step 1:



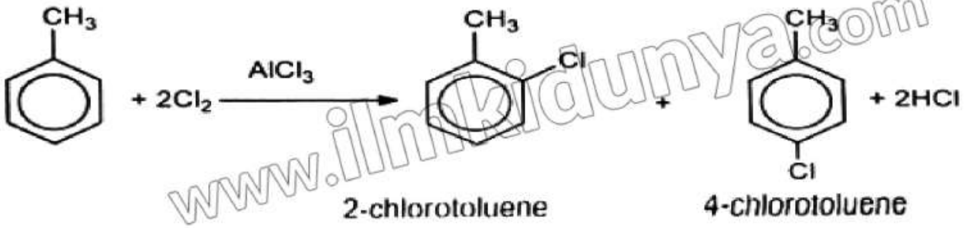
Step 2:



Step 3:



Halogenation of methylbenzene or other alkylarenes involved electrophilic attack at positions 2 or 4. The alkyl substituents are ring activating and increase electron cloud at position 2 and 4 in benzene ring. Similarly, hydroxyl group and amino groups also activate the benzene ring by pumping electrons in it through p-orbitals bridge. When methylbenzene is reacted with chlorine gas, using an anhydrous aluminium chloride catalyst, two products can be formed.



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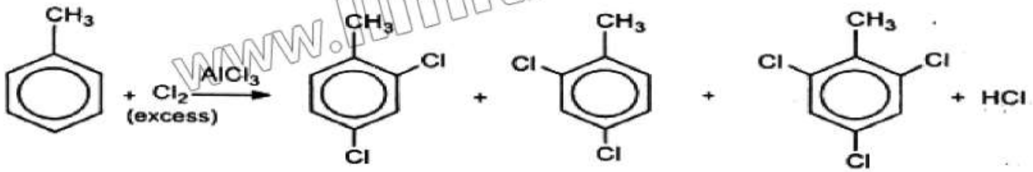
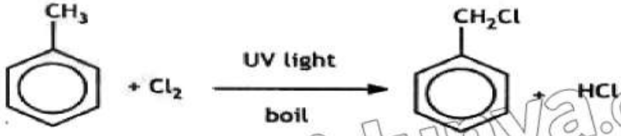
If excess chlorine gas is used, we get a mixture of 2,4-dichlorotoluene, 2,6- dichlorotoluene and 2,4,6-trichlorotoluene.



2,4-dichlorotoluene 4,6-dichlorotoluene 2,4,6-trichlorotoluene

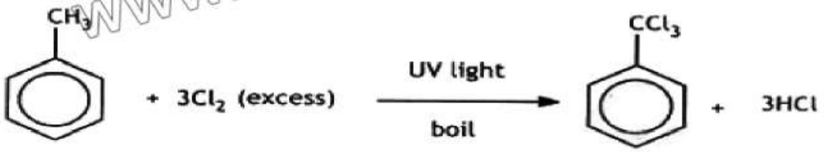
Side Chain Halogenation

When chlorine will react with alkyl side chain of alkylbenzene in the presence of ultraviolet (UV) light or strong sunlight. This reaction follows free-radical substitution mechanism. When chlorine gas is passed over boiling methylbenzene in the presence of UV light, the following reaction takes place.



chloromethylbenzene

Remember that there is no substitution into the benzene ring under these conditions. In excess of chlorine, eventually all three of the hydrogen atoms on the methyl side-chain will be replaced by chlorine atoms.



trichloromethylbenzene

Nitration

The nitration of benzene is another example of electrophilic substitution. Nitration refers to the introduction of nitro group(—NO_2) in benzene molecule. In this reaction the electrophile is the nitryl cation or nitronium ion (NO_2^+). This is made from a mixture of concentrated nitric acid and concentrated sulfuric acid.

This 'nitrating mixture' is refluxed with benzene at between 25 °C and 60 °C to make nitrobenzene.

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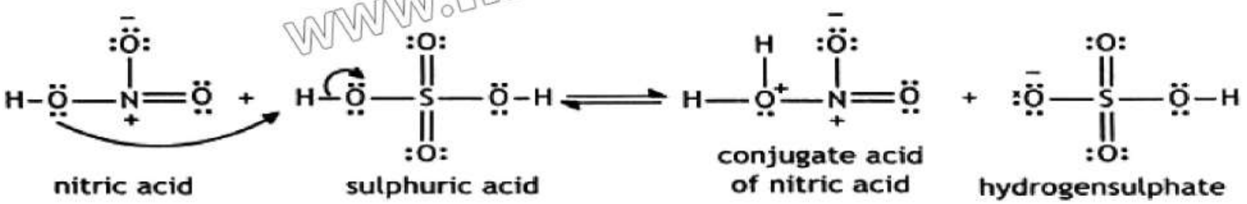
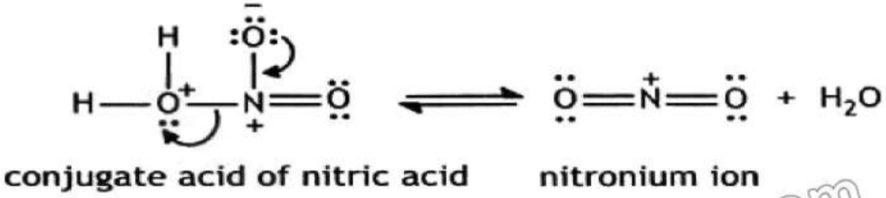
Mechanism

Step 1: Generation of Nitronium ion.

In this step, the electrophile nitronium ion (NO_2^+) is generated, when nitric acid reacts with sulphuric acid.





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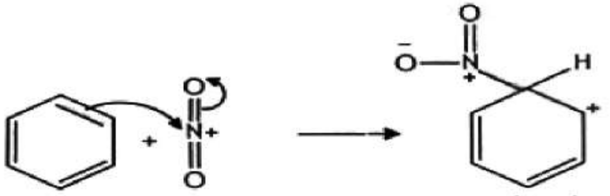
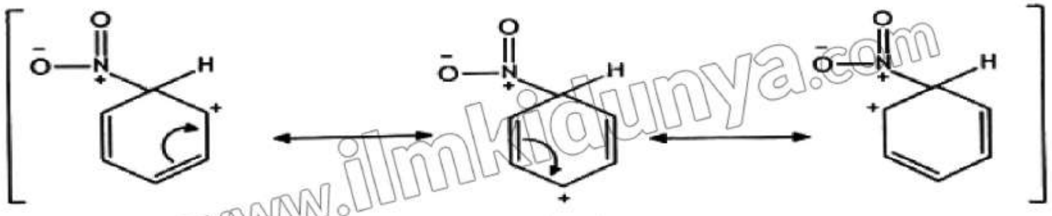
Step 2: Formation of Arenium ion (Sigma Complex)

In this step, the electrophile (NO_2^+) attacks the high electron density of pi (π) bonding system of benzene. A pair of electrons from the benzene ring is donated to the nitrogen atom of nitronium ion (NO_2^+) forming covalent bond. Resultantly, the delocalized pi (π) electron ring of benzene molecule is broken giving rise to an unstable intermediate called arenium ion.



arenium ion
(resonance stabilized)

The arenium ion has four pi (π) electrons and a positive charge delocalized over five carbon atoms. It undergoes resonance stabilization as follows:



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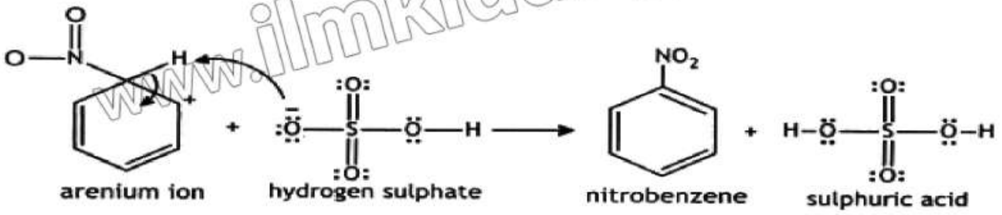
arenium ion
(resonance stabilized)

Step 3: Deprotonation of Arenium ion/Regeneration of Catalyst.



Finally, the delocalized pi (π) electrons ring of benzene molecule is restored when two electrons are donated to the ring from heterolytic cleavage of C—H bond, leaving hydrogen ion behind. In this way the stability of benzene ring is retained.

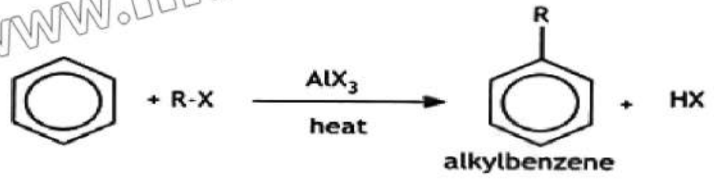
Friedel–Crafts reaction

In 1877 the French chemist Charles Friedel and his co-worker (an American chemist James Crafts) discovered that when benzene is heated with a alkyl halide and acyl halide in presence of aluminium chloride, alkylbenzene and phenylketon are obtained respectively. They studied the following two reactions.

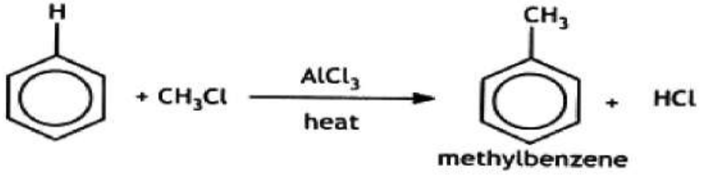
(i) Alkylation

The introduction of alkyl group in benzene ring when it is heated with chloroalkane in the presence of aluminium chloride (Lewis acid) is called Fridel-Craft alkylation. The aluminium chloride acts as catalyst in this reaction.

General Reaction:



Example:



Mechanism:

Step 1: Generation of Electrophile (CH_3^+).

In this step, the electrophile is generated which is methyl cation in this reaction.

$$CH_3—Cl: + AlCl_3 \longrightarrow CH_3^+ + AlCl_4^-$$

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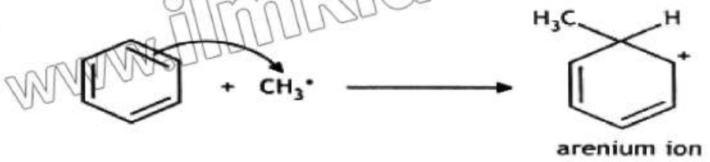
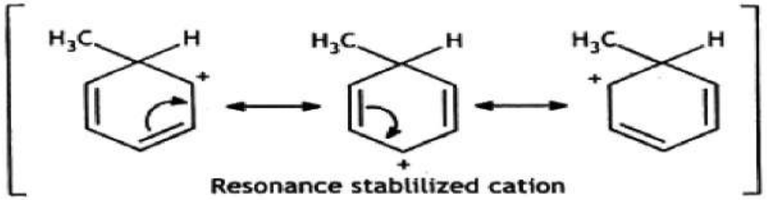
Step 2: Formation of Arenium ion.

This step involves the attack of electrophile (CH_3^+) on benzene ring, rupturing the ring and gives arenium ion.

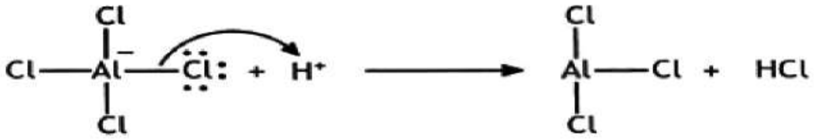


The arenium ion undergoes resonance stabilization as follows:



Step 3: Deprotonation of Arenium ion/Regeneration of Catalyst.

In this step, the pi electron cloud of benzene molecule is restored by loss of hydrogen ion and catalyst is regenerated.



The aluminium chloride is regenerated at the end of reaction, so it acts as catalyst.

Concept Assessment Exercise 8.3

- How does chloroethane react with benzene molecule? Name the electrophile and end product of this reaction.
- Which two roles are being played by aluminium chloride ($AlCl_3$) in Friedel-Craft alkylation?

ii. Acylation

The reaction in which acyl group is introduced in benzene ring when acyl halide is reacted with benzene in presence of catalyst, aluminium trihalide (AlX_3) is called acylation. The product obtained in this reaction is phenylethanone (phenylacetone).

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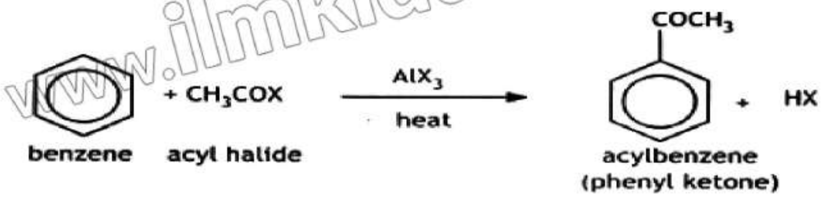
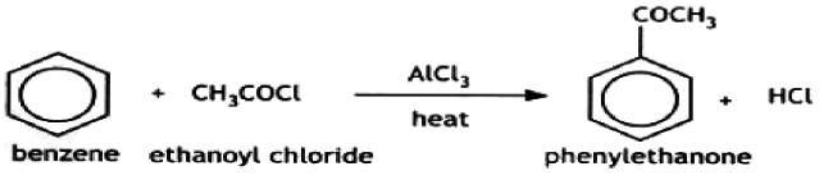
General Reaction:



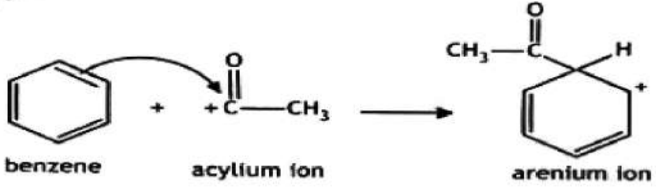
Example:



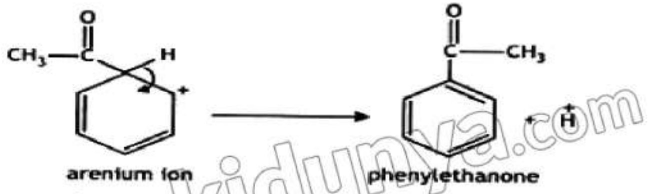
Mechanism:

Step 1: In this step, an electrophile called acylium ion (acyl cation) is generated.

Step 2: Then acyl cation reacts with benzene to form the intermediate arenium ion.



Step 3: The final step involves rearrangement where the benzene pi (π) electron ring is restored forming phenylethanone. The hydrogen ion eliminated reacts with tetrachloroaluminate(III) to regenerate aluminium chloride ($AlCl_3$).



$$[AlCl_4]^- + \overset{+}{H} \longrightarrow AlCl_3 + HCl$$

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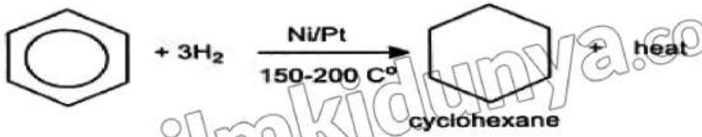
8.3.2 Addition Reaction

Benzene has a delocalized π-electron cloud, which typically allows for addition reactions. However, under normal conditions, benzene does not undergo addition reactions as readily as alkenes. This is because the π-electron cloud in benzene is part of a highly stable conjugated system known as an aromatic ring. The delocalized π-electrons in the aromatic ring of benzene circulate continuously across all six carbon atoms, making them less available for chemical reactions. Breaking this stable aromatic system requires harsh or vigorous conditions, such as high temperature, high pressure, or strong reagents.

The aluminium chloride ($AlCl_3$) carries halogen with itself in Friedel-Craft reaction, so it is called halogen carrier.

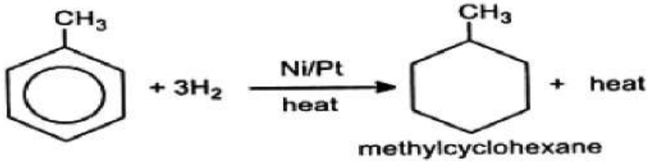
Hydrogenation

Hydrogenation is the addition of hydrogen molecules across the carbon atoms of benzene molecule, converting it into cyclohexane. This reaction takes place in the presence of catalysts, like nickel (Ni), platinum (Pt) or palladium (Pd) at temperature 150-200 C° and 20-30 atm pressure.



Role of Catalyst: The catalyst used provides surface area to hydrogen molecules breaking them into individual hydrogen atoms. The catalyst interacts with benzene molecule making it more reactive by weakening its pi (π) electron system. Six hydrogen atoms add to the six carbon atoms of benzene molecule to give cyclohexane, breaking the aromatic ring. The cyclohexane molecule releases from the catalyst surface and the catalyst is ready for more reactions.

Similarly, methylbenzene is hydrogenated to methylcyclohexane under the same reaction conditions.



Difference Between Addition Reactions and Electrophilic Substitution Reactions

The unsaturation in benzene seems that it shows addition reactions readily like alkenes, but benzene is quite reluctant to undergo addition reactions. Unlike alkenes, it requires rather harsh conditions to show addition reactions.

The key difference between addition reactions and electrophilic aromatic substitution reactions is what happens to the intermediate (a positively charged ion) formed in the first step of their mechanisms when an electrophile attacks. Remember from grade 11 that the halogenation of an alkene is a two-step process: first, a bridged halonium ion intermediate is formed, and then in the second step, a halide ion attacks the positively charged intermediate, giving a saturated product.

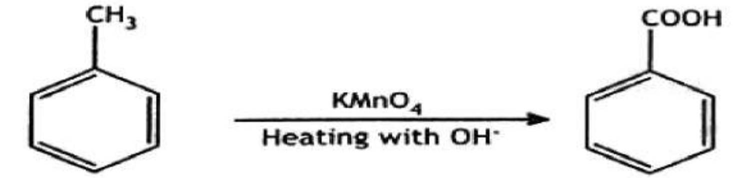
In contrast, the electrophilic aromatic substitution reaction of benzene involves the formation of a cation intermediate (arenium ion) in the first step. In the second step, the cation is stabilized by the loss of a hydrogen ion, rather than by the attack of a nucleophile (anion). This process results in a nucleophile substituting a hydrogen atom in the benzene molecule, leading to the formation of a substituted product.

8.3.3 Oxidation Reactions

Benzene can show oxidation reactions as other hydrocarbons do. However, unlike alkenes and alkynes, benzene and alkanes are quite resistant to oxidation by general oxidizing agents. However, they can be oxidized under certain conditions. In alkylbenzenes, the aliphatic side chain is more likely to be oxidized than the aromatic ring, although this requires prolonged heating.

The presence of the benzene ring in an alkylarene, such as methylbenzene, has significant influence of side chain reactions. For example, alkanes are not usually oxidized by a oxidizing agent such as potassium manganate(VII), but the methyl side-chain of methylbenzene is oxidized by hot alkaline or hot acidic potassium manganate(VII) to produce benzoic acid. This is because the benzene ring alkylarenes makes the alkyl side-chain more reactive.

In alkylbenzenes, the oxidation reactions can involve both aromatic ring and side alkyl chain of alkylarenes, depending upon the conditions used. Oxidation of benzene ring requires more aggressive conditions while alkyl side-chain can be oxidized under a bit gentle conditions. The carbon of alkyl side-chain closest to the benzene ring is oxidized to carboxylic acid group. In this topic, we will limit ourselves to the oxidation of the side chain on the benzene ring, resulting in benzoic acid.



methylbenzene

benzoic acid

1-ethyl-3-methylbenzene

benzene-1,3-dioic acid

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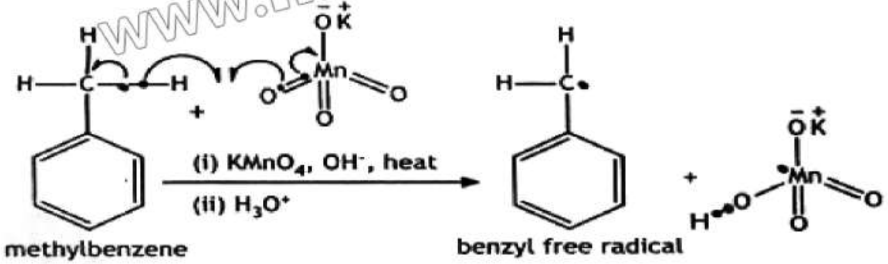
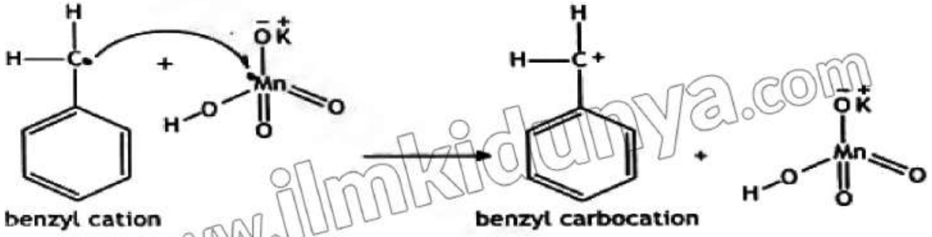
Mechanism involves the following three steps:

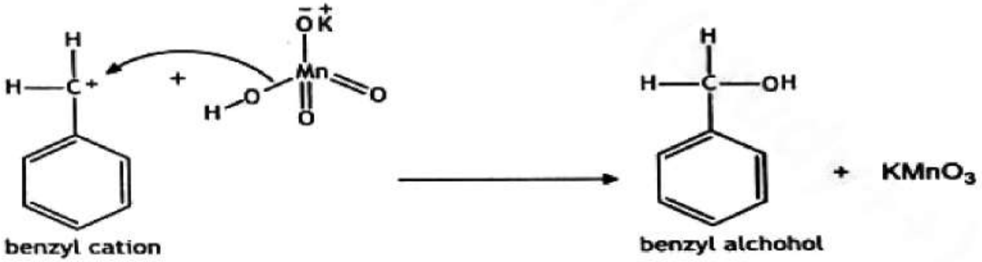
i. Hot alkaline potassium manganate (VII) abstracts a benzylic hydrogen atom as a free radical from the methyl side chain of methylbenzene, oxidizing it and leaving behind a benzyl radical.



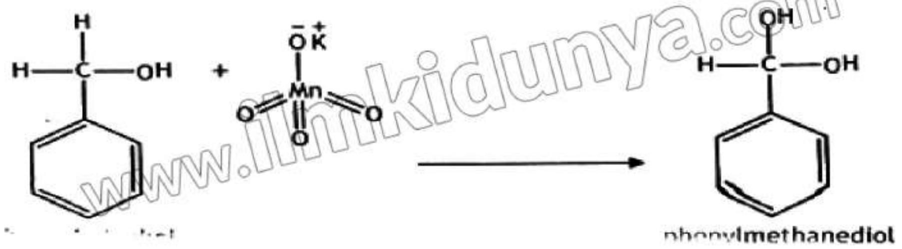
The benzyl free radical changes to benzyl cation after reacting with the odd-electron intermediate of potassium manganate (VII).



The benzyl cation abstracts hydroxyl group (-OH) from the potassium hydrogenmanganate, which is unstable.



In the next step, the alkaline potassium manganate (VII) further oxidizes benzylic carbon to give diol, as in the previous step.



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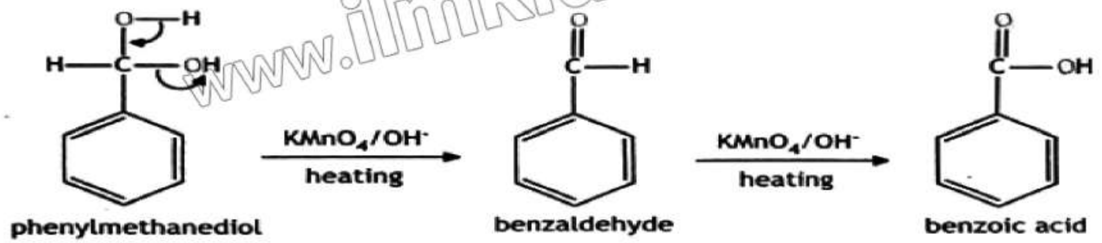
Phenylmethanediol is oxidized by the same oxidizing agent to benzaldehyde which further oxidizes to benzoic acid.



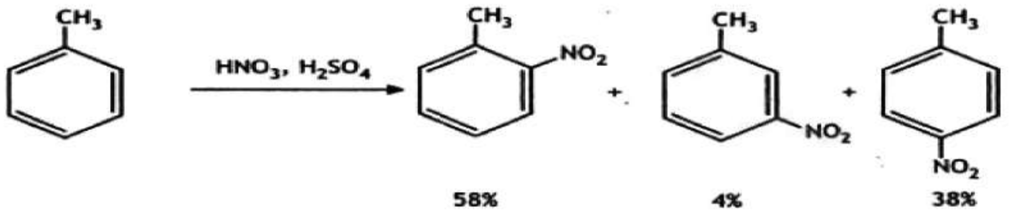
In these reactions, the first carbon of the side chain is oxidized always. In alkyls bigger than methyl, all carbon atoms next to the first one give rise to carbon dioxide formation.

8.4 Electrophilic aromatic substitution in substituted arenes

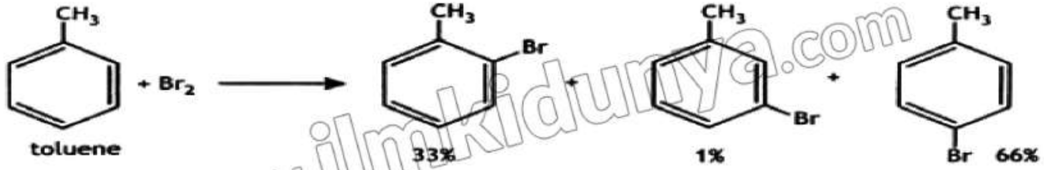
We have already studied that benzene molecule can undergo electrophilic aromatic substitution reactions, forming only one mono-substituted benzene. The substituent attacks any carbon in the benzene ring because all the six carbon atoms are equivalent.

When a second electrophile reacts with a monosubstituted benzene ring, it forms three different disubstituted benzene isomers. This occurs because the benzene ring offers three possible positions (carbons) where the second substituent can attach relative to the first. The position of the second electrophile in each of these isomeric disubstituted benzene molecules varies in relation to the position of the first substituent on the ring.

For example, methylbenzene reacts with nitric acid and sulfuric acids, forming three disubstituted benzene isomers with the ratio given.



If this reaction is carried out in a random way, the distribution of the three isomers formed would be 40:40:20. It indicates that we obtain two parts of 2-nitromethylbenzene, two parts of 3-nitromethylbenzene and one part of 4-nitromethylbenzene. Other mono-substituted benzene compounds can also undergo such random aromatic substitution reactions as given below.



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In the light of the above data, it is concluded that

i. *the orientation* of the incoming group is determined by the nature of the substituent already bonded to the ring, rather than the nature of the incoming electrophile.

ii. Some substituents direct the incoming electrophile to the 2-position (ortho position) and 4-position (para position), while others guide it to the 3-position (meta position).

There are three possible positions on the benzene ring where a second group (electrophile) can attack. The position of this attack is determined by the nature of the substituents already bonded to the benzene ring. Based on this, substituents are categorized into two classes.

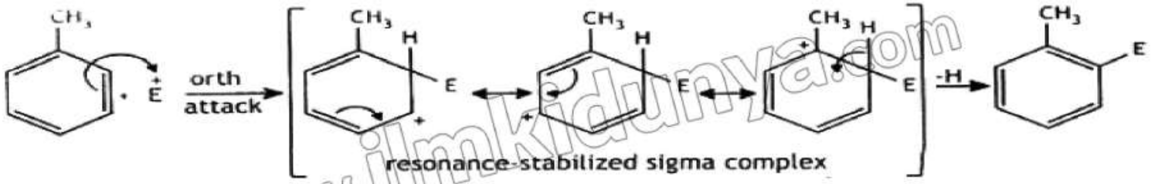
(a) Ring-Activating or Ortho/Para Directing Substituents

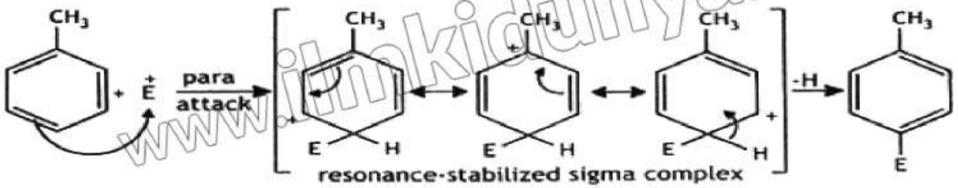
Substituents that increase the reactivity of benzene ring compared to single benzene molecule are called ring-activating substituents. These substituents are capable of donating electrons to the benzene ring through electron-donating resonance effect, increasing electron cloud relatively on all carbon atoms (positions) in benzene ring. This makes benzene molecule more reactive toward the incoming electrophile compared to single benzene molecule itself.

The ring-activating substituents are also called ortho/para directing substituents because they direct the incoming electrophile to the 2- and 4-positions (ortho-para positions). These substituents increase electron cloud at carbon-2 and carbon-4 compared to single benzene molecule. Due to higher electron cloud at carbon-2 and carbon-4 and lower electron cloud at carbon-3 (meta position), the next electrophile will attack ortho and para positions of the benzene molecule.

Key Information
The halogen groups are ring-deactivating by electron-withdrawing inductive effect, but ortho-para directing by electron-donating resonance effect. The resonance effect dominates the electron-withdrawing inductive effect, so halogen groups are ortho-para directing groups.

To explain the 2,4-directing effect of electron-donating substituents we need to focus on the electron distribution pattern in the arenium ion involved in electrophilic aromatic substitution reactions of benzene. Consider the arenium intermediate (sigma complex) formed in electrophilic attack on toluene.

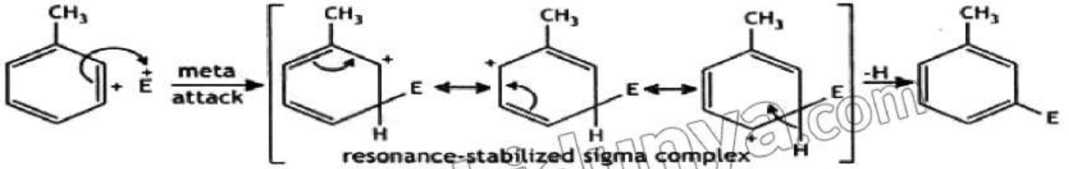




Both in ortho and para attack, a resonance structure is formed possessing positive charge on the carbon directly connected to the substituent. This resonance structure is the most stable one among all because its positive charge is stabilized more than that resulting from the meta attack. Such substituents are ring-activating and ortho para directing.

Inductive effect of substituents in benzene molecule diminishes with distance.

Electron-donating substituents will be more effective at these positions to stabilize the intermediate cation, by spreading out its charge.



On the other hand, in meta attack, none of the three arenium ions has positive charge on the carbon atom directly bonded to the substituent, making alky substituents less effective at this position.

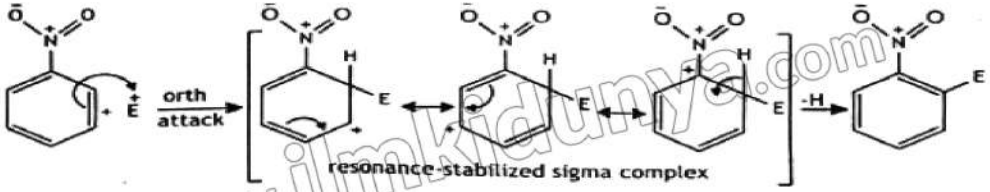
Examples of 2 and 4 directing substituents include alkyl group (-R), hydroxyl group (-OH), amino group ($-NH_2$), alkoxy group (-OR) and halo group (-X) etc.

Key Information
All halo group (-X) are ortho and para directing due to resonance effect but deactivating due to inductive effect.

(b) Ring-Deactivating or Meta-Directing Substituents

On the other hand, some substituents direct the incoming electrophile to the carbon-3 (meta position). These substituents withdraw electrons from the benzene ring through inductive effect, making overall benzene ring electron deficient and less reactive. Such substituents possess a partial or full positive charge on the atom directly connected to the benzene ring.

To explain 3-directing (meta-directing) effect of electron-withdrawing substituents, we need to focus on the electron distribution pattern in the arenium ion involved in electrophilic aromatic substitution reactions of benzene. Consider the arenium intermediate formed in nitration of benzene.



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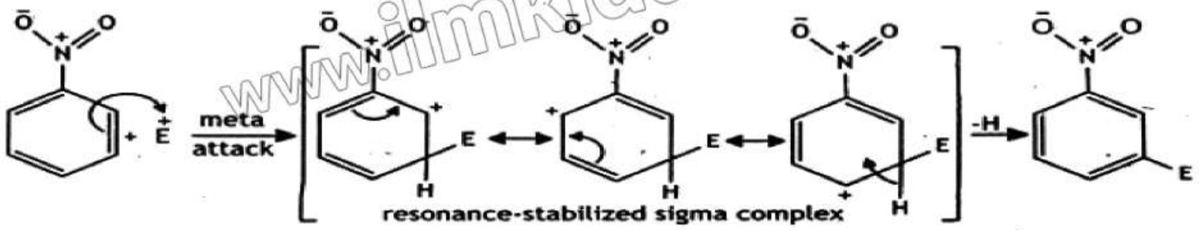

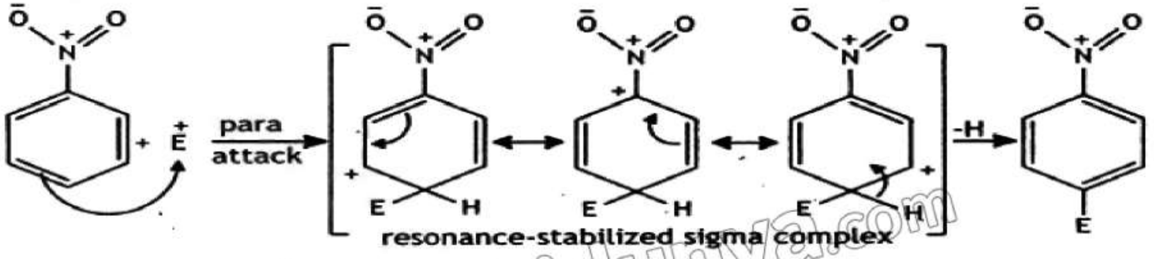

In light of this explanation, electron-withdrawing (meta) substituents destabilize the arenium ions of ortho and para attack more than the arenium ion of meta attack. This is because the positive Therefore, such substituents invite electrophiles at meta position and are called meta-directing substituents.

Examples of 3-directing groups: $-NO_2$, -CHO, -COOH etc

Key Information
The substituents that direct the incoming electrophile at ortho/para position are called ortha/para directing groups while those inviting electrophile at meta position are called meta directing groups.

Concept Assessment Exercise 8.4

- Why is aldehyde group (-CHO) termed as 3-directing substituent?
- How a 2 and 4-directing substituents release electrons to benzene ring?

KEY POINTS

- Benzene was discovered by Michael Faraday.
- The name aromatic comes from the word "aroma" meaning fragrance. Benzene was obtained from benzoic acid which, in turn, was extracted form the gum of benzoin, a resin of balsam tree.
- It was found that all aromatic compounds do not give pleasant fragrance.
- All aromatic compounds contain at least one benzene ring so aromatic compounds were declared the benzene ring containing compounds.

- The x-ray diffraction technique proved that the molecular formula of benzene molecule is C_6H_6 which suggests low hydrogen-to-carbon ratio (H:C).
- The molecular formula of benzene also proposes high unsaturation in its molecule, so it shows addition reactions.
- Benzene molecule, however, shows addition reactions less readily than alkenes which means that benzene is highly stable.
- The remarkable stability of benzene molecule is due to delocalization of pi (π) electron cloud in the ring.
- The delocalization of pi (π) electron cloud on unhybrid p-orbitals bridge on six carbon atoms of benzene ring is called resonance.
- Resonance gives extra stability and lower energy to benzene ring compared to hypothetical 1,2,3-cyclohexatrience molecule that has localized pi (π) bonds.
- Benzene has no defined structure like water because it has no pi (π) bond at fixed position. Rather, its pi (π) bonds are circulating across benzene ring continuously.
- There are many structures that contribute to understanding actual structure of benzene. These structures are called resonance contributors.
- Kekule, after 40 years struggle, in 1864 saw a daydream, watching a snake biting its tail. He was the first to propose that benzene has ring structure. Before Kekule, all chemists thought benzene to be having open structure.
- Kekule, however, failed in understanding that benzene has equal carbon-carbon bond lengths and bond strengths.
- A German chemist, Johannes Thiele, in 1899, presented the idea of partial double bonds between carbon atoms in benzene showing delocalized pi (π) bonds.
- The carbon-carbon bonds in benzene are neither single nor double, rather in between (partial double bonds).
- Benzene shows substitution reactions like alkanes and addition reactions like alkenes.
- The exceptional high stability of benzene is attributed to resonance.
- Resonance is the delocalization of pi (π) electron cloud in benzene ring on the unhybrid p-orbital bridge of six carbon atoms resulting in continuous circulation of pi (π) electron cloud.
- Benzene shows addition reactions under vigorous conditions like hydrogenation in the presence of nickel catalyst to give cyclohexane.
- Alkylbenzene undergoes oxidation of side alkyl chain in potassium manganate(VII) and produces carboxylic acid.
- Benzene can show electrophilic substitution reactions involving breakage of pi (π) electron ring forming an intermediate (arenium ion). After very short interval, the pi (π) electron ring is restored and give rise to substituted benzene.
- The attack of second electrophile on benzene ring is dictated by the substituent already attached to the ring.
- If the substituent bonded to the ring is electron donating, it means it activates the ring paving the way for the next electrophile to attack carbon 2 and 4 (ortho/para directing).
- In case, the group already bonded to the ring is electron-withdrawing, it deactivates the ring, removing electron cloud from carbon-2 and 4, relatively making electron cloud greater at position 3 on the ring.

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References for Further Information

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- Chemistry by George Facer
- Chemistry-The molecular nature of matter and change by Silberberg.
- Chemistry by Peter Cann and Peter Hughes.
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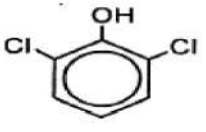
- Chemistry by Christopher Talbot, Richard Harwood and Christopher Coates.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. The IUPAC name of the following compound is



a) 1,3-dichlorophenol
b) 2,6-dichlorophenol
c) 2-hydroxy-1,3-dichlorobenzene
d) 1,5-dichlorophenol

ii. The type of intermolecular forces in benzene are
a) Dipole-dipole forces
b) London dispersion forces
c) hydrogen bonding
d) ion-dipole forces

iii. Which one of the following carbon atom in monosubstituted benzene ring is called meta carbon?
a) carbon 1 b) carbon 2 c) carbon 3 d. carbon 4

iv. The unsaturated nature of benzene can be justified by
a) Hydrogenation
b) nitration
c) alkylation
d) oxidation

v. Which one of the following challenges was faced by Kekule's structure of benzene?
a) benzene is immiscible with water
b) benzene is hexagonal
b) benzene is less reactive than alkenes
d) benzene is planar

vi. Benzene molecule has
a) three double bonds
b) hexagonal planar ring
b) sp^3 hybridization
d) three single bonds

vii. The C-C-C bond angle in benzene molecule is
a) 180° b) 120° c) 90° d) 109.5°

viii. Delocalization of pi (π) electrons in benzene molecule is because
a) each carbon is sp^2 hybridized
b) it is hexagonal
c) it is unsaturated
d) it has 5 unhybrid 2p orbitals

ix. The electrophile used in bromination of benzene molecule is
a) bromide ion
b) bromonium ion
c) aluminium bromide
d) bromine molecule

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x. The electrophile used in Friedel-Craft acylation is

a) arenium ion b) acylium ion c) hydrogen ion d) nitronium ion

xi. Aromatic hydrocarbons are found in the extracts of many plants. Their common characteristic is that they have

a) pleasant smell b) benzene unit

c) coloured compounds d) pleasant taste

xii. Which one of the following compounds can easily be nitrated?

a) Benzene b) phenol

c) nitrobenzene d) benzaldehyde

xiii. The most reactive compound, in terms of addition reactions, among the following is:

a) propene b) ethyne c) propane d) benzene

2. Short Answer Questions

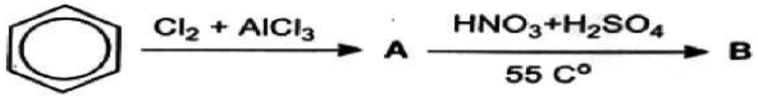
i. Cyclohexene decolourizes bromine water whereas benzene cannot, why?

ii. Consider the synthesis of 3-chlorobenzoic acid from methylbenzene given:

b) Name the intermediate A.

c) Write down the reagents and conditions for reaction 1 and reaction 2.

iii. Predict the products and their structural formulae of the following chemical reactions of benzene.



iv. In Friedel-Craft acylation of benzene, the aluminium chloride ($AlCl_3$) acts as Lewis acid. Justify the statement.

v. Explain the difference between halogenation of benzene when reacted with

a. Cl_2 and $AlCl_3$ b. Cl_2 and UV light

vi. Explain how is arenium ion formed in electrophilic substitution reactions of benzene?

vii. State the difference between substitution reactions of alkanes and benzene.

viii. Explain the structure on benzene with the help of atomic orbital treatment.

ix. How can unhybrid 2p-orbitals of benzene adopt a doughnut shape? Show diagram.

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3. Long Answer Questions

i. Benzene reacts with bromine.
  a. Write the balanced chemical equation.
  b. Name the catalyst used.
  c. What is the visual observation during this reaction?

ii. Benzene also reacts halogenoalkanes.
  a. Name the catalyst used.
  b. Using 2-bromopropane, write the formula of electrophile formed.
  c. Name the product of this reaction.
  d. Write down curly arrows mechanism for this reaction showing all the three steps, i.e generation of electrophile, formation of carbocation and the final product.

iii. The exceptional stability of benzene molecule is due to resonance in it.
  a. Why benzene has delocalized carbon-carbon double bond?
  b. Why benzene has energy lower than hypothetical cyclohexa-1,3,5-trien?
  c. The carbon-carbon bonds are partial double bonds. Comment.

iv. Benzene is more stable compounds than expected by chemists.
  a. Explain the stability of benzene molecule with reference to resonance energy.
  b. Draw the diagram showing resonance energy.

v. The electrophilic attack on a mono-substituted benzene is governed by the substituent already attached to benzene ring.
  a. Define meta-directing substituents. Give two examples.
  b. Explain the ortho/para and meta-directing effects of different substituents referring to different electron distribution pattern in arenium ion.

vi. A nitrobenzene undergoes nitration much more slowly than benzene. Explain why this happens and predict how the rate would change if a methoxy group were present instead.

vii. Toluene undergoes bromination in the presence of $FeBr_3$. Predict the major product(s) and justify the position(s) of substitution.

viii. Chlorobenzene is treated with nitric acid and sulfuric acid. Explain which position the NO_2 group is most likely to occupy and why, considering both resonance and inductive effects of Cl.

ix. You are asked to synthesize 4-nitrotoluene from benzene in the fewest steps possible. What steps would you take, and in what order? Justify your sequence based on directing effects.

x. Design a synthesis for m-bromonitrobenzene starting from benzene.

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HALOGENOALKANES

Student Learning Outcomes (SLOs)

- Describe production of halogenoalkanes i.e. reaction of benzene with Cl_2 and Br_2 in the presence of catalyst.
- Compare the reactivity of halogenoalkane and halogenoarene using chloroethane and chlorobenzene as examples.
- Predict the major product(s) based on the reaction conditions and the molecular structure of the halogenoalkane.
- Analyze the mechanism and products of a reaction pathway involving a halogenoalkane, and use retro-synthesis to deduce the starting materials.
- Describe the SN_1 and SN_2 mechanisns of nucleophilic substitution in halogenoalkanes including the effects of alkyl groups.
- Identify that primary halogenoalkanes tend to react via the SN_2 mechanism, tertiary halogenoalkanes via the SN_1 mechanism, and secondary halogenoalkanes by a mixture of the two, depending on structure.
- Explain the different reactivities of halogenoalkanes (with particular reference to the relative strengths of the C-X bonds as exemplified by the reactions of halogenoalkanes with aqueous silver nitrate).

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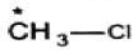
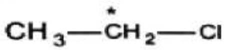
Halogenoalkanes also known as alkyl halides are compounds in which one hydrogen atom of alkanes has been replaced by a halogen atom. They are also known as halogen derivatives of alkanes. general formula of halogenoalkanes is R-X. The general formula of halogenoarenes is Ar–X, where Ar is an aryl or arene group.

Recall *that alkyl halides* are classified into primary, secondary and tertiary alkyls halides.

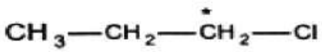
- Alkyl halide in which halogen atom is attached with primary carbon are called primary alkyl halide. A primary carbon is a carbon that is bonded to only other carbon atom of none, as in case of methane.


$\overset{*}{C}H_3-Cl$

Methyl chloride
Chloromethane


$CH_3-\overset{*}{C}H_2-Cl$

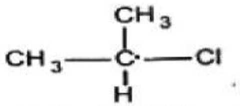
Ehyl chloride
Chloroethane


$CH_3-CH_2-\overset{*}{C}H_2-Cl$

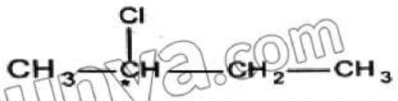
n-Propyl chloride
Chloropropane.

($\dot{C}$ is primary carbon atom)

- Alkyl halides in which a halogen atom is attached to a secondary carbon atom is called secondary alkyl halide. Secondary carbon is carbon to which two alkyl groups are attached.


$CH_3-\underset{H}{\overset{CH_3}{\dot{C}}}-Cl$

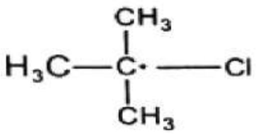
Iso-Propyl chloride (2-Chloro propane)


$CH_3-\overset{Cl}{\dot{C}H}-CH_2-CH_3$

Sec- Butyl chloride (2-Chlorobutane)

($\dot{C}$ is secondary carbon atom)

- Alkyl halides, in which a halogen atom is attached to a tertiary carbon are called tertiary alkyl halides. Tertiary carbon is carbon to which three alkyl groups are attached.


$H_3C-\underset{CH_3}{\overset{CH_3}{\dot{C}}}-Cl$

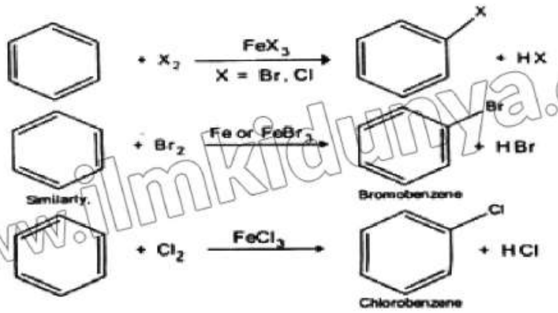
t-Bytyl chloride
2-Chloro-2-methyl-propane.

($\dot{C}$ is tertiary C-atom)

Alkyl halides have high melting and boiling points as compared to Alkanes.

9.1 Preparations of Halogenoarenes

Halogenation of benzene occurs with halogens (X_2) in the presence of Fe or Lewis acid catalyst FeX_3.



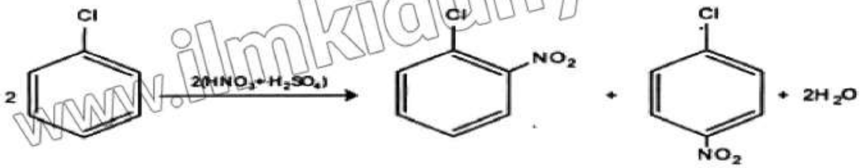
9.2 Reactivity of Halogenoalkanes

The strength of the C—X bond is an important factor that determines the reactivity of alkyl halides and aryl halides. The alkyl halide molecule is polarized due to the higher electronegativity of halogens compared to C. Thus, carbon receives a partial positive charge, while the halogens receive a partial negative charge. The halogen becomes nucleophilic in nature, which can be replaced by another nucleophile for example, chloroethane can undergo a nucleophilic substitution reaction. In this reaction, the nucleophile attacks the carbon atom that is attached to the chlorine atom. This results in the replacement of chlorine by a nucleophile.

$$CH_3-CH_2-Cl + Nu^- \rightarrow CH_3-CH_2-Nu + Cl^-$$

In chlorobenzene, the lone pair of electrons on chlorine atoms are delocalized over the ring, giving the C—Cl bond the character of a partial double bond. Therefore, the C—Cl bond is more difficult to break. Thus, the chlorine atom cannot be replaced by a nucleophile. Chlorine increases the ring electron density due to resonance. Thus, chlorobenzene undergoes an electrophilic substitution reaction. In this reaction, one of the hydrogen atoms of benzene in the ortho and para position is replaced by an electrophile.

For example, nitration of chlorobenzene gives a mixture of o-nitrochloro-benzene and p-nitrochloro-benzene is obtained.



9.3 Reactions of Halogenoalkanes or Alkyl Halides

In an alkyl halide molecule, the carbon-halogen bond is polarized due to the more electronegative nature of halogen than carbon. So, halogen atoms induce dipolar character in carbon-halogen bonds. The electron density is drawn more towards halogen atom. As a result, the halogen atom acquires a partial negative charge and carbon atom partial positive charge. This is called the inductive effect.

$$C^{\delta+}-X^{\delta-}$$

This polar character of the C—X bond is responsible for characteristic chemical reactions of alkyl halides.

Alkyl halides undergo two types of reactions

- Nucleophilic substitution reactions (SN Reactions)
- Elimination reaction

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9.3.1 Nucleophilic substitution (SN) reactions of Alkyl halides

The reaction in which a halogen atom of an alkyl halide is substituted or replaced by a strong nucleophile is known as the nucleophilic substitution reaction. The general representation of such reactions is given below.

These reactions are called the nucleophilic substation or SN reactions.

Substrate, nucleophile and Leaving Group

Substrate Molecule

The alkyl halide molecule on which a nucleophile attacks is called a substrate molecule.

Nucleophile

It is species having lone pair of electrons and donate a pair of electrons to electrophilic carbon of alkyl halide. (It may be neutral or negatively charge).

Examples of Nucleophiles

HO^-	Hydroxide ion	NH_2^-	Amino group
$C_2H_5O^-$	Ethoxide ion	Cl^-	Chloride ion
HS^-	Hydrogen sulphide ion	Br^-	Bromide ion
SCN^-	Thio cyanate ion	$\ddot{N}H_3$	Ammonia
$H_2\ddot{O}:$	Water		

Leaving Group (LG)

The halogen of alkyl halide is called the leaving group. The leaving group is also a nucleophile. It departs with an unshared pair of electrons. The incoming nucleophile must be stronger than the departing ones, Cl^-, Br^-, I^-, HSO^-_4 are good leaving groups. Poor leaving groups are OH^-, OR and NH^-_2, Iodide ion is a good nucleophile as well as a good leaving group.

There are two fundamental events in a nucleophilic substitution reaction:

1. **Breaking of the δ bond between carbon and halogen.**
2. **Formation of the new δ bond between carbon and the attacking nucleophile.**

   The substitution reaction is greatly influenced by the nature of the attacking nucleophile, the substrate, and the leaving group. In primary or secondary alkyl halides, attack by the incoming nucleophile and displacement of the leaving group occurs in one step, but in bulky tertiary alkyl halides, attack by the incoming nucleophile and displacement of the leaving group occurs in two steps. Thus, these substitution reactions follow two different mechanisms known as SN_1 and SN_2 reactions.

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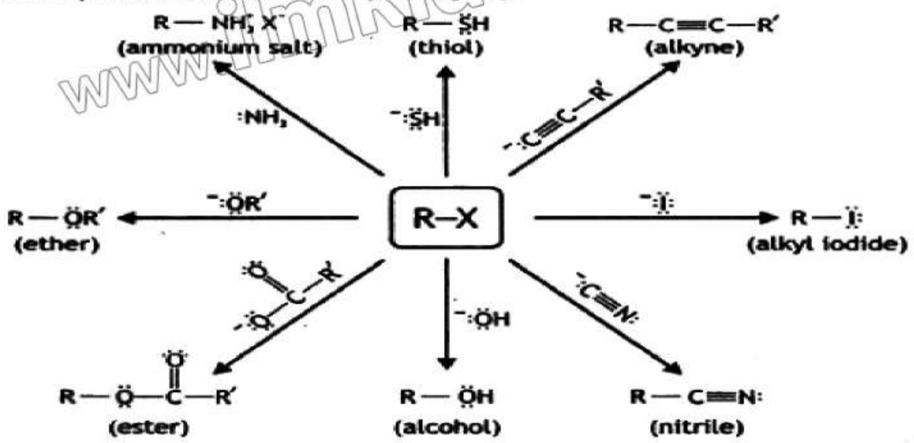
Examples of Nucleophilic Substitution Reactions



Carbocations and their Stability

Carbocation

A carbon atom that is attached to three atoms or a group of atoms and possesses a unit positive charge is known as carbocation.

Stability

The general stability order of simple alkyl carbocations is:

3° (most stable) > 2° > 1° > methyl (least stable)

Fig. 9.1 Stability order of carbocations

This is because alkyl groups are weak electron-donating due to hyperconjugation and inductive effects. The stability order of carbocation increases with an increase in alkyl groups.

SN$_1$ Mechanism

SN$_1$ is a unimolecular nucleophilic substitution reaction.

It is two step reaction mechanism in which the substrate R-X first ionizes reversibly into Carbonium ion (R$^+$) and X$^-$ ions. This is a slow and rate determining step.

Reaction with aqueous silver nitrate: When a haloalkane reacts with aqueous silver nitrate ($AgNO_3$), the silver ion (Ag^+) in the solution is exchanged with the halide ion (X^-) in the haloalkane. A precipitate of silver halide is formed. Alkyl fluoride does not react readily with $AgNO_3$ because C–F is strong, so fluoride ion is not displaced.

$$R\text{-}X + AgNO_3 \longrightarrow R\text{—}NO_3 + AgX$$

Where X is = Cl, Br, I

The colour of the precipitate depends on the halogens present.

AgCl: White precipitate which is soluble in NH_4OH solution.

AgBr: Cream coloured precipitate which is partially soluble NH_4OH solution.

AgI: Yellow precipitate which is insoluble in NH_4OH solution.

9.6 Alkyl Halides and Retrosynthesis

Alkylhalides are good starting materials to produce a verity of organic compounds. You can break down the analysis of a reaction pathway involving halogenoalkane. Consider the reaction between a haloalkane and a nucleophile. The mechanism involves the nucleophile attacking the carbon bonded to the halogen atom and the halogen departs.

$$R\text{—}X + Nu^- \longrightarrow R\text{—}Nu + X^-$$

Let's perform retro-synthesis to deduce the starting materials. For this, we work backwards from the product R-Nu to identify the starting materials. For this purpose you can consider the following reaction.

$$R\text{—}X \Rightarrow R^+ + X^-$$

The starting material for this reaction is a haloalkane which could give the same product. Suppose you want to prepare ethyl alcohol. To find the starting compound, work backwards from ethyl alcohol.

$$CH_3-CH_2-OH \Rightarrow CH_3-\overset{+}{C}H_2 + OH^-$$

So, starting material for this reaction is:

$$CH_3\text{—}CH_2\text{—}Br$$

$$CH_3\text{—}CH_2\text{—}Br + OH^- \Rightarrow CH_3\text{—}CH_2\text{—}OH + Br^-$$

KEY POINTS

- Halogenoalkanes, also known as alkyl halides are compounds in which one hydrogen atom of alkanes has been replaced by a halogen atom.
- Halogenation of benzene occurs with halogens (X_2) in the presence of Fe or Lewis acid catalyst FeX_3.
- The alkyl halide molecule is polarized due to the higher electronegativity of halogens compared to C.
- In chlorobenzene, the lone-pair of electrons on chlorine atoms is delocalized over the ring, giving the C–Cl bond the character of a partial double bond.
- The reactions in which the halogen atom of an alkyl halide is substituted or replaced by a strong nucleophile are known as nucleophilic substitution reactions.

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- A carbon atom that is attached to three atoms or a group of atoms and possesses a unit positive charge is known as carbocation.

  The general stability order of simple alkyl carbocations is:

$$\underset{\text{(most stable)}}{3^\circ} > 2^\circ > 1^\circ > \underset{\text{(least stable)}}{\text{methyl}}$$

- SN_1 is two-step reaction mechanism in which the substrate R-X first ionizes reversibly into Carbonium ion (R^+) and X^- ions.
- SN_2 is a Bimolecular nucleophilic substitution reaction that occurs in a single step.
- A common test to assess the reactivity of haloalkanes is their reaction with aqueous silver nitrate ($AgNO_3$).
- Alkyl halides are good starting materials to produce a variety of organic compounds.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which catalyst is commonly used in the halogenation of benzene with Cl_2 or Br_2?

a) H_2SO_4 b) $FeCl_3$ c) $AlCl_3$ d) NaOH

ii. In the reaction of benzene with Cl_2 in the presence of a catalyst, the product is:

a) Chloromethane b) Chlorobenzene
c) Dichloromethane d) Benzyl chloride

iii. What is the major product of the reaction between benzene and Br_2 with $FeBr_3$ as a catalyst?

a) Benzene bromide b) Bromobenzene
c) Dibromobenzene d) Bromomethane

iv. Which mechanism do primary halogenoalkanes typically follow in nucleophilic substitution reactions?

a) SN_1 b) SN_2 c) SN_1 and SN_2 both d) None of these

v. What type of bond is broken in the nucleophilic substitution reaction of a halogenoalkane?

a) C—H b) C—O c) C—X (where X is a halogen) d) C—C

vi. Which factor does NOT significantly affect the rate of SN_1 reactions?

a) Stability of the carbocation b) Solvent polarity
c) Strength of the nucleophile d) Leaving group ability

vii. Which halogenoalkane is more reactive in an SN_2 reaction?

a) Chloromethane b) Chlorobenzene c) Chloroethane d) All of these

viii. The C—Cl bond in chlorobenzene is less reactive towards nucleophilic substitution because:

a) The C—Cl bond is too strong b) The phenyl ring stabilizes the chlorine
c) Resonance effect makes the bond partially double
d) Steric hindrance from the benzene ring

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Organic hydroxyl compounds are a class of organic compounds that contain one or more hydroxyl groups (—OH) attached to a carbon atom. The presence of a hydroxyl group significantly affects the properties and reactivity of these compounds. Organic hydroxy compounds can be classified into several categories based on the nature of the carbon atom to which the hydroxyl group is attached. The main categories of hydroxy organic *organic* compounds are as follows:

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1. Alcohols

Alcohols are the simplest types of organic hydroxy compounds in which the hydroxyl group is attached to a saturated carbon atom (sp^3 hybridized).

For example;

Methanol (CH_3OH): The simplest alcohol, often used as a solvent and antifreeze.

Ethanol (C_2H_5OH): Found in alcoholic beverages, used as a solvent and fuel.

Isopropanol (C_3H_7OH): Also known as isopropyl alcohol, used as a disinfectant and solvent.

2. Phenols

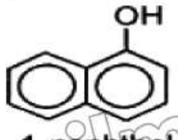
Phenols have a hydroxyl group attached directly to an aromatic ring (benzene ring). They are used in the manufacture of plastics, medicines, and as antiseptics and disinfectants.

phenol

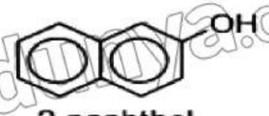
3. Naphthols

Naphthols are a set of organic compounds with the chemical formula $C_{10}H_7OH$. They are derivatives of naphthalene and consist of a naphthalene ring system bonded to a hydroxyl group. Naphthols exist in two isomeric forms:

1. **1-Naphthol:** Also known as α-naphthol, the hydroxyl group is attached to the first carbon atom of the naphthalene ring.
2. **2-Naphthol:** Also known as β-naphthol, the hydroxyl group is attached to the second carbon atom of the naphthalene ring.



1-naphthol



2-naphthol

These compounds are commonly used in the synthesis of dyes, pigments, and other organic chemicals. They also have applications in the manufacture of pharmaceuticals, agrochemicals, and in various chemical reactions as intermediates.

10.1 Preparation of Esters

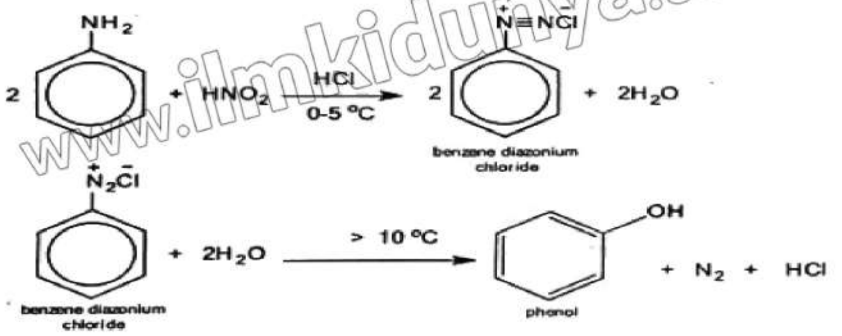
An ester is an organic compound formed by the addition of an acid to an alcohol. Esters are used in a variety of applications, such as the production of fragrances, flavourings, and pharmaceuticals. Esters can be prepared directly by reacting acyl halides with alcohols. Ethanoyl chloride, for example, reacts immediately with cold ethanol to form ethyl ethanoate. The reaction is very exothermic. A steamy acidic gas, (hydrogen chloride), is released. The oxygen atom of the alcohol, which has one lone pair of electrons, attacks electrophilic carbonyl carbon (acyl chloride). This attack results in the formation of the tetrahedral intermediate. In the subsequent step, the chloride ion (a good leaving group) departs and rapidly loses a proton to yield the ester.

$$CH_3COCl + CH_3CH_2OH \longrightarrow CH_3COOCH_2CH_3 + HCl$$

10.2 Preparation of Phenol

Phenol can be produced by the reaction of phenylamine with HNO_3 or $NaNO_3$ and dilute acid below 10°C to produce the diazonium salt.

Benzene diazonium chloride can be prepared by the reaction of aniline with nitrous acid (HNO_2) in the presence of hydrochloric acid. If the temperature is greater than 10°C, hydrolysis of benzene diazonium chloride takes place and phenol is formed.



10.3 Acidity of water, phenol and ethanol

Acidity refers to the stability of the conjugate base formed by proton donation. Water is an acid and base. It is autoionized, but the autoionization constant of water is very low ($k_w = 1 \times 10^{-14}$). Therefore, water is a weak acid. Phenol is a stronger acid than water. The reason for this is that the phenoxide ion which is formed after the proton is lost, undergoes resonance stabilization. The negative charge of the phenoxide ion is delocalized into the ring. Therefore, phenoxide ions are stable. So, K_a of phenol (1.3×10^{-10}) is higher than that of water (1.8×10^{-16}).

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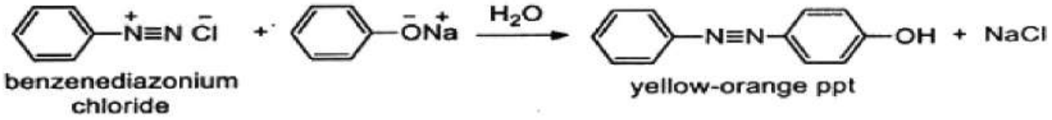
(c) Reaction of phenol with diazonium salt

Phenol is dissolved in sodium hydroxide solution to give a solution of sodium phenoxide. When this solution is cooled in ice, and cold benzene diazonium chloride solution is added, a yellow-orange solution or precipitate is formed. The product is one of the simplest azo-compounds which are used as azo dyes. Azo-dyes are synthetic dyes that do not occur naturally. In azo-dyes, two benzene rings are linked by a nitrogen bridge.

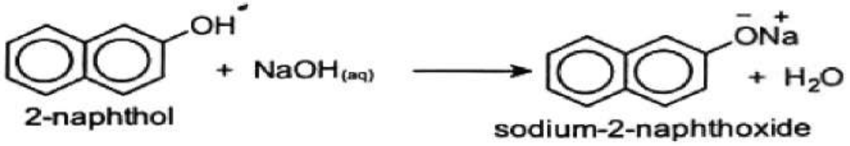


10.5 Reactions of Naphthols

General reactions of simple phenol can also be applied to other phenolic compounds such as naphthols. Naphthols behave like simple phenols in chemical reactions.

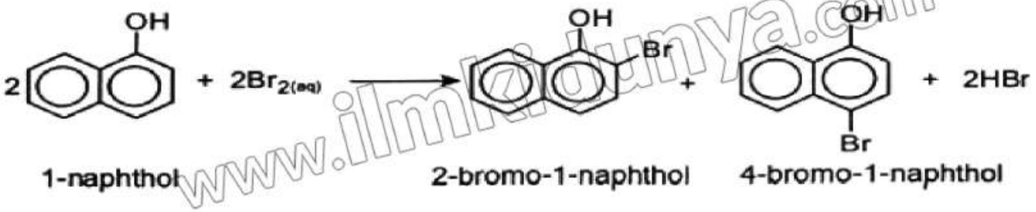
1. Reaction with sodium hydroxide

Naphthols dissolve in sodium hydroxide solution producing naphthoxide.



2. Reaction with bromine water

1-Naphthol decolourizes bromine water with a substitution of bromine at 2- and 4-positions.



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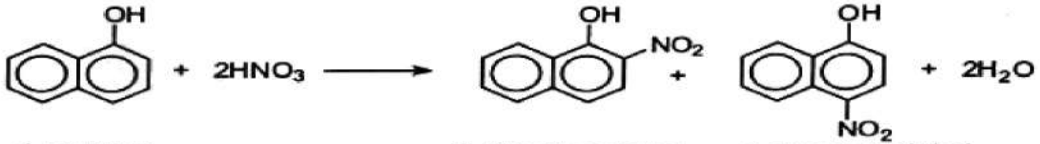
2-naphthol decolourizes bromine water with a substitution at the position between the OH group and the other ring. Position 4 is cluttered with the other ring.

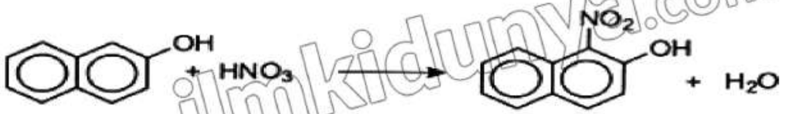
2-naphthol 1-bromo-2-naphthol

3. Reaction with nitric acid

Nitration occurs like bromination. 1-naphthol gives substitution at 2- and 4-positions.



1-naphthol 2-nitro-1-naphthol 4-nitro-1-naphthol

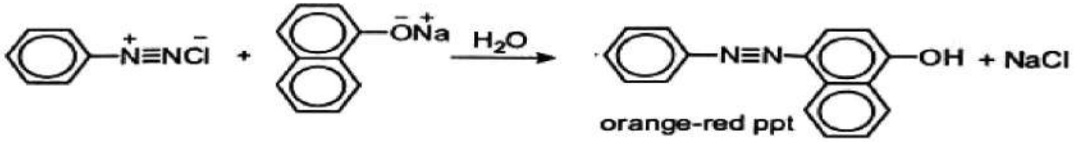


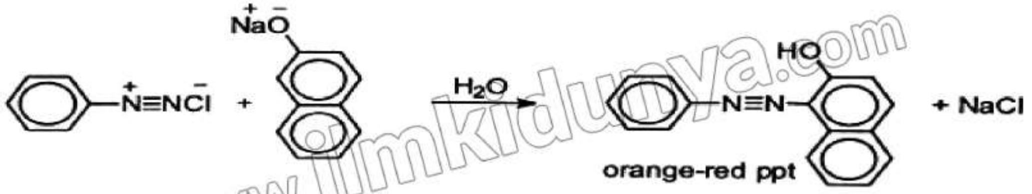
2-naphthol 1-nitro-2-naphthol

4. Reaction with diazonium chloride

Naphthols react with diazonium salt to give azo compounds. 1-naphthol reacts with diazonium salt in exactly the same conditions as with phenol. The 1-naphthol is dissolved in NaOH solution to produce an ion like the phenol. This solution is ice-cooled and mixed with the diazonium salt solution. An intense orange-red precipitate of an azo compound is produced. With 1-naphthol reaction occurs at position 4.

With 2-naphthol reaction occurs at a position between the OH group and the other ring.





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ix. Explain the resonance stabilization of the phenoxide ion and how it contributes to the acidity of phenol.

x. Compare the acidities of phenol, ethanol, and water. Provide a brief explanation for the differences in their acid strengths.

xi. Predict the products of the reaction of 1-naphthol with NaOH and bromine water. Provide the balanced chemical equations and indicate the positions of the substituents.

3. Long Answer Questions

1. Compare and contrast the reactivity of phenol, benzene, and ethanol in electrophilic aromatic substitution reactions. Explain the role of the hydroxyl group in phenol and its influence on these reactions.
2. Describe the acidity of phenol in terms of its ability to donate protons. Compare its acidity to that of water and ethanol and explain the molecular basis for the differences observed.
3. Describe how 2-naphthol will undergo a reaction with bromine water and nitric acid.
4. Predict the products if methanol is used instead of ethanol in the reaction with ethanoyl chloride. Provide the balanced chemical equation.
5. Write the balanced chemical equations for the reactions of phenol with NaOH and sodium metal. Describe the products formed in each reaction.
6. Explain the reaction of phenol with bromine water
7. Describe the reaction of phenol with dilute nitric acid at room temperature. What are the products, and why do they form in the observed positions on the aromatic ring?
8. Discuss the similarities and differences in the directing effects of the hydroxyl group in phenol and 1-naphthol.
9. Phenol is more acidic than ethanol. Analyze the structure of phenol to explain this difference in acidity.
10. Phenol reacts with bromine water to form a white precipitate without needing a catalyst. What does this suggest about the electron density of the aromatic ring in phenol?

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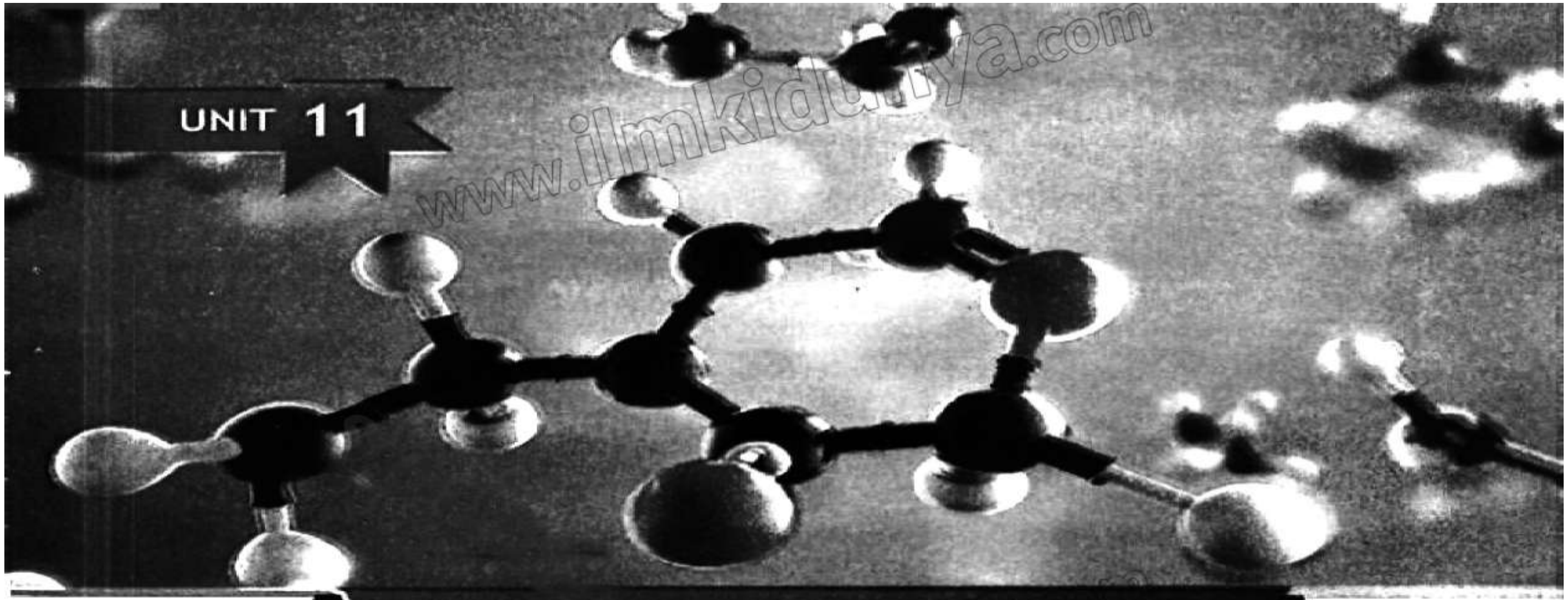

UNIT 11

CARBONYL COMPOUNDS

Student Learning Outcomes (SLOs)

- State the reactions by which benzoic acid can be produced: reaction of an alkylbenzene with hot alkaline $KMnO_4$ and then dilute acid, exemplified by methyl benzene.
- Describe the reaction of carboxylic acids with PCl_3, and heat, PCl_5, or $SOCl_2$ to form acyl chlodides.
- Recognise that some carboxylic acids can be further oxidized: a. the oxidation of methanoic acid with Fehling`s solution or Tollen`s reagent or acidified $KMnO_4$ or acidified $K_2Cr_2O_7$ to carbon dioxide and water. b. the oxidation of ethanedioic acid with warm acidified $KMnO_4$ to carbon dioxide.
- Explain the relative acidities of carboxylic acids, phenols and alcohols.
- Explain the relative acidities of chlorine-substituted carboxylic acids.
- Recall the reactions by which esters can be produced: reaction of alcohols with acyl chlorides using the formation of ethyl ethanoate and phenyl benzoate as examples.
- Recall the reactions(reagents and conditions) by which acyl chlorides can be produced: reaction of carboxylic acids with PCl_3 and heat, PCl_5, or $SOCl_2$.
- Describe the following reactions of acyl chlorides: (check either bullets or add a,b, c,d): a. hydrolysis on addition of water at room temperature to give the carboxylic acid and HCl. b. reaction with an alcohol at room temperature to produce an ester and HCl. c. reaction with phenol at room temperature to produce an ester and HCl. d. reaction with ammonia at room temperature to produce an amide and HCl. e. reaction with a primary or secondary amine at room temperature to produce an amide and HCl.
- Describe the addition-elimination mechanism of acyl chlorides in reactions.
- Explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and halogenoarenes (aryl chlorides).

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Carbonyl compounds are a class of organic substances characterized by the presence of a carbonyl group (C=O). A carbonyl group consists of a carbon atom doubly bonded to an oxygen atom. This functional group is very reactive and acts as the main structural feature of many organic molecules. Carbonyl compounds can be broadly divided into two main types based on the nature of the atoms or groups attached to the carbonyl carbon:

Aldehydes: In aldehydes, the carbonyl group is attached to at least one hydrogen atom and one alkyl or aryl group. The general formula for aldehydes is RCHO, where R can be hydrogen, alkyl or aryl.

Example: Formaldehyde (HCHO), Acetaldehyde (CH_3CHO)

Ketones: In ketones, a carbonyl group is attached to two alkyl or aryl groups. The general formula for ketones is RCOR', where R and R' can be alkyl or aryl.

Example: acetone (CH_3COCH_3), butanone ($CH_3COC_2H_5$)

In addition to aldehydes and ketones, the carbonyl group is also present in several other important classes of compounds:

Carboxylic acids: These contain a carbonyl group. attached to a hydroxyl group (-OH) and an alkyl or aryl group. The general formula is RCOOH.

Example: acetic acid (CH_3COOH), benzoic acid (C_6H_5COOH)

Esters: Recall that Esters formed by the reaction of carboxylic acids and alcohols have a carbonyl group attached to an alkoxy group (-OR) and an alkyl or aryl group. The general formula is RCOOR'.

Aliphatic carboxylic acids have the carboxyl group attached to an open chain of carbon atoms.

Example: ethyl acetate ($CH_3COOCH_2CH_3$), methyl benzoate $C_6H_5COOCH_3$

Amides: Contains a carbonyl group attached to a nitrogen atom (which can be attached to hydrogen atoms or alkyl groups) and an alkyl or aryl group. The general formula is RCONR'R".

Example: Acetamide (CH_3CONH_2), N,N-Dimethylacetamide $CH_3CON(CH_3)_2$

Anhydrides: Anhydrides formed by the reaction of two carboxylic acids contain two carbonyl groups linked to an oxygen atom. The general formula is $(RCO)_2O$.

This chapter focuses on the properties and reactions of carboxylic acids, acyl chlorides and related compounds such as esters and alkylbenzenes. It introduces the key chemical changes involved in the conversion of alkylbenzenes to benzoic acid and explores how carboxylic acids can react with chlorinating agents such as PCl_3, PCl_5 and $SOCl_2$ to form acyl chlorides. Overall, the chapter provides a comprehensive overview of the chemical behaviour and transformations of carboxylic acids and their derivatives.

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11.1 Acidity

Carboxylic acids are acidic simple organic compounds (pK_a ~ 5). But they are weak acids compared to mineral acids like HCl or H_2SO_4. (Remember the lower the pK_a, the stronger the acid)

Table 11.1: pK_a value of organic acids

Carboxylic acid	Structure	pKa
Ethanoic acid	CH_3CO_2H	4.7
Propanoic acid	$CH_3CH_2CO_2H$	4.9
Fluoroethanoic acid	CH_2FCO_2H	2.6
Chloroethanoic acid	CH_2ClCO_2H	2.9
Dichloroethanoic acid	$CHCl_2CO_2H$	1.3
Trichloroethanoic acid	CCl_3CO_2H	0.9
Nitroethanoic acid	$O_2NCH_2CO_2H$	1.7

Acidity order of chlorine substituted acetic acid is:

$$CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$$

The electron-withdrawing group bonded to the carbon atom next to the carboxyl group (COOH) makes the acid stronger. Due to electron withdrawing group electrons will move away from oxygen. Hence decreases the charge density on the oxygen atom of the carboxylate ion which stabilizes the group and makes it less likely to bond with an H^+ ion. For example, chloroacetic acid is 100 times stronger acid than acetic acid.

The electron-donating group (Alkyl) strengthens the O—H bond in the acid's —COOH group. It donates a negative charge towards the group of the carboxylate ion, making it more likely to accept an H+ ion, hence acidic strength decreases. For example, formic acid is more acidic than acetic acid.

11.2 Preparation of Benzoic Acids

By the oxidation of Alkyl Benzenes

Benzoic acid can be prepared by the oxidation of alkyl benzene, when treated with hot alkaline $KMnO_4$. The mixture is finally hydrolyzed with dilute acid.

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11.3 Reactivity

The carboxyl group shows the chemistry of both the carbonyl ($-\overset{\overset{O}{\|}}{C}-$) and the hydroxyl of an (—OH) groups. In most reactions, the carboxyl group is retained. However, the reactivity of these molecules is due to the presence of the carbonyl group.

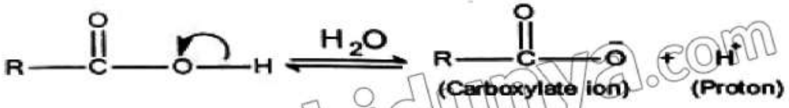
11.4 Reactions of Carboxylic Acids

Carboxylic acids undergo the following types of reactions.

1. The reaction in which hydrogen atom of —OH group of the carboxyl group is involved (salt formation).
2. The reaction in which the OH group is replaced by another group.
3. The reactions involving carboxyl group as a whole.

11.4.1 Reaction involving H-atom of the carboxyl group (Acidic properties of Carboxylic acid)

Carboxylic acids are weaker acids than mineral acids. They produce H^+ ion when dissolved in water

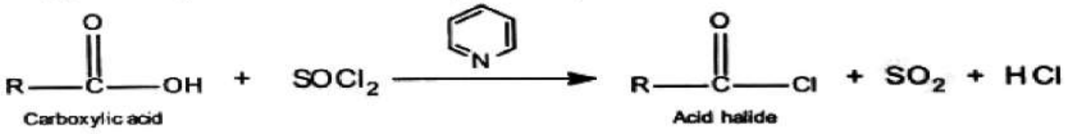


11.4.2 Reaction involving the OH group of Carboxylic acid

(Preparation of derivatives of Carboxylic acid)

The addition of a nucleophile to the carboxyl group is always followed by the displacement of the —OH group by some other group producing a carboxylic acid derivative. The —OH group can thus be replaced by X, OR, and NH_2 to form halides, esters, and amides respectively.

1. **Reaction with Thionyl Chloride (Preparation of Acyl Chlorides)**
   - Acyl chlorides are prepared by treating the carboxylic acid with thionyl chloride, ($SOCl_2$), in the presence of a base (Pyridine).



2. **Reaction with Phosphorus halides**

   Phosphorus(III) chloride reacts with carboxylic acids at room temperature producing acyl chloride and phosphorus acid.

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

ethanoic acid ethanoyl chloride

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Phosphorus(V) chloride reacts with carboxylic acids in a cold state producing acyl chloride and phosphorus oxychloride with the evolution of fumes of hydrogen chloride.

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

ethanoic acid ethanoyl chloride

11.4.3 Oxidation Reactions

Some carboxylic acids like methanoic acid and ehandioic acid can be further oxidized by some oxidizing agents. For example;

(i) Methanoic acid is oxidized to carbon dioxide and water by the Tollen`s reagent with the formation of a silver mirror.

$$HCOOH + 2OH^- + 2Ag(NH_3)_2^+ \rightarrow CO_2 + 2H_2O + 2Ag\downarrow + 4NH_3$$

(ii) Methanoic acid is also oxidized to carbon dioxide and water by Fehling`s solution with the formation of red precipitates of copper(I)oxide.

$$HCOOH + 4OH^- + 2Cu^{2+} \rightarrow CO_2 + 3H_2O + Cu_2O\downarrow$$

(iii) Etanedioic acid is oxidized to carbon dioxide by warm potassium manganate(VII) solution acidified with dilute sulphuric acid. In this reaction, the purple colour of $KMnO_4$ is changed into a light pink colour due to its reduction into manganese(II) ions.

$$(COOH)_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow 10CO_2 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

11.4.4 Comparing Strengths of Carboxylic acids, Phenols and Alcohols

The relative strengths of weak acids are compared by their pK_a values. The smaller the pK_a value, the stronger the acid. The pK_a value of an acid depends on the stability of it conjugate base it forms after donating a proton.

CH_3COOH $CH_3COO^- + H^+$ $pK_a = 4.76$

C_6H_5OH $C_6H_5O^- + H^+$ $pK_a = 10$

CH_3CH_2OH $CH_3CH_2O^- + H^+$ $pK_a =$ about 16

Ethanoate ion is stabilized due to resonance. It spreads over the whole of the COO^- group between the two electronegative atoms.

Phenoxide ion is also stabilized due to resonance. A negative charge spreads over the ring but between less electronegative atoms. So, it is less stable than ethanoate ion. Phenols are, therefore, less acidic than carboxylic acids.

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Ethoxide ion on the other hand has no delocalization of the negative charge. It will readily combine with H^+ to reform ethanol. So, ethanol is less likely to lose H^+ ions. It is hardly acidic. The acidic strength of these compounds is in the following order.

etanoic acid > phenol > ethanol

11.5 Reaction of Acyl chlorides

1. Reaction of Acyl chlorides with alcohols (Formation of esters)

Acyl halides react vigorously with alcohols at room temperature to produce esters. For example,

$$CH_3COCl + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCl$$

ethanoyl chloride   ethanol   ethylethanoate

$$C_6H_5COCl + CH_3CH_2OH \rightarrow C_6H_5COOCH_2CH_3 + HCl$$

benzoyl chloride   ethanol   ethyl benzoate

2. Reaction of acyl chloride with phenol

Acyl chloride reacts with phenol at room temperature to produce an ester.

$$CH_3COCl + C_6H_5OH \rightarrow CH_3COOC_6H_5 + HCl$$

phenylethanoate

3. Reaction with water (Hydrolysis)

Acyl halides hydrolyse with water at room temperature to produce carboxylic acids and hydrochloric acid.

$$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$$

4. Reaction with ammonia (Formation of amides)

Acyl halides react with ammonia at room temperature to produce amides. The hydrogen chloride produced reacts with excess ammonia to give ammonium chloride.

$$CH_3COCl + NH_3 \rightarrow CH_3CONH_2 + HCl$$

ethanamide

$$HCl + NH_3 \rightarrow NH_4Cl$$

5. Reaction with primary and secondary amines **(Formation of N-substituted amides)**

Primary and secondary amines react in a similar way as ammonia at room temperature to produce N-substituted amides. The hydrogen chloride reacts with excess amine to give ammonium salt.

$$CH_3COCl + CH_3NH_2 \rightarrow CH_3CONHCH_3 + HCl$$

ethanoyl chloride   methanamide   N-methylmethanamide

$$HCl + CH_3NH_2 \rightarrow [CH_3NH_3]Cl$$

Methyl ammonium chloride

$$CH_3COCl + (CH_3)_2NH \rightarrow CH_3CONH(CH_3)_2 + HCl$$

N-methylmetanamide   N,N-dimethylmethanamide

$$HCl + (CH_3)_2NH \rightarrow [(CH_3)_2NH_2]^+Cl^-$$

dimethyl ammonium chloride

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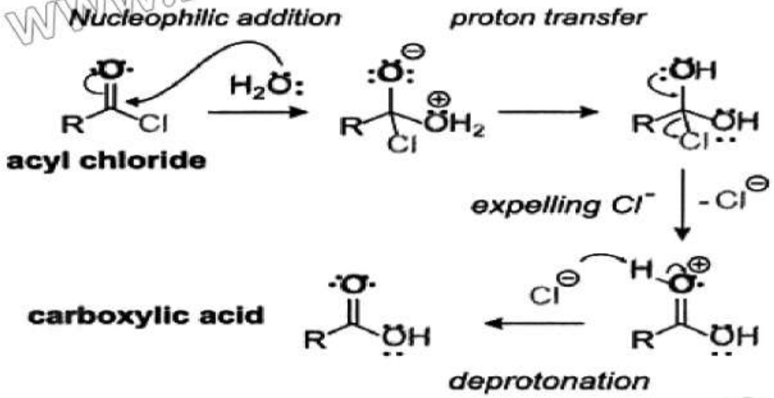
11.5.1 General mechanism of the reactions of acyl chlorides with nucleophiles



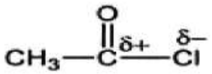
11.5.2 Comparison of Hydrolysis of Acyl chlorides , Alkyl chlorides, and Aryl chlorides

The ease of hydrolysis of these compounds is in the following order.

Acyl chlorides > Alkyl chlorides > Aryl chlorides

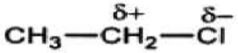
This trend can be explained on the basis of the strength of the C—Cl bond.

- In acyl chlorides, the carbonyl carbon atom is attached to two electronegative atoms (O and Cl), pulling electrons away. The carbonyl carbon is highly electron deficient. The nucleophile can easily attack it and displace the chlorine atom. So, the hydrolysis occurs most readily.



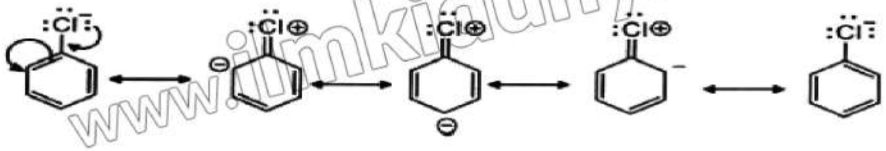
$$CH_3-\overset{\overset{O}{\|}}{C}^{\delta+}-\overset{\delta-}{Cl}$$

- In alkyl chlorides, the carbon atom is attached to only one electronegative atom, which pulls electrons away. The carbon atom is therefore less electron deficient than the carbonyl carbon atom. Hydrolysis requires a stronger nucleophile than water.



$$CH_3-\overset{\delta+}{CH_2}-\overset{\delta-}{Cl}$$

- In aryl chlorides, the lone pair of chlorine is involved in resonance and is delocalized over the ring. The C-Cl bond, therefore has some double bond character. As a result, the C-Cl bond is difficult to break, even by a strong nucleophile. So, hydrolysis will not occur.



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KEY POINTS

- Carboxylic acids are the most acidic simple organic compounds (pK_a - 5).
- The electron-withdrawing group bonded to the carbon atom next to the carboxyl group (COOH) makes the acid stronger.
- The carboxyl group shows the chemistry of both the carbonyl ($-\overset{O}{\overset{\|}{C}}-$) and the hydroxyl of an (−OH) group.
- The −OH group of carboxylic acids can be replaced by X, OR, and NH_2 to form halides, esters, and amides respectively.
- Phosphorus(III)chloride reacts with carboxylic acids at room temperature producing acyl chloride and phosphorus acid.
- Methanoic acid is oxidized to carbon dioxide and water by Tollen`s reagent with the formation of a silver mirror.
- Methanoic acid is also oxidized to carbon dioxide and water by Fehling`s solution with the formation of red precipitates of copper(I)oxide.
- Phenoxide ion is stabilized due to resonance. Ethoxide ion on the other hand has no delocalization of the negative charge.
- Acyl halides react vigorously with alcohols at room temperature to produce esters.
- Acyl chloride reacts with phenol at room temperature to produce an ester.
- Acyl halides hydrolyse with water at room temperature to produce carboxylic acids and hydrochloric acid.
- Acyl halides react with ammonia at room temperature to produce amides.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which reagent would you use to convert toluene to benzoic acid?

a) $KMnO_4$ and dilute acid b) Fehling's solution

c) PCl_5 d) $SOCl_2$

ii. What is the main product of the reaction between acetic acid and PCl_5?

a) Ethyl acetate b) Acetyl chloride

c) Acetic anhydride d) Acetone

iii. Which of the following is a strong oxidizing agent for the oxidation of methanoic acid?

a) PCl_5 b) $SOCl_2$ c) $KMnO_4$ d) PCl_3

iv. In terms of acidity, which of the following is the most acidic?

a) Methanol b) Phenol c) Formic acid d) Benzoic acid

v. What happens when benzoyl chloride reacts with water?

a) Benzoic acid and HCl are formed. b) Benzene and water are formed.

c) Phenol and water are formed. d) Benzoate and water are formed.

vi. The mechanism by which acyl chlorides react with alcohols is:

a) Addition	b) Elimination
c) Addition-elimination	d) Substitution

vii. Which of the following acyl chlorides is expected to hydrolyze most readily?

a) Methyl chloride	b) Acetyl chloride
c) Phenyl chloride	d) Benzyl chloride

viii. When formic acid is oxidized, which of the following is formed?

a) Water only	b) Carbon dioxide only
c) Methanol only	d) Water and carbon dioxide

ix. The relative acidity of chlorinated carboxylic acids is primarily due to:

a) Increased stability of the conjugate base.

b) Electron-donating effects of the chlorine atom.

c) Lowering of the carboxylate pK_a.

d) Increased electron density around the carbonyl group.

x. The addition-elimination reaction mechanism of acyl chlorides involves:

a) Nucleophilic attack on the carbonyl carbon.

b) Addition of HCl to the carbonyl group.

c) Electrophilic substitution on the benzene ring.

d) Radical addition to the carbonyl group.

xi. Why are carboxylic acids more acidic than phenols and alcohols?

a) Carboxylic acids have a lower molecular weight.

b) Carboxylic acids are better at forming hydrogen bonds.

c) The carboxylate anion is resonance-stabilized.

d) Carboxylic acids have a higher boiling point.

xii. How does chlorine substitution affect the acidity of carboxylic acids?

a) It increases acidity by donating electrons.

b) It decreases acidity by withdrawing electrons.

c) It increases acidity by withdrawing electrons.

xiii. Which of the following statements about the addition-elimination mechanism of acyl chlorides is correct?

a) The nucleophile attacks the carbonyl carbon, forming a tetrahedral intermediate.

b) The nucleophile attacks the chlorine atom directly.

c) The reaction involves a free radical intermediate.

d) The acyl chloride first forms a carbocation intermediate.

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xiv. What is the major difference in the oxidation products of ethanedioic acid and methanoic acid when treated with warm acidified $KMnO_4$?

a) Ethanedioic acid produces carbon dioxide, while methanoic acid produces formaldehyde.

b) Ethanedioic acid produces carbon monoxide, while methanoic acid produces carbon dioxide and water.

c) Ethanedioic acid produces carbon dioxide, while methanoic acid produces carbon dioxide and water.

d) Ethanedioic acid produces acetic acid, while methanoic acid produces carbon dioxide.

2. Short Answer Questions

i. Write the equation for the reaction of acetic acid with $SOCl_2$.

ii. Explain why methanoic acid can be oxidized while other carboxylic acids cannot.

iii. What products are formed when ethanedioic acid is oxidized with warm acidified $KMnO_4$?

iv. Describe the mechanism of acyl chloride hydrolysis with water.

v. What is the difference in reactivity between acyl chlorides and alkyl chlorides?

vi. Explain the influence of chlorine substitution on the acidity of carboxylic acids.

vii. What product results from the reaction of acyl chlorides with phenol?

viii. Methylbenzene can be oxidized to benzoic acid using hot, alkaline KMnO4 and then dilute acid.

a. Describe the role of potassium permanganate in the oxidation of methylbenzene.

b. Explain why the reaction mixture needs to be acidified after oxidation.

ix. Carboxylic acids can be converted to acyl chlorides using PCl_3, PCl_5 or $SOCl_2$.

a. Write the balanced chemical equation for the reaction of acetic acid with PCl5.

b. Compare the by-products formed when using PCl_3 and $SOCl_2$ for this conversion.

x. Methanoic acid can be oxidized by Fehling's solution, Tollen's reagent, acidified $KMnO_4$, or acidified $K_2Cr_2O_7$.

a. Outline the changes observed when methanoic acid is treated with Tollen's reagent.

b. Write the balanced chemical equation for the oxidation of methanoic acid with acidified $KMnO_4$.

xi. Carboxylic acids are generally more acidic than phenols and alcohols.

a. Explain why carboxylic acids are more acidic than alcohols.

b. Discuss the effect of electron-withdrawing groups on the acidity of carboxylic acids.

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3. Long Answer Questions

i. Describe the process of converting toluene to benzoic acid using hot alkaline $KMnO_4$ and then dilute acid. Include the mechanism and discuss the reasons for the choice of reagent.

ii. Explain the relative acidities of carboxylic acids, phenols, and alcohols. Provide examples and discuss how substituents can affect acidity.

iii. Compare the reactivity and hydrolysis of acyl chlorides with alkyl and aryl chlorides. Explain the factors that affect their reactivity.

iv. Esters can be formed from alcohols and acyl chlorides, exemplified by the formation of phenyl benzoate. Write the balanced chemical equation for the formation of phenyl benzoate from benzoyl chloride and phenol.

v. Acyl chlorides hydrolyze rapidly in water, while aryl chlorides are resistant. Analyze the electronic structures of these compounds to explain this contrast in reactivity.

vi. Given three compounds: ethanoyl chloride, chloromethane, and chlorobenzene, predict which one hydrolyzes the fastest and explain your reasoning with reference to bond polarity and resonance.

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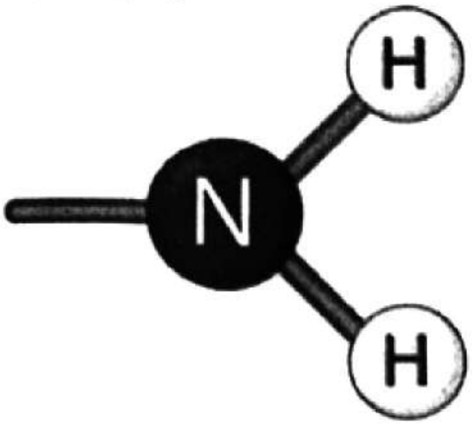
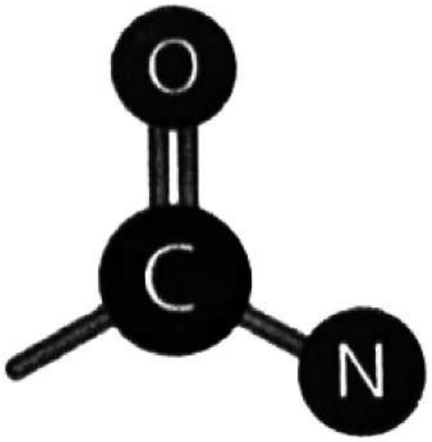
UNIT 12





NITROGEN COMPOUNDS

Student Learning Outcomes (SLOs)

- Recall the reactions (reagents and conditions) by which primary and secondary amines are produced.
  - (a) Reaction of halogenoalkanes with NH_3 in ethanol heated under pressure.
  - (b) Reaction of halogenoalkanes with primary amines in ethanol, heated in a sealed tube/ under pressure.
  - (c) The reaction of amides with $LiAlH_4$.
  - (d) The reduction of nitriles with $LiAlH_4$ or H_2/Ni.
- Describe the reactions by which nitriles can be produced: reaction of a halogenoalkane with KCN in ethanol and heat.
- Recall the reactions by which hydroxyl nitriles can be produced: the reaction of aldehydes and ketones with HCN, KCN as catalyst, and heat.
- Describe the hydrolysis of nitriles with dilute acid or dilute alkali followed by acidification.
- Descrbe the basicity of aqueous solutions of amides.
- Describe the reaction of phenylamine with $Br_2(aq)$ at room temperature.
- Describe the reaction of phenylamine with HNO_2 and dilute acid below 10 °C to produce the diazonium salt; further warming of the diazonium salt with water to give phenol.
- Explain the relative basicities of aqueous ammonia, ethylamine, and phenylamine.

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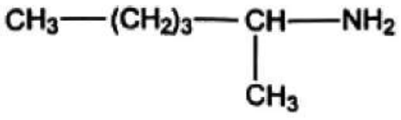
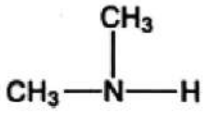
- Identify the properties of azo compounds (some examples include: (a) describe the coupling of benzenediazonium chloride with phenol in $NaOH_{(aq)}$ to form an azo compound. (b) Identify the azo group (c) state that azo compounds are often used as dyes (d) recognize that other azo dyes can be formed via a similar route.
- Identify the reactions (reagents and conditions) by which amides are produced (some examples include; (a) the reaction between ammonia and acyl chloride at room temperature (b) the reaction between a primary amine and an acyl chloride at room temperature.
- Describe the reactions of amides (some examples include: (a) hydrolysis with aqueous alkali or aqueous acid (b) the reduction of the CO group in amides with $LiAlH_4$ to for an amine.
- Explain why amides are much weaker bases than amines.
- Describe the acid-bas properties of amino acids and the formation of zwitterions.
- Describe the formation of amide (peptide) bonds between amino acids to give di- and tripeptides.
- Predict the results of electrophoresis on mixtures of amino acids and dipeptides at varying pHs.

In this chapter, we are going to look at the chemistry of some nitrogen compounds such as amines, amides, and nitriles. Amides are one of the most important functional groups of organic chemistry. Amides are weak bases compared to amines, but they play an important role in many chemical reactions. Amines are the building blocks of many organic compounds. Amines are the building blocks for amino acids, which are the building blocks for proteins. Nitriles are used in the synthesis of amines and other valuable organic compounds. These compounds have a wide range applications in the formation of dyes, drugs, and other materials.

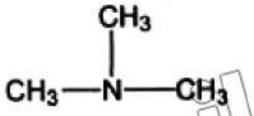
$CH_3—CH_2—NH_2$ Ethyl amine (Primary amine)



$CH_3—(CH_2)_3—\underset{\underset{CH_3}{|}}{CH}—NH_2$ 2-Hexyl amine (Primary amine)



$CH_3—\overset{\overset{CH_3}{|}}{N}—H$ Dimethyl amine (a sec-amine)



$CH_3—\overset{\overset{CH_3}{|}}{N}—CH_3$ Trimethly amine (a ter-amine)

Pyridine (a ter-amine)

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12.1 Preparation of Amines

Recall that primary and secondary amines can be prepared by various chemical reactions, depending on the desired structure and starting materials. For example;

1. By the reaction of Alkyl Halides with ammonia

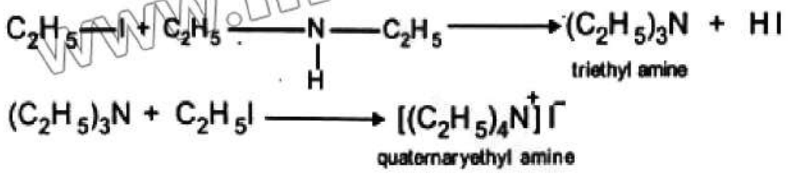
When an ethanolic solution of ammonia is heated with an alkyl halide in a sealed tube at 100 °C, we get a mixture of amines together with their salts. The salt formed reacts with excess ammonia to produce free amine.

$$NH_3 + CH_3CH_2Br \longrightarrow CH_3CH_2NH_3^+ + Br^-$$
$$CH_3CH_2NH_3^+Br^- + NH_3 \longrightarrow \underset{\text{ethylamine}}{CH_3CH_2NH_2} + NH_4^+Br^-$$

The reaction does not stop at the primary amine. The ethyl amine reacts with bromoethane in the same way in two steps producing a secondary amine.

$$CH_3CH_2Br + CH_3CH_2NH_2 \longrightarrow (CH_3CH_2)_2NH_2^+Br^-$$
$$(CH_3CH_2)_2NH_2^+Br^- + NH_3 \longrightarrow \underset{\text{diethylamine}}{(CH_3CH_2)_2NH} + NH_4^+Br^-$$

Secondary amine further reacts with ammonia to give tertiary amine, which forms quaternary ammonium salt.



$$C_2H_5{-}I + C_2H_5{-}\underset{\displaystyle H}{\overset{}{N}}{-}C_2H_5 \longrightarrow \underset{\text{triethyl amine}}{(C_2H_5)_3N} + HI$$
$$(C_2H_5)_3N + C_2H_5I \longrightarrow \underset{\text{quaternaryethyl amine}}{[(C_2H_5)_4N^+]I^-}$$

At the end of the reaction, the addition of strong alkali such as KOH liberates free amines from their salts, but the quaternary salt is unaffected. The three types of amines are separated by fractional distillation. Using excess ammonia primary amine is produced but the yield is low.

2. By the reductions of nitrogen containing functional groups:

Compounds containing nitrogen such as nitriles, and amides are reduced to amino group by various reducing agents.

(a) Reduction of Nitriles

Reduction of alkyl or aryl nitriles gives primary amines. The reduction may be brought about by reducing agent i.e. $LiAlH_4$, or sodium in ethanol.

$$\underset{\text{Nitrile}}{R-C\equiv N:} + 4[H] \xrightarrow[\text{Reducing agent}]{LiAlH_4} \underset{\text{Amine}}{R-CH_2-NH_2}$$

(b) Catalytic Reduction of nitriles

Nitriles on reaction with hydrogen gas in the presence of catalyst nickel give primary amines.

$$CH_3CH_2C\equiv N + 2H_2 \xrightarrow{Ni} CH_3CH_2CH_2\text{-}NH_2$$

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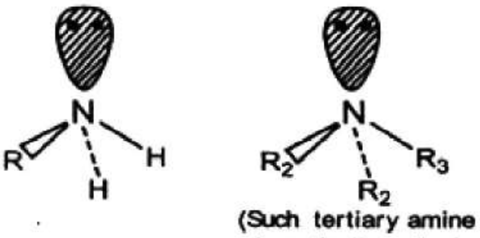
(c). Reduction of Amides

When an amide is treated with reducing agent $LiAlH_4$, -CO group of amide is reduced to $-CH_2$ and the primary amine is formed.

$$CH_3CONH_2 + 2[H] \longrightarrow CH_3CH_2NH_2 + H_2O$$

12.2 Basicity of amines



(Such tertiary amine is optically active)

In amines, the nitrogen atom is sp^3-hybridized and has a nearly tetrahedral structure. It forms three sigma bonds with its three sp^3-hybrid orbitals while the fourth non-bonding sp^3-hybrid carries a pair of electrons.

The lone pair of electrons on the nitrogen atom makes them basic in nature. The lone pair in amines behaves in the same way as in ammonia. When an amine is dissolved in water, the nitrogen lone pair accepts protons from water molecules to produce alkyl ammonium ions and hydroxide ions. The formation of hydroxide ions makes the solution alkaline. So the aqueous solutions of amines are alkaline. However, amines are more basic than ammonia.

$$RNH_2 + H\text{-}OH \longrightarrow [RNH_3]^+ + OH^-$$

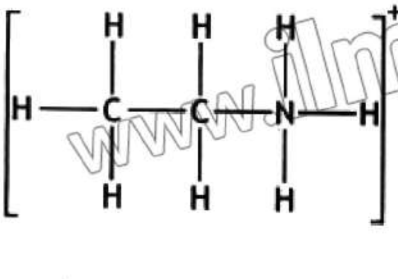
12.2.1 Relative basicities of aqueous ammonia, ethyl amine and phenylamine

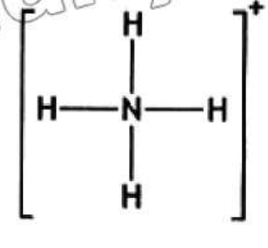
The relative strengths of weak bases are determined from their pK_b values. pK_b values of these bases are as follows;

Base	pK_b
Ammonia	4.75
Ethyl amine	3.27
Phenylamine	9.36

The lower the pKb value the stronger the base. Thus, ethylamine is a stronger base than ammonia, which in turns is stronger than phenylamine. Two factors determine the basic strength of the substrate.

- The ease with which its lone pair can capture the hydrogen ion H^+.
- Stability of the ion formed after receiving the H^+ ion. Ethylamine and ammonia have the following structure.





An ethyl group is an electron-donating group. This increases the electron density of the nitrogen atoms. This makes the nitrogen lone pair more electron-rich and more attractive to hydrogen ions. The ethyl ammonium ion formed which is more stable than the simple ammonium ion formed from *ammonia*. This is because the ethyl group reduces its positive charge.

Both reasons make ethyl amine more basic than ammonia.

Phenyl amine is an aromatic primary amine. The lone pair of electrons on nitrogen is involved in resonance and delocalizing over the ring. So this lone pair can no longer combine with proton, H^+. Thus the intensity of negative charge around the nitrogen atom is much less than in ammonia. Hence, phenylamine is a much weaker base than ammonia. The order of basic ability of these compounds is as follows;

phenylamine < ammonia < ethyl amine

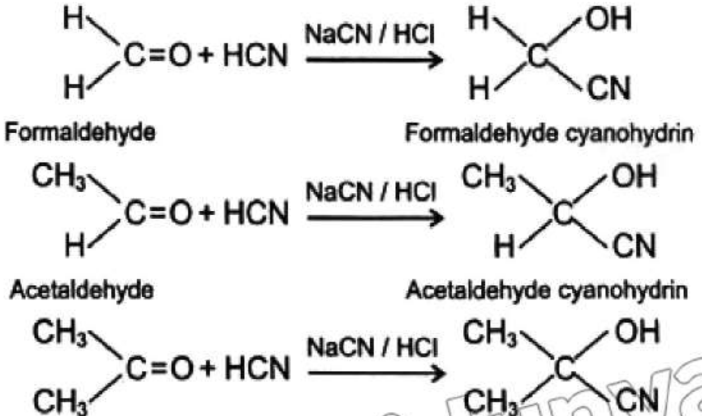
12.3 Formation of Nitriles

1. Recall that nitriles are prepared by heating halogenoalkane and potassium cyanide in ethanol.
   Halogenoalkanes on heating with KCN in ethanol produce alkyl cyanides or nitriles.

$$CH_3Br + KCN \longrightarrow \underset{\text{Cyano methane}}{CH_3CN} + KBr$$

$$CH_3CH_2Br + KCN \longrightarrow \underset{\text{Cyano ethane}}{CH_3CH_2CN} + KBr$$

2. Recall that aldehydes and ketones add hydrogen cyanide across the carbon-oxygen double bond forming compounds known as cyanohydrins. Since, HCN is a highly toxic gas, the aldehyde or ketone is mixed with a solution of KCN in water containing a little HCl. The KCN catalyses this reaction. It reacts with HCl to produce HCN, but the solution still contains some free cyanide ions which catalyze the reaction.



Note that the formation of nitriles results in an increase in the length of the carbon chain because of the extra carbon in the CN group. This reaction is often used in organic synthesis to increase the carbon chain.

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12.4 Hydrolysis of nitriles

Hydrolysis of nitriles can occur with both dilute acid or dilute alkali.

Acid hydrolysis of nitriles

When a nitrile is heated with a dilute acid such as dilute hydrochloric acid or dilute sulphuric acid, a carboxylic acid is formed.

$$\underset{\text{ethanenitrile}}{CH_3CN_{(aq)}} + 2H_2O_{(l)} + HCl_{(aq)} \longrightarrow \underset{\text{ethanoic acid}}{CH_3COOH_{(aq)}} + NH_4Cl_{(aq)}$$

Alkaline hydrolysis of nitriles

When a nitrile is heated with a dilute sodium hydroxide solution, a salt of carboxylic acid is produced, which on acidification with dilute hydrochloric acid gives free carboxylic acid.

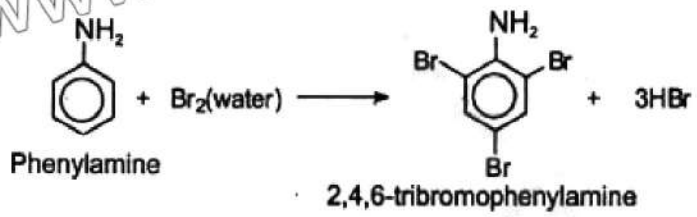
$$CH_3CN_{(aq)} + H_2O_{(l)} + NaOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + NH_{3(g)}$$

$$CH_3COONa_{(aq)} + HCl_{(aq)} \longrightarrow CH_3COOH_{(aq)} + NaCl_{(aq)}$$

12.5 Phenylamine and Azo Compounds

(a) Reaction of phenylamine with bromine water

When bromine water is added to an aqueous solution of phenylamine at room temperature, the reddish-brown colour of bromine is decolourized and a white precipitate of 2,4,6-tribromophenylamine is produced.



(b) Reaction of phenylamine with HNO_2 or $NaNO_2$

(Preparation of Diazonium Salts)

The solution of phenylamine in hydrochloric acid is cooled in ice (below 5 °C). The sodium or potassium nitrite solution is also ice-cooled. The ice-cooled solution of nitrite is slowly added to the phenylamine solution. A solution containing phenyl diazonium chloride is produced. It is also known as benzene diazonium chloride. The temperature of the reaction mixture should never go above 5 °C. Diazonium salts are highly unstable and tend to decompose readily above 10 °C.

Warming its aqueous solution decomposes it to phenol.

$$C_6H_5NH_2 + HNO_2 \xrightarrow{HCl} \underset{\text{Benzene diazonium chloride}}{C_6H_5{-}\overset{+}{N}{\equiv}N\overset{-}{Cl}} + 2H_2O$$

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12.6 Reactions of benzene diazonium chloride

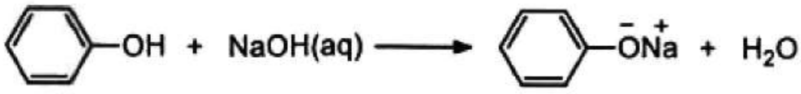
1. Reaction of benzene diazonium chloride with water

Warming of diazonium salt reacts with water to give phenol.

$$C_6H_5\overset{+}{N}\equiv N\overset{-}{Cl} + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$$

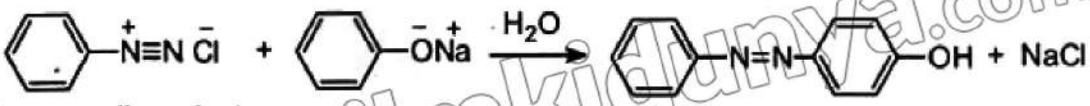
2. Reaction of benzene diazonium chloride with phenol

Recall when phenol is dissolved in sodium hydroxide solution and its ice-cold solution is mixed with ice-cold solution of diazonium chloride. A coupling reaction between phenoxide and diazonium ion takes place producing a yellow-orange solution or precipitate. The product is one of the simplest compounds called azo compounds. These are strongly coloured compounds and are known as azo-dyes. Azo compounds are used as dyes.



phenol

sodium phenoxide

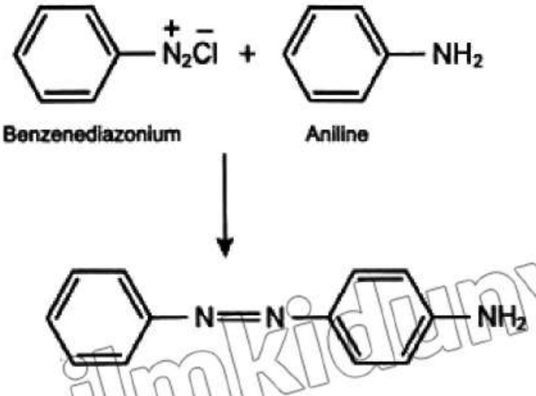


benzenediazonium chloride

(yellow-orange ppt)
p-hydroxyazobenzene
(4-(phenylazo)phenol)

Azo-dyes make up more than 60% of the total dyes. About 70% of all industrial dyes are azo compounds. The -N = N- unit is called an azo group. Compounds containing this functional group are called azo dyes. In azo-dyes, two benzene rings are linked by a nitrogen bridge.

Other dyes can also be produced from diazonium salts via a similar route. For example, when ice cold solution of benzene diazonium chloride is shaken with phenylamine. A yellow solid dye is produced, which is known as aniline yellow.



p-aminoazobenzene
(Azo Derivative)

For more examples see unit 10

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12.7 Preparation of Amides

1. By the reaction of acyl chloride with ammonia

Acyl halides react with ammonia at room temperature to produce amides. The hydroge chloride produced reacts with excess ammonia to give ammonium chloride.

$$CH_3COCl + NH_3 \longrightarrow \underset{\text{ethanamide}}{CH_3CONH_2} + HCl$$

$$HCl + NH_3 \longrightarrow NH_4Cl$$

2. By the reaction of acyl chloride with primary amines

Primary amines react in a similar way as ammonia at room temperature to produce N-substituted amides. The hydrogen chloride reacts with excess amine to give ammonium salt.

$$\underset{\text{ethanoyl chloride}}{CH_3COCl} + \underset{\text{methanamide}}{CH_3NH_2} \longrightarrow \underset{\text{N-methylmethanamide}}{CH_3CONHCH_3} + HCl$$

12.7.1 Reactions of amides

1. Reduction of Amides

When an amide is treated with reducing agent LiAlH$_4$, $-CO$ of amide is reduced to $-CH_2$ and a primary amine is formed. The carbon chain remains intact in this reaction

$$CH_3CONH_2 + 2[H] \longrightarrow CH_3CH_2NH_2 + H_2O$$

2. Hydrolysis of amides

Hydrolysis of amide can occur in both acidic and basic mediums.

(a) Acid hydrolysis of amides

When an amide is heated with dilute acids such as dilute hydrochloric acid or dilute sulphuric acid, a carboxylic is formed.

$$\underset{\text{ethanenitrile}}{CH_3CONH_{2(aq)}} + H_2O_{(l)} + HCl_{(aq)} \longrightarrow \underset{\text{ethanoic acid}}{CH_3COOH_{(aq)}} + NH_4Cl_{(aq)}$$

(b) Alkaline hydrolysis of amides

When an amide is heated with a dilute sodium hydroxide solution, a salt of carboxylic acid is produced with the liberation of ammonia gas. Carboxylic salt on acidification with dilute hydrochloric acid gives free carboxylic acid.

$$CH_3CONH_{2(aq)} + NaOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + NH_{3(g)}$$

$$CH_3COONa_{(aq)} + HCl_{(aq)} \longrightarrow CH_3COOH_{(aq)} + NaCl_{(aq)}$$

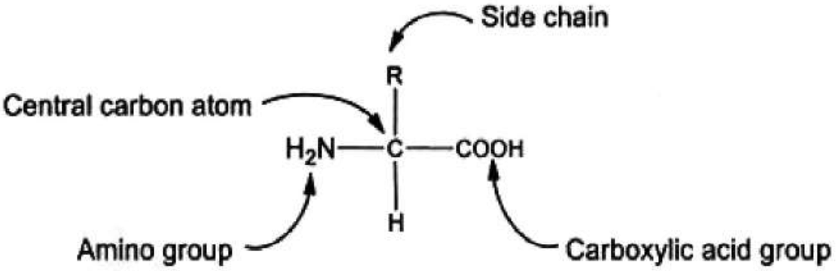
12.7.2 Basicity of amides

Amides are much weaker bases than amines. The amido group has a carbonyl group which is extremely electronegative. It pulls electrons towards it by resonance as well as inductive effect. So, its NH$_2$ group has little protonation ability. In amines, the lone pair of electrons on nitrogen is not delocalized. Moreover, alkyl group tends to increase electron density around nitrogen atoms. So amines have a strong ability to attract proton (H$^+$).

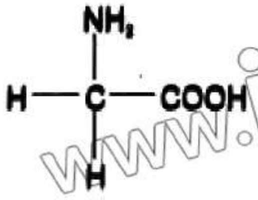
12.8 Amino Acids

The compounds containing an amino group, $-NH_2$, and a carboxylic acid group, $-COOH$ are called *amino acids*

An amino acid has two functional groups. What are those? Amino acids are the building blocks of protein synthesis. Twenty different amino acids are involved in protein synthesis. Out of twenty amino acids, our bodies can synthesize only ten amino acids. Such amino acids are called **non-essential amino acids.** The remaining ten are called **essential amino acids.** Essential amino acids must be present in our diet. Why? The general formula for an amino acid is:

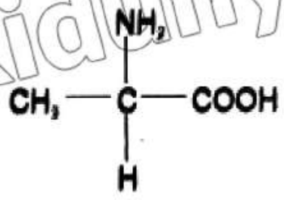


The amino acids generally have the amino group attached to the carbon atom next to the $-COOH$ group. They are known as 2-amino acids or alpha-amino acids.



$$H-\overset{NH_2}{\underset{H}{C}}-COOH$$

2-aminoethanoic acid



$$CH_3-\overset{NH_2}{\underset{H}{C}}-COOH$$

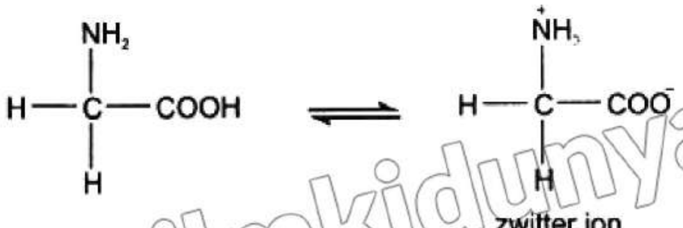
2-aminopropanoic acid.

12.8.1 Physical properties of amino acids

An amino acid has both a basic amine group and an acidic carboxylic acid group.

There is an internal transfer of a hydrogen ion from the $-COOH$ group to the $-NH_2$ group to leave an ion with both a negative and a positive charge. This is called a ***zwitter ion***.

A zwitterion has no overall electrical charge but contains separate parts which are positively and negatively charged.



$$H-\overset{NH_2}{\underset{H}{C}}-COOH \rightleftharpoons H-\overset{\overset{+}{N}H_3}{\underset{H}{C}}-COO^-$$

This is the form that amino acids exist in even in the solid state. In amino acids, the intermolecular forces are much stronger ionic attractions between one ion and its neighbours. These ionic attractions need more energy to break and so the amino acids have high melting points.

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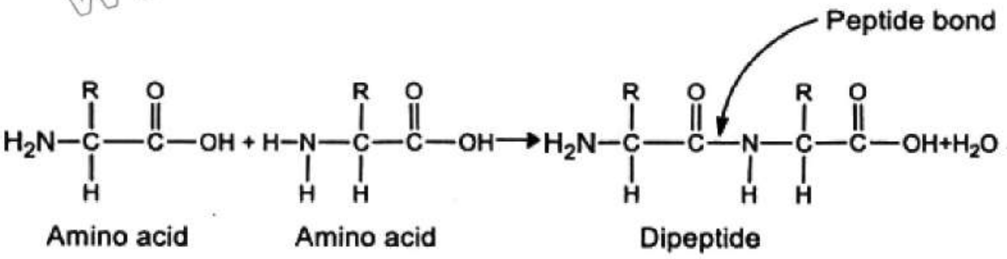
12.8.2 Formation of peptide bond

Molecules of amino acids join through the amino (-NH_2) group of one molecule and the carboxyl (-COOH) group of another molecule by eliminating a water molecule.



$$H_2N-\overset{R}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH + H-\underset{H}{N}-\overset{R}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH \rightarrow H_2N-\overset{R}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\overset{R}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH+H_2O$$

The linkage $-\overset{O}{\overset{\|}{C}}-NH-$ which joins two amino acid units is called a **peptide bond.** The resulting molecule is called a dipeptide. There is still an amino group on the left and a carboxyl group on the right. Each of these groups can react further to join more amino acid units. When a dipeptide combines with another amino acid molecule, the resulting molecule is called a tripeptide. In this way, thousands of amino acid units join to form a giant protein molecule.

12.8.3 Behaviour of amino acids and dipeptides in an electric field

Electrophoresis is a technique that can be used to separate charged molecules, such as amino acids and peptides. This method takes advantage of the movement of these molecules in the presence of an electric field. The speed at which these molecules move in the electric field is influenced by the pH of the medium. With the pH of the medium, the degree of ionization of amino acids changes. At the cathode, amino acids usually exist in the protonated state (as $-NH_3^+$) and move towards it at low pH. When the pH is high, amino acids exist in their deprotonated state (COO^-). As a result, they migrate towards the positive anode. The movement of dipeptides in an electric field depends on the net charge on the molecules, similarly. Altering the pH changes the charge on amino acid and dipeptide molecules.

KEY POINTS

- When an ethanolic solution of ammonia is heated with an alkyl halide in a sealed tube at 100°C, we get a mixture of amines together with their salts.
- The reduction of alkyl or aryl nitriles gives primary amines.
- When an amide is treated with reducing agent $LiAlH_4$, $-CO$ group g of amide is reduced to $-CH_2$, and a primary amine is formed.
- The lower the pKb value the stronger the base
- Halogenoalkanes on heating with KCN in ethanol produce alkyl cyanides or nitriles
- When a nitrile is heated with dilute acids such as dilute hydrochloric acid or dilute sulphuric acid, a carboxylic is formed.
- Acyl halides react with ammonia at room temperature to produce amides.

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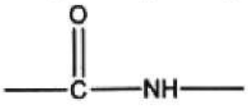
- When an amide is treated with reducing agent $LiAlH_4$, $-CO$ of amide is reduced to $-CH_2$ and primary amine is formed.
- When an amide is heated with a dilute sodium hydroxide solution, a salt of carboxylic *acid* is produced with the liberation of ammonia gas.
- The compounds containing an amino group, $-NH_2$, and a carboxylic acid group, $-COOH$ are called amino acids.
- A zwitterion has no overall electrical charge but contains separate parts which are positively and negatively charged.
- The linkage  $-\overset{\overset{\displaystyle O}{\|}}{C}-NH-$ which joins two amino acid units is called a **peptide bond.**

EXERCISE

1. Multiple Choice Questions (MCQs)

i. What is the reagent and condition used to convert halogenoalkanes to primary amines?
   a) NH_3 in ethanol, heated under pressure
   b) H_2SO_4 in water, room temperature
   c) $LiAlH_4$ in dry ether, reflux
   d) KOH in ethanol, heated under pressure

ii. Which of the following produces hydroxyl nitriles from aldehydes and ketones?
   a) H_2O, H_2SO_4, heat
   b) HCN, KCN as a catalyst, heat
   c) NH_3 in ethanol, heated under pressure
   d) Br_2, light, room temperature

iii. Which reaction is used to produce secondary amines from halogenoalkanes?
   a) Reaction with ammonia in ethanol
   b) Reaction with primary amines in ethanol
   c) Reaction with $LiAlH_4$
   d) Reaction with HCN and KCN

iv. Which reagent is used to convert nitriles to primary amines?
   a) H_2O, HCl, reflux b) H_2/Pt, room temperature
   c) H_2/Ni or $LiAlH_4$ d) Br_2, room temperature

v. What is the final product of the hydrolysis of nitriles with dilute acid?
   a) Alcohol b) Ketone c) Carboxylic acid d) Aldehyde

vi. What is the structure of the azo group in azo compounds?
   a) $R_1\text{-}N{=}N\text{-}R_2$ b) $R_1\text{-}C{\equiv}N\text{-}R_2$ c) $R_1\text{-}NH_2\text{-}R_2$ d) $R_1\text{-}O\text{-}R_2$

vii. What product is formed when phenylamine reacts with $Br_{2(aq)}$ at room temperature?
   a) Phenol b) Phenylamine bromide
   c) 2,4,6-tribromophenylamine d) An azo compound

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viii. What is the basicity order among aqueous ammonia, ethylamine, and phenylamine?
   a) Ethylamine > Aqueous ammonia > Phenylamine
   b) Phenylamine > Ethylamine > Aqueous ammonia
   c) Aqueous ammonia > Ethylamine > Phenylamine
   d) Aqueous ammonia > Phenylamine > Ethylamine

ix. What happens when benzenediazonium chloride reacts with phenol in $NaOH_{(aq)}$?
   a) Formation of phenylhydrazine
   b) Formation of an azo compound
   c) Formation of a nitro compound
   d) Formation of an ester

x. What is the role of peptide bonds in proteins?
   a) Provide structural support   b) Store energy
   c) Link amino acids   d) Bind with DNA

xi. Hydrolysis of nitriles with dilute acid produces:
   a) Amides   b) Carboxylic acids   c) Alcohols   d) Amines

xii. Phenylamine reacts with $Br_{2(aq)}$ at room temperature to give:
   a) Trihalogenated product   b) Monohalogenated product
   c) Dihalogenated product   d) No reaction

2. Short Answer Questions

i. Explain the conditions and reagents required for the reaction between a halogenoalkane and KCN to form a nitrile.

ii. Describe the hydrolysis of amides using aqueous acid or aqueous alkali. What is the final product of this reaction?

iii. Discuss the reaction of phenylamine with HNO_2 and dilute acid below 5°C. What is the major product formed?

iv. Describe the acid-base properties of amino acids and how they can form zwitterions.

v. Explain why amides are much weaker bases than amines. What structural aspect contributes to this difference?

vi. Compare the basicity of aqueous ammonia, ethylamine, and phenylamine, and explain the observed trends

   i. Outline the steps and conditions required to hydrolyze a nitrile to a carboxylic acid using dilute acid.

   ii. Describe the hydrolysis of an amide under acidic and basic conditions.

vii. Predict the results of electrophoresis on mixtures of amino acids at pH 3 and pH 11.

   i. Compare the reduction of nitriles and amides using $LiAlH_4$.

   ii. Analyse the significance of diazonium salts in synthetic organic chemistry.

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3. Long Answer Questions

i. Describe the steps and conditions involved in the hydrolysis of nitriles with dilute acid or alkali followed by acidification. What is the final product of this reaction?

ii. Explain the relative basicities of aqueous ammonia, ethylamine, and phenylamine. What factors contribute to these differences in basicity?

iii. Discuss the formation of amide (peptide) bonds between amino acids to give di- and tripeptides. What role do these bonds play in biological systems?

iv. Describe the reaction of phenylamine with HNO_2 and dilute acid below 1°C to produce the diazonium salt. What is the significance of this reaction in organic chemistry?

v. Predict the results of electrophoresis on mixtures of amino acids and dipeptides at different pH. What changes might you observe at different pH, and why?

vi. Describe the acid-base properties of amino acids and the formation of zwitterions. Discuss the significance of zwitterions in the behavior of amino acids in different pH environments.

vii. Describe the formation of amide (peptide) bonds between amino acids to give di- and tripeptides

viii. Predict and explain the results of electrophoresis on mixtures of amino acids and dipeptides at different pH. Discuss how the charge and size of the molecules affect their migration during electrophoresis.

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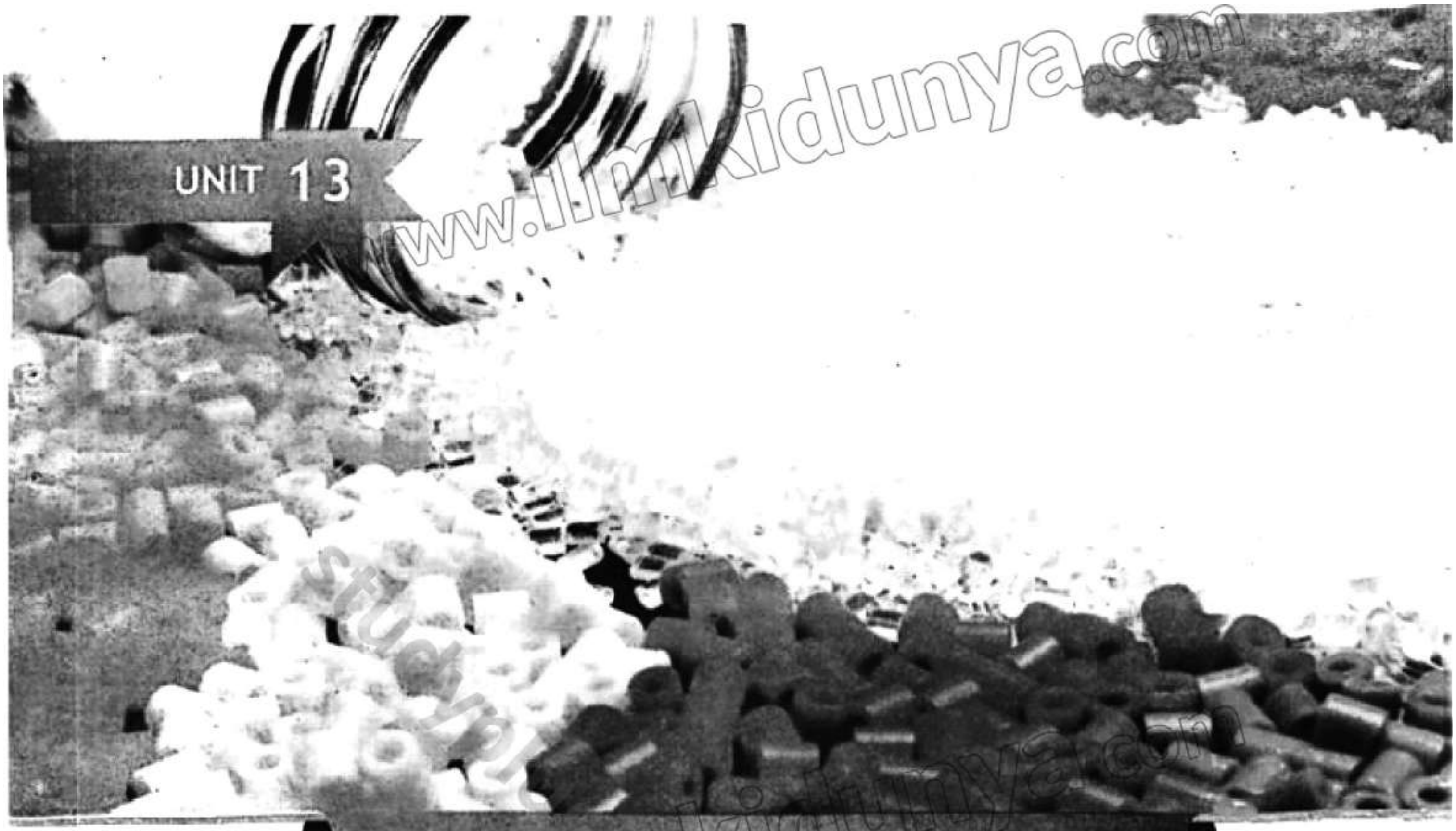
UNIT 13



POLYMERS

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Student Learning Outcomes (SLOs)

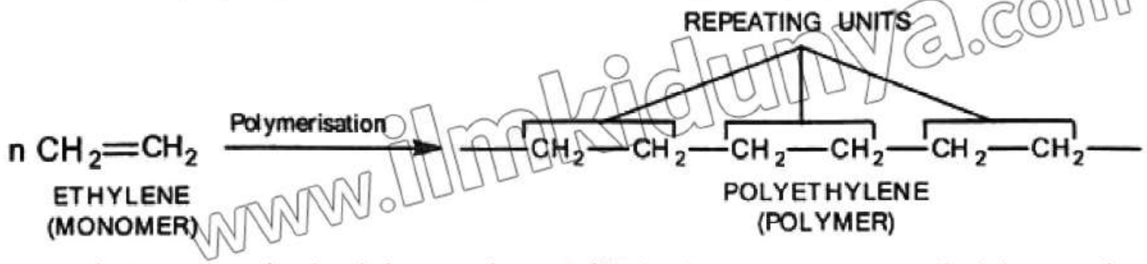
- Explain the chemical processes and properties of PVC and nylon, and the applications of these polymers in the industry.
- Describe the condensation reaction of ammonia or an amine with an acyl chloride at room temperature to give an amide.
- Discuss the importance of chemical industries in the economy of Pakistan, and describe the raw materials that are available in the country for various chemical industries.
- Describe the chemical processes of addition and condensation polymerization and the differences between them. Examples include:
  - a) addition polymers such as polyethene and polychloroethene, PVC,
  - b) polyesters (from reactions of diols and dicarboxylic or dioyl acid, and from hydroxycarboxylic acid),
  - c) polyamides (from reactions of a diamine and a dicarboxylic acid, or between amino acids.
- Identify the polymer formed, the monomer present in a section of polymer, and classify them as one of the two polymers.
- Deduce the repeating unit of a polymer obtained from a given monomer or pair of monomers and identify the monomes present in a given section of a polymer molecule.
- Predict the type of polymerization reaction for a given monomer or pairs of monomers.

- Explain the challenges associated with the disposal of non-biodegradable polymers.
- Recognise that poly(alkenes) are chemically inert and can therefore be difficult to *biodegrade*.
- Recognise that some polymers can be degraded by the action of light.
- Recognise that polyesters and polyamides are biodegradable by acid and alkaline hydrolysis.
- Outline the use of polymers to create artificial organs in biomedical science.

13.1 Synthetic Polymers

Polymers are high molecular weight compounds whose structures are made up of a large number of simple repeating units. The repeating units are usually obtained from low molecular weight simple compounds referred to as monomers. The reaction by which monomers are converted into polymers is known as polymerization.

The formation of polyethylene from ethylene is an example of polymerisation reaction.



Polymers that are synthesized from only one kind of monomer are called homopolymers. Polymers that are prepared from more than two different monomers are called copolymers. Polymers made up of three different monomers are called terpolymers.

13.2 Classification of Polymers

There are two main types of polymers: Addition polymers and Condensation polymers.

1. Addition Polymers

Addition polymers are formed by combining alkene monomers, resulting in just one huge molecule. These reactions are catalysed by peroxides or acids. The reactions require a pressure of 1000 atmospheres at 2000 °C. With the so-called Ziegler catalysts, which consist of trialkylaluminum $Al(R)_3$ and titanium tetrachloride $TiCl_4$ in an inert solvent, much lower temperatures and pressures can be used.

The polymer backbone consists of carbon atoms that originally formed a double bond. Nothing is lost. Monomers add to each other.

For example, polyvinyl chloride (PVC) is obtained by polymerization of vinyl chloride. PVC is used to manufacture artificial leather, floor coverings, corrugated roofing materials and gramophone records.

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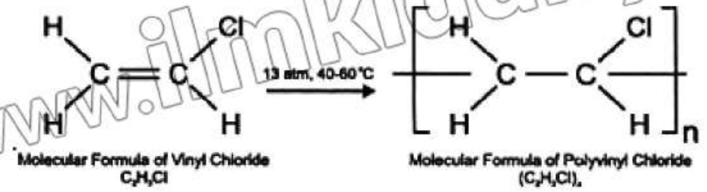


Vinyl chloride is obtained from acetylene by treatment with HCl in the presence of $HgCl_2$.

$$HC\equiv CH + HCl \xrightarrow{HgCl_2} CH_2{=}CH{-}Cl$$

Acetylene Vinyl chloride

2. Condensation Polymers

Condensation polymers are formed by the combination of monomers with the elimination of simple molecules such as H_2O, NH_3 or ROH. There are two main types of condensation polymers: Polyesters and Polyamides.

(a) Polyamides

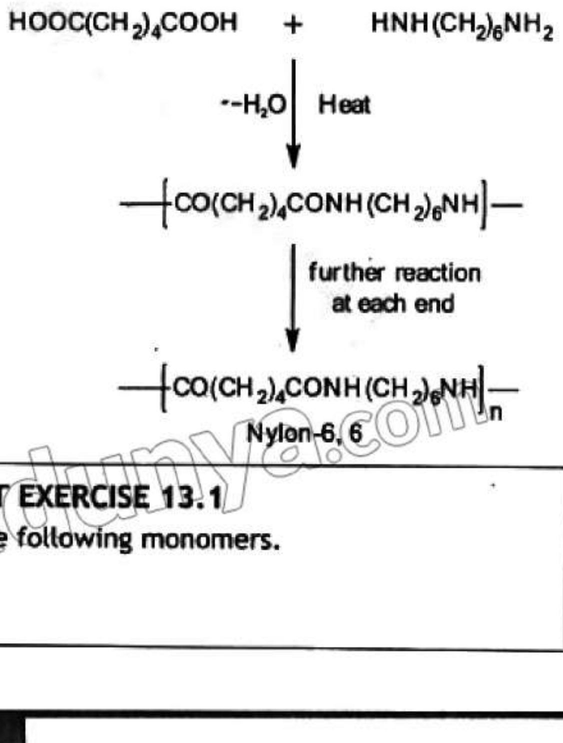
Polyamides can be made from a variety of different reactants.

(i) Nylon-6,6

Here's an example of making a polyamide from a diamine and a dicarboxylic acid. A hydroxyl (-OH) group from the dicarboxylic acid reacts with a hydrogen atom from one of the diamine's amine groups, forming water. This results in an amide linkage between the diamine and the dicarboxylic acid. Because both molecules have two functional groups, one at each end, the process happens again. This creates a long polyamide polymer chain. This polyamide is called Nylon-6,6.

It is obtained by heating adipic acid with hexamethylene diamine under nitrogen at 2000C. Nylon-6,6 derives its name from its starting materials, adipic acid and hexamethylene diamine, which have six carbons.

Nylon-6,6 was developed as a synthetic fiber for the production of stocking and other apparel. It was introduced to the public at the New York World's Fair in 1939. It is also used to make fibers for clothing and carpeting, filaments for fishing lines and ropes, bristles for brushes, and moulded objects such as gears and bearings.



CONCEPT ASSESSMENT EXERCISE 13.1

Predict the type of polymerisation reaction for the following monomers.

(i) Propylene $CH_3{-}CH{=}CH_2$

(ii) HO-A-OH + HOOC-B-COOH

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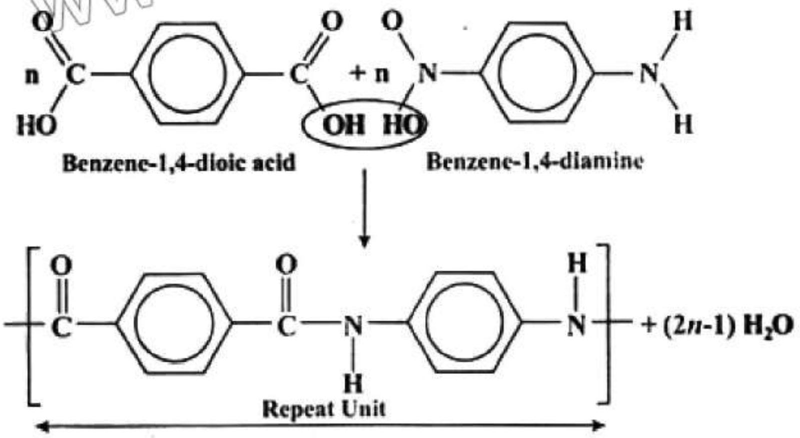
(ii) Kevlar

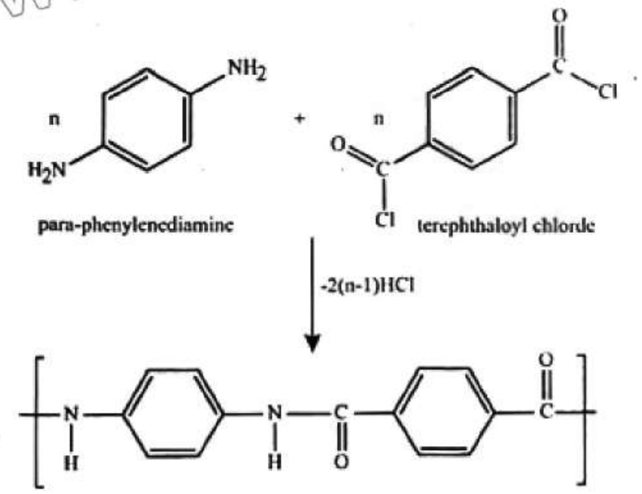
Kevlar is another polyamide. Its monomers are, benzene-1,4-dicarboxylic acid and benzene-1,4-diamine.



Kevlar is a strong and light weight polymer. It is woven into textile materials which is light weight, strong, corrosion and heat resistant. It is used for making bullet and fireproof vests, crash helmets, body of aircraft, boats etc.

CONCEPT ASSESSMENT EXERCISE 13.2

A polymer can be made from monomers benzene-1,4- dioyl chloride and benzene-1,4-diamine. Draw its repeat unit.



Kevlar

(iii) Poly peptide

Poly peptide is produced by the polymerisation of amino acid molecules. The bond between two amino acid molecules is produced with the elimination of water molecules.

$$n\,NH_2\text{-}CH_2\text{-}COOH + n\,NH_2\text{-}CH_2\text{-}COOH \rightarrow [\text{-}NH\text{-}CH_2\text{-}COO\text{-}NH\text{-}\ COO\text{-}]_n + 2(n\text{-}1)\ H_2O$$

aminoetanoic acid polypeptide

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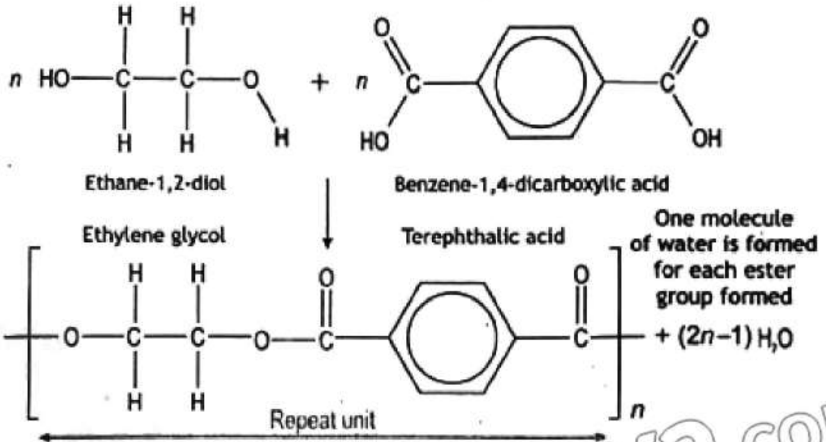
(b) Polyesters

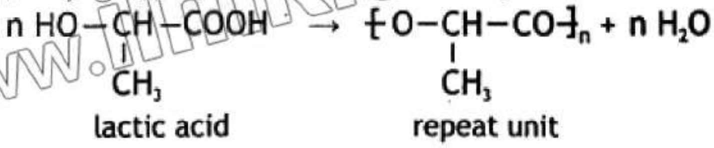
Polyesters are produced by the condensation of diols and dicarboxylic acids. For example,

(i) **Terylene:** The most common polyester is called terylene. It is also known as polyethylenetere phthalate (PET). It is made from monomers, ethane-1,2-diol and benzene-1,4-dicarboxylic acid.



(iv) **Polymerisation of hydroxycarboxylic acid.**

Hydroxy carboxylic acids also form polyesters. For example, polylactic acid. It is made from a monomer, 2-hydroxypropanoic acid (lactic acid).



$$n\,HO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH \rightarrow \left[O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CO\right]_n + n\,H_2O$$

lactic acid repeat unit

CONCEPT ASSESSMENT EXERCISE 13.3

Draw the monomer that makes the following condensation polymer.

$$[-O-CH_2-CH_2-CO-]_n$$

Polyester readily react with alkalis but slowly with acids. Terylene is used for making plastic bottles, clothing and carpets.

13.4 Biodegradable and Non-biodegradable Polymers

The polymers which can be decomposed by the action of microorganisms are called biodegradable polymers. For example, polyamides and polyesters. These polymers have hydrolysable amino or ester groups which can easily be broken by enzymes, acids, and alkalis.

The polymers which cannot be decomposed by the action of microorganisms are called non-biodegradable polymers. Polymers formed from addition polymerisation are unreactive or inert as they are non-polar and saturated. This makes it difficult to break down and biodegrade. Some can be recycled to form new polymers for a different purpose.

For instance, polyethylene, polypropylene, polyvinyl chloride, and polyethylene terephthalate (PET). These polymers contain long chains of carbon atoms which are chemically inert. They

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have non-polar bonds. These polymers are causing harm to the environment as they can remain intact over the years. They can also enter our food chain.

Some polymers can be degraded by ultraviolet light. For example, polyethylene, polypropylene, and polystyrene. Ultraviolet light breaks down the polymer chains and leads to the weakening of materials.

13.4.1 Long term effects of non-biodegradable polymers.

Non-biodegradable polymers accumulate in the environment. They do not decompose naturally. These materials in the presence of sunlight, water, and air produce highly toxic pollutants. These pollutants can enter the water and cause water pollution.

13.5 Polymer Hydrolysis

Condensed polymers can be broken down by hydrolysis reactions. This can be done under acidic or basic conditions.

For polyesters, the hydrolysis products are

(a) Acid hydrolysis (with hydrochloric acid catalyst) - diol and dicarboxylic acid
(b) Alkaline hydrolysis (heated with sodium hydroxide) - diol and carboxylic acid salt

For polyamides, the hydrolysis products are

(a) Acid hydrolysis - dicarboxylic acid and ammonium ions
(b) Alkaline hydrolysis - sodium salts of its monomers (dicarboxylic acid salt and diamine).

When proteins are hydrolyzed by acid, amino acids are formed, but the amine group accepts a proton to become $-NH_3^+$.

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13.6 Artificial Organs

Artificial organ is a biological device or tissue created by scientists to replace, replicate, or augment a functional naturally occurring organ. Artificial organs can be used as a substitute for organ donors and as a medical education tool. Types of Artificial Organs There are three main types of artificial organs, depending on the material scientists use to create them.

1. **Mechanical Artificial Organs:** Mechanical artificial organs are entirely made of non-living polymers like plastics and metals.
2. **Biomechanical Organs**: Biomassical organs contain both Living Cells and Non-Living Materials. Biological organs or Biosynthetic organs can be transformed from living cells to Biomass.
3. **Biological Organs:** Biological organs are specialized structures within living organisms that perform specific functions in our body. They are composed of different tissues that work together to carry out particular tasks. For example, heart, lungs, liver, brain, kidneys etc. They are part of larger organ systems, such as the digestive, respiratory, circulatory, and nervous systems, which coordinate to support life processes. Each organ contributes to the overall function of the organism in a precise and interdependent way.

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13.7 Importance of Chemical Industries

The chemical industry is a major contributor to Pakistan's economy. It is accounting for around 4.5 % of the country's total exports and 12% of its total imports. It is also a key factor in the growth of forward-oriented industries such as Pakistan's automobile industry, textiles and leather goods, shoes, furniture, food and beverages, etc. On the other hand, chemicals are also used in backward-oriented industries like surfactants which are essential for oil refiners and extractors. Pakistan's chemical industry has experienced rapid growth in recent years due to various factors such as rising domestic demand, improved raw material availability, improved government policies, increased foreign investment, advances in technology, and increased regional integration. Therefore, the chemical industry is influencing international trade and increasing economic competitiveness.

13.7.1 The list of raw materials used in chemical industry in Pakistan

The main raw materials are fossil fuels (coal, natural gas, and oil), air, water, salt, limestone, sulphur, and specialized raw materials such as phosphates and fluorides.

Pakistan also has mineral deposits such as coal, copper, gold, chromite, mineral salt, bauxite, and many other minerals. Various precious and semi-precious minerals are also mined.

Some of the main raw materials used in the chemical industry in Pakistan are:

Soapstone

It is one of the main raw materials in the chemical industry of Pakistan. 85% of it is also used in other industries like textiles, paper, soap, detergents, leather, food, etc.

Polyvinyl chloride (PVC)

In Pakistan, PVC is mainly used for the production of pipes, fittings, cables, profiles and footwear. It is also used in medical devices, packaging materials, and consumer products. PVC demand is driven by the construction industry, which accounts for approximately 70% of total consumption.

Resin

Resin is a synthetic organic polymer used to make plastics, adhesives, paints, coatings, and other products. Resin production is mainly based on petrochemical raw materials such as petroleum, ethylene, and propylene.

Soda Ash

Soda ash is the common name for sodium carbonate, which is used to make glass, detergents, paper, textiles, and other products. Pakistan is mainly based on natural resources such as rock salt and limestone.

Hydrogen Peroxide

This chemical compound is used for bleaching, disinfecting, oxygenating and other applications. In Pakistan, the production of hydrogen peroxide is largely based on imported raw materials such as anthraquinone and hydrogen gas.

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KEY POINTS

- Polymers are high molecular weight compounds whose structures are made up of. a large number of simple repeating units.
- The reaction by which monomers are converted into polymers is known as polymerization.
- Polymers that are synthesized from only one kind of monomer are called homopolymers.
- Polymers that are prepared from two different monomers are called copolymers.
- Addition polymers are formed by combining alkene monomers, resulting in just one huge molecule.
- Condensation polymers are formed by the combination of monomers with the elimination of simple molecules such as H_2O.
- Polyesters and Polyamides are condensation polymers
- Poly peptide is produced by the polymerisation of amino acid molecules.
- Polyesters are produced by the condensation of diols and dicarboxylic acids.
- Polyamide are produced by the condensation of diamines and dicarboxylic acids.
- The polymers which can be decomposed by the action of microorganisms are called biodegradable polymers.
- The polymers which cannot be decomposed by the action of microorganisms are called non-biodegradable polymers.
- Ultra violet light breaks down the polymer chains and leads to weakening of materials.
- Artificial organ is a biological device or tissue created by scientists to replace, replicate, or augment a functional naturally occurring organ.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which polymer is produced by polymerizing vinyl chloride?

a) Nylon b) Polyethylene c) PVC d) PET

ii. What small molecule is typically released during the formation of an amide from an amine and an acyl chloride?

a) Water b) Methane c) Hydrogen chloride d) Oxygen

iii. Which raw material is abundantly available in Pakistan for the fertilizer industry?

a) Limestone b) Natural gas c) Coal d) Iron ore

iv. What type of polymerization involves monomers with double bonds?

a) Addition polymerization b) Condensation polymerization
c) Radical polymerization d) Ionic polymerization

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v. Which of the following is an example of a polyamide?

a) PET b) Nylon c) PVC d) Polyethylene

vi. Which polymer can be degraded by hydrolysis?

a) Polyethylene b) PVC c) Nylon d) Polypropylene

vii. In what form is PVC often used in medical applications?

a) Rigid form b) Flexible form c) Foam form d) Powder form

viii. Which reaction forms a polyester?

a) Ethylene + chlorine b) Ethylene glycol + terephthalic acid

c) Hexamethylenediamine + adipic acid d) Propylene + ammonia

ix. Which polymerization method produces polyethylene?

a) Addition polymerization b) Condensation polymerization

c) Anionic polymerization d) Cationic polymerization

x. What is a common use of nylon in the textile industry?

a) Insulation b) Gears c) Clothing d) Packaging

2. Short Answer Questions

i. Explain the process of producing PVC from vinyl chloride.

ii. Describe the chemical reaction between an amine and an acyl chloride to form an amide.

iii. How do chemical industries contribute to the economy of Pakistan?

iv. Identify the raw materials available in Pakistan for the chemical industry.

v. Differentiate between addition and condensation polymerization.

vi. What are the environmental challenges associated with non-biodegradable polymers?

vii. How can polyesters and polyamides be degraded?

viii. What are the properties of nylon that make it suitable for use in textiles?

ix. Describe an application of polymers in biomedical science.

x. How is the disposal of poly(alkenes) challenging due to their chemical properties?

xi. Why is the hydrolysis of polyesters in an acidic environment faster than in a neutral environment?

xii. Compare the environmental benefits of using biodegradable polymers over traditional synthetic polymers

xiii. Predict the environmental impact of the widespread use of non-biodegradable polymers on marine ecosystems.

3. Long Answer Questions

- i. Discuss the synthesis, properties, and applications of PVC.
- ii. *Discuss the process of* producing nylon-6,6 and its applications in various industries.
- iii. Describe the importance of chemical industries in Pakistan and the raw materials available for these industries.
- iv. Compare and contrast addition and condensation polymerization with suitable examples.
- v. Explain the environmental impact of non-biodegradable polymers and suggest ways to mitigate these challenges.
- vi. Compare and contrast the chemical properties, production processes, and industrial applications of PVC and nylon, highlighting how these factors influence their respective environmental impacts and recycling potentials.
- vii. Differentiate between addition and condensation polymerization processes, using specific examples such as polyethylene, PVC, polyesters, and polyamides.
- viii. Give a variety of polymer structures, identify the monomers and classify each polymer as either an addition or condensation polymer.
- ix. Analyse the role of polymers in biomedical science, particularly in the creation of artificial organs. Discuss the properties required for polymers used in biomedical applications and the challenges associated with their development and use.
- x. Compare the environmental impact of the production and disposal of PVC and nylon, considering factors such as energy consumption, emissions, and waste management practices.

THINK TANK

1. Predict the type of polymerization reaction for a given set of two different monomers and justify your reasoning.
2. Evaluate the potential benefits and drawbacks of using polymers to create artificial organs.

Project

Propose a strategy for managing the disposal of non-biodegradable polymers in an environmentally friendly manner.

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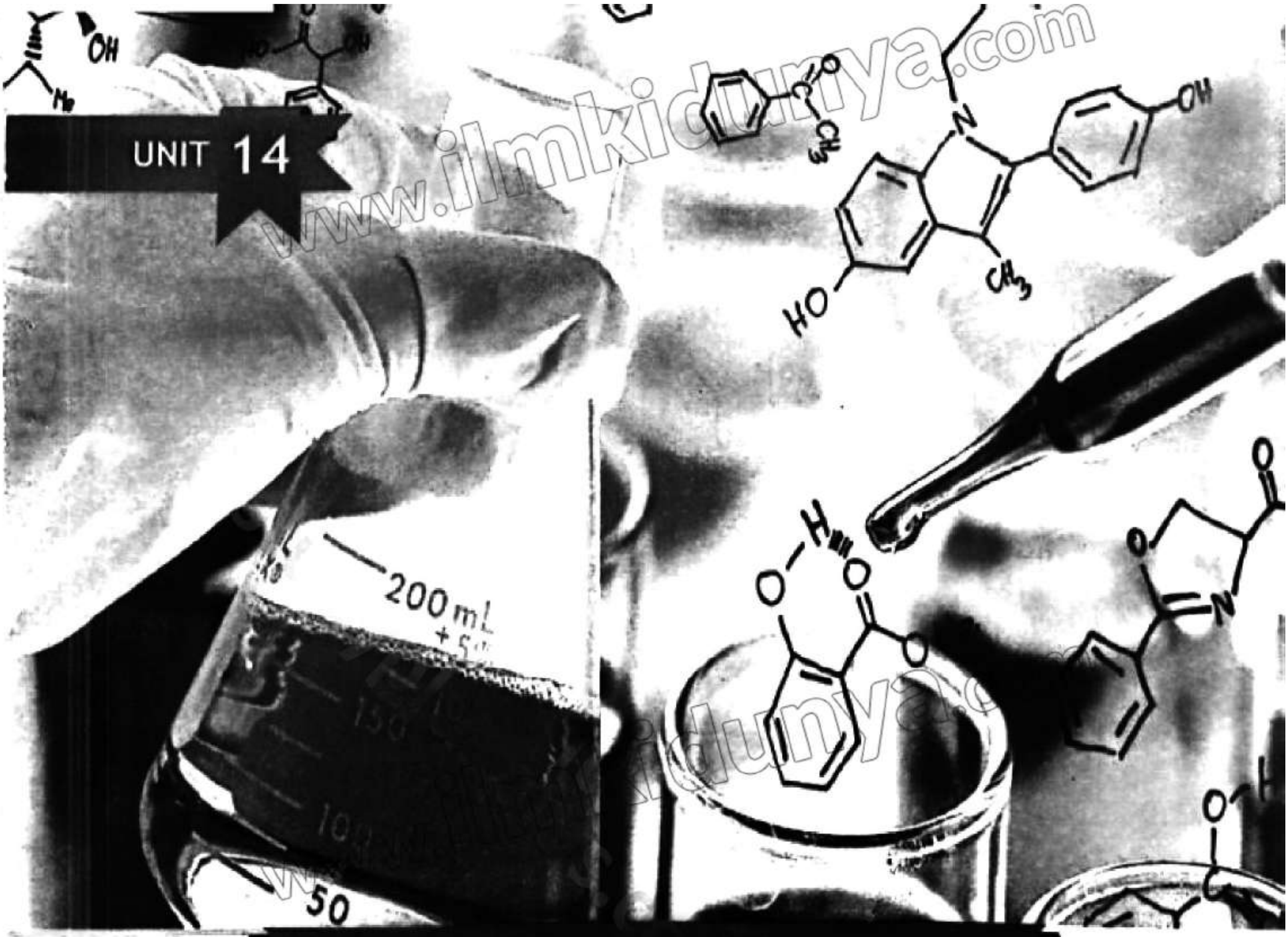
UNIT 14



ORGANIC SYNTHESIS

Artificial Intelligence In Organic Synthesis

Student Learning Outcomes (SLOs)

- Describe the use of Artificial Intelligence tools in designing organic molecules which may have the potential to be used as medicine (halicin can be used as an example).

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14.1 Influence of Artificial Intelligence on Pharmaceutical Research

Artificial intelligence (AI) has greatly influenced the area of pharmaceutical research and development, especially in the production of natural compounds with possible uses in medicine.

AI tools are being used in the pharmaceutical research due to the following advantages.

1. Data-driven discovery

AI can process vast amounts of chemical, biological, and pharmacological data to identify potential drug candidates. For example, hallicin was discovered using an artificial intelligence model trained on a dataset of known medicinal compounds. The model predicted the antibacterial properties of Halicin, which were not previously identified for this purpose.

2. Virtual Screening

Artificial intelligence (AI) technologies can conduct online screening of extensive collections of chemical compounds to pinpoint those that might interact with particular biological entities. This speeds up the initial stages of drug development, narrowing down the pool of possible candidates from millions to a more feasible size. In the case of Halicin, the AI algorithm examined over 100 million molecules across the ZINC15 database.

3. Molecular Generation

Generative models such as VAE (variable autoencoder) and generative adversarial networks (GAN) can generate new molecules with desired properties. These AI models learn the underlying patterns of chemical structures and create new compounds that can be synthesized and tested. These tools are particularly useful for exploring chemical states outside of known compounds.

4. Optimizing lead compounds

Artificial intelligence can help optimize lead compounds by predicting how changes in their chemical structure will affect their performance, stability and safety. This iterative process of design and testing is accelerated by AI's ability to predict features and recommend improvements.

5. Prediction of biological activity and toxicity

Machine learning algorithms can forecast the biological behaviour of substances and their possible toxicity, minimizing the necessity for thorough laboratory and animal testing. Through examining molecular configurations and relating them to existing information, machine learning can identify potentially dangerous substances at an early stage in their creation. Additionally, machine learning can aid in understanding how new medications work. By examining how potential drugs interact with living systems, machine learning can propose the molecular impacts of these drugs, which can inform subsequent enhancements and progress.

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14.2 Case Study: Hallicin

Hallicin was originally developed as a diabetes drug. It has been introduced as an antibiotic by artificial intelligence. The Massachusetts Institute of Technology (MIT) Cambridge researchers used a deep learning model trained on the molecular structures and bioactivity data of thousands of compounds. The model identified helicin as a potential antibiotic because of its predicted ability to disrupt bacterial cell membranes. This prediction was confirmed by laboratory tests that showed the effectiveness of hallicin against many antibiotic-resistant bacteria.

The success of Halicin underscores the power of AI to identify and optimize new drugs. We can hope for more efficient and effective development of therapeutics in the future.

14.3 Advantages of AI in drug development

Use of AI in drug development has following advantages

Speed: AI significantly reduces the time needed to find new drug candidates.

Cost-effectiveness: By narrowing down the list of potential candidates in a timely manner, AI reduces the costs associated with experimental testing.

Innovation: AI can investigate new chemical states that traditional methods may not account for, leading to the discovery of entirely new classes of drugs.

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KEY POINTS

- AI can process vast amounts of chemical, biological, and pharmacological data to identify potential drug candidates.
- Artificial intelligence (AI) technologies can conduct online screening of extensive collections of chemical compounds to pinpoint those that might interact with particular biological entities.
- Artificial intelligence can help optimize lead compounds by predicting how changes in their chemical structure will affect their performance, stability and safety.
- Hallicin was originally developed as a diabetes drug. It has been introduced as an antibiotic by artificial intelligence.
- AI significantly reduces the time needed to find new drug candidates.
- AI reduces the costs associated with experimental testing.

  References for futher studies
  - "AI: A Very Short Introduction" by Margaret A. Boden ".
  - Website: Blockly

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EXERCISE

1. Multiple Choice Questions (MCQs)

i. What is the primary function of AI in drug discovery as exemplified by the discovery of Halicin?

a) Manufacturing drugs b) Predicting biological activity and toxicity
c) Performing virtual screening d) Both B and C

ii. What was Halicin originally developed for before being repurposed as an antibiotic?

a) Cancer treatment b) Diabetes
c) Cardiovascular disease d) Alzheimer's disease

iii. Which database was used to screen molecules when discovering Halicin?

a) PubChem b) DrugBank c) ZINC15 d) ChemSpider

iv. What advantage does AI offer in the early stages of drug discovery?

a) Increased manufacturing speed b) Reduction in the need for clinical trials
c) Cost-effective narrowing down of potential candidates
d) Ensuring drug approval from regulatory bodies

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v. What was the original purpose of the compound Halicin before its antibiotic properties were discovered?

a) An anti-inflammatory agent b) A diabetes drug
c) A painkiller d) A cholesterol-lowering drug

2. Short Answer Questions

i. What is the significance of AI in predicting the biological activity and toxicity of compounds?

ii. Explain how AI models help in the optimization of lead compounds during drug discovery.

iii. Describe the process of virtual screening and its importance in the context of AI-driven drug discovery.

iv. What role did the deep learning model play in the discovery of Halicin as an antibiotic?

v. Why is MIT notable in the field of AI and drug discovery?

3. Long Answer Questions

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i. Discuss the various stages of drug discovery where AI tools are utilized, providing examples for each stage. How does AI improve the efficiency and effectiveness of these stages?

ii. Examine the case study of Halicin to illustrate the broader implications of AI in drug repurposing. What were the key steps involved, and how did AI contribute to each step? What does this case study suggest about the future of AI in medicinal chemistry?

UNIT 15

BIOCHEMISTRY

Student Learning Outcomes (SLOs)

- Explain the basis of classification and structure-function relationship of carbohydrates.
- Explain the role of various carbohydrates in health and diseases.
- Identify the nutritional importance of carbohydrates and their role as energy storage.
- Explain the bases of classification and structure-function relationships of proteins.
- Describe the role of various proteins in maintaining body functions and their nutritional importance.
- Describe the role of enzymes as biocatalyst and relate this role to various functions such as digestion of food.
- Identify factors that affect enzyme activity such as the effects of temperature and pH.
- Explain the role of inhibitors of enzymes catalyzed reactions.
- Describe the basis of classification and structure-function relationship of lipids.
- Identify the nutritional and biological importance of lipids.
- Identify the structural components of DNA and RNA.
- Differentiate between the structures of DNA polymer (double strand) and RNA (single strand).
- Relate DNA sequences to its function as storage of genetic information.
- Relate RNA sequence (transcript) to its role in transfer of information to protein (translation)

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- Identify the sources of minerals such as iron, calcium, phosphorous, and zinc.
- Describe the pole of iron, calcium, phosphorus, and zinc in nutrition.
- Explain why animals and humans have large glycogen deposits for sustainable muscular activities, Hibernating animals (polar bear, reptiles and amphibians) accumulate fat to meat energy resources during hibernation.
- Identify complex carbohydrates which provide lubrication to the elbow and knee.
- Describe fibrous proteins from hair and silk.
- Explain how cholesterol and amino acids serve as hormones.
- Identify insulin as a protein hormone whose deficiency leads to diabetes mellitus.
- Explain the role of minerals in structure and function.
- Identify calcium as a requirement for coagulation.
- Identify how milk proteins can be precipitated by lowering the pH using lemon juice.

Life requires energy. Where does this energy come from? Can you use sunlight directly for all life functions? Plants capture this energy and transform it into chemical energy. How? They store this energy in substances such as carbohydrates, proteins, and lipids. We need these compounds to exist. To ensure adequate nutrition, our food should have a balanced proportion of carbohydrates, proteins, and lipids. We also need enough amounts of vitamins, minerals, and fiber.

Certain compounds found in every living cell act as the cell's information and control centers. They can reproduce, store, and transmit genetic information. What are these compounds? This chapter will help you identify these important compounds.

15.1 Carbohydrates

Carbohydrates are the most abundant class of organic compounds. Carbohydrates are macromolecules composed of elements carbon, hydrogen, and oxygen. Each carbon is bonded to at least one oxygen atom. All carbohydrates contain an aldehyde or keto group and a hydroxyl group.

Carbohydrates have the general formula $C_x(H_2O)_y$. This formula suggests that they are hydrates of carbon with few exceptions. Recall that plants synthesize carbohydrates through photosynthesis.

$$6H_2O_{(\ell)} + 6CO_{2(g)} \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} C_6H_{12}O_{6(aq)} + 6O_{2(g)}$$

Plants convert glucose into starch and cellulose.

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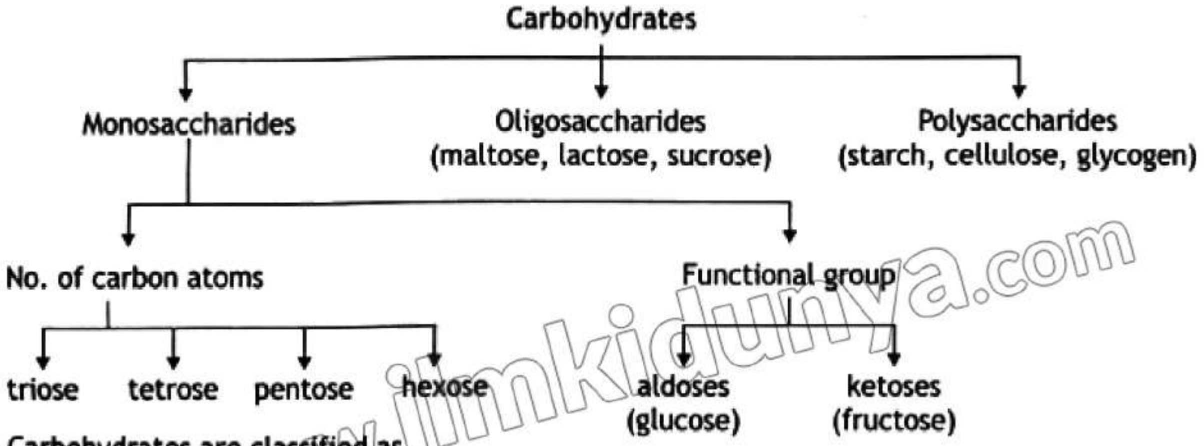
Functions of Carbohydrates

Functions of carbohydrates involve:

(a) Provide energy to cells.
(b) Provide structural support to the body.
(c) Support the organism's growth and development.

The complex structure of carbohydrates allows them to be stored easily and in great amounts. The branched complex carbohydrates can easily hydrolyse to produce small glucose molecules, which can easily be absorbed by the cells as an energy source.

15.1.2 Classification of Carbohydrates

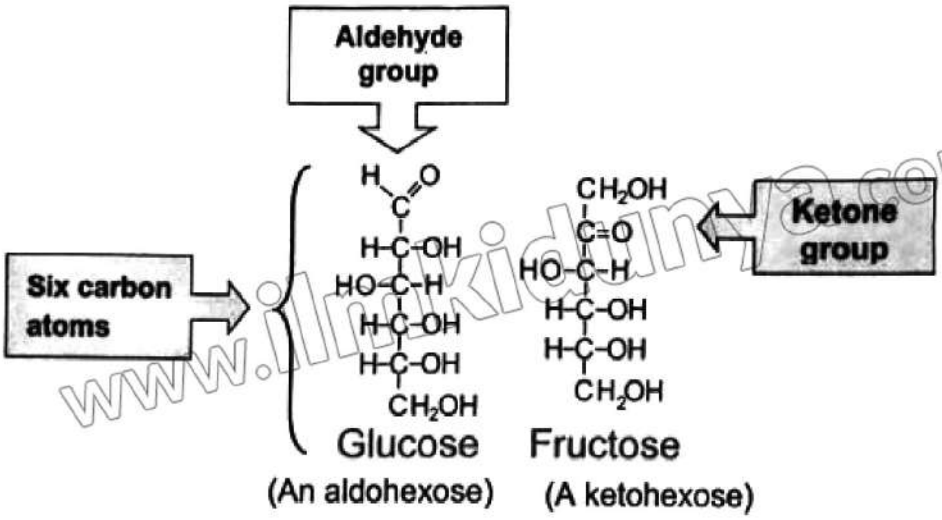


Carbohydrates are classified as

i) Monosaccharide
ii) Oligosaccharides
iii) Polysaccharides

1. Monosaccharides

Monosaccharides are the simplest carbohydrates. They cannot be hydrolyzed. They have general formula $(CH_2O)_n$ where n is 3 to 6 carbon atoms. They are further classified as trioses, tetroses, pentoses, hexoses etc. This classification is based on the number of carbon atoms they contain. The two most familiar monosaccharides are glucose and fructose. Both have



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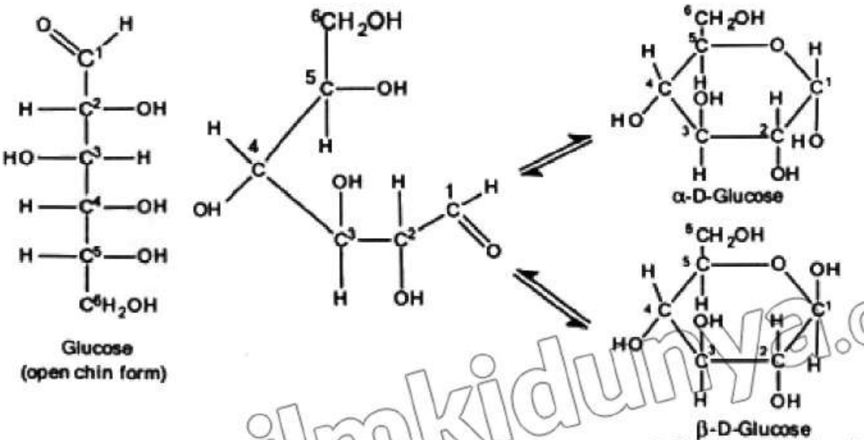
molecular formula $C_6H_{12}O_6$. Is glucose a pentose? Glucose is a pentahydroxy aldehyde, whereas fructose is a pentahydroxy ketone. Their open-chain structures are as follows. They are called simple sugars.

Some monosaccharide molecules can rotate the plane of plane-polarized light to the right (clockwise). They are called dextro-rotatory or dextrose sugars.

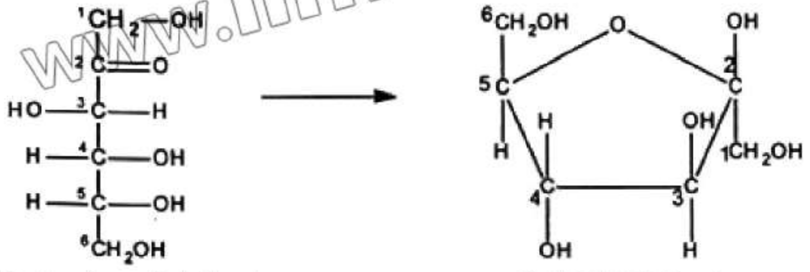
Glucose, manose, galactose, and dextrose sugars. Monosaccharides are white crystalline solid. They are soluble in water and have a sweet taste. They cannot be hydrolyzed. They are reducing in nature.



Glucose (open chin form)

α-D-Glucose

β-D-Glucose
D-Glucose(cyclic form)



Fructose (open chain form)

Fructose (cyclic form)

2. Oligosaccharides

Carbohydrates which upon hydrolysis from 2 to 10 molecules of monosaccharides or simple sugars are called oligosaccharides.

Therefore, depending upon the number of monosaccharide units they produce on hydrolysis, they are further classified as disaccharides, trisaccharides, etc. Prefixes di, tri, tetra, penta, etc. indicate the number of monosaccharide units, they produce on hydrolysis. They are white crystalline solids. They have a sweet taste and are soluble in water.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$

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CONCEPT ASSESSMENT EXERCISE 15.1

1. Classify sucrose, lactose and maltose as mono, di or tri-saccharides. Give reason.
2. Is galactose, a monosaccharide?
3. Raffinose, $C_{18}H_{32}O_{16}$ hydrolyses as follows. Is raffinose a disaccharide?

$$C_{18}H_{32}O_{16} + 2H_2O \longrightarrow 3C_6H_{12}O_6$$

3. Polysaccharides

The Carbohydrates which upon hydrolysis form hundreds to thousands of units of simple sugars are called polysaccharides. Starch and cellulose are polysaccharides. They are amorphous solids. They are tasteless and insoluble in water. They are non-reducing in nature.

Some common carbohydrates, with their structures are shown in Table 15.2:

Table 15.1: Some common carbohydrates, with their structures

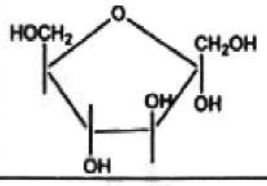
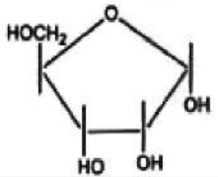
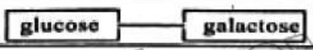
Name	Type	Structures	Occurrence
Glucose	Monosaccharide, aldose, hexose		Occurs abundantly in plants and animals
Fructose	Monosaccharide, ketose, hexose		In fruit and honey
Ribose	Monosaccharide, aldose, pentose		Component of the molecules of ribonucleic acid (RNA) and vitamin B_{12}
Sucrose	Disaccharide		Sugar cane, sugar beet (commonly simply called, 'sugar')
Maltose	Disaccharide		Malt
Lactose	Disaccharide		Milk
Starch	Polysaccharide	chains of glucose units	Plant storage organs, e.g. potato, wheat grain
Cellulose	Polysaccharide	Chains of glucose units (linked differently to those in starch)	Structural material of plants

Table 15.2: Summary of Carbohydrates

Carbohydrates		
Monosaccharides	**Disaccharides**	**Polysaccharides**
Glucose	Sucrose	Starch
Galactose	Maltose	Glycogen
Fructose	Lactose	Cellulose
Ribose		
Glyceraldehyde		

15.1.3 Carbohydrates and Health Conditions:

How do different types of carbohydrates impact health?

The type of carbohydrates you eat can affect your health. For example;

- Foods high in simple carbohydrates (added sugars), especially fructose, raise triglyceride levels, which can increase the risk of cardiovascular disease. Your body breaks down carbohydrates into simple sugars, which are absorbed into the bloodstream
- Monitoring your carbohydrate intake is critical to controlling blood sugar. It can cause diabetes.
- Excessive consumption of simple carbohydrates and high-calorie foods can promote weight gain or obesity.
- A high-fiber diet, including whole grains, can help lower cholesterol and reduce the risk of cardiovascular disease.
- Fiber-rich carbohydrates support the growth of beneficial gut bacteria and promote a healthy digestive system.

15.1.4 Nutritional importance of carbohydrates

There are five main functions of carbohydrates in the human body.

These are energy production, energy storage, macromolecule building, protein sparing, and fat metabolism support.

- Dietary carbohydrates provide glucose that the body's cells can use for energy. 1 g of glucose provides us with 15.6 kJ of energy.
- Excess glucose is converted to glycogen, a storage form of carbohydrates. It is also converted into fat and stored in the body's fat cells. Hundreds of grams of glycogen are stored in the liver and muscles. This glycogen is broken down into glucose when the body needs quick energy, such as during intense physical activity.
- Fiber is a type of carbohydrate that promotes good digestion by reducing constipation and lowering the risk of gastrointestinal disorders. Fiber can also help lower bad cholesterol and LDL levels, reducing your risk of heart disease.
- Carbohydrates play a role in various metabolic pathways. These can be converted into intermediate compounds that are used in the synthesis of other molecules such as amino acids and fatty acids.

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- Carbohydrates prevent protein from being used as an energy source. When enough carbohydrates are available, proteins can focus on their primary jobs, such as building and repairing tissue.
- Some glucose is converted to ribose and deoxyribose, which are essential building blocks of important macromolecules, such as RNA, DNA, and ATP.

15.1.5 Glycogen - A store house

What is glycogen? Glycogen is a type of stored glucose molecule made up of a large number of connected glucose molecules. It is the primary source of energy for our cells and is stored in our liver and muscles when the body does not need to use glucose for energy. When body requires energy due to a lack of glucose, the glycogen is reconverted into glucose and provides energy to the body in the form of ATP. This rapid glucose breakdown and release of energy is essential for the body cells, especially when we are in a state of high energy demand, such as when we exercise or respond to stress.

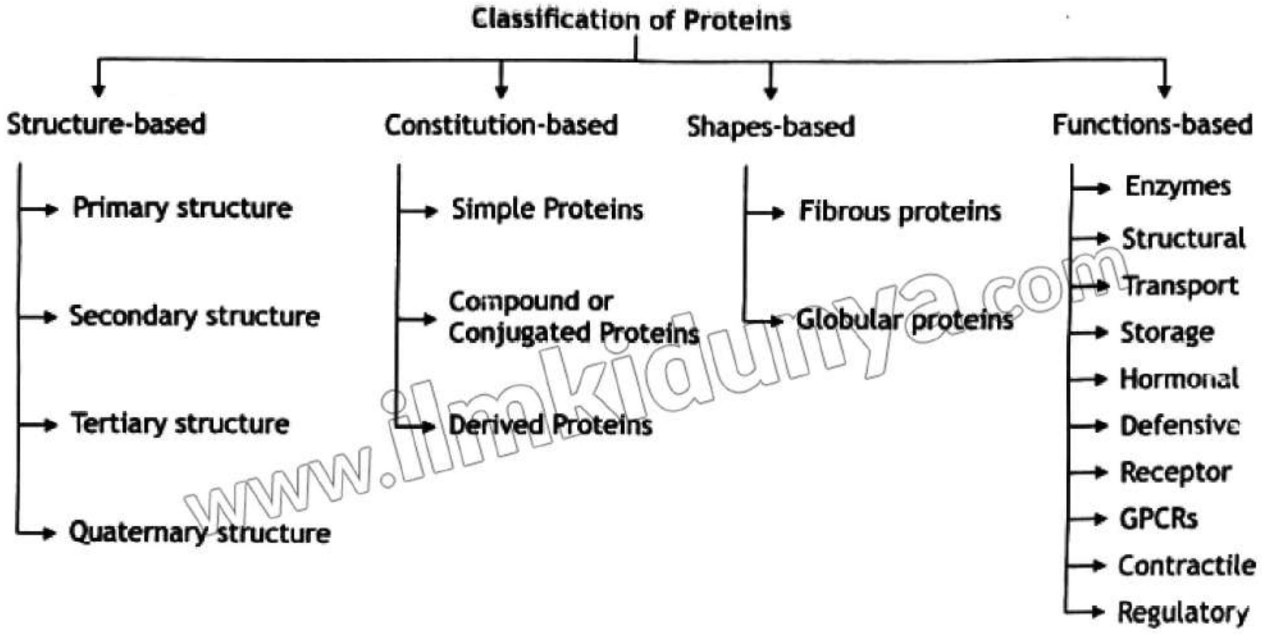
15.1.6 Complex carbohydrates for joint lubrication

We have special substances in our bodies that help our elbow and knee joints function smoothly. Three of these are glucosamine, glycosaminoglycans (GAGs), and proteoglycans. They play a vital role in maintaining joint health and flexibility. Glucosaminoglycans (CAGs) are the most abundant heteropolysaccharide in the body. They are long unbranched molecules containing a repeating disaccharide unit. GAGs are a major component of joint cartilage.

15.2 Proteins

Proteins are nitrogenous high molecular weight polymers. The building blocks of all **proteins** are the amino acids, therefore, all proteins produce amino acids on hydrolysis. Proteins are complex nitrogenous substances that produce amino acids on complete hydrolysis.

15.2.1 Classification of Proteins



Proteins are large complex molecules that play an important role in various biological processes. The classification of proteins is based on their structure, function, and the sequence of amino acids that make up their primary structure. The relationship between protein structure and function is closely related because the specific three-dimensional arrangement of a protein determines its function. Here is an overview of the basis of protein classification and the relationship between structure and function:

1. Structure-based classification:

Based on their structure, proteins can be divided into four major categories:

1. Primary structure
2. Secondary structure
3. Tertiary structure
4. Quaternary structure

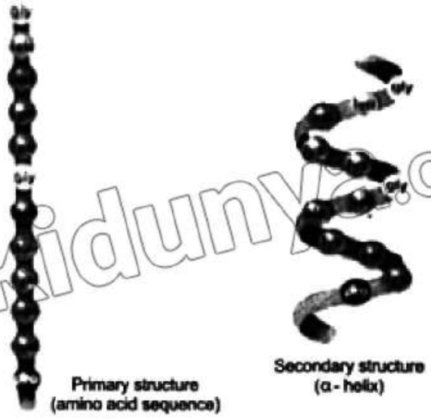
The structure of a protein depends upon the spatial arrangement of polypeptide chains present in proteins. Since three spatial arrangements are possible, proteins have the following four structures.

a) The Primary Structure of Proteins

The sequence of amino acids in a peptide chain is called primary structure. Amino acids are linked with one another through peptide bonds. The arrangement of these acids is called primary structure.

b) The Secondary Structure of Proteins

Peptide chains may acquire a spiral shape or may be present in a zig-zag manner. This coiling or zig-zagging of a polypeptide is called the secondary structure of a protein. It is due to H-Bond. For example, collagen.



Primary structure (amino acid sequence)

Secondary structure (α - helix)

Tertiary structure (folded individual peptied)

Quaternary protein structure is a protein consisting of more than one amino acid chain.

Fig 15.1

c) The Tertiary Structure of Proteins

The twisting or folding of polypeptide chains represents a tertiary structure of proteins. For example, myoglobin.

d) Quaternary Proteins

Quaternary means four. This is the fourth phase in the creation of a protein.

Quaternary protein is the arrangement of multiple folded protein or coiling protein molecules in a multi-subunit complex. Different types of bonding interactions including hydrogen bonding, salt bridges, and disulfide bonds hold the various chains into a particular geometry. For example, haemoglobin.

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15.2.2 Classification of Proteins based on Constitution

On the basis of constitution proteins are classified into three groups:

1. Simple Proteins
2. Compound or Conjugated Proteins
3. Derived Proteins

Simple Proteins

Proteins which on complete hydrolysis produce only the amino acids from which they are formed are called simple proteins. For example, albumins, globulins, collagens, etc.

Composite or Conjugated Proteins

Proteins composed of simple proteins (apoproteins) and non-protein groups called prosthetic groups are called composite or conjugated proteins. For example, lipoproteins, glycoproteins, phosphoproteins, nucleoproteins, hemoproteins, etc.

Derived proteins

Proteins consisting of simple or conjugated proteins partially hydrolyzed by acids, bases, or enzymes. For example, peptones. Peptides, proteoses, proteans, etc.

15.2.3 Classification of Proteins based on Shapes

Proteins are classified into two groups on the basis of their shapes.

1. Fibrous proteins
2. Globular proteins

Fibrous proteins

Proteins that are made up of elongated or fibrous polypeptide chains are called fibrous proteins. They form fibers of large sheets. Examples of fibrous proteins include keratins, collagens, myosins, and elastins. Hair and the outer layer of skin are composed of keratin. Connective tissues contain collagen. Myosins are muscle proteins and are capable of contraction and extension.

Globular proteins

Proteins that are water-soluble and possess a shape like a sphere or a globe upon folding are called globular proteins. These proteins are usually soluble in acids, water, alcohol, and bases—for example, albumin of eggs and haemoglobin.

15.2.4 Classification of Proteins on the basis of Functions

They can be classified based on their functions into several categories.

1. Enzymes:

Protein that facilitates the biochemical reactions. For example, lactase that breaks down lactose into glucose and galactose. Catalase catalyzes the decomposition of hydrogen peroxide into water and oxygen.

2. Structural Proteins:

Proteins that provide support and shape to cells and tissues. For example, Collagen which is found in connective tissues, provides strength and elasticity.

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3. Transport Proteins:

Protein that facilitates the movement of substances across membranes. For example, haemoglobin carries oxygen in red blood cells.

4. Storage Proteins:

Proteins that store nutrients and ions. For example, ferritin. It stores iron in the liver and spleen. The casein stores calcium in milk.

5. Hormonal Proteins:

Proteins regulate physiological processes and serve as signalling molecules.
For example, insulin regulates glucose metabolism. Thyroid Hormones that control metabolism and growth.

6. Defensive Proteins:

Proteins that protect the organism against pathogens are called defensive proteins. For example, antibodies. They bind to and neutralize foreign substances like bacteria or viruses.

7. Receptor Proteins:

Proteins that bind to specific molecules and transmit signals into the cell are called receptor proteins. For example, insulin receptor that binds insulin and initiates cellular responses.

8. G Protein-Coupled Receptors (GPCRs):

Proteins that respond to various signaling molecules are called G protein-coupled receptors.

9. Contractile Proteins:

Proteins that enable muscle contraction and movement are called contractile proteins. For example, actin and myosin.

10. Regulatory Proteins:

Proteins that control the activity of other proteins.
For example, transcription factors that regulate gene expression. Cycling regulates the cell cycle.

15.1.5 Structure- Function relationship of Proteins

The primary structure is the amino acid sequence of a protein. For example, insulin. The secondary structure describes how the peptide backbone segments orient into a homogeneous sequence. For example, collagen. The tertiary protein structure describes how the whole protein molecule coils into a three-dimensional arrangement. For example, myoglobin. Quaternary structure describes the arrangement of multiple folded protein or coiling protein molecules in a multi-subunit complex. Different types of bonding interactions including hydrogen bonding, salt bridges, and disulfide bonds hold the various chains into a particular geometry. For example, hemoglobin.

15.2.6 Key roles of proteins in maintaining body function

Proteins are essential macromolecules that play a crucial role in the structure, function, and regulation of the body's tissues and organs. It's important to consume an adequate amount of protein through the diet to support these essential functions in the body. Good dietary sources of protein include meat, poultry, fish, eggs, dairy products, legumes, nuts, and seeds. They are

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made up of amino acids, which are the building blocks of life. The nutritional importance of proteins can be summarized as follows.

- Proteins play an important role in the formation of protoplasm. Protoplasm is the essence of all forms of life.
- Proteins like collagen and elastin provide structural support to tissues, tendons, ligaments, and skin. Enzymes act as biological catalysts, facilitating and speeding up chemical reactions in the body. They are involved in digestion, metabolism, and the synthesis of various molecules.
- Proteins such as insulin and growth hormones act as chemical messengers that regulate various physiological processes, including metabolism, growth, and development.
- Proteins like hemoglobin transport oxygen in the blood, while others facilitate the movement of nutrients, ions, and molecules across cell membranes.
- Proteins like actin and myosin are essential for muscle contraction, allowing for movement and locomotion.
- Antibodies are proteins produced by the immune system to identify and neutralize pathogens such as bacteria and viruses, playing a critical role in immune defense.
- Receptor proteins on cell surfaces interact with signaling molecules, enabling cells to respond to external stimuli and coordinate various physiological responses.
- Certain proteins act as enzyme inhibitors.
- Proteins store essential nutrients such as amino acids and metal ions for future use, ensuring a constant supply for the body's needs.

CONCEPT ASSESSMENT EXERCISE 15.2

1. What are proteins? Give its simple classifications.
2. Differentiate primary, secondary, and tertiary structure of Proteins.
3. What are polypeptides?

15.2.7 Fibrous Proteins for structure and support

Fibrous proteins are specialized proteins that play a structural or supportive role in our bodies. They are like building blocks, providing strength to different parts.

Silk fiber:

Silk is not only a material for clothing; It is composed of fibrous proteins. These proteins form long, strong structures that make silk fibers durable and flexible.

Keratin (in nails and hair):

Have you ever wondered why hair and nails are so strong? This is due to a protein called keratin. Keratin gives our hair and nails structure and strength and makes them elastic.

Myosin (in muscle cells):

Myosin is a special protein found in our muscles. It helps muscles contract and relax so we can move our bodies.

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Fibrin (in blood clots):

Fibrin is like a superhero in our blood. When we get a cut, fibrin helps in forming of a clot to stop bleeding. It forms a mesh to seal the wound and protect us.

Insulin also signals other body systems, such as how cells absorb amino acids. It has other positive effects on the body. Doctors use insulin to treat certain types of diabetes.

15.3 Precipitation of Milk Proteins

Acid precipitation is the process of reducing the pH (acidity) of milk by adding acidic substances such as lemon juice. The main proteins precipitated in the liquid are milk proteins (casein and whey). The casein proteins in milk are micelles (small clusters of proteins). The phosphate groups on the casein micelles cause them to be negatively charged. This leads to electrostatic repulsion between the micelles and the casein proteins. The lower the pH of milk, the less electrostatic repulsion the micelles have. The addition of lemon juice lowers the pH of milk. As a result, the micelles can move closer together and form large aggregates. This results in the milk coagulating or coagulating when the pH drops.

15.4 Enzymes

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(Greek word En means in and Zyme means yeast)

Enzymes are biocatalysts that alter the speed of metabolic activities in living bodies. Enzymes are complex protein molecules that are quite specific in action and sensitive to temperature and pH.

15.4.1 Role of Enzymes as a Biocatalyst

Metabolism refers to a series of chemical reactions that take place in living organisms in order to maintain life. These reactions enable organisms to grow, reproduce, maintain their structures, and respond to environmental conditions. Metabolism involves two main types of processes: anabolic and catabolic. Anabolic reactions involve the synthesis of larger molecules, while catabolic reactions involve the breakdown of larger molecules. Generally, enzymes are released in anabolic reactions and used in catabolic reactions. As a result, these biochemical reactions are essentially energy transfers. In metabolism, chemicals are converted from one state to another by enzymes. These enzymes play a critical role in metabolism, as they catalyze (i.e., accelerate) biochemical reactions and regulate metabolic pathways. The molecules on which the enzymes act are referred to as substrates. The enzymes convert these substrates into various molecules known as products.

How does Enzyme work?

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When an enzyme attaches to a substrate, a temporary Enzyme-Substrate Complex (ES) is formed. The ES complex then breaks down the enzyme product.

$$E + S \rightarrow \text{ES Complex} \rightarrow E + P$$

In 1894, German chemist Emil Fischer proposed the lock and key model to explain how enzymes work. In this model, enzymes and substrates have specific shapes that fit together perfectly. This model describes the specificity of enzymes.

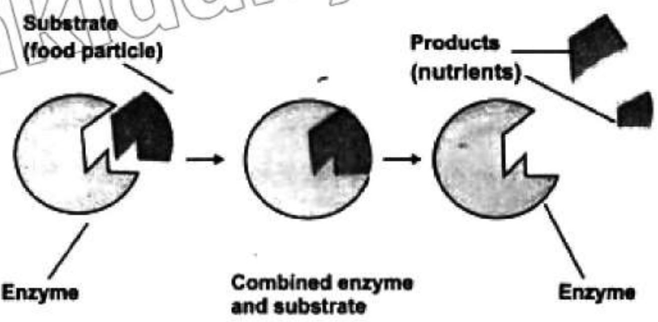

Fig 15.2 Lock and Key Model

In 1958, Daniel Koshland, an American biologist, proposed the induced-fit model to explain enzyme action. According to Koshland's model, active sites are not rigid structures but rather are moulded into the desired shape to perform their function. The "Induced fit model" is more acceptable than the "lock and key" model.

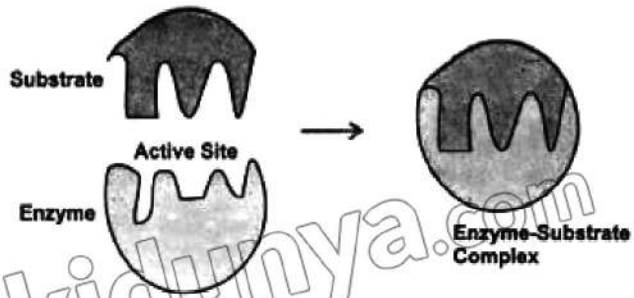

Fig 15.3 Induced Fit Model

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15.4.2 Factors Affecting Enzyme Activity

Enzymes are very sensitive to the environment in which they work. Any factor that can change the chemistry or shape of an enzyme molecule can affect its function. Here are some factors that can affect how fast enzymes work.

i) Temperature

Enzymes work at their maximum speed at a specific temperature called optimum temperature. For example, an animal enzyme works at 37 °C, a plant enzyme acts at 60 °C, etc. When the temperature increases, the activation energy increases and kinetic energy is added to the reaction, which speeds up the reaction. However, when the temperature is increased too much, the vibration of enzyme atoms increases, and the enzyme's globular structure is lost, resulting in enzyme denaturation, which slows down the enzyme's activity and can block it completely.

ii) Substrate concentration

When there are sufficient enzyme molecules for the reaction to take place, increasing the substrate concentration will increase the rate of reaction. However, if the enzyme concentration remains constant and the substrate concentration increases, there is a point at which the addition of substrate does not increase the reaction rate at all. If all the active sites are occupied (high amounts of substrate) of enzymes, no substrate molecule will find any free active sites. This type of saturation is known as the active site state and the reaction rate does not increase.

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iii) pH

All enzymes operate at maximum activity within a specific range of pH. This range is known as the optimum pH, and a small change in the pH of an enzyme either slows or stops the enzyme's activity. Each enzyme has its optimum pH value. For instance, the enzyme pepsin works in the stomach and is active in acidic environments (pH = 2) while the enzyme trypsin works in the small intestine and is active in alkaline conditions (pH = 8 to 9)

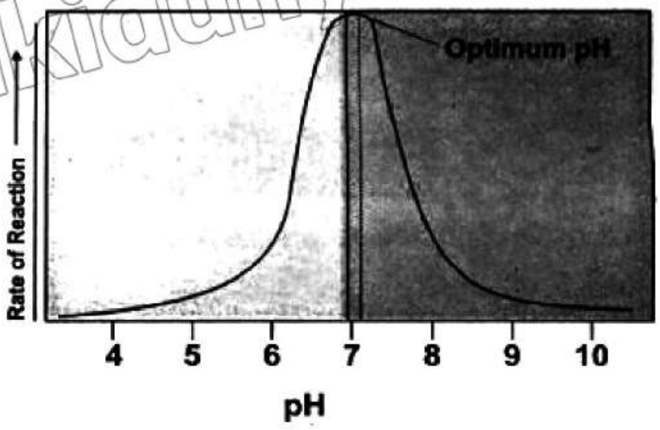

Fig 15.4: Effect of pH on Enzyme Activity

15.4.3 Role of Inhibitors in Enzyme Catalyzed Reactions

Inhibitors play a crucial role in regulating enzyme-catalyzed reactions by modulating the activity of enzymes. Inhibitors can be classified into two main types: competitive inhibitors and non-competitive inhibitors.

Competitive Inhibitors:

A competitive inhibitor is a molecule that is similar to the substrate and competes with it for the active site on the enzyme. It binds to the active site and prevents the substrate from attaching to the enzyme. For example, sarin, a nerve gas, acts as a competitive inhibitor to acetylcholine, a neurotransmitter. Sarin mimics acetylcholine's structure and competes for its active site, causing acetylcholine to build up in the synapses. Malonic acid is another example of a similar molecule. Malonic acid has a similar structure to succinic acid. Succinic acid is converted into fumaric acid on the succinate dehydrogenase enzyme, so malonic acid does not bind to the active sites on the substrate and therefore does not form a product.

Non-competitive Inhibitors:

Non-competitive inhibitors don't compete directly with the active site for the substrate but rather change the shape and form of the enzyme, reducing its ability to convert substrates to products. For example, mercury ions bind to the enzyme's thiol groups and change the shape and activity of the enzyme.

CONCEPT ASSESSMENT EXERCISE 15.3

1. What are enzymes? Why are they called biocatalysts?
2. How does enzyme work?
3. Differentiate between competitive and non-competitive enzymes inhibition.

15.5 Lipids

Lipids are naturally occurring heterogeneous groups of organic compounds of animals and plants origin, which are soluble in organic solvents. These include fats, waxes, oils, hormones and some membrane components. They function as energy-storing molecules and chemical messengers.

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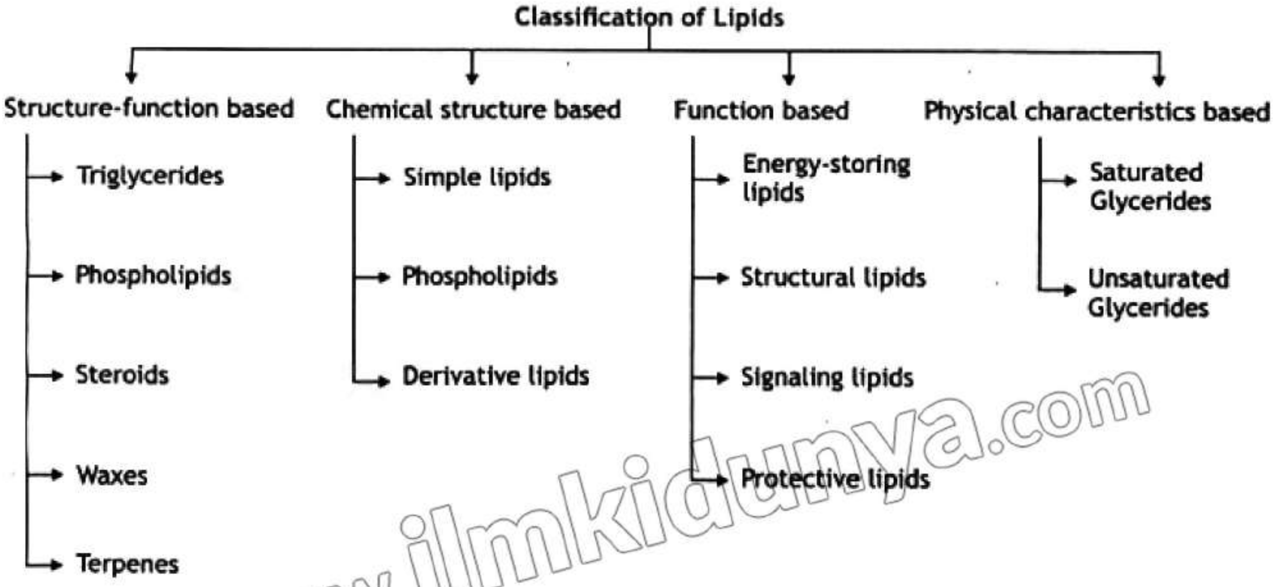
Lipids are the main constituents of cell membranes (cell walls), food storage molecules, and cholesterol.

All lipids are water insoluble, that's the one property they have in common.

15.5.1 Classification of Lipids

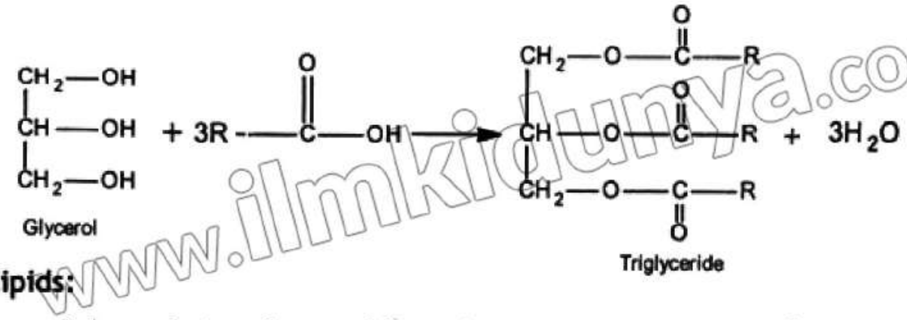


Lipids can be classified into the following classes. These categories highlight the structure-function relationships of lipids.

1. **Triglycerides:**

Fats and oils are made from two kinds of molecules, glycerol and three fatty acid. Since they contain three fatty acid units, they are called triglycerides. Fatty acids contain long hydrocarbon chains containing 12 to 22 carbon atoms and a carboxylic acid group at one end. They are the building blocks of most lipids. Examples include palmitic acid, oleic acid, and linoleic acid.

They are found in oils, butter, and adipose tissue. If the fatty acids are saturated, they form fats that are solid at room temperature, like butter. If they are unsaturated, they form oils which are liquid at room temperature, like olive oil, sunflower oil, cotton seed oil, etc.



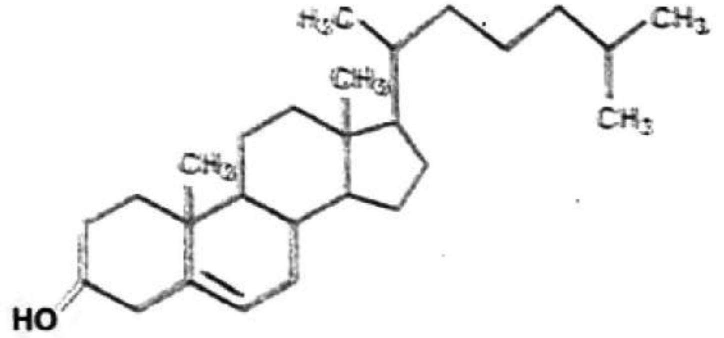
2. **Phospholipids:**

They are esters of glycerol, two fatty acids, and a phosphate group(PO_4^{3-}).

They are an integral part of cell membranes.

3. Steroids:

Steroids are organic compounds with a typical molecular structure containing four fused rings of carbon atoms (three six-membered and one five-membered). They function as structural components of cell membranes and are the precursors of various hormones. Examples: cholesterol, testosterone, estrogen.



Cholesterol

4. Waxes:

Waxes consist of long-chain fatty acids esterified to long-chain alcohols. They often act as a protective cover for plants and animals. Examples: lanoline, beeswax, carnauba wax, whale oil, etc.

5. Isoprenoids or Terpenes:

Lipids containing isoprene units (five-carbon units) are called terpenes or isoprenoids. They have various functions, including pigmentation in plants (carotenoids) and an electron carrier in cellular respiration (ubiquinone). Examples: pinene, camphor, menthol. Chlorophyll, and vitamin A.

15.5.2 Classification of lipids based on chemical structure

Based on chemical structure lipids are classified into the following groups

1. **Simple lipids:** These are composed of fatty acids and glycerol molecules. For examples;

DO YOU KNOW?

Lanoline serve as a protective coating for hair and skin, so it is used in skin creams and ointments. Carnauba wax is used automobile polish.

Triglycerides: Found in fats and oils, which act as the main energy store for organisms.

Waxes: Provide protection and water resistance to plants and animals.

Compound lipids: Contain additional components such as phosphoric acid, nitrogenous bases or proteins.

2. **Phospholipids:** These are essential components of cell membranes with a hydrophobic tail and a hydrophilic head.

Glycolipids: They participate in cell recognition and attachment, contain part of carbohydrates.

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3. **Derivative lipids:** They are formed by hydrolysis of simple, or complex lipids. For example;
   - (i) **Steroids:** Contain cholesterol, which is important for cell membrane structure, and hormones such as testosterone and estrogen.
   - (ii) **Prostaglandins:** Act as local hormones that influence inflammation, circulation and other physiological processes.

15.5.3 Classification of lipids on the bases of function:

Based on functions lipids are classified into the following classes

1. **Energy-storing lipids:**

Triglycerides: Stores energy in adipose tissue for future use.

2. **Structural lipids:**

Phospholipids: Form the basic structure of cell membranes.

Glycolipids: Promote membrane stability and cell recognition.

3. **Signaling lipids:**

Eicosanoids: Contain prostaglandins and leukotrienes that affect inflammation and the immune response.

4. **Protective lipids:**

Waxes: form a protective coating on plant and animal surfaces.

15.5.4 Classification of lipids on the basis of Physical Characteristics:

Based on physical characteristics lipids are classified into the following classes.

Saturated Glycerides: Fatty acids that contain only single bonds between carbon atoms are called saturated glycerides. They exist as solids at room temperature. Some examples of foods that contain high concentrations of saturated fats include butter, cheese, lard, and some fatty meats.

Unsaturated Glycerides: Fatty acids that contain at least one carbon-carbon double bond are called unsaturated glycerides. Oils are unsaturated glycerides. They exist in a liquid state at room temperature. Foods that contain higher concentrations of unsaturated fats include nuts, avocado, and vegetable oils such as canola oil and olive oil.

15.5.5 Nutritional and Biological Importance of Lipid

Lipids play three important biochemical roles:

1. As a storehouse of metabolic energy (Triglycerides)
2. As components of membranes
3. As messengers (Prostaglandins and Steroid Hormones)

One of the primary nutritional roles of lipids is to provide energy. For example, saturated, unsaturated, and trans fats provide approximately 9 calories per gram, compared to 4 calories per gram for carbohydrates and protein. Although fats are high in calories, they do not necessarily lead to weight gain if you track your total intake. Fats are also required for the absorption of essential nutrients such as fat-soluble vitamins A, D, and E.

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15.5.6 Essential Lipids

Lipids that are not produced by the body and enter the body through food are known as essential lipids. Polyunsaturated fatty acids (PFA) are the most important lipids and are found in the form of polyunsaturated fats (Omega-6 and Omega-3 fats). These fats are essential for hormone synthesis, cell membrane structure, brain, and vision health, and can help lower blood cholesterol levels. Omega-6 fatty acids are found in vegetable oils and nuts, while omega-3 fatty acids can be found in flax seeds, walnuts, and fatty fish.

15.5.7 Non-Essential Lipids

Monounsaturated fats are not required in the diet because the body can synthesize them from amino acids. However, they reduce the risk of cardiovascular disease. Non-essential lipids are present in olive oil, peanuts, and avocado. Saturated fats, trans fats, and cholesterol are found in the diet and increase the bad cholesterol levels in the blood. Trans fats come from processed and fried foods, while cholesterol comes from fatty animal foods.

[illegible]

Cholesterol is a building block of hormones. Our bodies use cholesterol to produce some important hormones. These hormones act like messengers, delivering important signals to different parts of our bodies. For example, cholesterol is essential to produce sex hormones such as estrogen and testosterone. These hormones play an important role in the development of secondary sexual characteristics and the regulation of the reproductive system.

[illegible]

Some hormones actually consist of amino acids linked together and are called peptide hormones. These hormones also act as messengers, but perform different tasks than hormones made from cholesterol. For example, insulin.

Insulin is a protein hormone produced by the pancreas and consists of two parts, the alpha chain (21 amino acids) and the beta chain (30 amino acids), connected by a bridge. Its molecular weight is 5,808 g/mol. When we eat, our body releases insulin, which helps cells absorb sugar for energy.

Its main function is to control the body's use of sugar and fat. It tells the liver, muscles, and fat cells to absorb sugar from the blood. Sugar is stored as glycogen in the liver and muscles and as triglycerides in adipose tissues.

Insulin prevents the body from using fat for energy. When blood sugar levels are low, the body uses stored sugar through glycogenolysis. Insulin deficiency leads to a condition called diabetes mellitus. Diabetes mellitus is a disorder in which the body does not produce enough or respond normally to insulin, causing blood sugar (glucose) levels to be abnormally high.

Hibernation is a process that occurs in many species, including polar bears, reptiles, and amphibians. Under favourable conditions, their body accumulates large amounts of fat. Due to the unbearable cold, the bodies of hibernating animals sleep longer than they would otherwise be able to survive. Animals undergo various physical changes during hibernation. Breathing becomes very slow. Also, body temperature decreases depending on the surrounding temperature. During hibernation, their metabolism slows down and they become less active. They often hide in secluded caves and caves so that no one disturbs their peaceful sleep and they are not hunted. During this time, stored fat is used to meet energy needs.

CONCEPT ASSESSMENT EXERCISE 15.4

1. What are triglycerides? Draw its structure

15.10 Nucleic Acids

Naturally occurring biomolecules that serve as the primary information-carrying molecules in cells are called nucleic acids.

Types of Nucleic Acids:

There are two types of nucleic acids.

1) Deoxyribonucleic acids (DNA)
2) Ribonucleic acid (RNA)

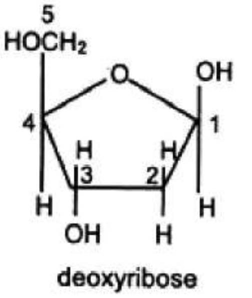
15.10.1 Structural Components of DNA and RNA

DNA consists of large polymeric molecules. Its monomers are called nucleotides. Four types of nucleotides are involved in the structure of DNA strands, which differ only from the base attached to carbon number 1 of the pentose sugar.

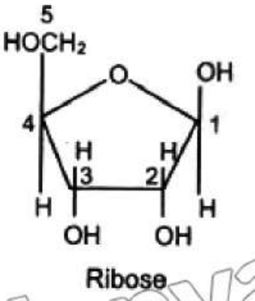
Components of Nucleotide

Each nucleotide consists of three components.

1) Pentose sugar or five-carbon sugar: In RNA pentose sugar is called ribose and in DNA it is called deoxyribose. In deoxyribose, the hydroxyl group at carbon number 2 of ribose is replaced by a hydrogen atom



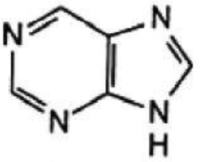
deoxyribose

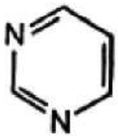


Ribose

1) **Nitrogenous base:** Four different types of nitrogenous bases are found in DNA: adenine (A), thymine (T), cytosine (C), and guanine (G). RNA, the thymine is replaced by uracil. (U)

Adenine and guanine are called purines which contain two-carbon nitrogen ring bases. While cytosine, thymine, and uracil are called pyrimidines which contain one-carbon nitrogen ring bases.





Pyrimidine

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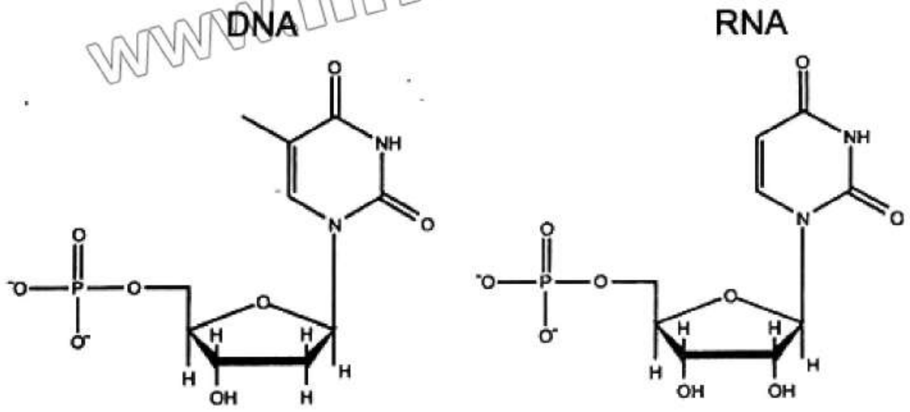
3) Phosphate unit: It is linked to C-5 of deoxyribose sugar in DNA and ribose sugar in RNA.

A simple structure of nucleotides is



15.10.2 Difference between RNA and DNA

1. RNA contains ribose sugar while DNA contains deoxyribose sugar.
2. Nitrogenous bases in DNA are cytosine, thymine, adenine, and guanine while in RNA thymine is replaced by uracil.
3. DNA is double-stranded while RNA is single-stranded, but the chain can fold back to itself to form a helical loop. The two strands in DNA are twisted into a double helix and are held in position by hydrogen bonds between complementary pairs of bases. The two stands are antiparallel i.e. they run in opposite directions.

DNA can store and transmit all the genetic information needed to build organisms. For instance, in human beings, the single fertilized egg cell carries the information for making legs, hands, head, liver, heart, kidneys, etc. DNA is found primarily in the cell nucleus.

Structure of DNA was discovered by J. Watson and Francis Crick in 1953. They were awarded the 1962 Nobel Prize for their work. This discovery initiated the field of molecular biology. Cancer research involves an extensive study of nucleic acids.

15.10.3 Structure of DNA

DNA exists in the spiral structure of a double helix, where two strands spiral around each other. The strands are joined together by hydrogen bonding between the bases of the two strands. The sequence of base pairs in a single strand is a genetic code that stores information needed to make proteins.

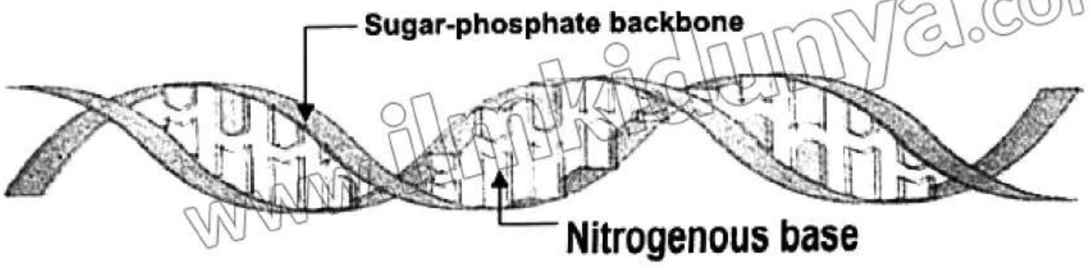


Figure 15.5 Structure of DNA

The double-stranded structure of DNA is the key to storing genetic information and transferring it from one generation to the next. The part of DNA that carries this genetic information is called genes. DNA is self-replicating. It copies the genetic information before a cell divides, so each daughter cell carries a copy of the correct genetic code can organism passed on to its offspring.

15.10.4 Structure of Ribonucleic Acid (RNA)

RNA exists as a single-stranded. It is created by DNA to carry genetic information. It is responsible for controlling the synthesis of new proteins by receiving, reading, decoding, and using the genetic information from DNA. DNA copies the genetic code in messenger RNA. The messenger RNA carries these copies into the cytoplasm to be synthesized into a protein. The genetic information in the mRNA is then translated with the aid of transfer RNA or ribosomal RNA which is used for protein synthesis. The resulting chain of amino acids called the polypeptide, is then sent to the Golgi Bodies to be processed and transformed into a protein.

Fig 15.6 Structure of RNA

Science Titbits (Chemistry in action)

The variation in DNA of individuals forms the basis of a method for identifying a person from samples of their hair, skin cells, or body fluid. Because DNA sequences like fingerprints are unique for each individual, this method is called DNA fingerprinting. Only a tiny sample is needed. The pattern is compared with the DNA of a sample from a known individual. If the DNA fingerprints are identical, it can be stated with a high degree of chemistry that the DNA in the known sample is from the individual.

CONCEPT ASSESSMENT EXERCISE 15.5

1. Write the names of structural components of DNA and RNA.
2. Which type of sugar is present in DNA?
3. What is the sugar unit in DNA?

15.11 Minerals of Biological Significance

Minerals are a type of nutrient that exists in the body. They are just as important as our oxygen to support life. They are also found in food in both organic and inorganic forms. Only 5% of the human body is made up of minerals. They are essential for every mental and physical process. They are also the most important factor in maintaining all physiological processes.

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Types of nutrients

What are macronutrients and micronutrients?

- *Macronutrients* are those nutrients that your body needs in large amounts. For example calcium, phosphorus, magnesium, and sulphur.
- Micronutrients are nutrients that your body does not need in large quantities. For example, iron, zinc, copper, and iodine.

15.11.1 Sources of Important Minerals

- Sources of Iron: Red meat, egg yolk, whole wheat, fish, spinach mustard etc.
- Sources of Calcium: Milk, cheese, egg yolk, beans, nuts, cabbage and green leafy vegetables.
- Sources of phosphorous: Egg yolk, cheese, milk, cabbage etc.
- Sources of Zinc: Oyster, red meat, chicken, beans, nuts, dairy products and some sea foods.

15.11.2 Role of important Minerals in nutrition

Role of Iron

Iron is an important mineral that helps maintain healthy blood. A lack of iron is called iron-deficiency anaemia, causing extreme fatigue and lightheadedness. It affects all ages, with children, women who are pregnant or menstruating, and people receiving kidney dialysis among those at the highest risk for this condition.

Iron is an important component of hemoglobin which is a protein in the red blood cells. Hemoglobin carries oxygen from the lungs to every part of the body. When iron levels are low, the red blood cells do not have enough oxygen transport, resulting in fatigue. Iron is also a component of myoglobin which carries and stores oxygen, especially in muscle tissue. Iron is essential for the development and growth of the brain in children. It is also necessary for the normal generation and functioning of different cells and hormones in the body. Iron deficiency anaemia is a condition in which iron levels are low. It can lead to extreme tiredness, dizziness, and other symptoms. It is most common in children and women who are pregnant, menstruating, or on dialysis.

Role of Calcium

Calcium is one of the most abundant minerals in the body. Calcium is associated with healthy bones and teeth. About 99% of the body's calcium is stored in bones, and the remaining 1% is found in blood, muscle, and other tissues.

Calcium is an essential component that plays an important role in blood coagulation. It also plays an important role in helping muscles to contract and regulating normal heart rhythms and nerve functions.

System integrity is determined by vitamin D status. Vitamin D deficiency leads to a decrease in the amount of ionized calcium in the body. This in turn leads to a reduction in the amount of calcium in the body's blood and tissues. Vitamin D deficiency causes rickets, osteomalacia, and osteoporosis.

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Role of Phosphorus

Phosphorus is a mineral found naturally in most foods and available in supplements. Phosphorus plays a variety of roles in your body. It plays a key role in the structure of your bones, teeth, and cell membranes, activating enzymes and maintaining your blood's pH level. Phosphorus plays a vital role in the proper functioning of your nerves and muscles (including your heart), as well as in the building blocks of your genes, DNA, RNA, and ATP (which are your body's primary sources of energy).

Role of Zinc

Zinc is the most important of all trace elements involved in humans. Your body contains about 2 gm of zinc. Zinc supports many functions in the human body. In addition to supporting the immune system, it enables the production of proteins and DNA, promotes wound healing, and influences child growth and development. The body needs zinc for the immune system to function properly. Low zinc levels can increase the risk of infections such as pneumonia. Zinc plays a role in maintaining healthy skin. It also plays an important role in promoting prostate health and testosterone levels.

CONCEPT ASSESSMENT EXERCISE 15.6

1. What is the biological significance of minerals?
2. What problems are caused by a deficiency of calcium and Phosphorus?
3. Give importance to zinc mineral.

KEY POINTS

- Carbohydrates have the general formula $C_x(H_2O)_y$.
- All carbohydrates contain an aldehyde or keto group and a hydroxyl group.
- Monosaccharides contain 3 to 6 carbon atoms.
- Carbohydrates which upon hydrolysis from 2 to 10 molecules of monosaccharides or simple sugars are called oligosaccharides.
- The Carbohydrates upon hydrolysis form hundreds to thousands of units of simple sugars are called polysaccharides.
- Glycogen is a type of stored glucose molecule made up of a large number of connected glucose molecules.
- Proteins are complex nitrogenous substances that produce amino acids on complete hydrolysis
- Enzymes are biocatalysts that alter the speed of metabolic activities in living bodies.
- Lipids are naturally occurring heterogeneous groups of organic compounds of animal and plant origin, which are soluble in organic solvents.
- Cholesterol is a building block of hormones.
- Naturally occurring biomolecules that serve as the primary information-carrying molecules in cells are called nucleic acids.
- Nucleic acids are present in every living cell as well as in viruses. They can reproduce, store and transmit genetic information. They are of two types of DNA and RNA.

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Nucleotide is the structural unit of DNA and consists of one sugar, one nitrogenous base and at least one phosphate.

- Minerals are nutrients and are as necessary as oxygen for life. They are constituents of teeth, bones, tissues, blood, muscles, and nerve tissues.
- Minerals are classified as major and trace minerals i.e. those required in appreciable quantity are major and those needed in low quantity are trace.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which carbohydrate is the primary source of quick energy in the body?

a) Starch b) Cellulose c) Glucose d) Glycogen

ii. What is the main structural component of plant cell walls?

a) Starch b) Cellulose c) Glycogen d) Chitin

ii. Which amino acid cannot be synthesized by the human body?

a) Glycine b) Glutamine c) Lysine d) Alanine

iv. Enzymes are primarily composed of:

a) Carbohydrates b) Lipids c) Proteins d) Nucleic acids

v. Which lipid is a major component of cell membranes?

a) Triglyceride b) Steroid c) Phospholipid d) Cholesterol

vi. RNA differs from DNA in that RNA:

a) Is double-stranded b) Contains thymine
c) Contains uracil d) Has a deoxyribose sugar

vii. What mineral is essential for oxygen transport in the blood?

a) Calcium b) Iron
c) Phosphorus d) Zinc

viii. Competitive inhibitors of enzymes:

a) Bind to the allosteric site b) Bind to the active site
c) Denature the enzyme d) Increase enzyme activity

ix. What is TRUE about enzymes?

a) They make biochemical reactions to proceed spontaneously
b) They lower the activation energy of a reaction
c) They are not very specific in their choice of substrates
d) They are needed in large quantities

x. The number of Carbon atoms in Hexose is:

a) One b) Four
c) Six d) Ten

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2. Short Answer Questions

i. Describe the primary structure of a protein.
ii. What is the role of dietary fiber in health?
iii. Explain how temperature affects enzyme activity.
iv. What is the function of hemoglobin?
v. Differentiate between saturated and unsaturated fatty acids.
vi. What is the main function of RNA
vii. Describe one function of cholesterol in the body.
viii. How do enzymes lower activation energy?
ix. Describe the lock and key mechanism of enzyme action.
x. Identify the nutritional importance of carbohydrates and their role as energy storage.
xi. Identify the differences between fibrous proteins and globular proteins?
xii. What role do antibodies play in the immune system?
xiii. What is the optimal pH for most human enzymes?
xiv. What happens to an enzyme when it becomes denatured?
xv. How does a non-competitive inhibitor differ from a competitive inhibitor?
xvi. How is glycogen used during exercise?
xvii. Identify the sources of minerals such as iron, calcium, phosphorous, and zinc.
xviii. How does insulin regulate blood glucose levels?

3. Long Answer Questions

i. Explain the role of proteins in the body and their nutritional importance, including examples.
ii. Describe the factors affecting enzyme activity and provide examples of how these factors can alter enzymatic reactions in the human body.
iii. Detail the classification of lipids and discuss their nutritional and biological importance.
iv. Describe the structure of DNA and RNA and explain how these structures relate to their functions in genetic information storage and transfer.
v. How would you categorize various carbohydrates based on their chemical structures, and what functions do these classifications suggest in biological systems?
vi. Describe the role of iron, calcium, phosphorus, and zinc in nutrition.
vii. Compare and contrast the effectiveness of glycogen and fat as energy storage molecules during prolonged physical activity.
viii. Analyze the mechanisms by which competitive and non-competitive inhibitors affect enzyme activity.
ix. Examine the role of proteins in maintaining body functions.
x. How would you treat a patient with a deficiency in one of these minerals, considering dietary and supplemental interventions?
xi. Identify how milk proteins can be precipitated by lowering the pH using lemon juice. How would you apply this principle to develop a new method for producing cheese?

UNIT 16

EMPIRICAL DATA COLLECTION AND ANALYSIS

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Student Learning Outcomes (SLOs)

- Differentiate between qualitative data and quantitative data (qualitative data includes all non-numerical information obtained from observation, not from measurement. Quantitative data are obtained from measurements and always associated with random error/uncertainties determined by use of apparatus and the human limitations such as reaction times)
- Justify the propagation of random errors in data processing shows the impact of the uncertainties on the final result. Some examples main include;

  *When we process data that contains random errors these as errors can propagate or accumulate throughout the calculation resulting in large uncertainties in the final result.
- For example if we measure the length and width of a rectangle to calculate its area, any small error in the measurement of length and width will propagate through the area calculation resulting in larger uncertainties in the final area measurement. This information is critical in the scientific research as it helps us assess the reliability of our data and draw valid conclusion from our experiments.
- Analyse the concept that experimental design and procedure usually lead to systematic errors in measurements, which causes are deviation in a particular direction.
- Justify that repeat trials and measurements will reduce random errors but not systematic errors.
- Explain that graphical techniques are an effective means of communicating the effect of an independent variable on a dependent variable and can lead to the determination of physical quantities.
- Discuss that sketched graphs have labelled but unscaled axes, and are used to show qualitative trends such as variables that are proportional or inversely proportional.
- Discuss that drawn graphs have labelled and scaled axes, and are used in quantitative measurements.

Analytical chemistry is mainly related to the chemical characterization of materials. Everything we use or consume is made up of chemicals and knowledge of the chemical composition of any substance is important in our daily life. Analytical chemistry plays an important role in nearly all aspects of chemistry, for example, agricultural, clinical, environmental, forensic, manufacturing, metallurgical, and pharmaceutical chemistry.

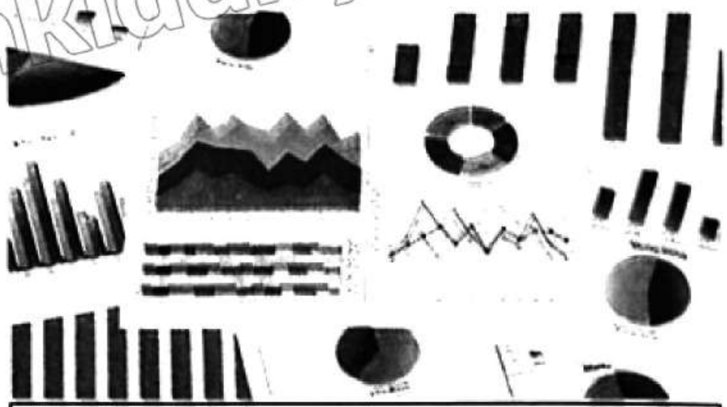

Fig 16.1

The percentage of nitrogen in fertilizers determines its value. The food quality is determined by the presence of essential nutrients, minerals and vitamins in it. The air quality is determined by monitoring the pollutants in it, which contaminate the air. In diabetics, blood glucose is monitored periodically. The presence of trace elements from gunpowder on a murder defendant's hand will prove a gun was fired. The efficacy of drugs is determined by their purity. Thus in every field of life analytical chemistry is involved in one way or the other.

16.1 Types of Data

Chemical characterisation data is of two types. Both are important for understanding chemical phenomena.

1. Qualitative data
2. Quantitative data

Qualitative data in chemistry refers to non-numeric information derived from observations about chemical characteristics and reactions. For example; observing the colour change of a reagent in a solution to determine the presence of specific ions or molecules, identifying the type of chemical reaction (e.g., exothermic, endothermic, or absorption), reporting the chemical sample's odour, colour and state (solid, liquid or gas). This means qualitative data is about describing the properties and behaviour of substances and reactions.

On the other hand, quantitative data refers to numerical measurements that are obtained from experiments. Quantitative data is obtained from instruments. For example concentration, weight, volume, temperature, etc. This means quantitative data, is about measuring and calculating certain numerical values.

Quantitative data are often obtained from measurements of substances and reactions. These measurements can include mass, volume, concentration, temperature, and other properties. Random error and uncertainty are always present in these measurements, which arise from the limitations of the apparatus used and human factors. For examples;

(1) For determining concentration of a substance burette, pipette, and volumetric flask is used for titrations. Inaccurate calibration of these glass wares, improper cleaning of glass ware, and human error in reading the meniscus are sources of errors. In a

titration experiment to determine the concentration of an acid, the volume of the titrant added from a burette is measured. Small errors in reading the meniscus level or *the initial* and final readings can lead to uncertainties in the calculated concentration.

(2) For mass measurement an analytical balance is used. Improper calibration of the balance, air currents in the laboratory, and cleanliness of the balance pan can cause error in measurement. Weighing a sample of a chemical compound for a reaction, even a slight draft in the lab or dust on the balance pan can introduce errors in the measurement.

16.2 Types of Errors

Error is the difference between the value or quantity obtained in an experiment and the value accepted in the experiment or in the literature. Primarily there are two types of errors in experiments.

(1) Random errors

Random error is the random difference between the observed value and the true value.

Random errors can be affected by:

(a) How easy the instrument or scale is to touch and read. A person reads the scale incorrectly.

(b) Changes in the environment, such as temperature fluctuations in the laboratory air currents in the room, etc.

Random errors will cause the result to deviate from the accepted value in either direction (either too high or too low). Repeating the experiment and working with the average of the results can help reduce the impact of random errors

(2) Systematic errors

Systematic error is a consistent repeatable error due to faulty equipment flawed experimental or human mistakes.

Systematic errors always pull the result away from the accepted value in the same direction (always too high or always too low).

For example, For instance, if an electronic balance is not zeroed (using a tare button), the mass weighing are always greater than they should be. If a volume is not read at eye level in a burette, the volumes are always lower than they should be because of a parallax (parabolic) error. If a cap is not kept on a spirit burner during calorimetry experiments, the alcohol evaporates, resulting in a larger mass loss. Repeating the test and working with the mean will not eliminate systematic errors.

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Measurement techniques are used.

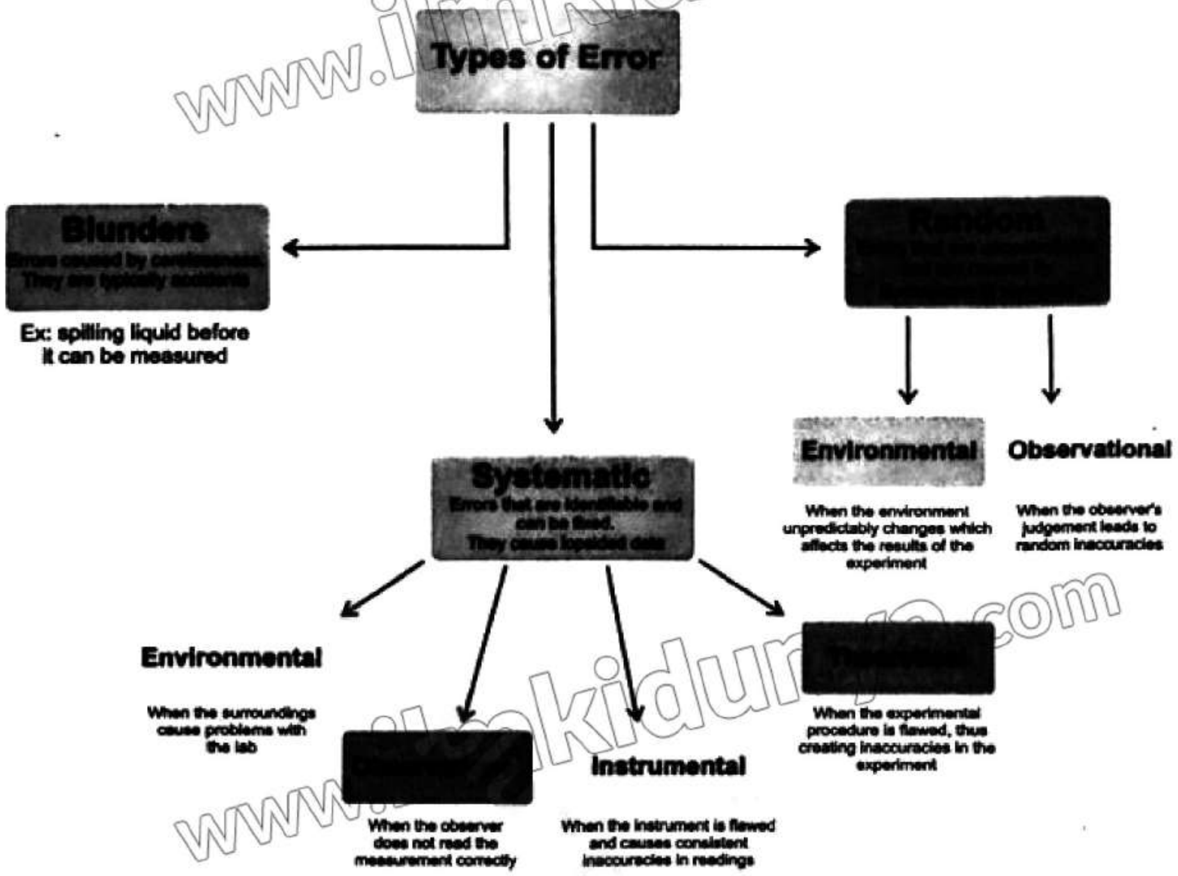

Fig 16.2

16.2.1 Propagation of random errors

When we process data that contains random errors, these errors can propagrate or accumulate throughout the calculations, resulting in larger uncertainties on the final result.

For example if we measure the length and width of a rectangle to calculate its area, any small error in the measurement of length and width will propagate through the area calculation, resulting in larger uncertainties in the final area measurement.

Let us consider an example: In the scale, the scale has division of 1cm, so the measurement can be nearest to 0.1cm

Length of the rectangle (L) = 10.0 cm

Uncertainty in length measurement (ΔL) = 0.1 cm

Width of the rectangle (W) = 5.0 cm

Uncertainty in width measurement (ΔW) = 0.1 cm

Area of rectangle = Length x Width

= 10 cm x 5 cm

= 50 cm^2

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Propagation of uncertainty:

The uncertainty in the area (Δ) an be calculated as follows;

$$\begin{aligned}\Delta A &= [\,W \times \Delta W\,] + [\,L \times \Delta L\,]\\ &= [\,5.0\text{ cm} \times 0.1\text{ cm}\,] + [\,10.0\text{ cm} \times 0.1\text{ cm}\,]\\ &= [\,0.5\text{ cm}^2\,] + [\,1.0\text{cm}^2\,]\\ &= 1.5\text{ cm}^2\end{aligned}$$

Calculated area of the rectangle is 50.0 cm^2

The uncertainty in the area is 1.5 cm^2

So, the final area of the rectangle can be reported as 50 ± 1.5 cm^2. This means due to uncertainty in the measured length and width, the area of the rectangle could be as low as 48.5 cm^2 or as high as 51.5 cm^2. This range of possible values allows us to understand the practical variability in our measurements. This information is critical in the scientific research as it helps us assess the reliability of our data and draw valid conclusion from our experiments.

16.2.2 Systematic errors and 'experimental design and procedure

The design and implementation of experiments are carefully planned to reduce errors, but they can inadvertently introduce systematic errors that consistently skew measurements away from the true value. These errors can be caused by various factors, including equipment calibration, environmental conditions, and human biases, leading to a decrease in the accuracy and reliability of experimental results.

Example1:

You have designed an experiment to determine the concentration of a Alizarin or any other compound in a solution using a spectrophotometer. The following systematic errors can occur:

Error in calibration: Before using the spectrophotometer, it needs to be calibrated with standard solutions of known concentrations. After that calibration curve is developed. If there's an error in the calibration process, such as incorrect standard solution preparation or inaccuracies in the calibration curve. All final results would be doubtful.

Sample Preparation: The way you prepare the sample can bring in systematic errors. For example, if you consistently add slightly more or less of the sample solution to the cuvette each time, it will increase the concentration and in turn the measured absorbance and thus the concentration.

Instrument performance: Over time, the spectrophotometer might drift in its performance, leading to consistent errors in absorbance (optical density) measurements. This could be due to factors like aging of the instrument's components or damage due to shifting and misuse.

Impurity effect:

The impurity effect can also be called matrix effect. In the matrix if the impurities are present other than your compound of interest, they can interfere in the optical density or light absorption intensity, giving rise an error in the concentration measurements.

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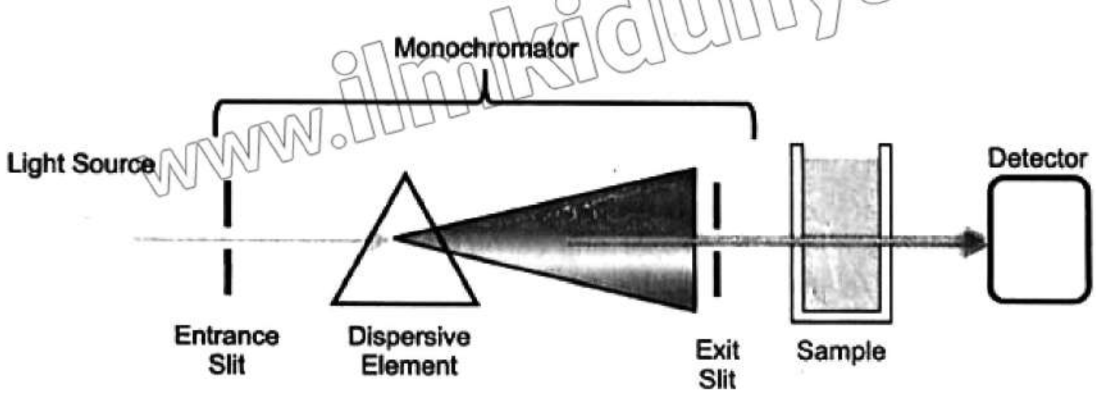


Fig 16.3

Example 2: If an analyst or student tries to find out the concentration of a reducing agent ($FeSO_4$) solution with the help of acidified $KMnO_4$ volumetrically, the following systematic errors can occur:

i) Error in volume measurements:

If a student measures the volume without properly calibrated burette pippet, or if the meniscus reading is inaccurate this will cause a deviation from the true value in the results.

ii) Impurity in analytical reagents:

If the reagents used like $KMnO_4$ or sulphuric acid has a degree of impurity in them the measured concentration will have a deviation from the true value of the sample concentration.

iii) Effect of temperature fluctuation:

The rate of the reaction and equilibrium is greatly affected by temperature changes which may lead to a potential error in the titration. For example, the rate of the reaction may increase by warming mixture of sulphuric acid and ferrous sulphate during titration, which leads to the deviation of concentration measurements from true value.

iv) Incomplete redox reaction:

If the redox reaction between oxidizing and reducing agents is not complete, it can lead to incorrect endpoint and consequently, the concentration calculations will become incorrect. This may be due to inhibitors present in the reaction mixture or due to inadequate stirring.

To avoid such systematic and random errors in the experiment, we should revise the experimental design and procedure.

16.3 Repeat trials and the elimination of errors

The random errors can be reduced by repeat trials and measurements in chemical analysis, as they help assess uncertainty or variability in the analysis. This assures a more accurate determination of the desired quantity. This is due to the fact that random errors are typically unpredictable, and variations usually occur in different readings. It makes it necessary to take repeated and concordant readings to estimate associated uncertainty, along with true value.

However, systematic errors cannot be eliminated by repeat trials, because systematic errors are consistent. These are determinate errors means they are predictable errors, and they happen due to certain known reasons. Systematic errors are caused by reasons such as incorrect calibration of instruments, impurity in analytical reagents, or due to temperature fluctuations. These reasons deviate the measurements in the same fashion either positive or negative.

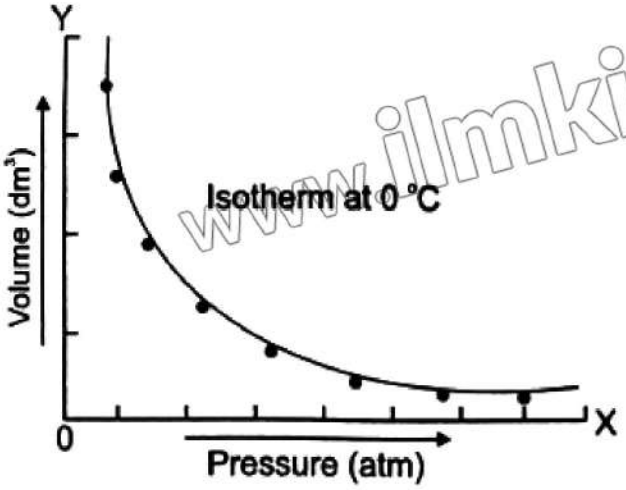
To rule out the systematic errors, it is necessary to control them after identifying the source of error. This can be achieved by proper and correct calibration of instruments, using high quality and the purest reagents available, and ensuring consistent conditions in the lab. This practice will minimise the impact of systematic errors on accuracy.

16.4 Graphical techniques and data of variables

Drawing graphs is an effective method to represent the relationship between two variables i.e. the effect of independent variable on a dependent variable.

Dependant variable: The variable that is affected by changes in the independent variable and this is usually plotted on y - axis.

Independent variable: It is manipulated or controlled by the individual who is doing experiment. It is plotted on x - axis.



Graph 16.4

Fig 16.5

For example, in the pressure-volume graph (Boyle's law), pressure is independent variable and the volume is the dependent variable.

By making a graph between two variables the relationship is visualised, and visually comprehended that how does an independent variable affects on the dependent variable. The graphs depict the relationship between variables, whether they are direct, inverse or more complex.

The graph can also be used to determine certain physical quantities, for example, the rate of change (slope = tanθ) between the variables. The slope can represent important physical properties like acceleration, rate of reaction, or consistency in a relationship.

Thus, the graphical method of representing data has greater visual appeal than a table and also represents relationships which may help in drawing extra plots.

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16.5 Sketched Graphs

16.5.1 Sketched Graphs; Unscaled but Labelled Axes

Sketched graph is a way of visual representation, whose purpose is to represent qualitative trends rather than precise mathematical values. These graphs have the following salient features.

Labelled Axes

The variables which are to be represented on x and y axis are labelled in the sketch graphs, but numerical values are missing in these graphs, i.e. they are not scaled. For example the in the graph 16.1 which is a sketched graph, the axes are labelled as volume and pressure but there is no value or units of pressure and volume along the axes.

Unscaled Axes

Since the graphs are unscaled there is no grid line or tick marks which correspond to specific numerical increments. The major focus of this graph is shape and direction of the line or the curve.

Uses and Advantages

Sketched graphs serve various purposes effectively:

Conceptual Comprehension:. They facilitate the visualization and explanation of variable behaviours, helping in the conceptual cognition of physical phenomena.

Preliminary Assessment: Sketched graphs are valuable in initial data scrutiny, helping to identify potential patterns and correlations before going into comprehensive quantitative analysis.

Educational Applications: Sketched graphs find frequent use in educational contexts to introduce principles and concepts without the complexity of precise numerical data.

Instant Visualizations: Generating sketched graphs offers a swift and effective means of illustrating relationships, making them beneficial for brainstorming, presentations, or rapid analyses.

16.5.2 Drawn Graphs with Labelled and Scaled Axes

Drawn graphs are quantitative, graphical representation of the relationship between two variables. They have labelled and scaled axes. They give very important quantitative information about the quantities being plotted. The scale tells the intervals of quantities on each axis using a suitable unit of measurement. Scaled axes ascertain that the data points are correctly represented with relation to each other. The scale determines the gaps at which values are placed along each axis. This ensures the precise measurements andcomparisons between different data points. For example, the temp-density graph's scale on the x-axis shows temperature, each mark denotes increments of one-degree celsius, ensuring that temperature gaps are accurately reflected.

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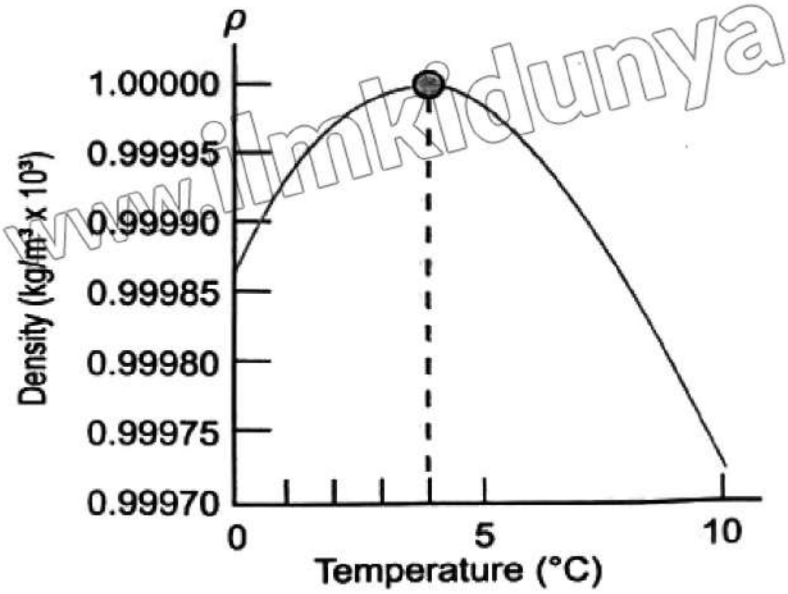
The density of water at different temperature

Temperature (°C)	Density (gcm^{-3})
100	0.9584
50	0.9880
25	0.9970
10	0.9997
6	0.9999
4	1.0000
0 (water)	0.9998
0 (ice)	0.9167



Graph 16.6: Scaled graph

It is more convenient to read patterns of increasing or decreasing order from a scaled graph, than by using a tabulated data.

Drawn graphs are useful for representing quantitative measurements, where numerical data is plotted. This includes variables such as density, distance, mass, temperature, or any other measurable quantity. By plotting data points on a graph, patterns, trends, and anomalies become visually apparent, aiding in data interpretation.

Drawn graphs are effective means for communicating results to a wide range of audience like general public. They successfully convey complex information in a visually accessible format, enabling easier understanding and interpretation of data.

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16.5.3 How to calculate slope of a graph

1. Pick any two points on the line: Label them as Point 1 (x_1,y_1) and Point 2 (x_2,y_2).
2. Find the vertical change (rise): Subtract the y-values: y_2-y_1.
3. Find the horizontal change (run): Subtract the x-values: x_2-x_1
4. Divide rise by run to get the slope:

$$\text{Slope} = tan\theta = \frac{\text{perpendicular}}{\text{base}}$$

$$m = tan\theta = \frac{y_2 - y_1}{x_2 - x_1}$$

This slope tells you how steep the line is. Positive means uphill, negative means downhill, zero means flat, and undefined means vertical.

KEY POINTS

- Analytical chemistry is mainly related with the chemical characterization of materials.
- Quantitative analysis deals with the determination of how much of one or more constituents is present.
- There are two types of errors in data collection and in analysis leading to faulty results namely Random Errors, and Systematic errors.
- Random errors occur due to natural variability in the measurement process and can be caused by factors such as limitations in the measuring instrument, fluctuations in environmental conditions etc.
- Systematic error can be caused by an imperfection in the equipment being used.
- Error that can occur due to negligence or carelessness during the measurement process.
- Systematic errors cannot be eliminated by repeat trials, because systematic errors are consistent.
- There are two types of graphs; sketch graphs and drawn graphs.
- Drawn graphs are useful for representing quantitative measurements, where numerical data is plotted.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which of the following is the example of qualitative analysis?
   a) Volumetry
   b) Spectrophotometry
   c) Gravimetry
   d) Precipitation

ii. During titration the burette is not correctly calibrated. The error that will generate due to this is categorised as:
   a) Random error
   b) Systematic error
   c) Indeterminate error
   d) Rough error

iii. Which error can be reduced or eliminated by taking repeat trials?
   a) Random errors
   b) Systematic error
   c) Determinate error
   d) Rough error

iv. Which one of the following gives more information?
   a) Information on x-axis
   b) Information on y-axis
   c) Information in un-scaled graph
   d) Information in scales graph

v. The density of water ___ from 4 °C to 0 °C.
   a) Increases
   b) Decreases
   c) Remains constant
   d) Fluctuates irregularly

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2. Short Answer Questions

i. Explain qualitative and quantitative analysis with examples.

ii. What are random errors, write few examples.

iii. How does the error propegates? Give an example.

iv. Explain with one example each of dependent variable and independent variable.

3. Long Answer Questions

i. Explain errors and their types in detail.

ii. What are few methods to eliminate errors in analysis.

UNIT 17

QUALITATIVE ANALYSIS
(Mass Spectrometry)

Student Learning Outcomes (SLOs)

- Analyse mass spectra in terms of m/ e values and isotopic abundances.
- Calculate the relative atomic mass of an element given the relative abundance of it's isotopes or it's mass spectrum.
- Deduce the molecular mass of an organic molecule from the molecular ion peak in the mass spectrum.
- Suggest the identity of molecules by simple fragmentation in a given mass spectrum.
- Deduce the number of C atoms "n" in a compound using the M+1 peak and the formula:

$$\text{Number of carbon-atoms} = \frac{\text{relative intensity of M+1 peak}}{0.01107 \times \text{relative intensity of } M^{+}}$$

- Deduce the presence of chlorine and bromine atoms in a compound using M+. peak in mass spectrum.

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General uses and instrumentation of Mass Spectrometry have already been discussed in grade XI. It is a very useful tool to analyse the number of isotopes of an element and their relative abundances. Furthermore, it is also used to determine the molecular masses and help in the structure determination of organic molecules, especially organic molecules. Another advanced benefit of mass spectrometry is the study of reaction mechanisms by finding fragmental masses of molecular fragment cations and intermediate cations formed during the reaction.

17.1 How to analyse a number of isotopes and their relative abundances of isotopes?

The number of peaks that appear on a proper m/z value in the mass spectrum tells us about the number of isotopes. For example, two peaks are seen in the mass spectrum of chlorine which shows that there are two isotopes of chlorine present in the natural sample. Similarly, three peaks in the hydrogen spectrum tell us about three isotopes of hydrogen namely protium, deuterium and tritium.

Secondly, the height of each peak tells us about the relative abundances of each isotope in terms of percentage.

17.2 Calculation of relative atomic masses:

The relative atomic mass of an element can be calculated by the given formula using the relative abundance of each isotope with its m/z value.

$$\text{Relative (avg.) atomic mass} = \frac{\sum \text{(mass number)} \times \text{(isotope abundance)}}{100}$$

For example, the study of the Boron(z=5) spectrum tells the number of isotopes with relative abundances of isotopes are as follows:

Mass number of boron =10

Relative abundance of boron=19.90%

Mass number=11

Relative abundance B-11= 80.10%

It's average atomic mass can be calculated by putting this information in the formula.

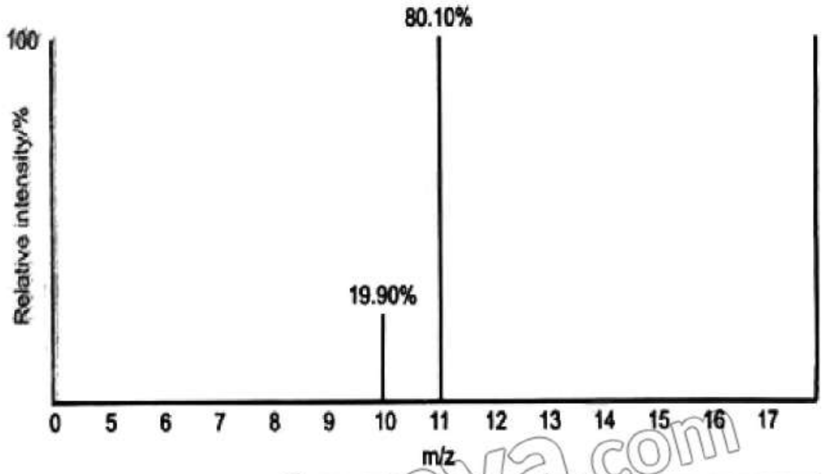

Fig 17.1: Mass spectrum of boron

$$\text{Avg. Atomic mass of Boron} = \frac{(10 \times 19.90) + (11 \times 80.10)}{100} = 10.801\text{amu}$$

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CONCEPT ASSESSMENT EXERCISE 17.1

Question: Using the given spectrum, calculate the average atomic mass of the element and find out to which element this spectrum belongs. You can take the help of the periodic table.

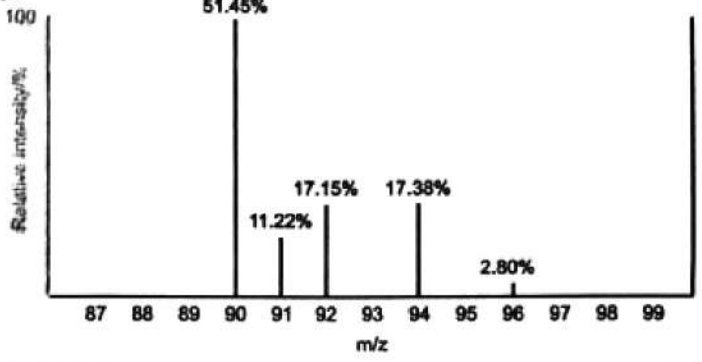

Fig 17.2:

17.3 Determination of molecular mass by molecular ion peak

The first thing to do is the identification of the molecular ion peak (M^+). The molecular ion peak is the peak in a mass spectrum that represents the molecular ion (symbol: M^+ peak). The molecular ion peak is the point with the largest mass-to-charge ratio after excluding any peaks caused by the presence of heavier isotopes. Then you check the m/z value of the molecular ion peak. Another important characteristic peak of a compound in mass spectrum is base peak. The base peak is due to the most abundant ion of the molecule which is given abundance of 100. The peak corresponding to the most abundant ion is called base peak.

The value of m/z of molecular ion peak is equal to the molecular mass because most of the ions carry +1 charge. If isotopes are present with greater mass but less relative abundance their peaks will arise at a greater m/z. For example, if an organic compound has ^{13}C isotope a smaller peak at (M+1) one m/z greater than the molecular ion peak.

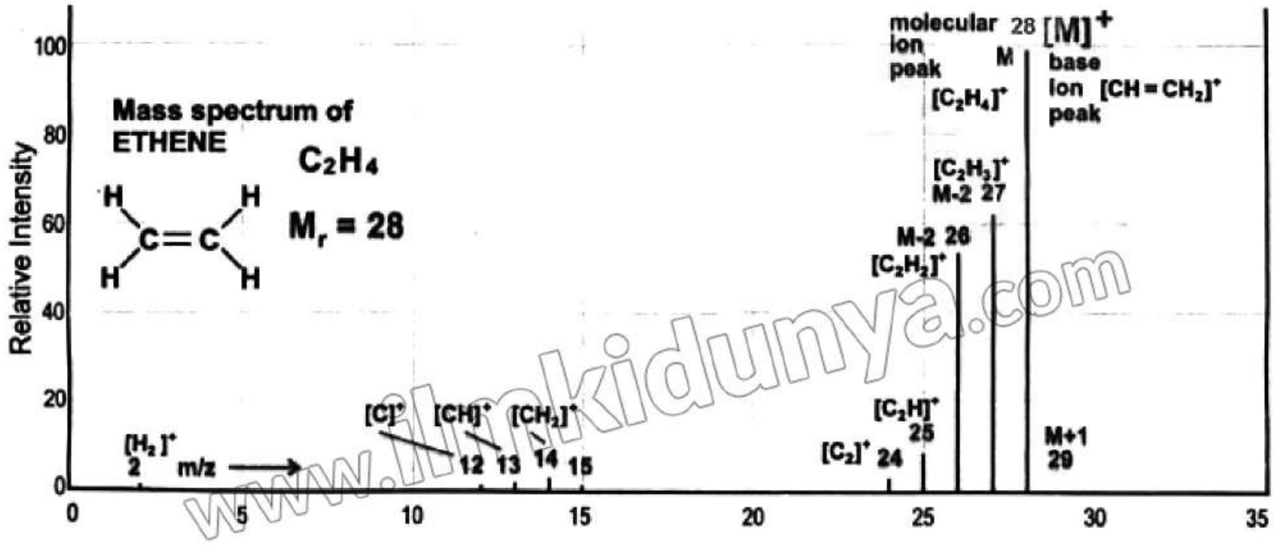

Fig 17.3 Mass spectrum of ethene

For example, the molecular ion or heaviest peak for hexane appears at 86 m/z. Let us explain the mass spectrum of the ethene molecule. In the figure the molecular ion peak appears at m/z= 28 which is equivalent to the molecular mass of ethene. The peak at 29 is the M+1 peak due to one of carbon in ethene that is C-13 isotope having 1% abundance. The peak is at m/z=30 is the M+2 peak due to the presence of both carbons as C-13 in ethene. M+2 peak usually much smaller than M+1 and M peaks. The other peaks are formed by all those fragment ions formed during the process of mass Spectrometry.

17.4 Identification of a molecule by fragmentation pattern

By the impact of electrons from the electron gun onto the molecules, molecule undergoes fragmentation. Dissociation of the bond depends on the type of functional group, usually the weakest bond breaks and the most stable fragments are formed. Among the fragments only cations are carried to the detector. In the mass s Mass spectrum of n-pentane s usually the fragments of m/z=15 and m/z=14 are formed corresponding to the (CH_3^+) methyl cation. Similarly, m/z=29 peak also appears which represents ethyl ($CH_3CH_2^+$) cation and m/z=43 for the propyl cation($CH_3CH_2CH_2^+$).

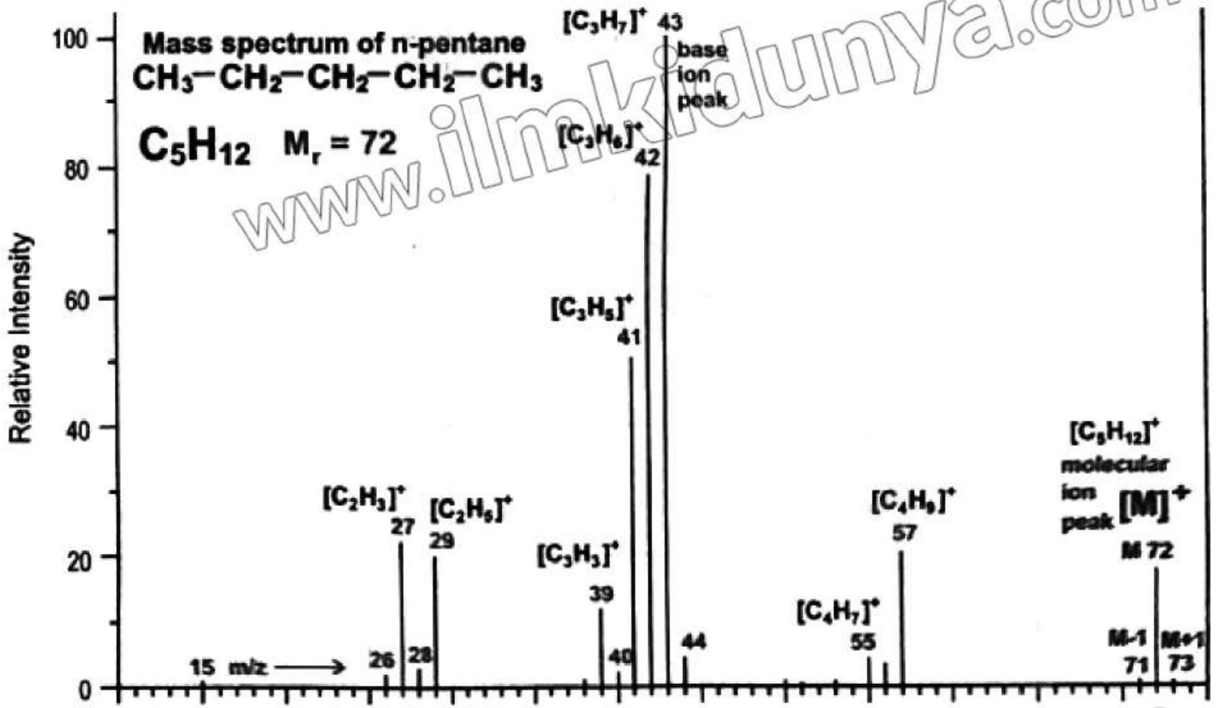

Fig 17.4: Mass spectrum of n-pentane

m/z=41 peak is formed 2 Hydrogen atoms from propyl cation to form propylene cation ($^+CH_2CH{=}CH_2$). Some stable ions are also formed by the rearrangement of unstable ions.

In the above fragmentation pattern of n-pentane given in the figure shows that molecular ion peak is formed at m/z=72. This molecular ion is fragmented by electron impact into ethyl radical and propyl cations. There are equal chances of the formation of ethyl cation(m/z=29) and propyl radical. During this fragmentation, CH_3^+ is also formed giving a peak at m/z=15. Thus the fragmentation pattern in the mass spectrum and molecular ion peak give considerable clues regarding the molecular structure.

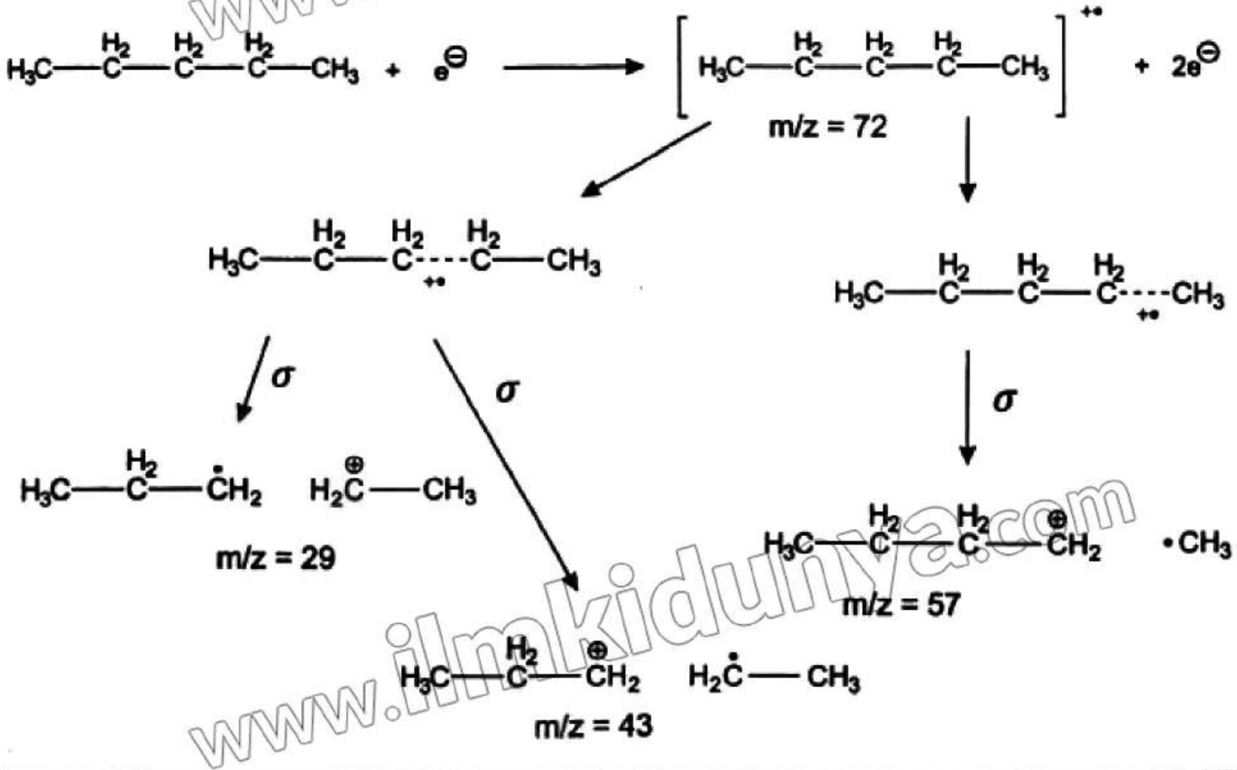

Fig 17.5: fragmentation pattern of n-pentane

Similarly for functional groups like alcohols, a peak with one less than the molecular ion peak M-1 appears by the loss of hydrogen from the OH group. By the loss of the OH group M-17 peak is obtained, this OH group can be a cation OH^+ giving rise to a peak at m/z=17 as well.

17. 5 Deduction of C-number in a molecule:

From intensities of the molecular ion and molecular ion plus one ($M^+ +1$), we can calculate the number of carbon atoms in a molecule by using the formula:

$$\text{Number of carbon-atoms} = \frac{100 \times \text{abundance of M+1 peak}}{1.1 \times \text{abundance of } M^+ \text{ peak}}$$

Example: Determine the molecular formula of a molecule with a molecular ion peak of relative abundance of 27.32% and M+1 peak with a relative intensity of 2.10%.

Solution: By putting the values of relative intensities in the above formula we get:

$$\text{Number of carbon-atoms} = \frac{100 \times 2.10}{1.1 \times 27.32}$$

$$6.94 \cong 7$$

So there are seven carbon atoms in this molecule.

17.6 Deduction of the presence of Chlorine and Bromine in a molecule

Both Chlorine and Bromine have considerable relative abundances of their heavier isotopes, so they can be recognised by peaks of greater m/z in their mass spectra.

Chlorine: The molecular ion peak (M^+) of chlorine appears at m/z = 35 due to greater relative abundance (75.77%). We get an additional peak of one-third height at M+2 due to the presence of heavy isotope Cl-37 with a relative abundance of 24.23%. The height of this peak confirms the presence of Chlorine.

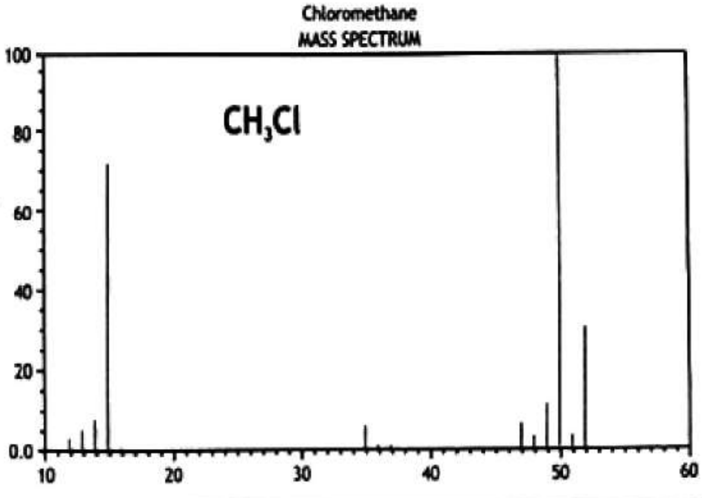

Fig 17.6: Mass spectrum of methyl chloride

The above spectrum of chloromethane shows the molecular ion peak at m/z=50 which is equivalent to molecular mass of CH_3Cl. Another considerable peak at m/z=52 represents the presence of heavy isotope Cl-37 with a relative abundance one third of the molecular ion peak.

Bromine: The two isotopes of bromine i.e. Br-79 and Br-81 have relative abundances of 50.50% and 49.50%, respectively. We should get molecular ion peak (M^+) at m/z=79 and another peak of approximately the same height at m/z= 81. This is the M+2 peak. As it is obvious from the mass spectrum of Bromoethane molecular ion peak appeared at m/z=108 which is equivalent to its molecular mass and the M^{+2} peak is slightly smaller at m/z= 110 representing the presence of heavier isotope Br-81.

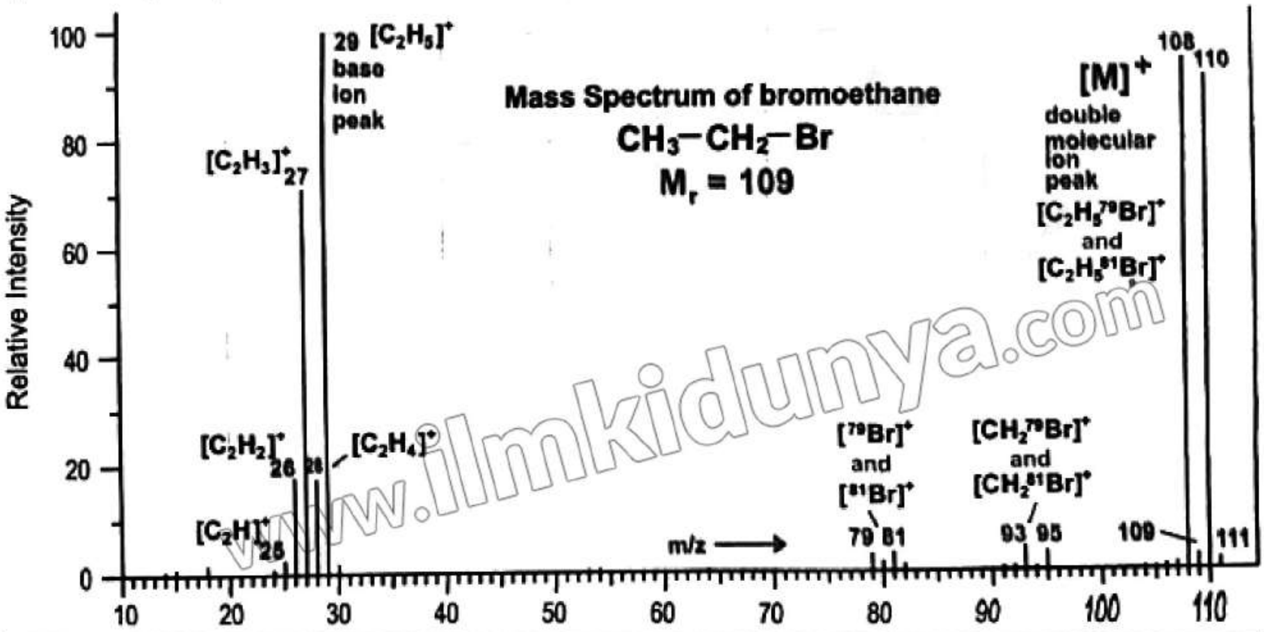

Fig 17.7: Mass spectrum of ethyl bromide

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KEY POINTS

- Mass Spectrometry is a very useful tool to analyse relative abundances of the isotopes of an element in a compound.
- The number of peaks that appear on a proper m/z value in the mass spectrum tells us about the number of isotopes.
- The height of each peak tell us about the relative abundances of each isotope in terms of percentage.
- The molecular ion peak is the peak in a mass spectrum that represents the molecular ion (symbol: M^{+} Peak).
- By the impact of electrons from the electron gun on to the molecules, molecule undergoes fragmentation.
- We can calculate number of carbon atoms in a molecule by using a formula using the information obtained by mass spectrum.

References:

1. Mass Spectrometry by Jürgen H Gross, 2004
2. Introduction to spectroscopy byDonald L Pavia, 2008
3. Spectra imagine courtesy by Google images

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EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which is not the field of mass spectrometry?

a) Molecular mass

b) Relative abundance of isotopes

c) Concentration of molecules in a sample

d) Molecular structure elucidation

ii. Average atomic mass of an element can be calculated by using:

a) IR spectroscopy

b) b. UV visible spectroscopy

b) Mass spectrometry

c) d. Nuclear magnetic resonance spectroscopy

iii. Molecular mass of a compound cannot be deduced by:

a) Molecular ion peak b) Base peak

c) M+1peak d) M+2 peak

iv. Why is m/z value taken equivalent to mass?

a) Charge is zero b) Charge of ions is equal to+1

c) Charge of irons is equal to -1 d) Mass is very high as compared to charge

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v. Fragments in mass spectrum are formed by the:

   a) Impact of electrons b) Impact of protons

   c) Chemical rearrangements d) Both A and C

vi. Bromine can be recognised by:

   a) Molecular ion peak b) M+1 peak

   c) M+2 peak d) M-1 peak

1. Short Answer Questions

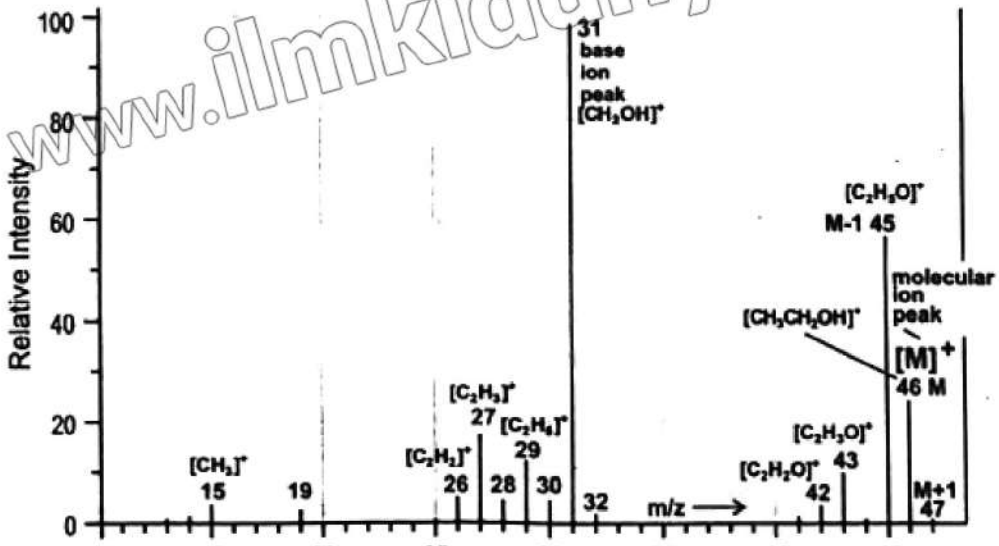
i. How can you calculate average atomic mass of an element using relative abundance is of all isotopes?

ii. How the number of carbon atoms in a molecule can be calculated by using intensities of the peaks in mass spectrum?

iii. How can you identify the presence of chlorine and bromine in the molecule using mass spectrum?

iv. What is the role of molecular ion peak in the determination of molecular mass of a substance?

v. Observe following mass spectrum of an organic compound "g" carefully and answer the given questions.



MS of the compound "g"

   a. Write few reactions that help to understand the fragmentation pattern of the sample molecule "g" whose MS is given.

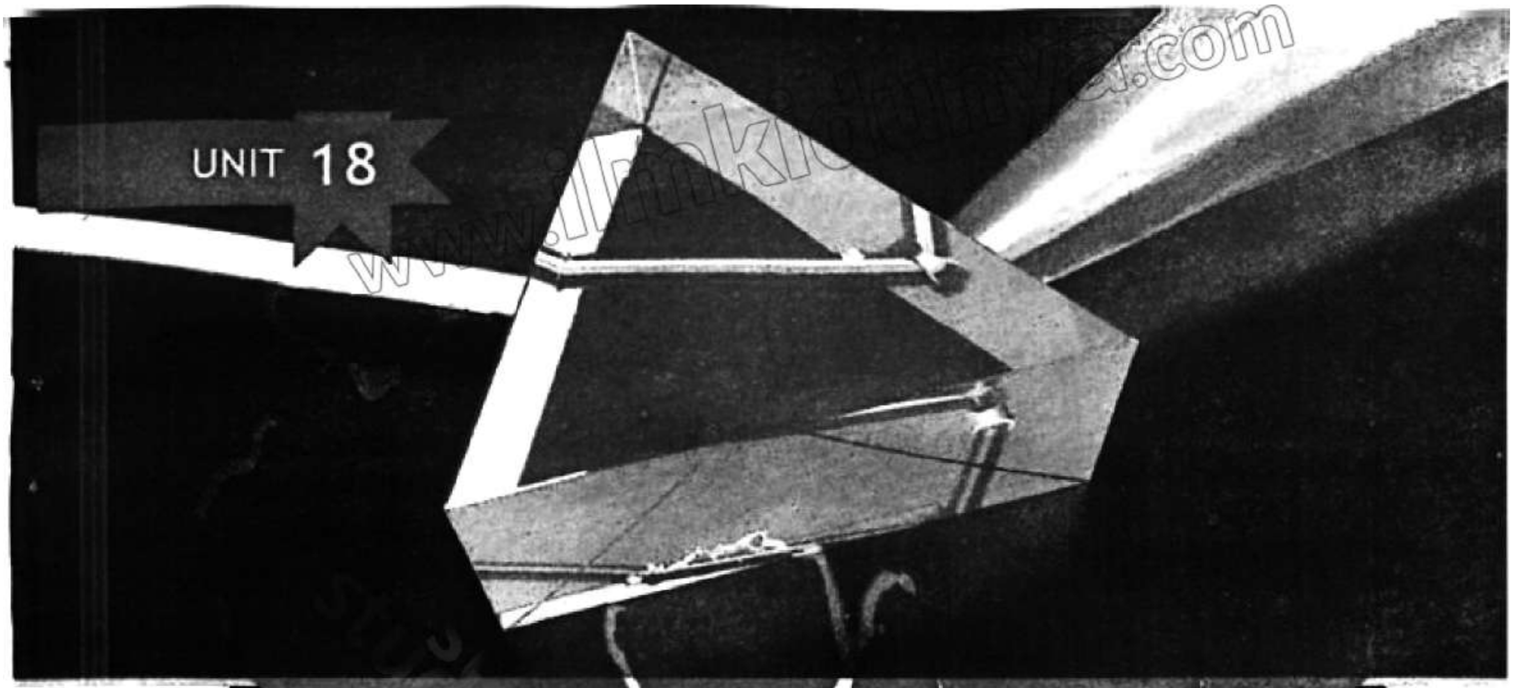
   b. Why is the peak at m/z 47 is not the molecular ion peak?

   c. What do you mean by a base-peak?

   d. What is the structural formula of the molecule g?

2. Long Answer Questions

i. Analyse in detail, the information obtained by the fragmentation pattern in mass spectrum, used for the structural elucidation of a molecule.



UNIT 18

SPECTROSCOPY

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[illegible] Outcomes (SLOs)

- Explain that the degree of unsaturation or Index of Hydrogen Deficiency (IHD) can be used to determine from a molecular formula the number of rings or multiple bonds in a molecule.
- Explore, how Mass Spectrometry (MS) proton nuclear magnetic resonance spectroscopy (1H NMR) and Infrared Spectroscopy (IR) are the techniques that can be used to help identify compounds, and to determine their structures.
- Interpret an infrared spectrum of a simple molecule to identify functional groups.
- Deduce possible structures of organic compounds using IR spectrum and molecular formula. (examples: phenol, acetone, ethanol).
- Predict weather a given molecule will absorb in the UV-Visible region.
- Predict the colour of a transition metal complex from its UV-Visible spectrum.
- Explain atomic emission and atomic absorption spectrum.
- Analyse different environments of carbon atoms present in a simple molecule using 13C-NMR spectrum.
- Using 13C-NMR to deduce possible structure of a simple molecule.
- Predict the number of peaks in 13C-NMR spectrum for a given molecule.
- Analyse different environments of protons present in a simple molecule using (proton) 1H-NMR spectrum.
- Use a (proton) 1H-NMR spectrum to deduce relative number of each type of proton present, the number of equivalent protons on the carbon atom adjacent to the one to which the given proton is attached.

- Deduce possible structures of the molecule.
- Predict the chemical shift and splitting patterns of the protons in the given molecule.
- Explain the use of Tetra methyl silane (TMS) as the standard for chemical shift measurement.
- Recognise the need for deuterated solvent e.g. $CDCl_3$ when obtaining a proton NMR spectrum.
- Describe the identification of O-H and N-H protons by proton exchange using D_2O

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Spectroscopy is a technique used for structural elucidation of the molecule. It is based on the interaction of atoms or molecules with electromagnetic radiations. Spectroscopy is a very powerful technique used by the chemists of the world to determine the composition and structure of any compound. It exploits the interaction of electromagnetic radiations with matter.

Electromagnetic Spectrum

The electromagnetic spectrum is the range of all frequencies of electromagnetic radiation.

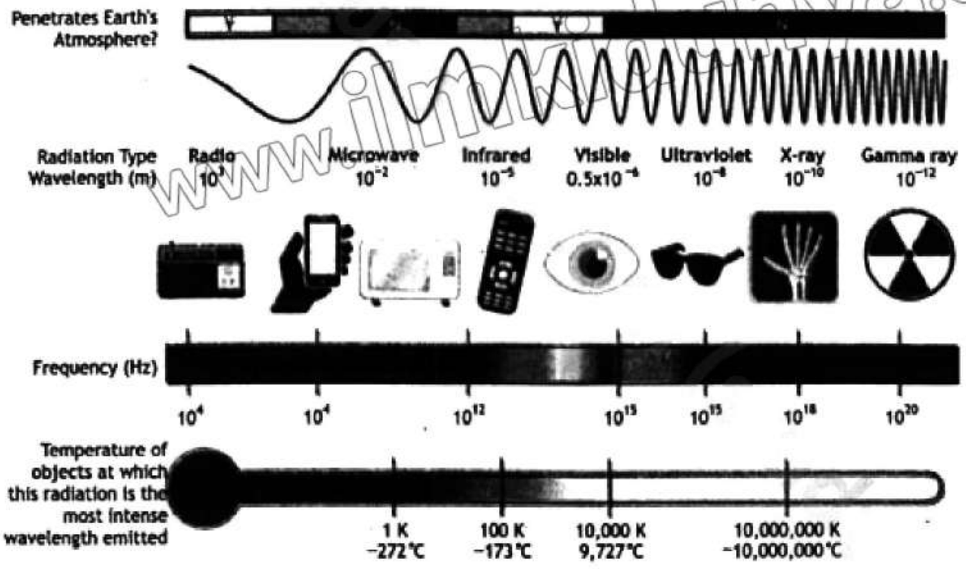

Fig 18.1: Electromagnetic Spectrum

18.1 Spectroscopic Techniques

The major spectroscopic techniques used for organic compounds are:

1. **UV-Visible** spectroscopy is used to find out the conjugation, predict the colour and concentration in compounds.
2. **IR-spectroscopy** is used for the determination of functional group in the organic compounds.
3. **NMR- spectroscopy** is used to find out the number of particular types of atoms in a molecule usually hydrogen-1and carbon-13.

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4. **Mass Spectrometry** is the technique used for finding out molecular masses, fragment mass, and relative atomic masses of isotopes of an element.
   Each molecule in a compound is very specific to absorb the electromagnetic radiations of a specific region. On absorbing specific wavelength of light each molecule undergoes a different type of change, that is observed. This gives the key to understand the structure of an organic compound.

18.2 Index of Hydrogen Deficiency or Unsaturation

The total number of rings and pi bonds can be determined by the use of index of hydrogen deficiency (IHD) or degree of unsaturation in an organic compound. It compares the molecular formula that contains all sigma bonds and the molecular formula of the given compound, in such a way that the difference of atoms which are deficient in the actual compound as compared to the fully saturated compound is obtained. A ring in the structural formula of organic compound contributes 1 in the degree of hydrogen deficiency.

Example 18.1

"Degrees of Unsaturation" (or "Index of Hydrogen Deficiency")

- In a hydrocarbon with no double bonds or rings, the number of hydrogens and carbons is related as follows:

  Number of hydrogens = (2 x number of carbons) + 2

- Each multiple bond or ring reduces the hydrogen count by 2, which we refer to as a "degree of unsaturation"
- The degrees of unsaturation in a molecule can be calculated from its molecular formula using the following calculation:

$$\text{Degrees of Unsaturation} = \frac{2C + 2 + N - H - X}{2}$$

C = #carbons
H = #hydrogens
N = #nitrogens
X = #halogens

- Note that this tells you the *sum* of [multiple bonds + rings], but does not specify exactly how many multiple bonds or rings are present.
- This simple and fast calculation is a useful first step to take when confronted with determining the structure of an unknown molecule.

Calculate the degree of unsaturation in ethene (C_2H_4)

The molecular formula of ethene is C_2H_4. To calculate the degree of unsaturation, we use the formula:

Degree of Unsaturation = (2C + 2 - H-X)/2

In this case, there are 2 carbon atoms and 4 hydrogen atoms and number of halogen atoms in the molecule. Substituting these values into the formula, we get:

Degree of Unsaturation = (2 x 2 + 2 - 4-0)/2 = 1

So the degree of unsaturation for ethene is 1.

CONCEPT ASSESSMENT EXERCISE 18.1

Calculate the degree of unsaturation in:

a. Benzene (C_6H_6) b. Ethyne(C_2H_2)

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18.3 IR Spectroscopy

IR spectroscopy makes use of interaction of infrared radiations with organic molecules. Its typical range of wave number is from 4000 cm^{-1} to 625 cm^{-1} and it is used to analyse the functional group present in an organic compound. Each functional group absorbs a *specific* component of the IR radiations thus it is recognised. This technique is widely used in organic and inorganic compounds. It helps in the identification of molecular structure. It has high scan speed, resolution and sensitivity which makes it a very useful tool.

18.3.1 Principle of IR spectroscopy

When an organic molecule having any functional group composed of some hetero atom is exposed to IR radiation, the electric field component of rays interacts with the dipole moment of the molecule. If the frequency of the infrared light matches the natural vibrational frequency of a bond or a collection of bonds within the molecule, absorption occurs.

The bonds start to vibrate with greater amplitude by the absorption of this energy. It leads to a change in the dipole moment of the particular bond in a molecule. More is the polarity of the bond more is the intensity of the absorption of the bond.

The frequencies of the radiations that are absorbed are the characteristic of the molecular structure and the functional groups that are present in the sample. By analysing the IR spectrum one can find out the molecular structure especially the functional groups.

The major components of infrared spectrophotometers are;

source of IR radiations, monochromator, sample chamber, detector, data collection and processing system etc.

18.3.2 Reading an IR spectrum

To interpret an infrared spectrum we have to analyse the absorption bands, in this way we can find out the functional groups present in the structure of organic compound.

Each peak in the IR spectrum corresponds to a specific bond. This provides a fingerprint of the compound.

First of all we correlate the absorption frequencies of the unknown compound with the reference for different type of bonds. We look for the major peaks and the associated functional groups by comparing it with the reference. Functional groups like C-H, C=O, O-H, N-H, are more common.

The finger print region below 1500 cm^{-1} is unique to each compound, aiding in compound identification.

18.3.3 Some common functional groups and their characteristic IR absorption ranges

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Table 18.1: functional groups with wavenumber and intensity

Functional Group	Wavenumber (cm^{-1})	Intensity
Akyl		
C—H	2853-2962	medium-strong
Alkenyl		
=C—H	3010-3095	medium
C=C	1620-1680	variable
Alkynyl		
≡C—H	3300	strong
C≡C	2100-2260	Variable
Aromatic		
Ar—H	3030	variable
C=C	1400-1600	variable
Alcohols, Phenols & Carboxylic Acids		
O—H (alcohols / phenols)	3200-3500	broad, strong
O—H (carboxylic acids)	2500-3000	broad, variable
C—H (alcohols)	1025-1060	Strong
Aldehydes, Ketones, Esters, Carboxylic acids & Amides		
C=O (Aldehydes)	1690-1740	strong
C=O (Ketones)	1680-1750	strong
C=O (Esters	1735-1750	strong
C=O (Carboxylic acids)	1710-1780	strong
C=O (Amides	1630-1690	strong
Amines		
N—H	3300-3500	medium

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Example 18.2:

Interpret the IR spectrum of a simple molecule, ethanol (C_2H_5OH)

Problem solving strategy

- Identify significant peaks.
- Compare these peaks to known wavenumber ranges for various functional groups.
- Use this information to deduce the presence of specific functional groups in the molecule.
- This method allows you to identify and confirm the functional groups in simple molecules using their IR spectra.

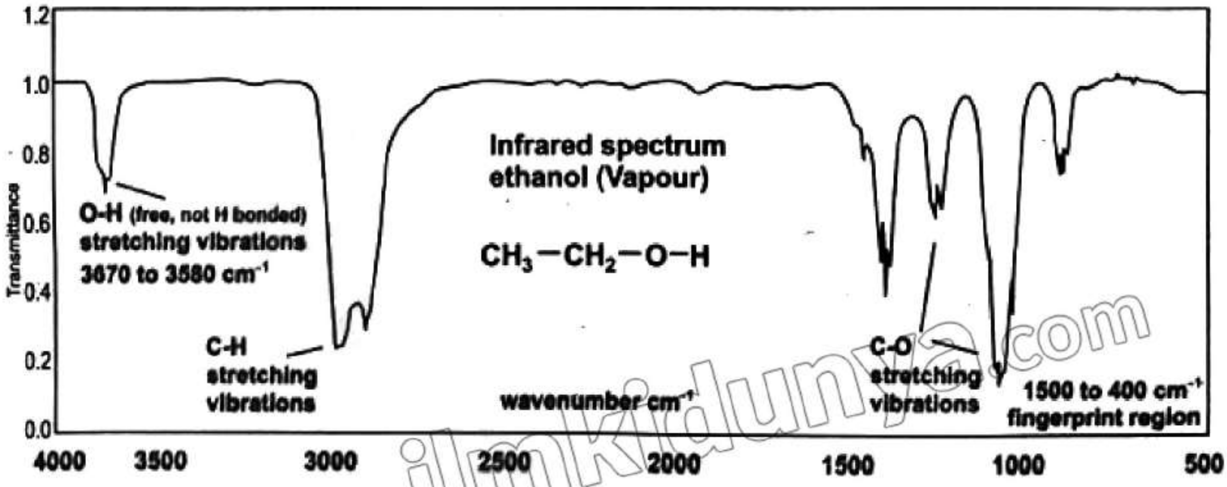

Fig 18.2: IR spectrum of ethanol

The IR spectrum of ethanol shows:

- A broad peak around 3300 cm^{-1}
- Peaks around 2850-2960 cm^{-1}
- A peak around 1050-1150 cm^{-1}

Solution

Match Peaks to Functional Groups:

- The broad peak at 3300 cm^{-1} suggests an O-H bond, confirming an alcohol functional group.
- The peaks in the 2850-2960 cm^{-1} range indicate C-H bonds, which are present in the ethyl group (C_2H_5).
- The peak around 1050-1150 cm^{-1} suggests a C-O bond, also supporting the presence of an alcohol group.

IR spectrum of acetone

This is IR spectrum of acetone (Fig 18.3) The strong absorption peak at 1700cm^{-1} to 1725cm^{-1} is the functional group C=O peak. With a small variation of wave number this peak is also visible *in the* spectrum of aldehydes, carboxylic acid and their *derivatives. At 1215cm*$^{-1}$ to1435cm^{-1} CH_2 vibration is observed. At nearly 3000cm^{-1} C-H vibration bands are seen.

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This information helps a lot in understanding the structure of the molecule.

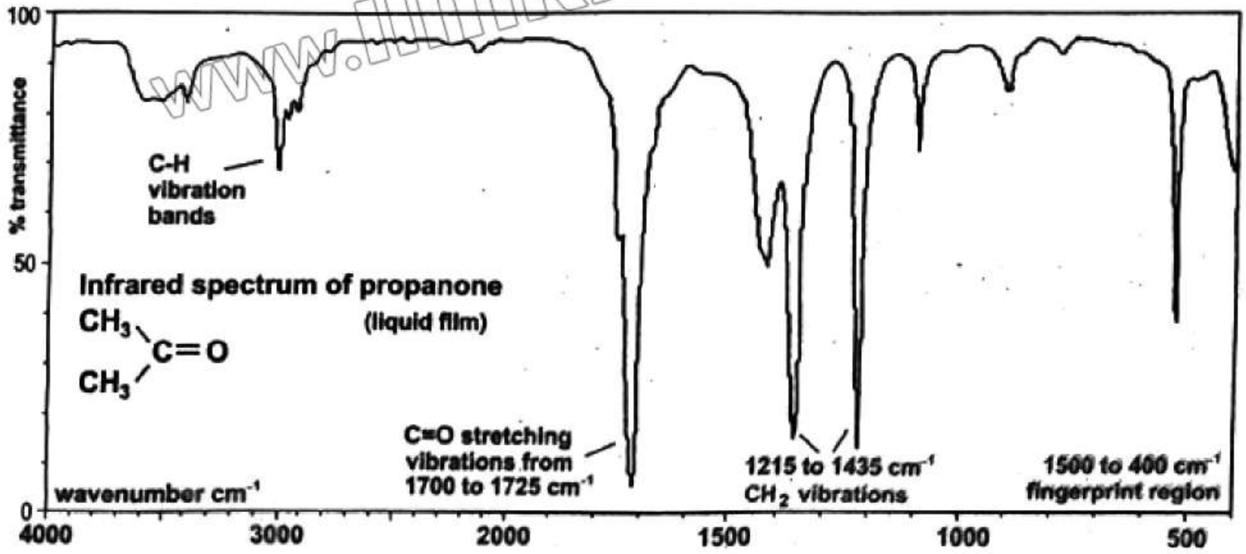

Fig 18.3: IR spectrum of acetone

IR spectrum of phenol

In the structure of phenol (Fig. 18.4) a broad and strong absorption peak represents O-H functional group attached with an aromatic ring. At around 1500 cm^{-1} conjugated double bonds absorb.

Each peak in the IR spectrum corresponds to a specific bond. This provides identification of the compound.

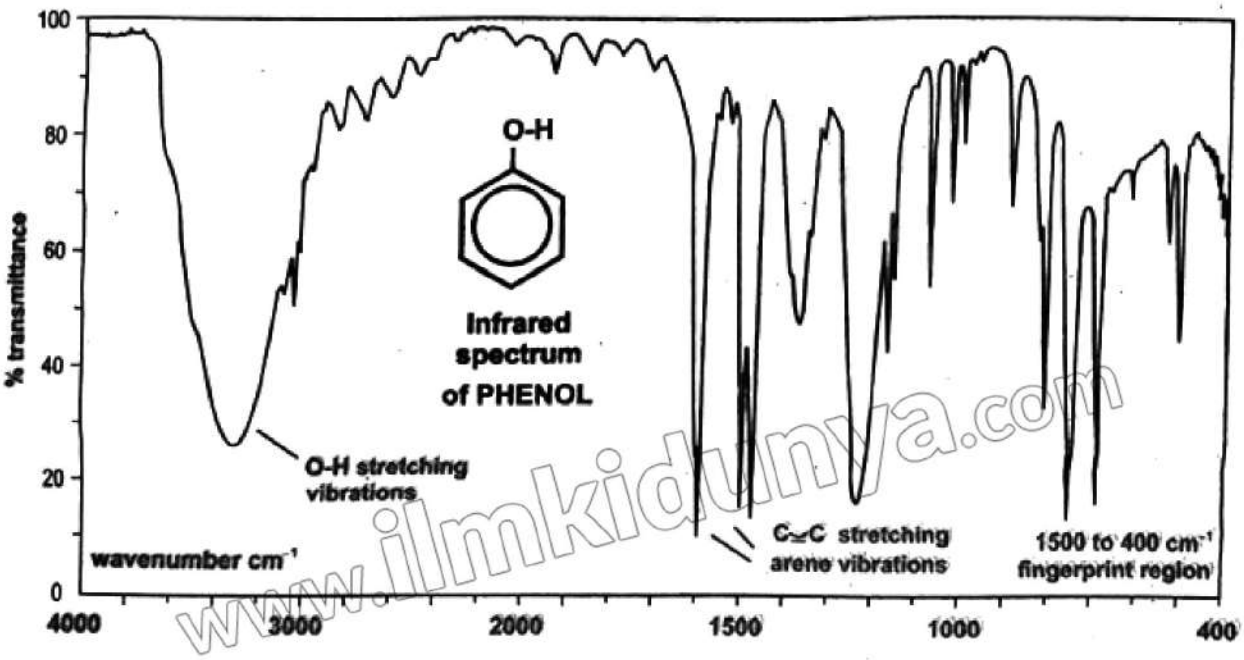

Fig 18.4: IR spectrum of phenol

18.4 UV-Visible Spectroscopy

It is the technique in which the UV and visible light absorption by any compound is measured. It's typical range of wavelength is from 200 nm-800 nm.

This technique involves the excitation of the electrons by the absorption of UV visible wavelength of light. The absorption of the light is directly proportional to the concentration of the sample having particular electrons available for excitation. UV visible spectroscopy is widely used in material sciences and biochemistry. This spectroscopy can be applied to a variety of sample types, including liquids, solids, and gases. It is used to find out the conjugation in unsaturated compounds. Usually the electronic excitations include π-π^* (pi to pi star transition), n-π^* (n to pi star transition), σ-σ^* (sigma to sigma star transition), and n-σ^* (n to sigma star transition). These transitions by the absorption of specific range of wavelength, provides the information about the molecular structure.

The coloured compounds absorb a small range of wavelength (400nm-800nm) in the visible region of electromagnetic radiations and transmit the rest of the wavelengths thus the colour appears.

The colour of the compound is not predicted by the wavelength of absorbed wavelength, but the wavelength that is reflected or transmitted.

Firstly, the wavelengths are identified that are absorbed by a coloured complex.
Secondly, we determine the energy required for the transition, the energy of the transition is related with wavelength of light absorbed. Shorter wavelength corresponds to blue and violet region while the longer wavelength region corresponds to red and orange regions.

The colour of the compound is complementary to the wavelength that are absorbed. If a complex absorbs blue or violet it will appear yellow or yellow-green etc.

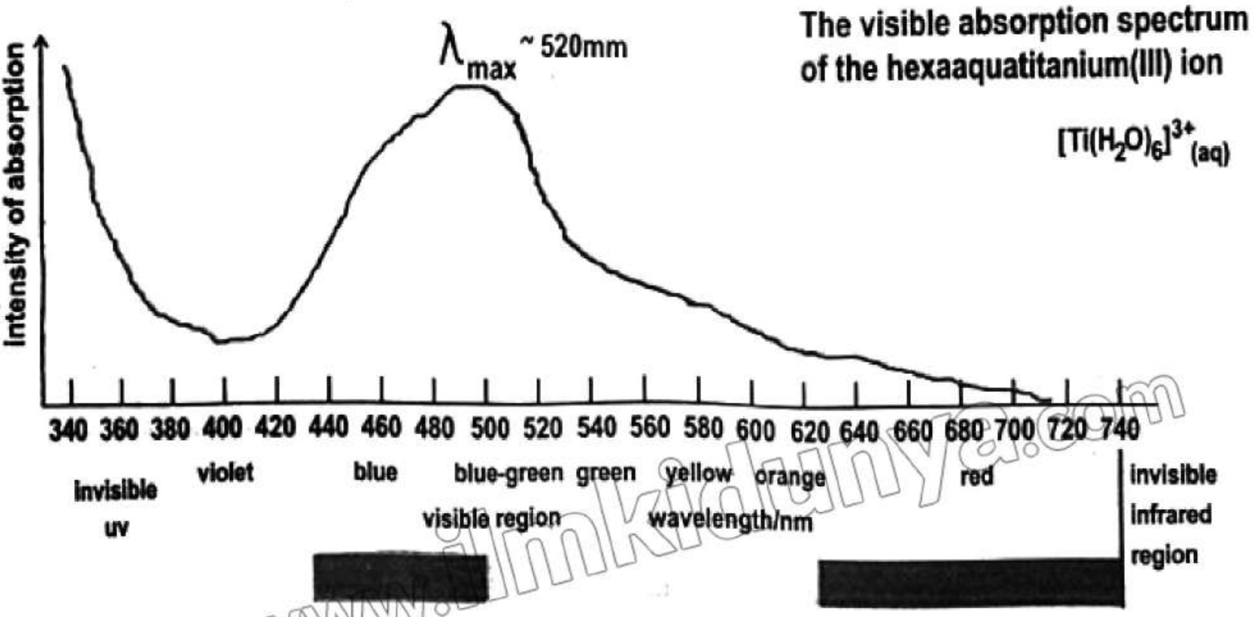

Fig 18.5: UV visible spectrum of $[Ti(H_2O)_6]^{3+}$

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Table 18.2

Wavelength Absorbed (nm)	[illegible]	[illegible] Absorbed
400-435	Yellow-Green	Violet
435-480	Yellow	Blue
480-490	Orange	Green-Blue
490-500	Red	Blue-Green
500-560	Purple	Green
560-580	Violet	Yellow-Green
580-595	Blue	Yellow
595-605	Green-Blue	Orange
605-700	Blue-Green	Red

The colour of a compound hexaaqua Titanium (III) $[Ti(H_2O)_6]^{3+}$ in figure 18.5 is violet as this compound absorbs the yellow and green colrours of visible wavelength of light, thus it appears violet. Another use of UV-Visible Spectroscopy is finding the concentration of a solution of unknown concentration quantitatively. Firstly, a standard curve is obtained by using standard solutions and analysing the intensity of absorption of particular band of wavelength. Secondly, the absorption of unknown solution is measured and compared with the standard curve.

CONCEPT ASSESSMENT EXERCISE 18.2

Q1. A compound absorbs the light with a wavelength of 500nm-560nm. What colour do you expect for this compound?

Q2. What wavelength do you suggest about the absorption of light by the components of air?

18.4.1 Predict whether a compound will absorb in the UV-visible region

To predict whether a compound will absorb in the UV-visible region, you need to understand the electronic structure of the compound, particularly the presence of certain types of electronic transitions. If a compound has conjugated double bonds, aromatic rings, or functional groups like carbonyls that enable π to π* or n to π* transitions, it is likely to absorb in the UV-visible region.

Example 1: Benzene (C_6H_6)

- Benzene has a conjugated π system with alternating double bonds.
- It exhibits π to π* transitions, absorbing in the UV region around 254 nm.

Example 2: 1,3-Butadiene (C_4H_6)

- 1,3-Butadiene has a conjugated system of double bonds (C=C-C=C).
- It shows π to π* transitions, absorbing in the UV region around 217 nm.

Example 3: Acetone (CH_3COCH_3)

- Acetone has a carbonyl group (C=O) which can undergo n to π* transitions.
- It absorbs in the UV region around 279 nm.

18.5 Atomic Emission Spectroscopy

Atomic emission spectroscopy is a powerful technique to quantify the elements by the measurement of the specific wavelength of light emitted from a pre-excited sample. The source of excitation may be flame, plasma, arc or spark. Atoms of any element emit light during de-excitation after the source have been abandoned. These characteristic emitted wavelengths are used to identify the element. The emitted light is dispersed by a diffraction grating or prism then detected by a detector. It is a very useful technique used to identify the elements in different samples.

When an atom absorbs energy (e.g., from heat, electrical energy, or light), its electrons get excited to higher energy levels. These excited electrons are unstable and eventually return to their ground state or a lower energy level. During this transition, the electrons release energy in the form of photons. The wavelength (colour) of the emitted light depends on the energy difference between the two levels. The spectrum appears as a series of discrete lines, each corresponding to a specific wavelength.

Each element has a unique emission spectrum, often referred to as its "fingerprint."

These lines are known as spectral lines and represent the quantized energy levels within the atom.

18.6 Atomic Absorption Spectrum

An atomic absorption spectrum is observed when free atoms in the ground state absorb specific wavelengths of light and get excited to higher energy levels. This absorption leads to dark lines in the spectrum at those specific wavelengths.

Atomic emission and absorption spectra are always line spectra and give same information as shown in figure that placement of the spectral lines according to wavelength is same in emission and absorption spectrum of potassium. Only difference in spectrum is that in AES bright lines appear on dark background, and in AAS dark lines are visible on bright background.

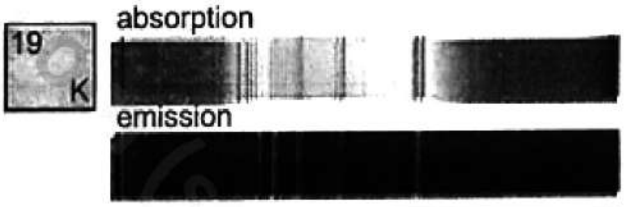

Fig 18.6: Atomic absorption and emission spectra of potassium

18.7 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy or magnetic resonance spectroscopy (MRS), is a spectroscopic technique based on re-orientation of atomic nuclei with non-zero nuclear spins in an external magnetic field. This re-orientation occurs with absorption of electromagnetic radiation in the radio frequency region from roughly 4 to 900 MHz, which depends on the isotopic nature of the nucleus and increased proportionally to the strength of the external magnetic field. Notably, the resonance frequency of each NMR-active nucleus depends on its chemical environment. As a result, NMR spectra provide information about individual functional groups present in the sample, as well as about connections between nearby nuclei in the same molecule. As the NMR spectra are

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unique or highly characteristic to individual compounds and functional groups, NMR spectroscopy is one of the most important methods to identify molecular structures, particularly of organic compounds.

18.7.1 Principle

All those nuclei which are Nuclear magnets or NMR active have a random orientation of their spins. When an external magnetic field is applied all these nuclei acquire two spin states; one with low energy ,and aligned with applied magnetic field (B^o)and the other with high energy and against the applied magnetic field. The energy difference between these two energy states corresponds to the radio wave frequency. By absorbing the same energy to flip their spins certain equivalent nuclear magnets thus resonate. When a spin returns to its ground state, the absorbed energy is emitted at the same frequency level. The emitted radio frequency signal gives the NMR spectrum of the compound.

18.7.2 NMR active nuclei

NMR active nuclei are those possessing a property called 'spin', whereby a charged nucleus spins about an axis and generates its own magnetic dipole moment, including hydrogen (^1H), the ^{13}C isotope of carbon, the ^{19}F isotope of fluorine, and the ^{31}P isotope of phosphorus, all have magnetic moments and therefore can be observed by NMR. Organic chemists use ^1H and ^{13}C NMR.

To be NMR-active, a nucleus must have a non-zero nuclear spin quantum number ($I \neq 0$). It is this non-zero spin that enables nuclei to interact with external magnetic fields and show signals in NMR. Atoms with both an odd number of protons and an odd number of neutrons, or an odd sum of protons and neutrons, exhibit half-integer values for the nuclear spin quantum number ($I = 1/2, 3/2, 5/2$, and so on). These atoms are NMR-active.

18.8 ^1H NMR (Proton NMR)

It is the application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen-1 nuclei within the molecules of a substance, in order to determine the structure of its molecules.

18.8.1 Use of Deuteratedsolvent

Deuterated (deuterium = ^2H, often symbolized as D) solvents especially for use in NMR are preferred, e.g. deuterated water, D_2O, deuterated acetone, $(CD_3)_2CO$. In the non-hydrogen solvents CS_2 and CCl_4 are frequently usedin order to avoid the interference of solvent protons in the analysis.

18.8.2 Tetramethylsilane (TMS) as standard of chemical shift

TMS (Tetra methyl silane $Si(CH_3)_4$) is a tetrahedral molecule, with all protons being chemically equivalent and highly shielded by electrons due to lesser electronegativity of silicon ,giving one single signal, used to define a chemical shift (δ) = 0 ppm. Proton NMR spectra of most organic compounds are characterized by chemical shifts in the range +14 to -4 ppm and by spin-spin coupling between protons.

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18.8.3 Nuclear spin flipping and chemical shift

Nuclear spin flipping is a quantum mechanical phenomenon where certain atomic nuclei absorb energy from an external source, leading to a change in their spin state.

If the nucleus is irradiated with electromagnetic radiation of the proper frequency, it can absorb energy and "flip" from the lower-energy spin state to the higher-energy state. This energy transition induces a change in the nuclear spin states.

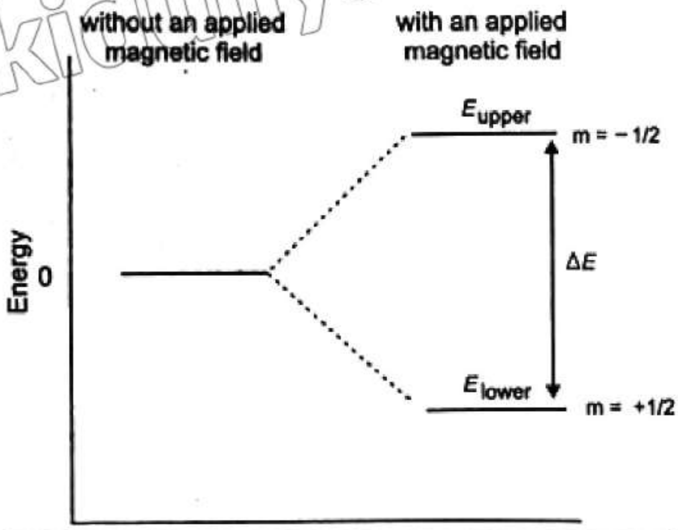

Fig 18.7: effect of external magnetic field

In nuclear magnetic resonance (NMR) spectroscopy, the chemical shift is the difference between the resonant frequency of an atomic nucleus and a standard in a magnetic field. It's expressed in parts per million (ppm) and is a key property for determining a molecule's structure.

The exact frequency required for resonance depends on the strength of the external magnetic field, the identity of the nucleus, and the electronic environment of the nucleus. The number of peaks tells you the number of different environments the hydrogen atoms are in. The ratio of the areas under the peaks tells the ratio of the numbers of hydrogen atoms in each of these environments.

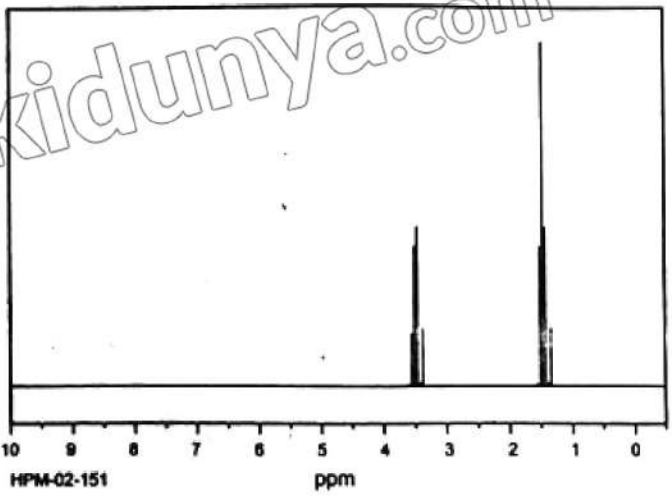

Fig 18.8: Proton NMR of Ethyl Chloride

Molecules have simple spectra. The spectrum of ethyl chloride shows a peak equivalent to three alike protons of methyl (CH_3) at 1.5 ppm and another at 3.5 ppm, corresponding to two similar protons of methylene with respect to reference peak. Two protons that absorb at 3.5 ppm are more near to highly electronegative chlorine, experience more external magnetic field due to more de-shielding as compared to the three protons absorbing at 1.5 ppm.

The spectrum of benzene consists of a single peak at 7.2 ppm due to the diamagnetic ring current. when the electron density is high around the nucleus, the opposing magnetic field to electrons is also bigger which in turn gives huge shielding. Deshielding is when electron density falls around the nucleus, the magnetic field opposing it reduces and then the nucleus feels more of the external magnetic field.

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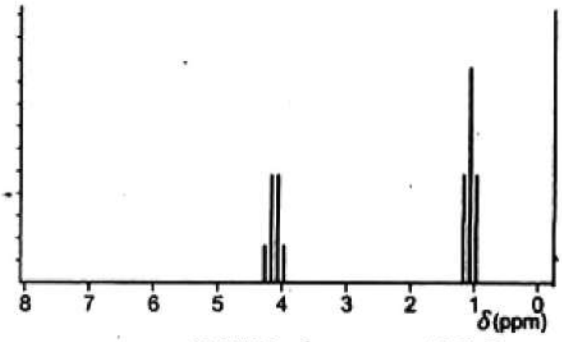
CONCEPT ASSESSMENT EXERCISE 18.3

Q1. How many peaks do you expect in the proton NMR of benzene?

Q2. Why the peak of two protons attached with alpha carbon of ethyl alcohol have greater chemical shift than the ethylene group of ethyl chloride?

Q3. Given is a H-NMR spectrum of an organic compound "x" with a molecular formula $C_4H_{10}O$. Deduce its structural formula by using its H-NMR spectrum.



H-NMR of compound "x"

18.8.4 Environment of a given proton (Multiplicity)

In hydrogen-1 NMR, all the hydrogen atoms attached to the same carbon have the same environment. However, hydrogen atoms on different carbons can also have the same environment, if the carbon atoms they are bonded to, exactly the same chemical groups with respect to each other.

If there are no hydrogens on the adjacent atoms, then the resonance will remain a single peak, a singlet. If there is one hydrogen on the adjacent atoms, the resonance will be split into two peaks of equal size, a doublet. If there are two equivalent protons are present on the adjacent carbon atom it will give a triplet signal, and if three protons present on adjacent C atom a quartet appears. This is governed by (N+1) rule and gives a valuable information about the neighbourhood of a given proton, shown in the figure.

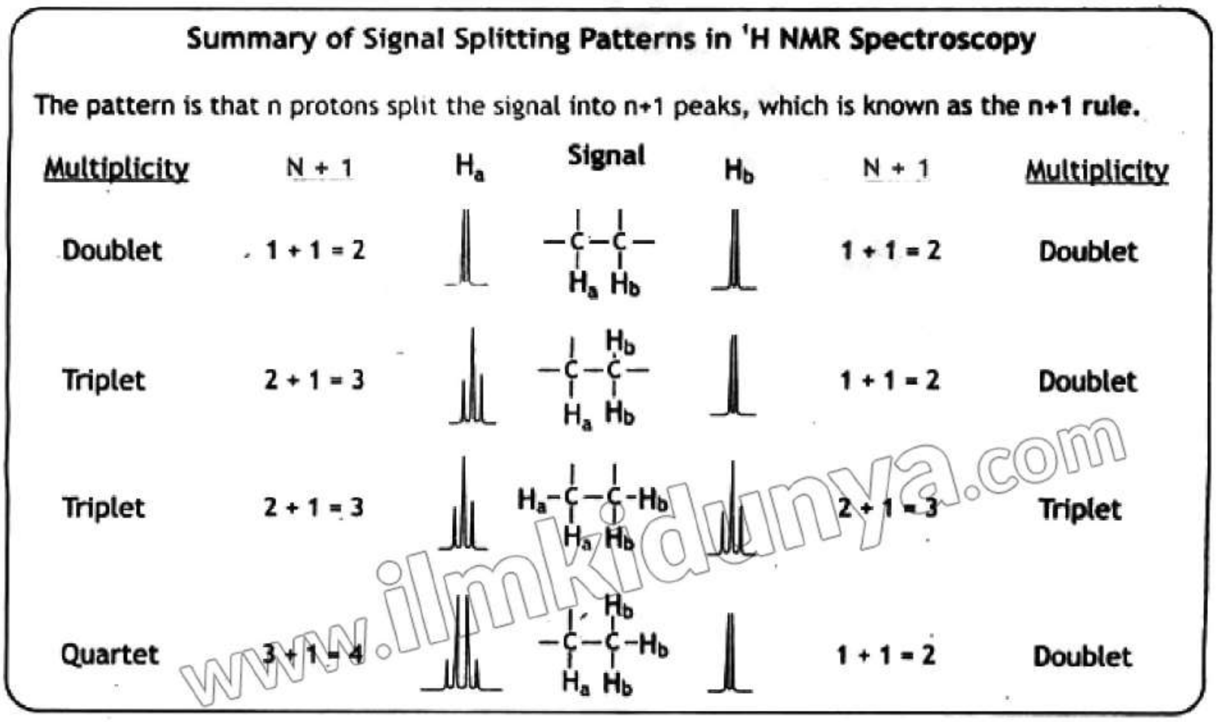


Fig 18.9: Multiplicity of NMR peaks

This is why in the given spectrum of ethyl chloride, CH_2 peak is a quartet because of 3 neighbouring protons and the CH_3 peak is a triplet due to 2 neighbouring protons of CH_2.

18.8.5 Proton exchange by D_2O

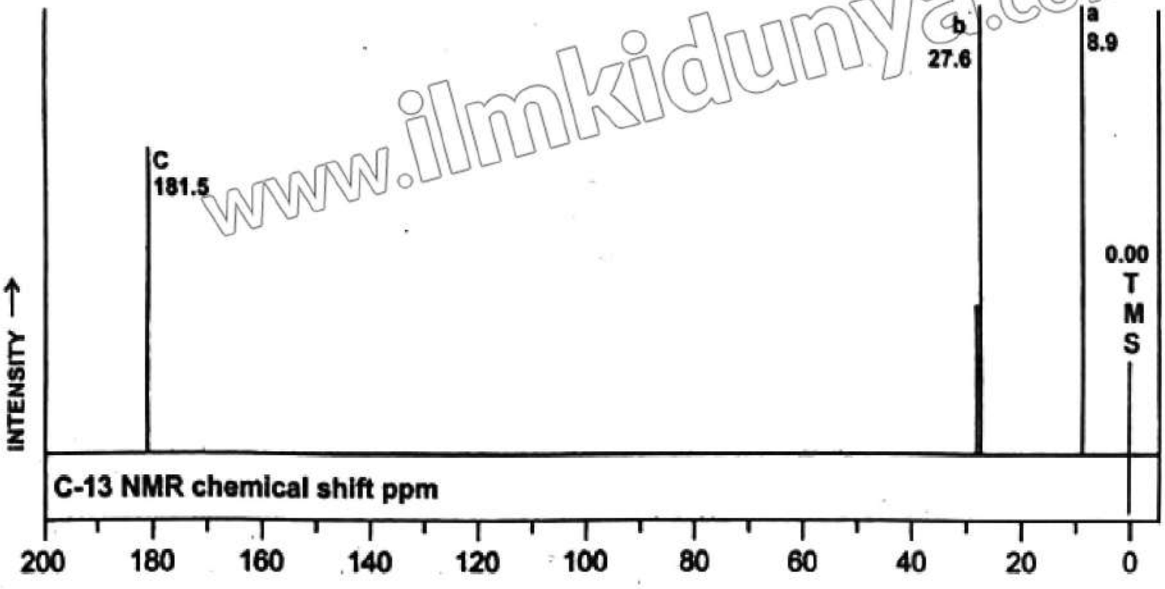
When an NMR sample that contains O-H or N-H protons is shaken with deuterium oxide (D_2O), the O-H or N-H protons exchange with the deuterium atoms in D_2O. This causes the corresponding NMR signals to disappear, which suggests the presence of an O-H or N-H proton. This is because deuterium is NMR inactive.

CONCEPT ASSESSMENT EXERCISE 18.4

Q1. How many peaks do you expect in the NMR spectrum of acetone? If it is a single peak describe the reason.

Q2. What would be the difference between the proton NMR spectrum of ethyl alcohol and ethyl chloride? Why is the chemical shift of OH proton in alcohol greater?

Q3. By using the information given in the C-13 NMR of the compound "y" answer the given questions.



C-13 NMR of the compound "y"

a. How many carbon atoms are present in compound "y"?
b. What is the chemical shift of CH_3 carbon out of these three values?
c. One C is dirty attached to two oxygen atoms, can you tell it's chemical shift?
d. Deduce the possible structure of compound "y" if its molecular mass is 74 amu.

18.9 Carbon-13 NMR

About 1% of all carbon atoms are the ^{13}C isotope; the rest (apart from tiny amounts of the radioactive C-14) is C-12. ^{13}CNMR is based on the magnetic properties of the ^{13}C nuclei. Carbon-13 nuclei are NMR active, hence a ^{13}C nucleus can behave as a small magnet. C-12 nuclei do not have this property.

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It means that it can also be aligned with an external magnetic field(B^o) or opposed to it. The alignment where it is opposed to the field is less stable (at a higher energy). It is possible to make it flip from the more stable alignment to the less stable one by supplying exactly the right amount of energy. It is possible to detect this interaction between the radio waves of just the right frequency and the ^{13}C nucleus as it flips from one orientation to the other as a peak on a graph. This flipping of the ^{13}C nucleus from one magnetic alignment to the other by the radio waves is known as the resonance condition.

18.9.1 Chemical shift in ^{13}C-NMR

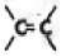
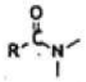
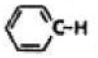
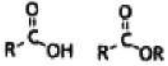
A peak at a chemical shift of 60 is said to be downfield of TMS. The further to the left a peak is, the more downfield it is. The chemical shifts for ^{13}C NMR are much bigger than for proton-NMR. In ^{13}C NMR, they range up to about 200 ppm depending on the environment of carbon.

18.9.2 Deduction of possible structure of molecule using ^{13}C-NMR

^{13}C-NMR of each different molecule is distinct. By analysing the peaks in spectrum and comparing these peaks with standard references can give the information about the types of carbon atoms present in the molecule. By a careful study of chemical shifts of all peaks in spectrum we can be able to recognise carbon atoms, or from where they belong i.e alkane, alkenes, alkynes and aromatic carbon atoms can easily be recognised based on their specific chemical shift range. The symmetrical molecules are simple and have less peaks in their NMR spectrum due to their identical positions.

Table 18.3: Chemical shift values of ^{13}C-NMR

Approximate Values of Chemical Shifts for ^{13}C NMR

$(CH_3)_4Si$	0	* I−C	-20 - 40		100 - 150		155 - 185
$R\text{-}CH_3$	8 - 30	Br−C	25 - 65		110 - 170		
$R\text{-}CH_2\text{-}R$	15 - 55	Cl−C	35 - 80				165 - 185
R_3CH	20 - 60	O−C	40 - 80	C=N	150 - 170		
R_4C	30 - 50	N−C	30 - 65	C≡N	110 - 140		190 - 220

Comparing these peak values with the appeared spectrum we can predict the structure of the molecule. Talking in general one spectroscopic technique solely does not fully work to structural elucidation. Combined information obtained from different spectroscopic techniques along with mass Spectrometry help resolve the structural formulae of organic compounds.

Let us discuss the ^{13}C-NMR spectrum of ethanol. In ethanol there are two distinct C atoms one is attached with highly electronegative O atom and the other with just three hydrogens and an alpha carbon atom. Carbon atom attached with the oxygen atom is highly de-shielded and represents a higher chemical shift and appears at 58 ppm. The second carbon atom which is methyl carbon, is slightly experiencing inductive effect thus it is better shielded. It's peak appears at 18 ppm.

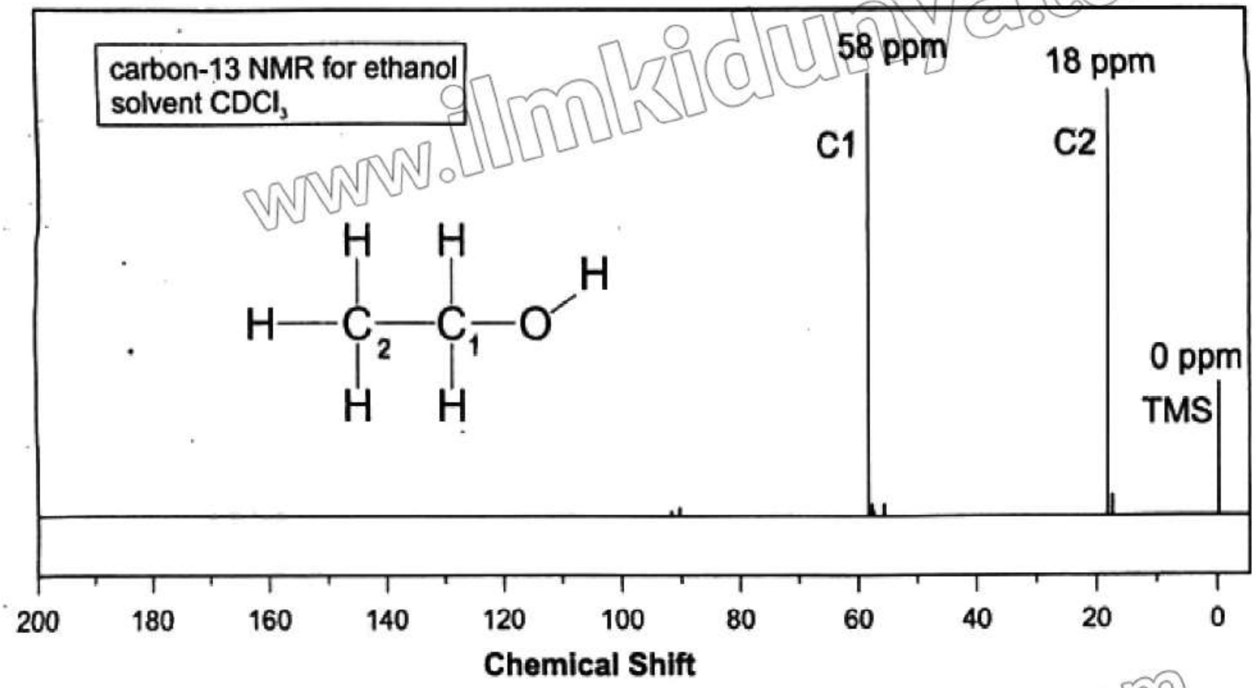


Fig 18.10: ^{13}C-NMR of ethanol

Lets take example of the acetone. In spite of having 3 carbon atoms, the spectrum is showing just two peaks. Both the methyl carbons are identical and better shielded appear at 30.8 ppm. The carbonyl carbon being more de-shielded shows it's peak at 206 ppm due to attachment with highly electronegative O atom.

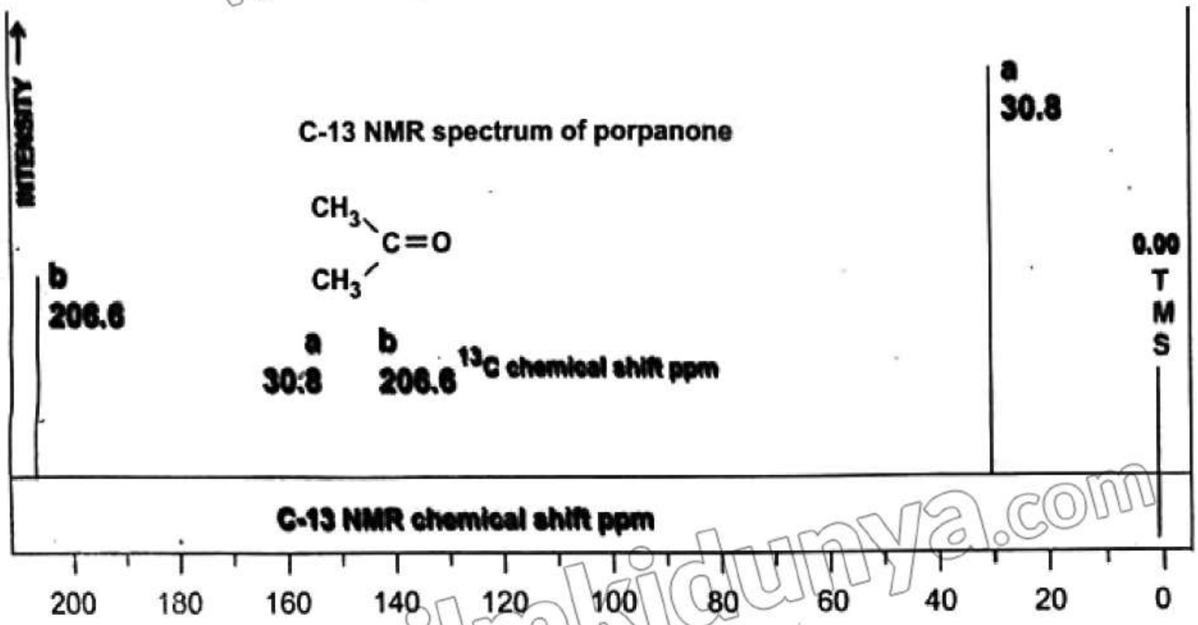


Fig 18.11: NMR spectrum of acetone

In the ^{13}C-NMR spectrum, each unique carbon environment in the molecule gives a separate peak. The number of peaks in the spectrum corresponds *to the number of chemically* different carbon atoms.

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18.9.3 Steps to Predict the Number of Peaks

- Look for symmetry in a molecule. Symmetrical carbons are equivalent and give one peak.
- Identify each unique carbon medium. Carbons in different chemical environments (different neighbouring atoms or bonds) produce distinct peaks.

Example 1: Ethanol (C_2H_5OH)

Structure: CH_3CH_2OH

Spectrum Analysis:

- CH_3 (methyl group): The carbon in the methyl group is bonded to three hydrogens and one carbon.
- CH_2 (methylene group): The carbon in the methylene group is bonded to two hydrogens, one carbon, and one oxygen.
- OH (hydroxyl group): Although the oxygen doesn't appear directly in the 13C-NMR spectrum, the carbon bonded to it will have a distinctive chemical shift due to the electronegativity of oxygen.

Number of Unique Carbons: 2

- Methyl carbon: One peak
- Methylene carbon: One peak

Expected Peaks: 2 peaks

Spectrum:

1. Methyl carbon: Appears around 10-20 ppm
2. Methylene carbon: Appears around 50-60 ppm

Example 2: Acetone (C_3H_6O)

Structure: $(CH_3)_2CO$

Spectrum Analysis:

- CH_3 (methyl groups): Both methyl groups are equivalent and bonded to the same carbonyl carbon.
- CO (carbonyl group): The carbonyl carbon is in a distinct environment due to its double bond with oxygen.

Number of Unique Carbons: 2

- Methyl carbons: One peak
- Carbonyl carbon: One peak

Expected Peaks: 2 peaks

Spectrum:

1. Methyl carbons: Appear around 20-30 ppm
2. Carbonyl carbon: Appears around 190-210 ppm

Example 3: Butane (C_4H_{10})

Structure: $CH_3CH_2CH_2CH_3$

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Spectrum Analysis:

- CH_3 (methyl groups): The two terminal methyl groups are equivalent.
- CH_2 (methylene groups): The two methylene groups are equivalent.

Number of Unique Carbons: 2

- Methyl carbons: One peak
- Methylene carbons: One peak

Expected Peaks: 2 peaks

Spectrum:

1. Methyl carbons: Appear around 10-20 ppm
2. Methylene carbons: Appear around 20-40 ppm

Example 4: Benzene (C_6H_6)

Structure: C_6H_6

Spectrum Analysis:

- Aromatic Carbons: All six carbons in the benzene ring are equivalent due to the symmetry of the molecule.

Number of Unique Carbons: 1

- Aromatic carbons: One peak

Expected Peaks: 1 peak

Spectrum:

- Aromatic carbons: Appear around 120-140 ppm

CONCEPT ASSESSMENT EXERCISE 18.5

Q1. How many types of C atoms are present in ethoxy ethane (diethyl ether)? Draw an approximate ^{13}C-NMR spectrum of this molecule taking help from the given table of chemical shifts.

Q2. Why are the chemical shifts in ^{13}C-NMR spectrum much greater as compared to the ^{1}H-NMR?

KEY POINTS

- Spectroscopy is a technique used for structural elucidation of the molecule. It is based on the interaction of atoms or molecules with electromagnetic radiaction.
- Mass Spectrometry is the technique used for finding out molecular masses, fragment mass, and relative atomic masses of isotopes of an element.
- The total number of rings and pi-bonds can be determined by the use of index of hydrogen deficiency (IHD) or degree of unsaturation in an organic compound.
- IR spectroscopy makes use of interaction of infrared radiations with organic molecule. It is used to analyse the functional group present in an organic compound.
- In UV-Visible spectroscopy the UV and visible light absorption by any compound is measured. It's typical range of wavelength is from 200 nm to 800 nm. *It is used to find* unsaturation and conjugation in an organic compound.

- The coloured compounds absorb small part in visible (400 nm-800 nm) region of electromagnetic radiations and transmit the rest of the wavelengths, thus the colour appears.
- Atomic emission spectroscopy is a powerful technique to quantify the elements by the measurement of the specific wavelength of light.
- NMR active nuclei are those possessing a property called 'spin', whereby a charged nucleus spins about an axis and generates its own magnetic dipole moment.
- TMS (Tetramethylsilane $Si(CH_3)_4$) is a tetrahedral molecule, with all protons being chemically equivalent and highly shielded by electrons. It works as a reference whose chemical shift is zero.
- When an NMR sample that contains O-H or N-H protons is shaken with deuterium oxide (D_2O), the O-H or N-H protons exchange with the deuterium atoms in D_2O, this is called deuterium exchange.

Reference

1. Organic spectroscopy and chromatography by M Younas, 2011
2. Introduction to Spectroscopy Donald L Pavia, 2008

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Select the correct choice from the given options.
Spectroscopy is a technique in which matter interacts with:

a) Light b) Sulphuric acid c) Magnetic field d) Plasma

ii. Which technique is used to detect conjugation in an unsaturated hydrocarbon.

a) NMR b) UV-Visible spectroscopy

b) Mass Spectrometry d) IR spectroscopy

iii. Coloured compounds absorb in the wavelength between:

a) 1nm to 200 nm b) 200 to 400 nm c) 400 to 600 nm d) 400 to 800 nm

iv. IR Spectroscopy is used to detect:

a) Functional group b) Conjugation c) Type of hydrogens d) Number of rings

v. Which radiations are used in NMR spectroscopy?

a) UV b) Visible c) X-rays d) Radio waves

vi. Which bond shows greater chemical shift in 1H NMR?

a) O-H b) N-H c) C-H d) SI-H

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2. Short Answer Questions

i. Write basic principle of IR spectroscopy.

ii. How can you identify functional group of an organic compound by using IR spectroscopy?

iii. With the help of UV- Visible spectrum of an unseen compound, how can you predict it's colour?

iv. Draw a rough UV-Visible spectrum of a compound which is yellow in colour.

v. Explain principles of AES and AAS.

vi. How is atomic absorption spectroscopy different from atomic emission spectroscopy?

vii. What are NMR active nuclei? How can you tell about a nucleus, whether it is NMR active or not?

viii. What is the effect of external magnetic field on the spinning nuclei?

ix. Explain chemical shift.

x. Why do the peaks in NMR spectrum split into doublet, triplets or quartets etc?

xi. What is deuterium exchange method and what is it's use?

xii. Why does acetone give a single peak in proton-NMR and two peaks in ^{13}C-NMR? Explain with reason.

xiii. What is TMS? Tell its significance?

xiv. Why deuterated solvents are used in proton NMR spectroscopy?

3. Long Answer Questions

i. Write the details of IR spectroscopy including its principle, spectrum and uses.

ii. Explain the uses of UV-visible spectroscopy.

iii. Nuclear magnetic resonance is a powerful tool for the elucidation of structures of organic compounds. Defend the statement.

iv. How is PMR different from CMR?

PROJECT

Draw approximate proton NMR spectrum and ^{13}C-NMR spectrum of 3-pentanone.

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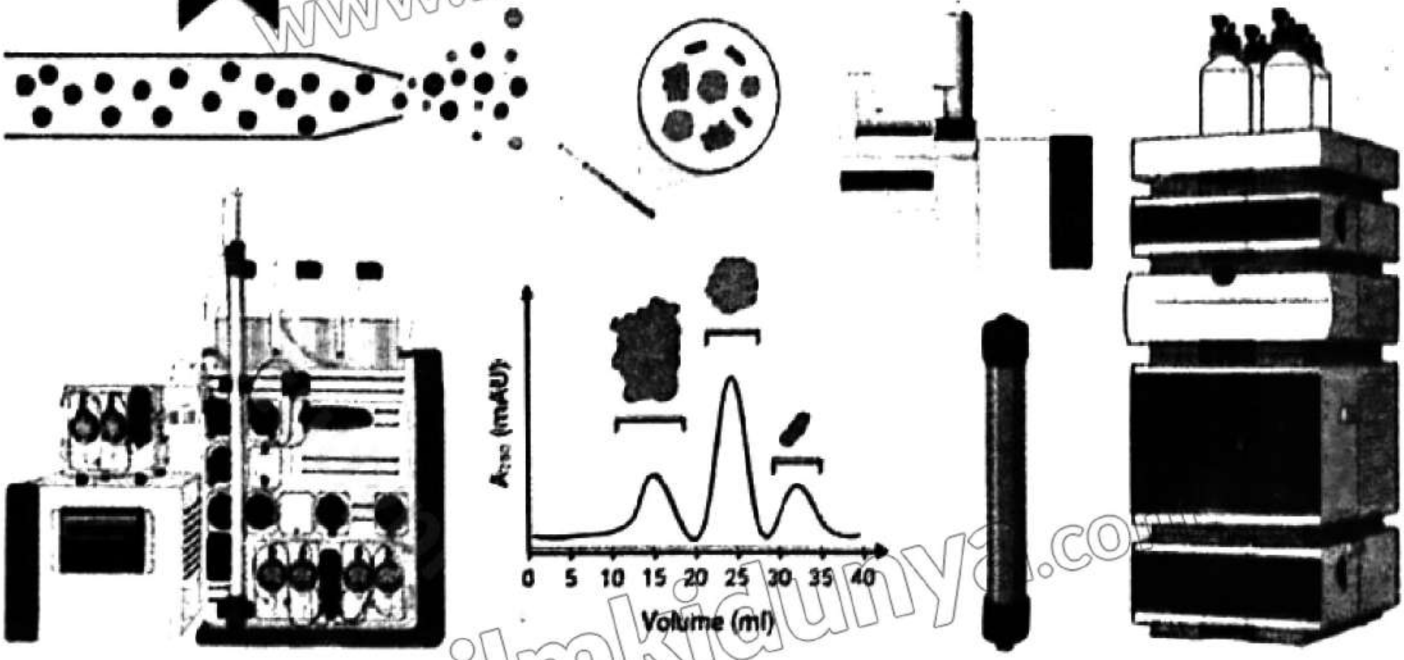
UNIT 19



CHROMATOGRAPHY

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Student Learning Outcomes (SLOs)

- Describe the terms stationary phase, mobile phase, Rf value, baseline and solvent front.
- Explain the principles and applications of thin layer chromatography in forensic chemistry and analysis of unknown materials.
- Interpret Rf values and retention times in chromatograms to determine the composition of a mixture.
- Explain the importance of selecting the appropriate stationary and mobile phase in chromatography and their impact on the separation of compounds.
- Describe the use of mass spectroscopy in combination with chromatography for identifying and qualifying small number of unknown materials in forensic analysis.

Chromatography is a fascinating lab technique that is useful for separating mixtures. It plays a vital role in various fields for example helping scientists to identify the components of medicines, assess the purity of water, and analyze the nutritional content of foods. Its name comes from Greek words meaning "color" and "to write," highlighting its ability to visually represent the different parts of a mixture based on their colors.

It has several significant applications in many pharmaceutical sectors, food and chemical industries. Chromatography is used to check the purity of compound. Environmental testing laboratories are using these techniques of Chromatography. It is also used in beverage, forensic and drug testing. One of the key advantages of chromatography is its ability to separate complex mixtures into their individual components, providing valuable information about composition and purity of compounds.

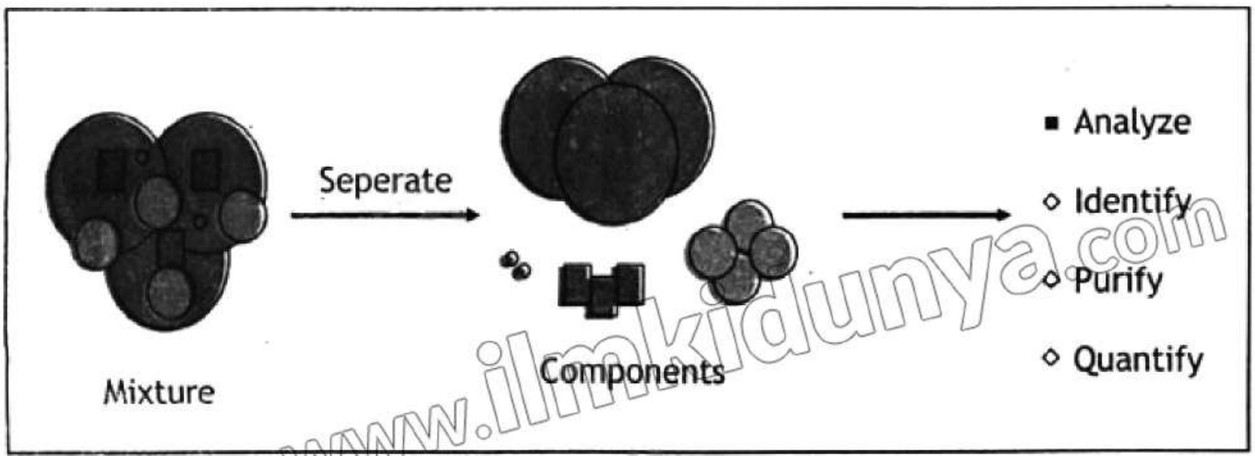

Fig 19.1: Process of chromatography

19.1 Main Components of Chromatography

Chromatography involves two phases: one that is stationary phase (usually a solid like glass or silica) and other one is mobile phase (usually a liquid or gas).

1. Stationary phase: The stationary phase doesn't move, while the mobile phase moves over it. The stationary phase is often packed into a tube while the mobile phase flows through it for example in column chromatography the stationary phase is packed in a column and mobile phase is run through the column. Stationary phase can be in solid or liquid phase coated on surface of solids.

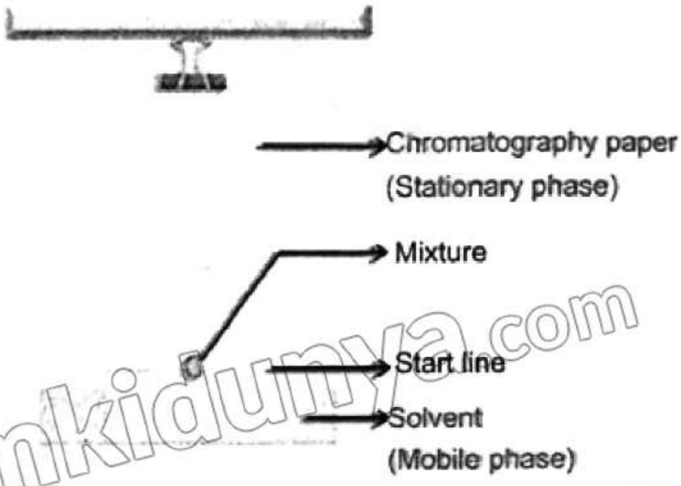

Fig:19.2 Stationary and mobile phase

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2. Mobile phase: In chromatography, the mobile phase is usually a liquid or gas that flows over the stationary phase. Liquid chromatography uses a liquid mobile phase, and gas chromatography uses a gas mobile phase. In Column chromatography, the mobile phase (either liquid or gas) passes through a column separating the mixture's components by sticking to the stationary phase at different rates.

3. R_f (retardation factor) value: Rf value of a compound is the ratio of the distance travelled by the solute to the distance travelled by the solvent.

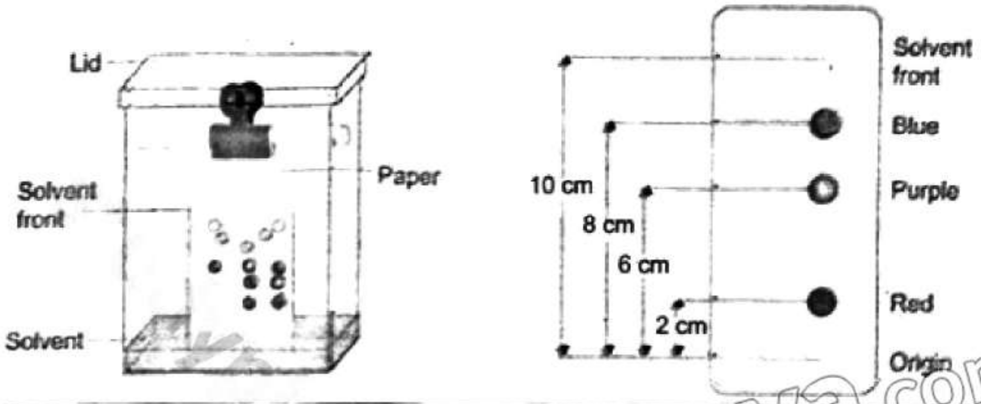

Fig :19.3 R_f calculations

In chromatographic analysis retention factors (R_f) is used to tell that how far a compound travels compared to the solvent front, providing valuable information for compound identification. It is calculated as the ratio of the distance travelled by the compound to the distance travelled by the solvent front from the baseline, where the sample was initially applied.

$$R_f \text{ Value} = \frac{\text{Distance from Baseline travelled by Solute(compound)}}{\text{Distance from base line travelled by solvent(Solvent front)}}$$

4: Solvent front: The level at which solvent reaches as it moves up the paper is called the solvent front. There is a dynamic equilibrium between the mobile and stationary phases as the components constantly move between the two phases.

5. The baseline: The baseline is the starting line from which the movement of components is measured. It is typically represented as a straight line on the chromatogram and is used as reference point and spots are placed at this level.

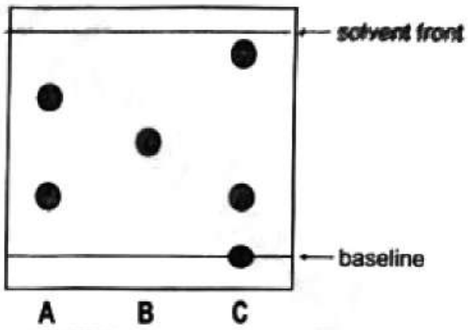

Fig 19.4 Paper Chromatogram

Do you Know

Chromatography is used in biochemical research for the separation and identification of chemical compounds of biological origin. In petroleum industry the technique is employed to analyze complex mixture of hydrocarbons.

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19.2 Thin Layer Chromatography

Thin-layer chromatography (TLC) separates substances based on how they interact with different surfaces. In TLC, substances move across a thin layer on a plate. Some substances stick more to this layer (the stationary phase) and move slowly, while others move faster. This separates the mixture into different parts, which appear as spots on the plate.

In the process of thin-layer chromatography (TLC), the mixture of substances are separated into its components with the help of a glass plate coated with a very thin layer of adsorbent, such as silica gel and alumina, as shown in the figure below.

The solution of the mixture to be separated is applied as a small spot at a distance of at least 2 cm. The plate is then placed in a closed jar containing a liquid termed as an eluant, which then rises up the plate carrying different components of the mixture to different heights.

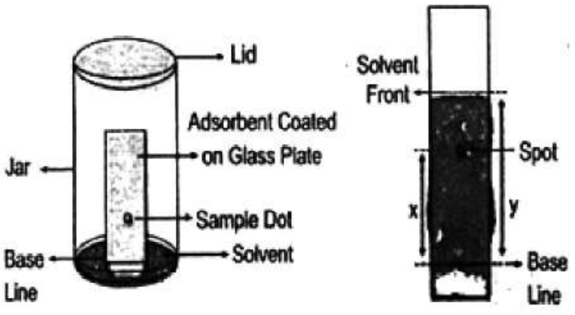

Fig 19.5: Thin Layer Chromatography

TLC is one of the fastest, least expensive, simplest and easiest chromatography technique. Thin Layer Chromatography plates are pre-made plates that are chemically inert and stable. They have a thin layer of stationary phase applied to their surface. This layer is fine and evenly thin.

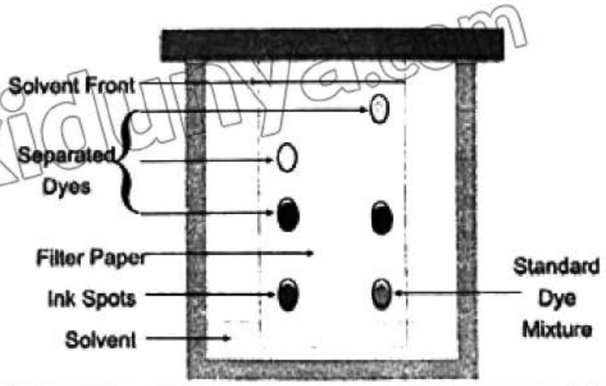

Fig 19.6 Chromatography Chamber

The plates are developed in a Chamber. It maintains a stable environment inside to help spots develop properly. It also prevents solvent evaporation and keeps the process free from dust.Mobile Phase in Thin Layer Chromatography is a solvent mixture or a single solvent. It needs to be free from particles. The purer the mobile phase, the better the spots will develop.

19.2.1 Working of thin Layer Chromatography

1. The stationary phase on the plate is coated with silica gel or Aluminum oxide and dried.
2. Use a pencil to make small marks at the bottom of the plate. Apply sample solutions to these marks by using capillary tube.
3. Pour the mobile phase in TLC chamber and add moistened filter paper to keep the humidity constant.
4. Put the plate in the chamber with the sample and close it with a lid.
5. Let the plate develop, making sure the sample spots stay above the mobile phase level without dipping into the solvent.
6. Once spots develop, remove the plates and let them dry. We can check the sample spots under a UV light.

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Group Activity:

Design an experiment to study the different component of following mixtures using thin layer chromatography.

(i) Colors of markers.
(ii) Pigments present in petals of hibiscus flower
(iii) Component of ink

Hint:

Teacher will provide

(i) three different brands of black water-based markers.
(ii) TLC plates
(iii) hibiscus flowers petals along with some small amount of alcohol and mortal and pestle
(iv) Sample of different kinds of inks.

19.2.2 Applications of thin Layer Chromatography (TLC)

1. Testing various medicines like sedatives, local anesthetics, and more.
2. Useful in biochemical analysis, separating substances obtained from food.
3. Identifying natural products such as essential oils and alkaloids.
4. Purifying samples and comparing them with authentic ones.
5. In the food industry, for separating and identifying colors, sweeteners, and preservatives.
6. Used in the cosmetic industry.
7. Useful in Organic synthesis.

19.2.3 Limitations of thin layer chromatography

1. Separation length is shorter compared to other chromatography methods.

2. Being an open system, factors like humidity and temperature can influence the final results.

3. This method is suitable for detecting very small amounts of substances.

19.2.4 Application of thin layer Chromatography in Forensic Chemistry

The application of TLC in forensic chemistry contributes significantly to the investigation and resolution of criminal cases by providing rapid and reliable separation and analysis of diverse forensic samples. Thin layer chromatography (TLC) finds several applications in forensic chemistry due to its ability to separate and analyze compounds within complex mixtures. Here are some key applications of TLC in forensic chemistry.

1. **Drug Analysis:** TLC is extensively used in the analysis of illicit (forbidden by law) drugs. Forensic chemists can separate and identify various drugs present in samples, such as cocaine and *heroin*. By comparing the separated compounds with known standards, scientists can determine the composition and purity of the drugs.

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2. **Poison Report:** In cases of suspected poisoning, TLC can be employed to analyze biological samples (e.g., blood, urine, tissues) for the presence of toxic compounds. This helps forensic scientists identify the poison involved.
3. **Trace Evidence findings:** TLC is valuable for analyzing trace evidence found in fibers, paints, and dyes. By separating and comparing the components of these materials with known standards or reference samples, forensic experts can link them to specific sources, aiding in criminal investigations.
4. **Gunshot Residue Analysis:** TLC can be used to analyze gunshot residue (GSR) collected from suspects or crime scenes.
5. **Explosives inspection:** Thin Layer Chromatography (TLC) is used to detect and analyze explosive residues. By separating and identifying components like nitroaromatics or nitrates, forensic chemists can determine if explosives are present in samples from crime scenes or suspected bomb-making facilities.
6. **Document Analysis:** Thin Layer Chromatography (TLC) helps to analyze ink and paper samples in questioned document cases. By separating the components of inks or paper coatings, forensic experts can compare questioned documents with known samples helping in document authentication or detecting forgeries.
7. **Scientific Screening:** Thin Layer Chromatography (TLC) is a preliminary screening tool in toxicology. It quickly identifies and separates drugs in biological samples, helping forensic scientists decide which samples need further analysis with more sensitive techniques like GC-MS or LC-MS.

In forensic chromatography labs, various techniques are used, each serving different purposes. These include gas chromatography, high-performance liquid chromatography (HPLC).

19.3 Interpretation of R_f Value

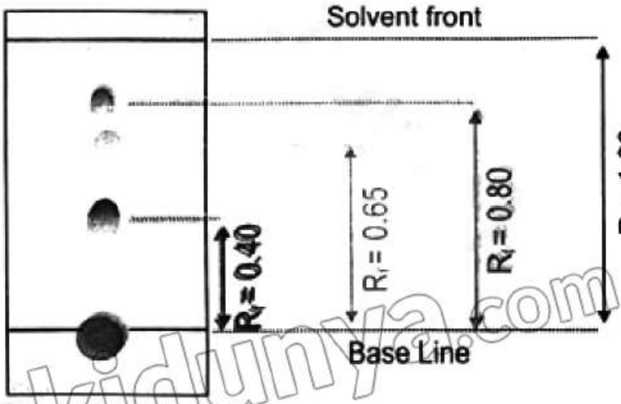

Fig 19.7 R_f Value

Retention factor (R_f) values in chromatography show how much a solute likes the stationary phase or the mobile phase. This helps to understand its properties, such as how polar it is, its relative size, and how well it dissolves.

Consistent R_f values allow for the identification of unknown substances by comparing them to known substances. Different R_f values indicate different compounds, while similar values suggest possible identity. Slight variations can occur due to interactions and concentration differences. Overall, R_f values are essential for analyzing properties and comparing substances in chromatography.

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19.3.1 Factors Affecting R_f Values

On the chromatography paper, a prepared sample solution containing component(A+B) is applied and processed through a mobile phase. Because of their different affinities with the mobile phase, analytes (A) and (B) are separated. The analytes, solvent front, and the point where the mixture (A+B) was administered are all measured relative to each other.

1. Solvent Impacts Retention Factors

As solvent transports the chemical along the plate, the solvent used has a significant impact on the chemical's retention factor value. Since R_f value is the ratio of distance travelled by solute and solvent, therefore solvent is the most important factor which affect the R_f value. It is observed that R_f value of compound is higher in polar solvent as compared to non-polar solvent. Sometimes mixture of solvents is used for TLC to adjust the R_f value.

2. Solute (Sample)

Solute or sample are also responsible for R_f value. The compounds which contain polar groups such as hydroxyl (OH) or amine (NH_2) are able to bind with silica of TLC plate. Therefore, it travels slower as compared to solvent. Therefore, R_f value to the polar compound is lower. Whereas non-polar compounds bind to the silica with a lesser extent. Hence solvent and solute travel faster towards the top end. Thus, R_f value of non-polar compounds is higher than polar compounds.

3. Temperature

At higher temperatures solubility of compounds is more therefore temperature affects the R_f values of a compound.

4. Thickness of silica layer

Silica of the TLC plate binds with solute/compound, thus thicker the silica layer stronger the binding and this results in lowering the R_f value.

19.3.2 Retention time

Retention time is used in column chromatographic technique. Retention time is the time taken for a sample molecule to travel through the column, from the time it is inserted into the machine to the time it is detected. Molecules in the gaseous mixture travel at different rates, therefore giving rise to different retention times.

a) Longer retention times are associated with:

Non-polar components in the mixture

They are more attracted to the non-polar liquid in the stationary phase

So non-polar molecules travel slower through the column

b) Shorter retention times are associated with:

Polar components in the mixture that prefer to interact with the carrier gas.

They are less attracted to the non-polar liquid in the stationary phase.

So polar molecules travel faster through the column.

These molecules may have lower boiling points and, therefore, are vaporized more readily.

19.4 Selection of Mobile and Stationary Phase

19.4.1 Selection of stationary phase

In general, an adsorbent is used as a stationary phase during the process of chromatography. It should have the following characteristics:

The stationary phase functions as an adsorbent and possesses the following traits

1. High and selective adsorption capacity
2. Finely divided to maximize surface area for adsorption
3. High mechanical stability to minimize dust formation
4. Chemically inert towards sample and eluting solvents
5. High purity
6. It should be easily available

The stationary phase is selected in such a way that the components of the sample have different solubilities in the phase. Hence, different components have different rates of movement through the stationary phase and as a result, can be separated from each other.

The second step in choosing the stationary and mobile phases is to determine the desired separation that you want to achieve.

If you want to separate a mixture of closely related compounds with high resolution, you can use a stationary phase with small particles and a mobile phase with low viscosity and high flow rate. This way, the components will have less diffusion and more interaction with the stationary phase, resulting in sharper peaks and better separation.

19.4.2 Selection of Mobile Phase in Chromatography

When choosing the right mobile phase in chromatography, factors are more important than specific factories. However, choosing solvents from reputable manufacturers with high-quality control standards is crucial for successful separations. Here are some key factors to consider.

Solvent purity

Use HPLC (High performance liquid chromatography) or MS (Mass spectrometry) to grade solvents to keep impurities low and prevent them from affecting your analysis. Buy solvents from companies with strong quality control to ensure they are pure and consistent for your experiments.

Solvent properties

Polarity: Consider the polarity of your analytes and match it to the mobile phase for optimal interaction.

Viscosity: Optimal viscosity ensures proper flow rate and peak shape.

Chemical reactivity: Choose solvents that are stable and won't degrade your analytes or the stationary phase.

UV transparency: If using UV detection, the solvent shouldn't absorb UV light at detection wavelength.

pH: For methods involving charged solute pH control is crucial.

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19.5 Use of Mass Spectrometry in Forensic Analysis

Mass spectrometry is an important analytical tool used in chemistry, biochemistry, pharmacy, medicine, and many related fields of science. It helps to analyze and investigate single cells and objects from outer space. Mass spectrometry is crucial for identifying the structure of unknown substances, analyzing environmental and forensic samples, and ensuring the quality control of drugs, foods, and polymers.

Mass spectrometry is a scientific method used in forensic science to analyze tiny bits of substances found at crime scenes. It helps detectives and scientists to figure out what substances are present in things like human tissue, drugs, or chemicals.

Mass spectrometers are instrumental in detecting and identifying atmospheric pollutants. In the realm of forensics, these devices are invaluable for drug testing, toxicology studies, and even the detection of explosive residues.

19.5.1 Mass spectrometry used in forensic science

In mass spectrometry, a sample is analyzed to determine its molecular composition through the generation of a spectrum that reveals the masses of its component parts.

The sample is injected into the mass spectrometer, either directly or after passing it through a chromatography-based instrument to separate it into its constituent components. An ionization chamber turns the components into charged ions, by removing at least one electron from the sample.

This form of ionization is called electron ionization (EI), which is one of the most common methods used.

The ions can then be accelerated in a mass analyzer and separated from one another using a magnetic field, which deflects the ions to different degrees based on their masses.

In the case of EI, once the sample components are separated, ion beams then enter a detector, which generates an electric signal proportional to the number of ions hitting it. This creates a mass spectrum that shows the mass-to-charge (m/z) ratio of the individual component ions that were in the sample. This spectrum enables a forensic analyst to determine exactly which compounds the sample is composed of, using a combination of mass spectrum.

For greater resolution, forensic analysts may use more sophisticated type of spectrometry, which separates sample components based on how long it takes for them to cross a certain distance within a vacuum, rather than separating fragments based on their mass-to-charge ratios.

Overall, mass spectrometry is a powerful tool that has greatly improved forensic science. It helps scientists find important clues in complex samples and provides valuable evidence that can be used to catch criminals and ensure justice is served.

Bugs can help solve a crime.

It's actually called forensic entomology. While bugs can't actually solve a crime, investigators are able to look inside of an insect's (typically a maggot) stomach and is able to determine how long a body has been decomposing.

19.5.2 Applications of Mass Spectrometry

Mass spectrometry could help to determine what toxin was used or if drugs were involved, it could identify what kind of drugs they were. This information is crucial in solving crimes and providing evidence in court cases.

Mass spectrometry is an efficient method to elucidate the chemical composition of a sample or molecule. More recently, it has been used to classify biological products, in particular proteins in a number of species. Usually, mass spectrometers can be used to classify unknown substances by molecular mass measurement, to measure known compounds, and to determine the structure and chemical properties of molecules.

19.5.4 Advantages of Mass spectrometry

1. Mass spectrometry can detect substances at very low concentrations (parts per million or even parts per billion).
2. It can accurately determine the atomic composition and molecular mass of a sample.
3. Mass spectrometry can analyze a wide range of compounds, including complex mixtures.

19.5.5 Disadvantages of Mass Spectrometry:

1. Mass Spectrum is less effective for identifying compounds of hydrocarbon producing similar ions.
2. Mass spectrometry cannot separate optical and geometric isomers, which are compounds with the same molecular formula but different structures.
3. The equipment is expensive and requires specialized training to operate and interpret results.

Combining mass spectrometry with other methods, like gas chromatography, can be used for improving separation and identification capabilities.

KEY POINTS

1. Chromatography separates compounds based on their attraction to the stationary phase, which doesn't move, and the mobile phase, which carries the compounds. More polar compounds move shorter distances, resulting in a lower R_f factor. For example, glucose, being very polar, moves a shorter distance.
2. Chromatography involves combining the substance with a liquid or gaseous mobile phase, leading to the separation of different components in the sample. Each component exits the stationary phase at a specific time called retention time.
3. Chromatography is crucial in protein purification strategies and for separating, isolating, and purifying proteins from complex samples.
4. Different chromatography methods use different stationary phases; for example, paper chromatography uses water bound to cellulose fiber while thin-layer chromatography (TLC) uses a glass plate coated with silica gel.
5. R_f value is the ratio of substance distance to solvent front distance. Higher R_f values indicate lower polarity, while lower values suggest higher polarity.

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6. In thin-layer chromatography (TLC), the mixture of substances are separated into its components with the help of a glass plate coated with a very thin layer of adsorbent, such as silica gel and alumina,
7. Polarity affects a chemical's attraction to other substances. More charge difference means more polarity. Increasing solvent polarity makes all mixture components move faster during chromatography.
8. Mass spectrometry, widely used in biology, chemistry, physics, clinical medicine, and space exploration, separates molecular ions based on mass and charge to determine compound molecular weight.
9. Mass spectrometry is used for both qualitative and quantitative analysis of chemical substances, helping classify sample elements and isotopes, determine molecular masses, assess sample purity, and calculate molar mass.
10. In Forensic mass spectrometry helps detectives and scientists figure out what substances are present in things like human tissue, drugs, or chemicals found at a crime.
11. During poisoning investigations, the detecting specific poisons can help detective to understand the situation better.

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EXERCISE

1. Multiple Choice Questions (MCQs)

i. In a scenario where a person may have died from a drug overdose at a crime scene, how can mass spectrometry contribute to determining the cause of death?

a) Mass spectrometry can detect the presence of a toxin but not specify which toxin.

b) Carpet fiber analysis can be utilized to match fibers found on the victim.

c) Tissue samples can be examined to identify both the presence and quantity of toxins.

d) Mass spectrometry can ascertain the presence of a toxin but not quantify it.

ii. Detecting amino acids by spraying the plate with ninhydrin solution exemplifies which type of chromatography?

a) Column chromatography
b) Thin layer chromatography
c) Paper chromatography
d) Liquid chromatography

iii. What does the retardation factor represent?

a) The ratio of the distance traveled by the substance from the baseline to the distance traveled by the solvent from the baseline.

b) The ratio of the distance traveled by the solvent from the baseline to the distance traveled by the substance from the baseline.

c) The ratio of the distance traveled by the substance from the top line to the distance traveled by the solvent from the top line.

d) The ratio of the distance traveled by the solvent from the top line to the distance traveled by the substance from the top line.

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iv. In chromatography, the stationary phase may be ____________ supported on a solid.

a) Solid or liquid
b) Liquid or gas
c) Solid only
d) Liquid only

v. *Which type* of chromatography involves separating substances in a mixture over a 0.2mm thick layer of an adsorbent?

a) Gas liquid
b) Column
c) thin layer
d) Paper

vi. What is the distance that the solute moves while undergoing one partition?

a) Retention distance
b) Distribution constant
c) Plate height
d) Column packing length

vii. In TLC substances are separated because of differences in________.

a) polarity
b) molecular size
c) concentration
d) electronegativity

viii. Which chromatographic technique is best suited for separating volatile compounds based on their interaction with a stationary phase?

a) Paper chromatography
b) Thin-layer chromatography (TLC)
c) Gas chromatography (GC)
d) High-performance liquid chromatography (HPLC)

ix. Which chromatographic technique is often used for monitoring the progress of reactions and identifying compounds based on their retention factors?

a) Paper chromatography
b) Thin-layer chromatography (TLC)
c) Column chromatography
d) Gas chromatography (GC)

2. Short Answer Questions

i. What causes colors to separate during chromatography?
ii. Is it possible for the R_f value to exceed 1?
iii. Explain the primary use of thin-layer chromatography (TLC)?
iv. Differentiate between thin-layer chromatography (TLC) and paper chromatography?
v. What do "stationary phase" and "mobile phase" refer to in chromatography?
vi. What type of chromatography is used in forensic science?
vii. Describe how you would analyze the chromatograms to determine if two ink samples are from the same source.
viii. Explain the importance of the solvent choice in chromatography and how it affects the separation process.
ix. Assess the limitations of paper chromatography when used to separate complex mixtures?
x. What are the essential characteristics of the substance used as a developer?

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3. Long Answer Questions

i. Is mass spectrometry quantitative or qualitative? Give a reason to support your answer.
ii. Evaluate the effectiveness of chromatography as a method for environmental monitoring of pollutants. What are the strengths and weaknesses in this application?
iii. Design an experiment to investigate the effectiveness of different chromatographic techniques in separating and identifying components of a mixture. Evaluate the experimental design, including the choice of chromatographic techniques, sample preparation methods, detection systems, and data analysis strategies. Discuss the potential challenges and limitations of the experiment.

THINK TANK

Group Activity

Teacher will divide the students into groups and Participants will use paper chromatography to solve a crime scene investigation by identifying and comparing ink samples from different suspects. Through this activity, participants will develop a practical understanding of chromatography techniques, enhance their problem-solving skills, and apply their knowledge in a forensic science context.

Outline for activity:

1. Recall basic concepts and principles of chromatography.
2. Explain the scenario where ink samples are found
3. Sample Preparation of chromatography strips
4. Analyze the separation process of ink components.
5. Evaluate and compare chromatograms to identify the matching ink sample.
6. Create a logical conclusion based on chromatographic analysis.
7. Evaluate the entire process.

GROUP PROJECT

Describe a scenario in which the results of a chromatography experiment could be misinterpreted. How would you ensure an accurate interpretation of chromatographic data?

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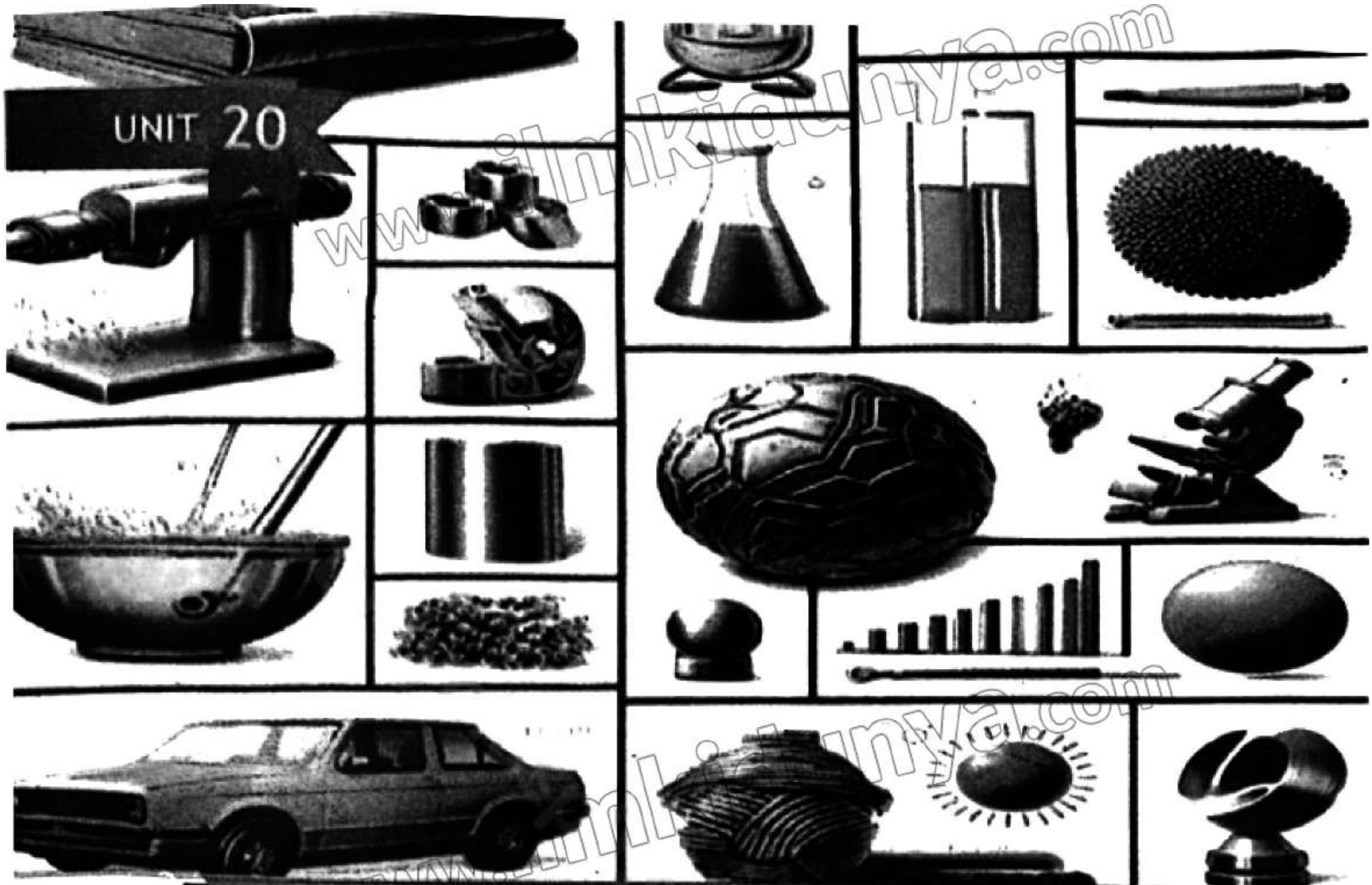

UNIT 20

MATERIALS

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Student Learning Outcomes (SLOs)

- Explain the properties of different materials and how they can be applied to desired structures.
- Explain the process of extracting material from ores and alloying them to achieve desired characteristics.
- Explain the mechanism of catalysts and how they increase the rate of a reaction while remaining unchanged at the end.
- Explain the challenges associated with recycling and toxicity of some materials produced through materials science.
- Explain the use of X-rays crystallography in analyzing structures.

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20.1 Material

A material is a substance or mixture that makes up an object. Everything around us is made from materials, each with unique properties. The materials can be soft or hard, flexible or stiff, and delicate or strong. Material can be used to describe something that is made of matter and exists in the physical world. There are many different types of materials. Some common examples of everyday materials are plastics, metals, fabric and glass.

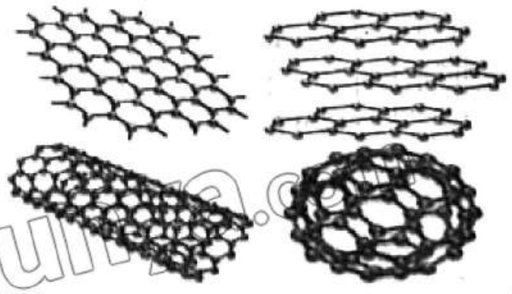
20.1.1 Properties of material

The properties of materials such as strength, flexibility, heat and electrical conductivity and melting and boiling points are key factors that determine how materials can be used. These properties are influenced by the material's chemical composition and internal structure. For example, metal, paper, wood and plastic come in a variety of shapes, sizes, colors, and compositions. Each item made from these materials has unique properties due to the specific materials used. When different substances are mixed they create a new material with its own set of characteristics.

Interesting Fact

Graphene is one of the strongest materials known. It conducts heat better than diamond,

and may conduct electricity better than silver. As it's two-dimensional, it could be used to detect single molecules of a gas - if a gas molecule were to stick to a sheet of graphene there would be a local change in the electrical resistance.



Processing methods, such as mixing, heating and cooling can alter a material's properties by changing its internal structure.

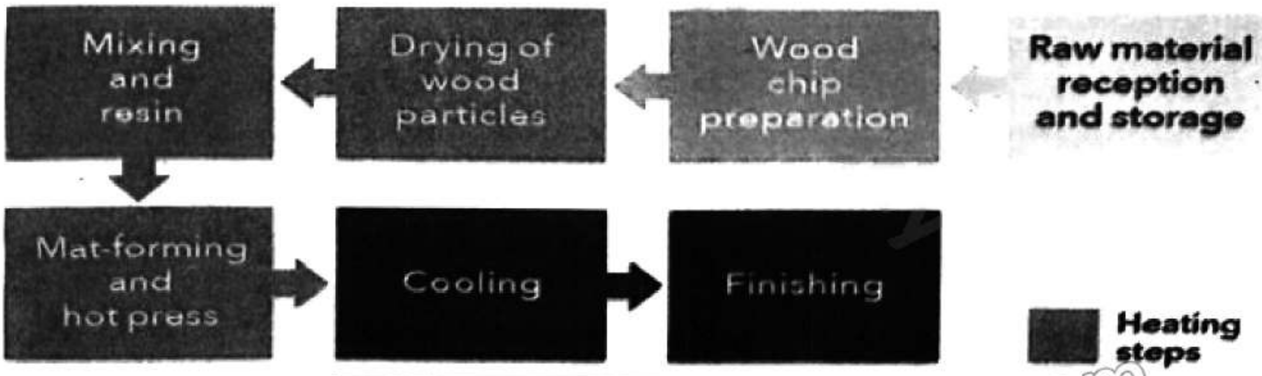


Fig 20.1 Processing Methods of Material

For instance, heating can increase the flexibility of some materials or change their conductivity. Cooling can make a material harder or more brittle.

Cost, color and texture are also important factors in determining how a material is used. For example, a material that is strong and lightweight might be chosen for applications where both strength and low weight are important such as in aerospace engineering.

Thus, the combination of material properties, processing techniques, and other factors like cost and appearance determines how materials are selected and used in different applications.

Some of the material and their structure and properties are as follows:

20.1.2 Alloys and metal compounds

Properties like shape and mass may be different for different objects even when they are made of the same material. Density is a useful property for making comparisons between different materials. Mixtures of metals called alloy is common example. By alloying some of the important properties of metals can be improved. Metals can be produced (smelted) from their ores by a variety of methods.

Fig 20.2 Metal Alloys

Fun Facts

Many alloys that contain **silver** in their name usually do not contain silver as one of their constituent elements. They are called 'silver' only because of their color. Examples of this are Tibetan silver and German silver.

Stainless steel is formed by mixing iron, small quantities of carbon and chromium is called 'stainless' because chromium gives it resistance from any kind of stain or iron rust.

Iron is the most used metal globally but it cannot be used in its pure form as it is soft and stretchable when heat is applied. At the same time if you add a very small amount of carbon to iron it becomes hard.

Copper is a good conductor of electricity and hence is used in wires to transmit electricity but the same copper when mixed with zinc or tin, we get alloys brass and bronze are not good conductors of electricity.

20.1.3 Properties of alloys

1.Alloys are stronger than the metals from which they are made.

2.Alloys are harder than the constituents' metals.

3.Alloys ere more resistant to corrosion.

4.Alloys have lower melting points than the constituent metals.

5.Alloys have lower electrical conductivity than pure metals.

6. They are characteristically shiny, and most are malleable (ability of a material to deform when compressed for example gold is very malleable and can be beaten to an extremely thin sheet) and ductile (can be drawn in the form of wires)

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Plastic

Fig 20.3 Plastics

All plastics are made from elements like hydrogen, carbon, oxygen, nitrogen, and other nonmetals. These elements are converted into long chains of molecules called polymers.

The word "poly" means many, and Polymers include plastics and rubber materials like polyethylene, nylon, polystyrene, and PVC. Most of the hydrocarbons used to make plastics come from oil and natural gas. During processing, other additives are mixed to give the plastics special characteristics.

Properties

1. They have low density.
2. Chemically inert or unreactive.
3. Good insulators and low thermal conductivity.
4. They can easily moulded into different shapes and size
5. They are light in weight and are chemically stable.
6. Plastic polymers are low cost easy to manufacture.
7. Plastics are used in electronic devices and house hold gadgets as insulators.

Ceramics

Fig 20.4 Ceramics

Ceramics include materials like cement, glass, and clay minerals such as porcelain. Tiles are made from silica, glass, and porcelain. Ceramics are compounds made from metallic and non-metallic elements. They are lightweight and provide excellent thermal insulation. The thickness of tiles can vary. Some ceramic materials can also be magnetic. A common type of ceramic magnet is made from strontium and iron oxides.

Properties

1. They are very hard.
2. Ceramics are brittle.
3. Stiffness and strengths are comparable to those of metals.
4. Poor conductors of heat and electricity.
5. Could be transparent, translucent or opaque.

Concrete

Concrete is one of the most commonly used building materials and is widely used today. Concrete is made from two main ingredients:

1. A mixture of water and cement (a binding agent).

2. Filler materials like sand, crushed stone, and gravel. To make concrete, a mix of Portland cement (10-15%) and water (15-20%) forms a paste. This paste is combined with the aggregates to create the final material.

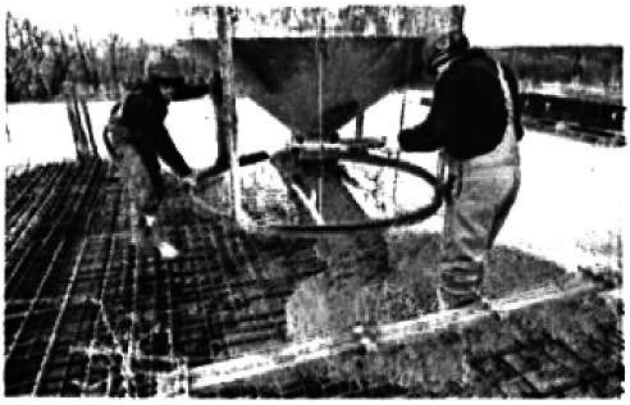

Fig 20.5 Concrete

Properties

1. It's affordable, durable, and can be molded into nearly any shape.
2. Concrete is a mixture of cement, water, sand and gravel that hardens over time to create a solid, strong substance.

Steel

Steel is another popular construction material. It is an alloy made mainly of iron with a small amount of carbon and sometimes other elements. The carbon makes steel strong and durable. Other elements like chromium, nickel, molybdenum, and silicon can be added to create different types of steel with various properties.

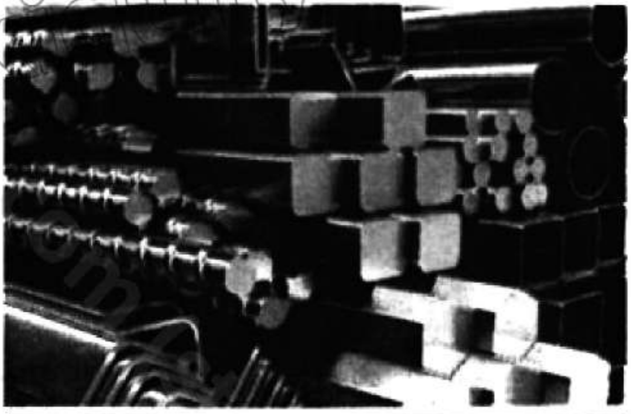

Fig 20.6 steel

Properties

1. Steel is a high-strength material and can be used for structural loads.
2. Steel is highly durable and rigid.
3. Steel is versatile material.
4. Most of steel are easily weldable.
6. Steel generally has lower thermal and electrical conductivity compared to other metals.
7. Steel can be completely recycled.
8. Steel can be alloyed with other elements such as chromium, nickel and molybdenum to resist corrosion.

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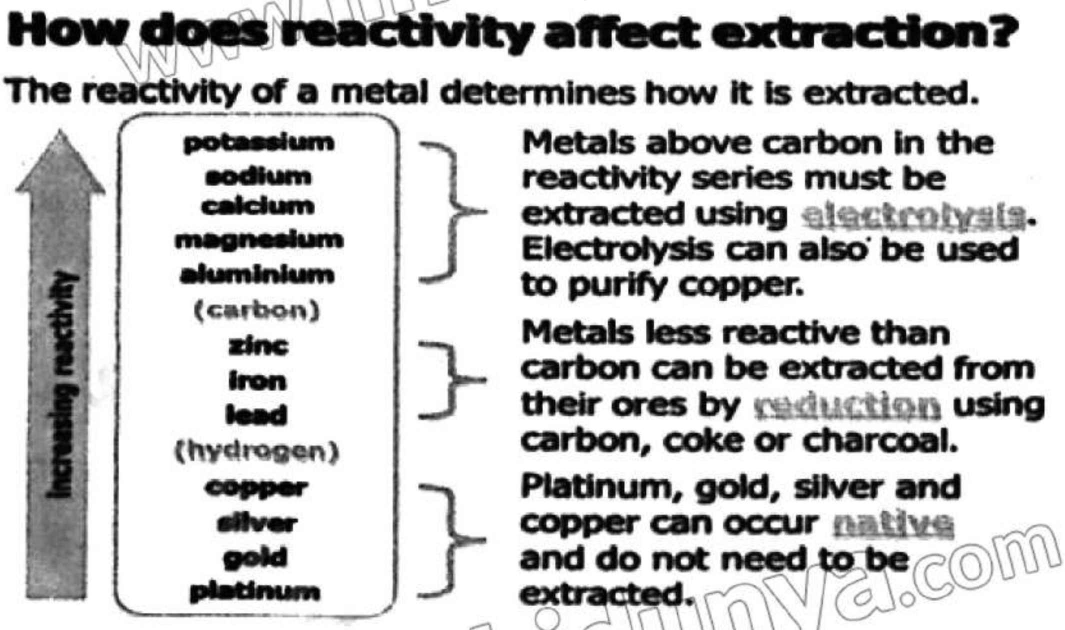
20.2 Extracting Material from Ores and Alloying



How does reactivity affect extraction?

The reactivity of a metal determines how it is extracted.

Metals above carbon in the reactivity series must be extracted using electrolysis. Electrolysis can also be used to purify copper.

Metals less reactive than carbon can be extracted from their ores by reduction using carbon, coke or charcoal.

Platinum, gold, silver and copper can occur native and do not need to be extracted.

Fig 20.7 How reactivity affects extraction

1. **Extraction:**
   - **Crushing and Grinding:**

     The extracted ore is broken into smaller fragments and subsequently reduced to a fine powder.
   - **Concentration:**

     Frequently employed techniques include flotation process, magnetic separation, and gravitational separation.
2. **Roasting:**

   The concentrated ore is heated in air below its melting point and converted into oxide. This process is called roasting. For example;

   The roasting for zinc blende (ZnS) , cinnabar (HgS) and copper pyrite ore.

$$2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO + 2SO_{2(g)}$$
$$HgS_{(s)} + O_{2(g)} \rightarrow Hg_{(l)} + SO_{2(g)}$$
$$2CuFeS_{2(s)} + O_{2(g)}\ ) \rightarrow Cu_2S_{(s)} + 2FeS_{(s)} + SO_{2(g)}$$

3. **Smelting:**

   The method to reduce metal ions to free metal is called smelting. This is done by heating ore with a reducing agent. The most common reducing agents are coke, carbon monoxide and hydrogen. Some examples are:

$$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(l)} + 3CO_{2(g)}$$

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$$WO_{3(s)} + 3H_{2(g)} \longrightarrow W_{(s)} + 3H_2O_{(l)}$$

$$ZnO_{(s)} + C_{(s)} \longrightarrow Zn_{(s)} + CO_{(g)}$$

However, smelting of copper ore is done in two steps.

i) The roasted copper ore is heated: with coke and sand at about 1100°C. The materials melt and separate into two layers. The bottom layer that contains mixture of Cu_2S and FeS is called matte. While the upper layer is a silicate slag formed by the reaction of FeO and sand

$$2FeS_{(s)} + O_{2(g)} \longrightarrow 2FeO_{(s)} + 2SO_{2(g)}$$

$$FeO_{(s)} + SiO_{2(s)} \longrightarrow FeSiO_{3(s)}$$

ii) **Bessemerization**

In this process air is blown through the molten copper matte in a Bessemer converter (Figure 20.8). Any remaining iron sulplide (FeS) is oxidized and removed as slag($FeSiO_3$). In the final smelting step cuprous sulphide (Cu_2S)is oxidized to form cuprous oxide, which reacts with remaining cuprous sulphide to form metallic copper.

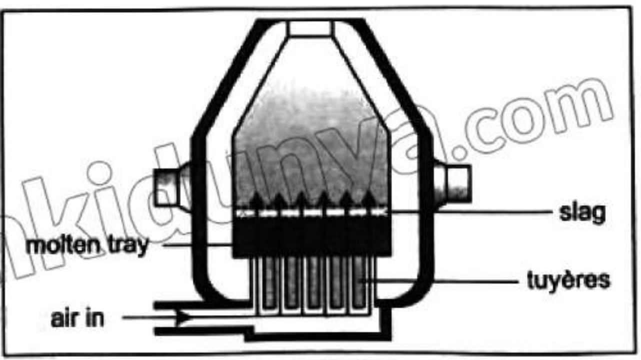

Fig 20.8 Bessemer converter

$$2Cu_2S_{(l)} + 3O_{2(g)} \longrightarrow 2Cu_2O_{(l)} + 2SO_{2(g)}$$

$$Cu_2S_{(l)} + 2Cu_2O_{(l)} \longrightarrow 6Cu_{(l)} + SO_{2(g)}$$

The product, called blister copper is about 97 to 99% pure Cu, with entrapped bubbles ofSO_2 gas. Bessemerization is also used to convert pure iron into steel.

4. Refining or purification of metals

The metal obtained as a result of smelting contains some impurities. So, it must be refined. Following methods may be used.

i) Electrolytic refining:

An electrolytic cell is used in electro-refining, in which impure metal acts as the anode and a sample of pure metal acts as the cathode. For example, electrolytic refining of copper is carried out in an electrolytic tank containing acidified copper sulphate solution as electrolyte (Figure20.9). Impure slabs of copper act as anode and pure copper sheets as cathode.

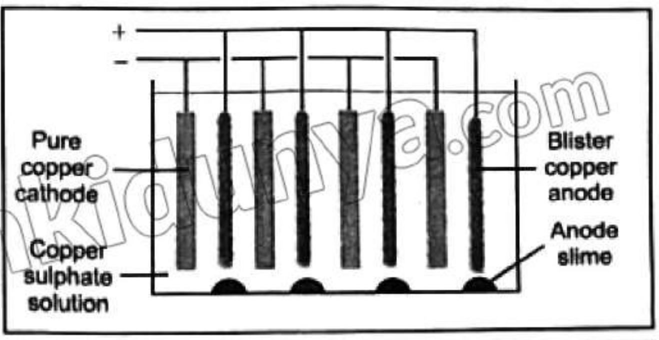

Fig 20.9 Electrolytic refining of copper

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On passing an electric current through the solution, impure copper dissolves forming Cu^{+2}ions. These Cu^{+2} ions gain electrons at the cathode and form Cu atoms, which are deposited on the cathode. In this way, pure copper is collected at the cathode. The impurities like Au and Ag fall off the anode as anode mud.

Reaction at anode:

$$Cu_{(s)} \longrightarrow Cu^{2+}{}_{(aq)} + 2e^-$$

Reaction at the cathode:

$$Cu^{2+}{}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

ii) Distillation:

Metals with relatively low melting points such as As, and Hg are refined by distillation.

5. Alloying:

Alloying is the process of combining a metal with one or more other elements to enhance its properties such as strength, ductility, corrosion resistance, and hardness.

Methods:

- **Melting and Mixing:** The base metal is melted, and the alloying elements are added to the molten metal. The mixture is thoroughly stirred to ensure uniform distribution of the elements.

  For example, steel is made by adding carbon and other elements like chromium, nickel, and manganese to iron.
- **Powder Metallurgy:** This involves mixing fine powdered metals and pressing them into a desired shape before heating them to bond the particles. This method is useful for creating alloys with specific properties.
- **Mechanical Alloying:** This involves repeatedly fracturing and welding a mixture of powder particles to produce an alloy. This method is used for creating advanced materials with unique properties.

6. Shaping

- **Casting:** The molten alloy is poured into moulds to achieve the desired shape.
- **Forging:** The metal or alloy is hammed or pressed while it is hot.
- **Rolling:** The metal or alloy is passed through rollers to produce sheets or other shapes.
- **Machining:** Cutting and shaping the metal or alloy using tools.

7. Heat Treatment:

- **Annealing:** Heating the metal or alloy to a specific temperature and then cooling it slowly to remove internal stresses and improve ductility.
- **Quenching:** Heating the metal or alloy and then cooling it rapidly in water or oil to increase hardness.
- **Tempering:** Heating the quenched metal or alloy to a lower temperature and then cooling it to achieve a balance between hardness and ductility.

Examples of alloys

- **Steel:** Iron alloyed with carbon
- **Bronze:** Copper alloyed with tin
- **Brass:** Copper alloyed with zinc

Interesting fact

Main purpose of making Alloy to decrease the intensity of corrosion of metals for example bronze is alloy of 90% copper and 10% tin. Bronze statues do not get affected by sun and rain. Stainless steel does not get stain with air or water and also does not rust. It is an alloy made from 74% iron ,18 %chromium and 8 % carbon.

20.2.1 Importance of Alloy making

1. Alloys help to increase the metal hardness.
2. The melting point of pure metals is very high and alloying helps to reduce the melting point range.
3. By alloying the resistance increases and cannot be influenced by chemicals or weather conditions.
4. The process of alloying changes the metal color when mixed together, two different metals or one metal and another non-metal.
5. Alloying helps in the good casting of metals, as pure metals tend to solidify when melted and contract as well. After they are alloyed, they tend to expand and result in a good casting.

20.3 Mechanism of Catalysts

20.3.1 What is Catalysis?

Catalysis is process when the speed of a chemical reaction is altered by a substance called a catalyst. This catalyst is not used up in the reaction and can be used over and over again. Usually, even a small amount of catalyst is enough to speed up the reaction. In these reactions, the catalyst often forms a temporary unstable substance before returning to its original form, allowing it to keep working in a cycle.

In the presence of catalyst less energy is needed to start a chemical reaction but the overall energy doesn't change. A catalyst can help with multiple reactions. Other substances can affect how well a catalyst works: inhibitors make it less effective, and promoters make it more effective and can also change the reaction temperature.

Catalyzed reactions have less activation energy (the energy needed to start the reaction) than uncatalyzed ones, so they happen faster at the same temperature and with the same number of reactants. The reaction speed depends on how often reactants meet during the slowest step, which usually involves the catalyst. The amount of catalyst affects the reaction rate. Even though catalysts aren't used up in the reaction, they can be stopped, weakened, or destroyed by other processes.

20.3.2. Mechanism of Catalysis

Transition metals make excellent catalysts as they have incompletely filled d-orbitals that allow them to both donate and accept electrons easily from other molecules.

A catalyst increases the rate of reaction by lowering the activation energy by providing an alternate pathway with lower activation energy.

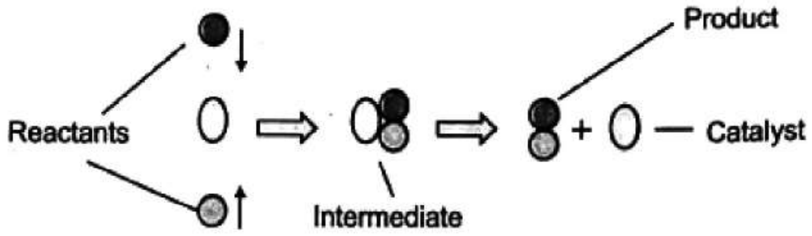

Fig 20.10 Mechanism of Catalysis

If the activation energy is reduced, more reactants can cross the energy barrier easily. Activation energy is the energy needed by reactants to start a reaction. The catalyst brings the reactants together by temporarily bonding with them. This makes it easier and quicker for the reactants to react together.

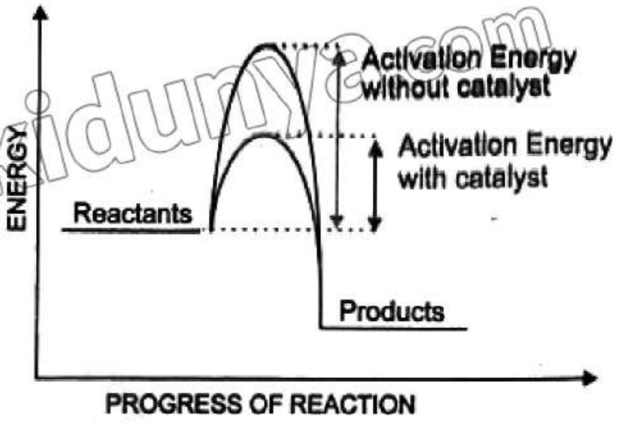

Fig 20.11 Catalytic Decomposition of H_2O_2

Example1

Catalytic Decomposition of Hydrogen Peroxide

Reaction: $2H_2O_2 \rightarrow 2H_2O + O_2$

Catalyst: Manganese dioxide (MnO_2)

- Hydrogen peroxide molecules adsorb on the surface of MnO_2.
- MnO_2 provides a surface that facilitates the breakdown of hydrogen peroxide into water and oxygen, involving a lower activation energy pathway compared to the uncatalyzed reaction.
- The decomposition proceeds via the formation of intermediate species involving the MnO_2 surface.
- Water and oxygen molecules desorb from the MnO_2 surface.
- MnO_2 remains unchanged and can catalyse further decomposition of hydrogen peroxide.

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Example 2

V_2O_5 is used as catalyst in the contact process for the preparation of sulfur trioxide from sulfur dioxide by oxidation.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

V_2O_5 is used as catalyst

Amazing Fact:

Recycling helps to save energy. If you recycle one glass bottle, it saves enough energy to light a 100-watt bulb for four hours, power a computer for 30 minutes, or a television for 20 minutes. Recycling one aluminum can saves enough energy to run a 55-inch HDTV to watch your favorite movie.

Fun fact about recycling:

Each ton (2,000 pounds) of recycled paper can save 17 trees, 380 gallons of oil, three cubic yards of landfill space, 4,000 kilowatts of energy, and 7,000 gallons of water. This represents a 64% energy savings, a 58% water savings, and 60 pounds less of air pollution.

20.4 Challenges Associated with Recycling

The recycling problem involves challenges in collecting, sorting, managing, and processing recyclable materials. These problems arise due to factors like poor waste management systems, improper waste disposal, lack of education and lack of awareness about recycling, and difficulty in separating recyclable from non-recyclable waste. Ensuring safe recycling practices and thorough testing of recycled materials is essential to minimize potential toxicological impacts.

Pollution occurs when non-recyclable materials mix with recyclables. If recycling costs more than the benefits, it might not be worth doing. Issues include knowing if we are recycling thermosetting plastics or thermoplastics. Some items, like chip bags and juice pouches, are hard to recycle because they are made of multiple layers of different materials.

Recycling and managing the toxicity of materials produced through materials science involve several challenges. Main challenges are as follows:

1. Complex Material Composition

- Modern materials often consist of multiple layers or composites, each made from different substances. Separating these components for recycling is technically challenging. It is often expensive.
- **Alloys** are designed for specific properties, but their mixed composition complicates recycling processes.

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2. Contaminants and Purity Issues

- Materials are generally contaminated with substances like oils, adhesives, or other residues. These materials require additional processing steps to remove before recycling.
- Recycled materials must have the required purity levels for reuse which is difficult, especially for high-tech applications.

3. Economic Viability

- The processes required to recycle advanced materials are often more expensive than producing new materials. This makes recycling less attractive.

4. Environmental and Health Risks

- Some materials, such as certain plastics, batteries, and electronic components, contain toxic substances (e.g., lead, mercury, cadmium). They pose health and environmental risks if not properly managed.
- Recycling processes can generate hazardous emissions or by-products that pose serious health issues.

5. Technological Limitations

- Recycling technologies may not yet be advanced enough to efficiently process certain materials.
- **Lifecycle Analysis:** Comprehensive lifecycle analyses are needed to fully understand the environmental impacts of materials from production to disposal, which can guide better design and recycling practices.

20.5 X-Ray Crystallographic Analysis

X-ray crystallography is a method that uses X-rays to find out the detailed structure of a crystal, including the arrangement of its atom sand molecules. This helps us understand how these atoms and molecules are bonded and any irregularities in the crystal.

This technique can be used on various substances like salts, minerals, metals, semiconductors and biological compounds (such as proteins, DNA, and vitamins).

X-ray crystallography is valuable in many fields, including biology, chemistry, and geology.

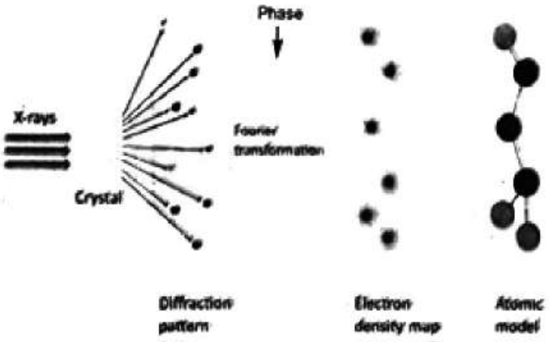

Fig 20.11 X-ray Crystallography

Barium tests are used to examine the digestive tract using a white powder Barium Sulphate. It is a chalky substance that you drink before they give you the X-ray which enables your doctor to make an accurate diagnosis.

20.5.1 Applications of X-ray Crystallography

X-ray crystallography is used to study many different molecules. It has been vital in many famous projects in chemistry. Early examples include determining the structures of simple crystals like quartz and salt. A notable achievement was discovering the double-helix structure of DNA by Franklin, Watson, and Crick in 1953. Other important molecules analyzed include Vitamin B12, insulin, and penicillin.

Some important applications of crystallography are as follows:

- X-ray crystallography helps in understanding the 3D structures of proteins and other biomolecules
- Determining the structures of DNA and RNA helps in understanding genetic information storage and transmission.
- By revealing the structure of target proteins, X-ray crystallography helps in identifying potential binding sites for new drugs.
- This technique helps in understanding the atomic structure of various materials, such as metals, ceramics, and polymers, leading to the development of new materials with desirable properties.
- It helps in structural determination of nanoparticles and the development of nanotechnology applications.
- Determining the structure of complex organic and inorganic compounds is fundamental for understanding their reactivity and properties.
- X-ray crystallography can help to explain the intermediates and transition states in chemical reactions.
- Determining the structures of minerals helps in understanding geological processes and the formation of natural resources.
- Studying how minerals change under different temperature and pressure conditions.
- Understanding the arrangement of atoms in solids can explain various physical properties such as conductivity, magnetism, and optical properties.
- Understanding the crystalline structures of pollutants can help in developing methods for their removal or neutralization.

KEY POINTS

1. Each item is made up of various materials and when one substance is mixed with another, it creates a unique material with specific qualities.
2. Homogeneous mixture formed by mixing metal with other metal or nonmetals in a certain proportion is called an alloy.
3. By making alloys some of the important properties of metals can be improved.
4. Recycling is the process of collecting, processing of materials that would otherwise be discarded as waste, converting them into new products.
5. The toxicity of materials produced through recycling can vary significantly depending on the type of material and the recycling process used.

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6. A catalyst provides an alternate pathway for the reaction that has a lower activation energy. When activation energy is lower, more reactant particles have enough energy to react, so the reaction occurs faster.
7. X-ray crystallography uses electromagnetic radiation (specifically, X-rays) to determine the molecular and atomic structure of a crystal. The structure of the crystal causes the X-rays to diffract in specific directions.
10. X-ray crystallography is a technique used to determine the atomic and molecular structure of a crystal by measuring the angles and intensities of X-rays diffracted through the crystal lattice.
11. X-ray crystallography provides detailed information about the arrangement of atoms within the crystal, crucial for understanding the structure and function of various materials, including biological molecules like proteins.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which process is used to purify metals to the desired purity?

a) Smelting b) Refining c) Grinding d) concentration

ii. How do catalysts speed up chemical reactions?

a) By increasing the activation energy

b) By providing an alternative pathway with lower activation energy

c) By being consumed in the reaction

d) By increasing the temperature of the reaction

iii. X-ray crystallography is primarily used to:

a) Measure the density of materials b) Determine atomic structures

c) Conduct chemical reactions d) Separate metal ores

iv. Which material is known for its high thermal resistance and brittleness?

a) Metal b) Polymer c) Ceramic d) Composite

v. Heating the metal to a specific temperature and then cooling it slowly to remove internal stresses and improve ductility is called?

a) Annealing b) Quenching c) machining d) Forging

vi. Tiles are made from

a) silica b) glass c) porcelain d) all of these

vii. The concentrated ore is heated in air below its melting point and converted into oxide. This process is called?

a) Concentration b) Smelting c) Roasting d) Bessemerization

viii. Which of the following materials is NOT considered a ceramic?

a) Cement b) Nylon c) Glass d) Porcelain

ix. What is the primary function of additives mixed with plastics during processing?

a) To reduce the cost of production
b) To enhance the colour of plastics
c) To give plastics special characteristics
d) To make plastics biodegradable

x. Which property is common to both plastics and ceramics?

a) High electrical conductivity
b) High density
c) Lightweight
d) High thermal conductivity

2. Short Answer Questions

i. Compare and contrast the properties of plastics and ceramics?

ii. Comment on the environmental impact of using steel and plastics in construction?

iii. Describe the properties and uses of ceramics?

iv. What is the process of smelting in metal extraction?

v. Explain the role of a catalyst in a chemical reaction?

vi. Give an example of an alloy and its components.

vii. What is concentration in the context of ore processing?

viii. How does refining improve the quality of metals?

ix. List four applications of x-ray crystallography?

3. Long Answer Questions

i. Explain the entire process of extracting a metal from its ore, including the steps of concentration, smelting, and refining.

ii. Describe the mechanism of catalysts in detail and give examples of their applications in both industrial contexts.

iii. Analyse the environmental and economic challenges associated with recycling materials.

iv. Elaborate on the principles and applications of X-ray crystallography. How does it contribute to our understanding of both biological molecules and synthetic materials?

Activity

Poster Design on Recycling

Objective:

To educate students about the importance of recycling and to encourage them to creatively express their knowledge and ideas through poster design.

Groups:

Divide the class into small groups of 3-4 students. Assign each group a specific aspect of recycling to focus on (e.g., plastic recycling, electronic waste, composting etc).

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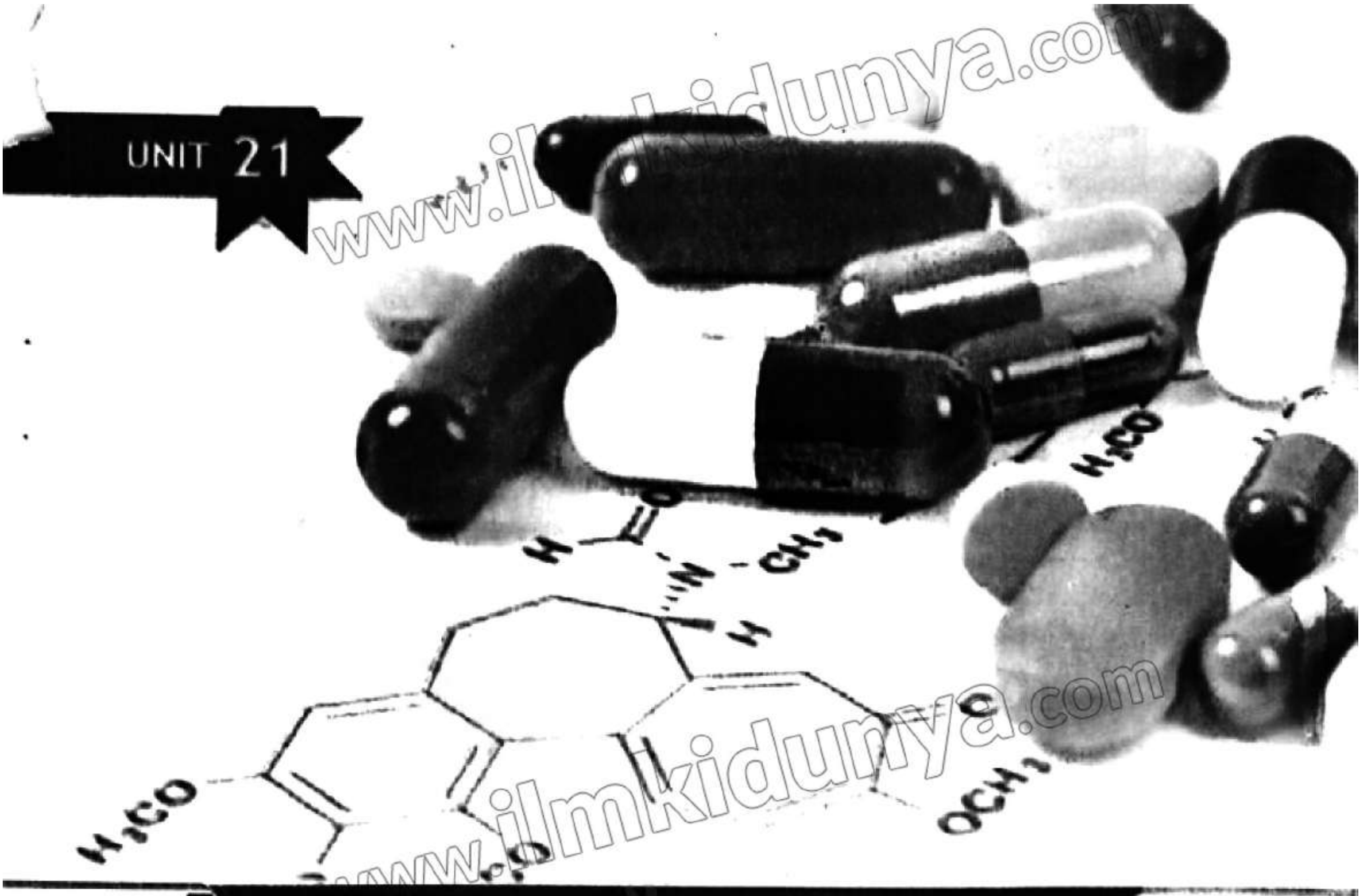
UNIT 21



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MEDICINE

Student Learning Outcomes (SLOs)

- Recognise the concept of therapeutic index and therapeutic window in relation to drug administration.
- Explain the mechanism of action and uses aspirin and penicillin and explain the chemical structure of the same.
- Describe the mechanism of action of opiates and the concept of opioid receptors in the brain.
- Describe the pH regulation of stomach and its relation to the concept of non-specific reactions and active metabolites.
- Recognised the challenges in treating viral infections with drugs and the concept of antiviral medications.

21.1 Therapeutic Index

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The therapeutic window, also known as the therapeutic range or therapeutic index, indicates the range of drug amounts in the body that bring about the desired therapeutic effects with minimum adverse effects. This means, it expresses the dosage range in which a medication can be both effective and safe.

21.1.1 Key Components of therapeutic index

1. **Minimum Effective Concentration (MEC):**
   This is the lowest amount of a drug in the bloodstream that triggers the desired therapeutic effect. Below this concentration, the drug may not be effective.
2. **Maximum Tolerated Concentration (MTC):**
   This signifies the highest amount of a drug in the bloodstream that a patient can bear without experiencing severe side effects or toxicity.
   The therapeutic window acts as a safety zone for drug administration, ensuring that the drug is potent enough to be effective while staying within safe limits to prevent harm to the patient. Falling below the MEC may result in inadequate treatment, while surpassing the MTC can lead to toxicity.

21.1.2 Factors Influencing the Therapeutic Window:

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a. **Individual Variability:** People may metabolize drugs differently due to genetic factors, age, or overall health.
b. **Drug Interactions:** The simultaneous use of multiple medications can modify the concentrations of each drug.
c. **Patient Characteristics:** Factors like age, weight, and pre-existing medical conditions can affect how a drug is absorbed, distributed, metabolized, and eliminated.

21.2 Mechanism of Drug Action

Drug action refers to certain biochemical or physiological effects that the drug produces in the body to produce a therapeutic response. A drug's mechanism of action is the molecular or cellular process by which a drug exerts its pharmacological effects.

Aspirin and penicillin are two fundamental medications in medicine, each with unique mechanisms of action, applications, and chemical compositions. Let's explore each one in detail.

21.2.1 Aspirin

Mechanism of Action:

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The primary mode of action of aspirin involves the inhibition of the enzyme cyclooxygenase (COX). This enzyme plays a vital role in the synthesis of prostaglandins. Prostaglandins contribute to the development of inflammation, pain, and fever, while thromboxanes are involved in platelet aggregation, and are essential for blood clotting. By blocking COX, aspirin reduces inflammation, pain, and fever, and also inhibits blood clot formation by preventing thromboxane production.

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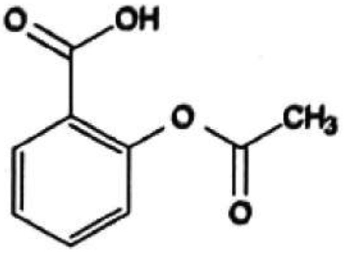
Uses:

Aspirin is utilized for various purposes, including:

1. Pain relief: for headaches, muscle pain, and mild arthritis.
2. Anti-inflammatory effects: to alleviate inflammation.
3. Antipyretic properties: to reduce fever.
4. Anticoagulant effects: in low doses, it prevents heart attacks and strokes by inhibiting blood clot formation.

Chemical Structure:

The chemical name of aspirin is acetylsalicylic acid. It consists of an aromatic ring (benzene ring) linked to a carboxylic acid group (–COOH) and an ester group (–$COOCH_3$). The structure can be simplified as:



Aspirin

21.2.2 Penicillin

Mechanism of Action:

Penicillin binds to the β-lactam ring on the transpeptid enzyme, preventing it from cross-linking and preventing new cell walls from forming. By inhibiting these enzymes, penicillin disrupts the formation of a normal cell wall in bacteria. This leads to a weakened cell wall that eventually ruptures, causing the bacteria to die due to osmotic pressure.

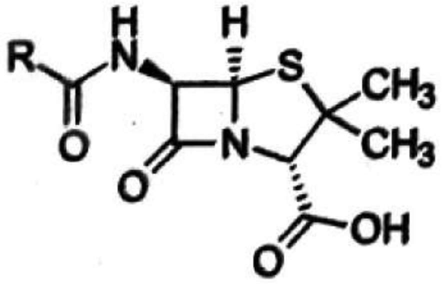
Uses:

Penicillin antibiotics are employed in the treatment of various bacterial infections, such as:

1. Pneumonia and other respiratory tract infections.
2. Meningitis.
3. Skin infections.
4. Syphilis.
5. Throat infections

Chemical Structure:

The key structural feature of the penicillins is the four-membered β-lactam ring; this structural moiety is essential for penicillin's antibacterial activity. The β-lactam ring is itself fused to a five-membered thiazolidine ring.



Penicillin

21.2 .3 OPIATES

Opiates, also called opioids are a class of drugs that include the illegal drug heroin, synthetic opioids such as fentanyl, and legal prescription pain relievers such as oxycodone, hydrocodone, codeine, morphine, and many others.

They are known for their strong pain-relieving effects. They induce euphoria and, unfortunately, addiction. The mechanism of action of opiates involves their interaction with opioid receptors located in the brain and throughout the central nervous system.

21.2.4 Opioid receptors:

Three main types of opioid receptors include:

1. *Mu (μ) receptors: These are mainly responsible for the analgesic effects of opiates and are the main targets of most clinically used opioids. Activation of mu receptors can also cause respiratory depression, euphoria, and physical dependence.*
2. Delta (δ) receptors: Their function is not fully understood, but they are thought to affect pain-relieving mechanisms and may play a role in mood regulation.
3. Kappa (κ) receptors: Activation of kappa receptors can cause pain and relief, but in some cases, they are also associated with dysphoria and hallucinations.

Mechanism of Action:

Opiates bind to opioid receptors located on certain cells in the brain, spinal cord, and other body areas. These receptors are part of the body's natural pain relief system and are often activated by endorphins which are naturally occurring hormones. Opiates, when bound, stimulate the endorphins, producing powerful analgesic effects to blunt the pain sensation.

Research indicates that commonly used drugs, such as opiates, alcohol, nicotine, amphetamines, and cocaine, trigger a neurochemical reaction that significantly boosts dopamine release by brain neurons in the reward centre. This results in feelings of euphoria and well-being.

Therapeutic Uses of Opioids

1. **Pain Management:**
   Opioids are used to treat moderate to severe pain, especially when other pain relievers are ineffective.
2. **Cough Suppression:**
   Some opiates have antitussive (cough suppressant) effects.
3. **Diarrhea Treatment:**
   Opioids can decrease bowel motility, relieving diarrhoea.

Risks and Considerations:

While opiates are effective for pain relief and have legitimate medical uses, their potential for abuse, addiction, and overdose is a serious issue. The euphoric effect can lead to abuse, and long-term use can result in tolerance (requiring higher doses for the same effect) and physical dependence and addiction. Abrupt discontinuation of the drug can cause withdrawal symptoms. Overdose, especially with potent synthetic opioids like fentanyl, can lead to death.

21.3 pH Regulation in the Stomach

The stomach's pH regulation is a dynamic process for proper digestion and enzyme activation. Parietal cells in the gastric glands release hydrochloric acid into the stomach lumen. This acid maintains an acidic environment in the stomach. This tightly controlled process is essential for breaking down ingested food. This acidification aids in activating digestive enzymes, denaturing proteins, and eliminating harmful microorganisms in food.

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pH Level in the Stomach:

The stomach's pH typically ranges from 1.5 to 3.5, creating an acidic environment necessary for optimal enzyme function, especially pepsin for protein breakdown.

Control Mechanisms:

Various factors, such as food presence, hormonal signals (gastrin), and neural signals, regulate HCl release.

21.4 Non-Specific Reactions and Active Metabolites

1. Non-Specific Reactions:

The reactions that occur without specificity to a particular substrate are called non-specific reactions. For instance, the low pH of the stomach lumen helps kill pathogens in the food and break down complex food molecules like proteins, lipids, and carbohydrates. The stomach`s HCl unfolds proteins, making them more accessible for enzymatic digestion by pepsin.

2. Active Metabolites:

What is a metabolite? A metabolite is a biologically active form of a drug or substance produced by the body's metabolic processes. The stomach's pH can affect the formation of metabolically active drugs. Some medications undergo significant metabolism in the stomach due to the acidic environment and enzyme activity. These metabolites can metabolize the drug or render it inactive.

21.5 Viral Infections and Their Treatment

Unlike bacteria, viruses lack many cellular structures and metabolic pathways, making it difficult to target them without affecting the host cells. Therefore, treating viral infections with pharmaceuticals presents unique challenges.

Antiviral drugs are developed to disrupt the viral life cycle by targeting different stages of replication. This can include preventing the virus from entering host cells, inhibiting the replication of the viral genome, or stopping the release of new virus particles.

Enzyme inhibition is a common mechanism of action for numerous antiviral drugs, as they focus on viral enzymes essential for replication. Protease inhibitors, reverse transcriptase inhibitors, and polymerase inhibitors are examples of medications that break the viral life cycle.

In addition to enzyme inhibition, some antiviral drugs enhance the host's immune response to viral infections. For instance, interferons are proteins that can boost the immune system's ability to combat viruses. Viral protease inhibitors specifically target the activity of viral proteases, which are enzymes essential for processing viral proteins. These inhibitors are frequently used in the treatment of HIV and hepatitis C virus infections.

To combat drug resistance and viral diversity, combination therapy involving multiple antiviral agents with different mechanisms of action is commonly used. This strategy aims to reduce the risk of resistance development and improve treatment effectiveness.

21.5.1 Challenges in Treating Viral Infections

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Virus and bacteria possess different structures. Viruses can develop a protective covering around themselves. Unlike bacteria viruses do not have cell walls which can be attacked by antibiotics.

Therefore, the treatment of viral infections poses many challenges. For instance;

1. Viruses multiply inside host cells, using the host's ribosomes. Therefore treating viral infection without harming the host cell requires specific antiviral agents.
2. Viruses can mutate rapidly, producing new strains. This quick mutation rate can cause resistance to antiviral medications, complicating ongoing treatment.
3. Viruses lack cellular structures like a cell wall or metabolic pathways, which are common targets for antibacterial drugs. This limits the potential targets for antiviral medications.
4. Some viruses develop protective covering and can remain dormant in the body for a longer period.
5. Medications for viral infection may affect host cell functions, leading to toxic side effects. Balancing the selectivity of antiviral drugs is essential to minimize harm to the host.

21.6 Concept of Antiviral Drugs

Antiviral drugs are a class of medicines particularly used to treat viral infections. Drugs that combat viral infections are called antiviral drugs. Viruses are among the major pathogenic agents that cause several serious diseases in humans, animals, and plants. Antiviral medications disrupt the viral life cycle by inhibiting specific stages of replication, such as blocking virus entry into host cells.

KEY POINTS

- The therapeutic window, also known as the therapeutic range or therapeutic index, indicates the range of drug concentrations in the body that bring about the desired therapeutic effects with minimum adverse effects.
- The simultaneous use of multiple medications can modify the concentrations of each drug.
- Drug action refers to certain biochemical or physiological effects that the drug produces in the body to produce a therapeutic response.
- The primary mode of action of aspirin involves the inhibition of the enzyme cyclooxygenase (COX).
- The chemical name of aspirin is acetylsalicylic acid.
- The key structural feature of the penicillins is the four-membered β-lactam ring; this structural moiety is essential for penicillin's antibacterial activity.
- Opiates are compounds that have strong pain-relieving effects.
- Opioids are used to treat moderate to severe pain, especially when other pain relievers are ineffective.
- The stomach's pH regulation is a dynamic process for proper digestion and enzyme activation.

- The stomach's pH typically ranges from 1.5 to 3.5
- The reactions that occur without specificity to a particular substrate are called non-specific reactions.
- A metabolite is a biologically active form of a drug or substance produced by the body's metabolic processes.
- Virus and bacteria possess different structures. Viruses can develop a protective covering around themselves.
- Unlike bacteria viruses do not have cell walls which can be attacked by antibiotics.
- Antiviral drugs are a class of medicines particularly used to treat viral infections.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. What is the significance of maintaining an acidic pH in the stomach for digestion?

a) Enhances the absorption of lipids
b) Facilitates the activation of digestive enzymes
c) Promotes the breakdown of carbohydrates
d) Increases the secretion of bile

ii. Which opioid receptor is primarily responsible for the analgesic effects of opiates?

a) Delta (δ) receptors
b) Kappa (κ) receptors
c) Mu (μ) receptors
d) Sigma (σ) receptors

iii. What is a major challenge in developing broad-spectrum antiviral drugs?

a) High mutation rate of viruses
b) Lack of selectivity
c) Limited understanding of viral replication
d) Inability to target host cells

iv. Why is understanding the mechanism of action of a drug essential for healthcare professionals?

a) To identify potential side effects
b) To determine the optimal dosage
c) To assess drug interactions
d) All of the above

v. Which of the following best describes the therapeutic window?

a) The range of drug concentrations that is toxic
b) The range of drug concentrations that produces therapeutic effects without causing significant adverse effects
c) The range of drug concentrations that is ineffective
d) The range of drug concentrations that causes adverse effects

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vi. If a drug's concentration in the bloodstream falls below the MEC, what is the most likely outcome?

a) The patient will experience toxicity

b) The drug will have no therapeutic effect

c) The patient will experience severe side effects

d) The drug will be at its maximum effectiveness

vii. What is the primary therapeutic use of aspirin?

a) Antibacterial b) Analgesic and anti-inflammatory

c) Antiviral d) Antifungal

viii. Penicillin is most effective against which type of organisms?

a) Viruses b) Fungi c) Gram-positive bacteria d) Protozoa

ix. How does penicillin inhibit bacterial growth?

a) By disrupting bacterial DNA synthesis

b) By inhibiting the enzyme responsible for cell wall synthesis

c) By disrupting bacterial protein synthesis

D. By inhibiting bacterial RNA synthesis

x. Which of the following is a common therapeutic use of opiates?

a) Treating bacterial infections b) Reducing inflammation

c) Relieving severe pain d) Lowering blood pressure

xi. Why can long-term use of opiates lead to addiction?

a) Because they inhibit serotonin reuptake

b) Because they cause irreversible binding to receptors

c) Because they increase dopamine release in the brain

d) Because they decrease the production of natural endorphins

2. Short Answer Questions

i. Explain the role of hydrochloric acid in the stomach and its impact on the activation of digestive enzymes.

ii. Briefly describe how opioids activate mu receptors and how this activation leads to pain relief.

iii. Discuss two challenges in developing antiviral drugs and provide potential strategies to overcome them.

iv. How does the secretion of hydrochloric acid influence the digestion?

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3. Long Answer Questions

i. Discuss the link between the mechanism of action of opioids and the potential for drug addiction.
ii. Analyse the challenges involved in developing antiviral drugs.
iii. Explain the relationship between the Minimum Effective Concentration (MEC) and the Maximum Tolerated Concentration (MTC). How do these parameters define the therapeutic window?
iv. Describe the chemical structure of aspirin and penicillin, highlighting the functional groups that are critical for their mechanisms of action. Explain how these structures relate to their respective therapeutic uses.
v. A patient presents with symptoms of a bacterial infection. The doctor prescribes penicillin. Explain how penicillin works to treat the infection. Discuss potential resistance mechanisms that bacteria might employ against penicillin and how these mechanisms can be overcome.
vi. Identify and describe the main types of opioid receptors in the brain. Discuss their roles in pain modulation and the physiological effects of their activation by opiates.
vii. Analyse the impact of long-term opiate use on brain chemistry and function. Discuss the changes in receptor density and neurotransmitter levels that occur with prolonged exposure to opiates. Evaluate the implications of these changes for treatment options and recovery strategies for opiate addiction.

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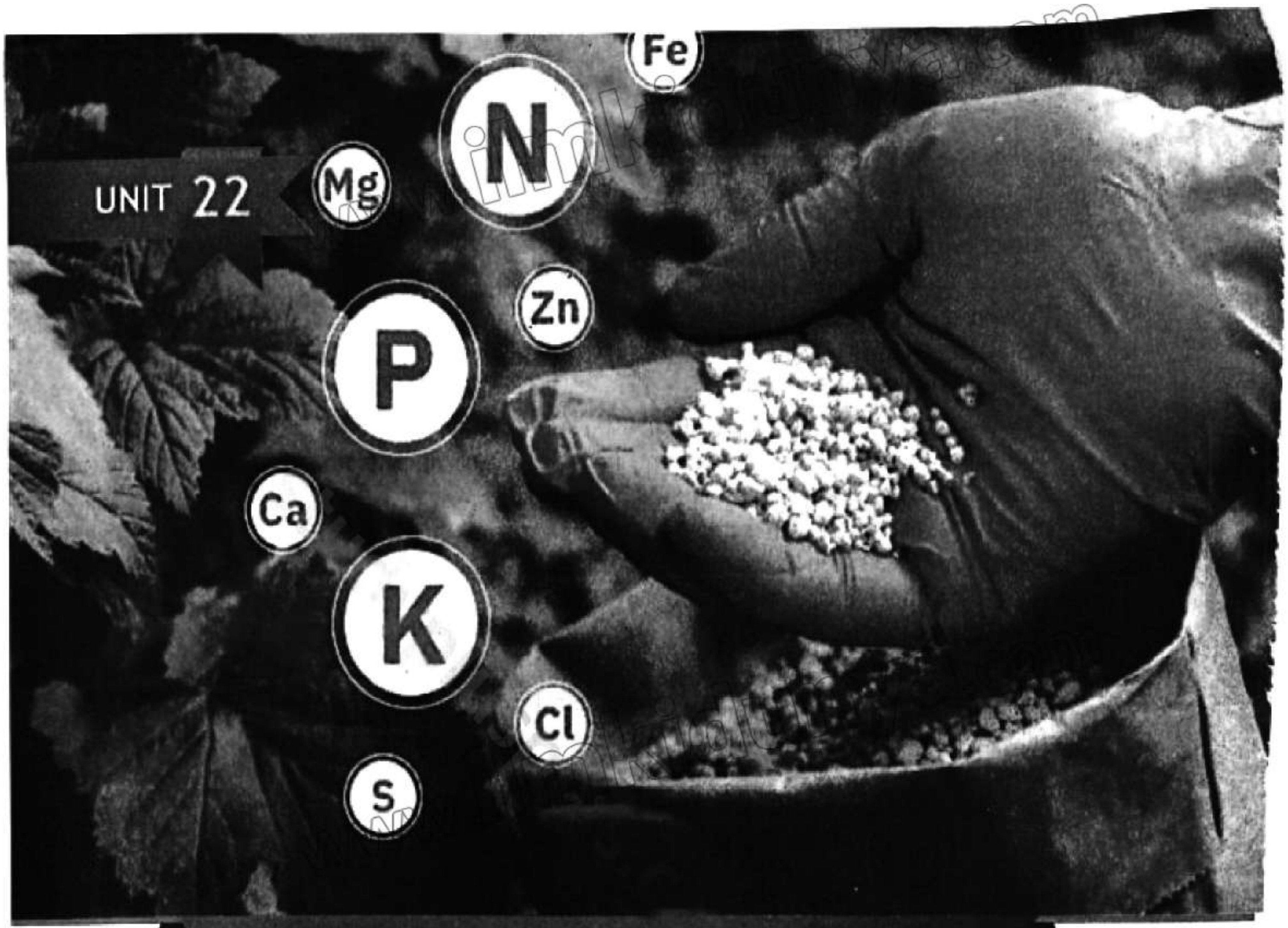
UNIT 22



AGRICULTURE

Student Learning Outcomes (SLOs)

- Explain the chemical composition and function of different types of fertilizers, including their role in providing essentials nutrients to crops and the impact of their applications on the soil health
- Identify the different types of pesticides used in agriculture and describe their mode of action, including the potential benefits and risks associated with their use.
- Identify the chemical reactions that occur when acid rain falls on crops and soil and explain the effects it has on crop growth, including nutrient uptake and crop yield.
- Explain the basics of genetic engineering and how it is used in agriculture, including the development of genetically modified crops and the potential benefits and risks associated with their use.
- Explain how changes in temperature, precipitation, and extreme weather events can affect crop growth and yield, including the potential for crop failure food storages, as well as the potential to develop new crop varieties that are more resilient to changing climate conditions.

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This chapter covers basic aspects of agriculture such as fertilizers and plant protection products (pesticides), advantages and disadvantages of pesticides. Learn about the effects of acid rain on plants and soil. You will also learn the basics of genetic engineering and modified crops and the pros and cons of their use. Finally, you will learn how extreme weather events, such as climate change, temperature fluctuations, etc. affect plants.

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22.1 Fertilizer

Fertilizers are natural or artificial substances containing elements that improve plant growth and productivity. Fertilizers increase the natural fertility of the soil or replace the elements taken from the soil by previous crops.

The fertility of the soil is the quality of the soil that allows the production of compounds in sufficient quantity that plants need for their growth. Other factors such as light, humidity, temperature and soil structure are also important for plant growth. If the soil fertility is not good, natural or artificial materials can be added to provide the plant with the necessary nutrients.

Historically, fertilizers are obtained from either natural or man-made sources: compost; animal manure, manure, harvested minerals, crop rotation, and human (and natural industrial) byproducts (e.g., fish processing waste, blood meal, animal by-products from animal slaughter, etc.). However, from the late 19th century onwards, after advances in plant nutrition were made, a synthetic-based agricultural industry began to develop. This shift transformed the world's food system, enabling large-scale, industrialized agriculture and large-scale harvests.

Nutrients in organic products are gradually released while the substance decomposes over time, while artificially synthesized inorganic products allow for the rapid uptake of nutrients by plants. However, the organic type of fertilizer is better for the soil and the ecosystem in the long run.

22.2 Composition of Fertilizers

Chemical fertilizers contain all nutrients. They contain nitrogen, phosphorus, and potassium as macronutrients and zinc, manganese, copper, iron, calcium, boron, magnesium, and molybdenum as trace elements.

22.1.1 Function of different types of Fertilizers

- **Nitrogen fertilizers**

N-fertilizers are especially useful in the middle phases of a plant's life cycle when the plant needs the most support to keep growing and leafing out. The two most popular types of chemical nitrogen-based fertilizers are ammonium nitrate, calcium ammonium nitrate, and urea. Nitrogen fertilizer must be applied at the start of the season.

- **Phosphorus fertilizers**

Phosphorus fertilizers serve to reinforce roots and stems, and are crucial at all stages of the plant's growth cycle. They also boost flowering, seed production, and fruit. Important P-fertilizers are superphosphate, triple superphosphate, diammonium phosphate, ammonium dihydrogen phosphate, and ammonium polyphosphate.

- **Potassium fertilizers**

Potassium fertilizers promote root development in plants. Potassium helps plants maintain healthy photosynthesis and limits the spread of diseases. Leaves may become yellow or brown around the edges if your plants are lacking in potassium. If you don't add potassium fertilizer on time, the leaves will wither and fall off. Some examples of potash-type fertilizers are potassium chloride (KCl), potassium sulphate (K_2SO_4), and potassium nitrate (KNO_3).

22.1.2 Impact of fertilizers on soil health

Whether in synthetic or organic fertilizer types, the right nutrients applied at the right stage of plant growth are essential for a healthy crop, which in turn leads to improved crop yields. Imbalanced application of fertilizers can change soil pH and increase pest attack, acidification and soil erosion, resulting in reduced soil organic carbon and beneficial organisms, reduced plant growth and yield, and even greenhouse gas emissions.

22.3 Pesticides

The chemical substances used in agriculture to control or kill pests including insects, fungi, rodents, and weeds are called pesticides. Pests can damage crops and reduce yields. There are numerous types of pesticides. Each pesticide has its mechanism of action. Common types of pesticides are as follows:

Insecticides:

Insecticides are chemicals used to control insects. For example;

- **Organophosphates and Carbamates:** These chemicals inhibit enzyme the acetylcholinesterase, which is involved in transforming nerve signals to insects. This causes an increase in acetylcholine, which in turn causes overstimulation of the nervous system and paralysis of insects.
- **Pyrethroids:** The chemicals disrupt sodium channels in insect neurons, producing repetitive nerve impulses and paralysis.
- **Neonicotinoids:** These chemicals affect the nicotinic acetylcholine receptors in the insect nervous system, disrupting the transmission of nerve signals and causing paralysis.

1. **Herbicides:** Herbicides are chemicals used to control unwanted plants also called weeds. For example;

- **Glyphosate:** Glyphosate is a widely used herbicide that controls broadleaf weeds and grasses It inhibits protein production and ultimately kills the plant.
- **2,4-D and Dicamba:** These herbicides stimulate the effects of the plant hormone auxin, leading to uncontrolled growth and eventual death.
- **Paraquat:** Paraquat acts by inhibiting photosynthesis and causes the death of a plant.

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2. **Fungicides:** Fungicides are pesticides that kill or prevent the growth of fungi and their spores. They are used to control fungi that damage plants. For example;

- **Triazoles:** Triazoles control the biosynthesis of ergosterol, which is an important component of fungal cell membranes. They break membrane integrity and cause cell death.
- **Strobilurins:** They interrupt the electron transport chain in fungal mitochondria, hence interrupting energy production and causing cell death.
- Copper-based fungicides: They cause cell death by interrupting various cellular processes in fungi.
- **Rodent poisons:** These chemicals disrupt blood clotting by inhibiting vitamin K, causing internal bleeding in rodents.
- **Zinc phosphide:** They react with stomach acid to form phosphine gas, toxic to rodents.

3. **Nematicides:** A nematicide is a type of pesticide used to kill plant-parasitic nematodes. For example;

- **Organophosphates:** They disrupt the nervous system of nematodes.
- **Biopesticides:** Biopesticides are a type of pesticide derived from natural materials such as animals, plants, bacteria, and certain minerals. For example, canola oil and baking soda are considered biopesticides. They can control nematode populations through various mechanisms.

22.4 Benefits and Risks of Pesticides

The use of pesticides in agriculture and other industries can have benefits and risks. It is important to find a balance between effective pest control and minimizing harm to human health and the environment.

22.4.1 Benefits of Pesticides

Pesticides are beneficial in many ways.

1. Pesticides help protect plants from pests and diseases. Hence contribute to increasing yield and food production.
2. Pesticides can control the spread of disease between plants, animals and humans. Therefore, they contribute to reducing the risk of epidemics and improving human health.
3. The use of pesticides can be more cost-effective than alternative pest control methods.
4. Pesticides can promote the production of higher-quality fruits and vegetables by preventing damage caused by pests. Hence contributing to food security and stability worldwide.

22.4.2 Negative aspects of Pesticides

Pesticides also pose many risks.

1. Pesticides can be carcinogenic, and neurotoxic. So, they can cause adverse health effects to farmers, co-workers, and consumers.
2. Pesticides can have negative effects on non-target organisms. Beneficial insects, birds, and aquatic organisms can also be affected by pesticides. Runoff water from fields can contaminate water sources and harm aquatic organisms.

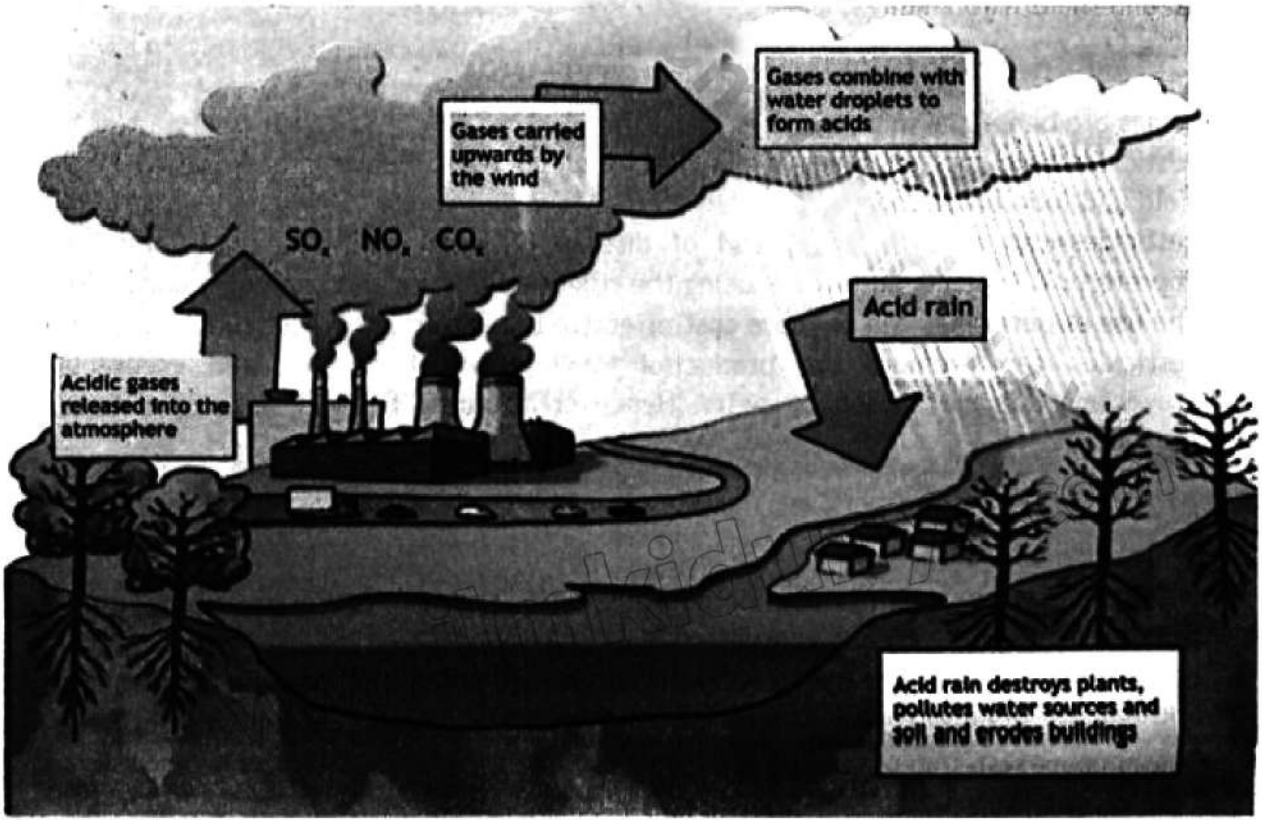
3. Leftover residues of pesticides on fruits, vegetables, and other crops, can cause health effects on consumers.
4. Over time, pests can develop resistance against certain pesticides, making them less effective. This can lead to the use of stronger or more toxic pesticides, which can further aggravate environmental and health issues.
5. Pesticides can reduce the number of beneficial insects, causing imbalances in the ecosystem and loss of biodiversity.
6. Pesticides can also be harmful to pollinators such as bees, which play a key role in pollinating many crops. Pollinator population declines can cause far-reaching agricultural consequences.
7. The inappropriate use or disposal of pesticides can lead to soil and water contamination, causing environmental pollution.

22.5 Acid Rain

Normal rainwater is saturated with carbon dioxide. It has pH of 5.6. Rain with a pH lower than 5.6 is called acid rain. Acid rain is caused by air pollution from sulphur oxides (SO_x) and nitrogen oxides (NO_x), dissolved in rainwater producing sulfuric acid (H_2SO_4) and nitric acid (HNO_3), respectively. As a result, rainwater has a pH as low as 2.1. This value is lower than that of lemon juice or vinegar. When acid rain falls on plants and soil, it can cause a number of chemical reactions. These reactions affect soil chemistry, nutrient availability, and ultimately crop growth and yield.

22.5.1 Impact of acid rain on soil:

Effects of acid rain on crops and soil can be devastating in many ways.



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- Acid rain lowers the pH of the soil and makes it more acidic. Increased acidity can cause important nutrients such as calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), and sodium (Na^+) to leach from the soil and be replaced by hydrogen ions (H^+) of acid rain. This reaction reduces the availability of these essential nutrients to plants. So, the required nutrients are leached away from the soil.

Example:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

- Increased acidity of soil causes the leaching of aluminium from the soil.

$$Al_2O_3 + 3H_2SO_4 + 6H_2O \rightarrow 2Al(OH)_3 + 3SO_4^{2-} + 6H^+$$

Aluminium ions are poisonous to plants and can kill them. It also makes it difficult for plants to absorb water.

- Direct acid rain can damage the waxy surface of leaves, increasing water loss and making plants more susceptible to disease and the environment.
- Studies have shown that acid rain can significantly affect the performance of sensitive plants such as soybeans, wheat, and peanuts by changing their physiological and biochemical processes. Soy and wheat crops are sensitive to changes in soil pH. Acid rain can reduce soybean and wheat yields by reducing nitrogen fixation in soybeans and affecting the nutrition of both crops.
- Acid rain can negatively affect soil microbial communities, which play an important role in nutrient cycling and decomposition of organic matter. This can further affect nutrient availability and soil structure, affecting crop yields.

All of the factors mentioned above reduce crop yield.

22.6 Genetic Engineering

Genetic engineering also called genetic modification is a technique used to change an organism's gene to enhance the capabilities of the organism. This means genetic engineering is the process of altering an organism's genome. This can range from changing one single DNA base to deleting or inserting a whole region of DNA.

Table 22.1: GM crops

Alfalfa	Melon	Rose	Flax, Linseed
Argentine Canola	Papaya	Soybean	Potato
Carnation	Petunia	Squash	Tomato
Chicory	Plum	Sugar Beet	Maize
Cotton	Polish canola	Sweet pepper	Rice
Creeping Bentgrass	Poplar	Tobacco	Wheat

For example, genetic engineering can produce more efficient or nutritious crop plants. In agriculture, genetic engineering is applied to develop genetically modified (GM) crops with desired traits such as increased yield, resistance to pests and diseases, and tolerance to stresses like *drought*, salinity, and extreme temperature changes.

Basics of Genetic Engineering:

Genetic engineering is practised in four basic steps.

1. Scientists first identify a desired trait, such as drought tolerance or pest resistance.
2. The gene responsible for this trait is identified and isolated from the organism.
3. Using various techniques, the isolated gene is inserted into the target plant's genome.
4. The genetically modified plant is grown and tested to ensure it has acquired the desired traits and is safe for consumption and the environment.

22.6.1 Use of Genetics in Agriculture:

Genetic engineering has led to the development of many genetically modified crops, including

- Crops like soybeans, corn, and cotton have been engineered to tolerate specific herbicides (e.g., glyphosate). This has enabled farmers to control weeds without harming the crops.
- Bt crops (e.g., Bt corn, Bt cotton) contain a gene from the bacterium Bacillus thuringiensis, which produces a protein which is toxic to specific insects. This has reduced the need to use chemical pesticides.
- Some crops have been engineered for resistance against viruses, fungi, and bacteria. For instance, rainbow papaya which is resistant to the papaya ringspot virus.
- Some crops have been developed to deal with vitamin A deficiency. For example, Golden *rice* is genetically modified to produce beta-carotene, a precursor of vitamin A.

22.6.2 Potential Benefits of Genetically Modified Crops

Some of the benefits of genetic engineering in agriculture are as follows.

- It has increased crop yields.
- It has reduced production costs for food or medicine.
- It has reduced the need for pesticides.
- It has improved food composition and food quality.
- It has produced crops resistant to pests and diseases.
- It has improved food safety, and medical benefits for the growing population.

22.6.3 Potential Risks of Genetically Modified Crops

Little information is available about the long-term impact of GM crops on humans. Genetically modified foods may cause antibiotic-resistant diseases. GM crop cultivation may reduce agricultural biodiversity. Genetically modified crops may result in the development of disease-resistant pests. Cross-pollination of genetically modified genes with wild relatives may lead to unforeseen consequences.

Changes in temperature, precipitation patterns, and extreme weather events can significantly impact crop growth and yield in various ways.

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22.7 Impacts of Climate Change on Agriculture

Changes in temperature, precipitation, and extreme weather events can affect crop growth and yield.

Effects of temperature Changes

How does temperature stress affect plants?

Heat stress causes dehydration and affects plant growth and development. High temperatures affect their photosynthesis, respiration, and water absorption. In extreme cases, this can cause slow growth, reduced yield, and even crop failure.

Similarly, cold temperatures can damage crops. Cold can kill young plants or damage their structures, resulting in reduced or complete yield loss.

Effects of Precipitation Changes

Precipitation is essential for crop health. It provides the water and nutrients needed for plant growth and development. When it rains sufficient, the crop can absorb the water and nutrients it needs, and the soil around it stays moist and fertile. This allows the plants to grow and produce large and healthy crops. Heavy rainfall can leach essential nutrients from the soil, reducing crop availability. Therefore, an optimal amount of rainfall is necessary for optimal crop growth and yields. Drought conditions can lead to moisture stress, causing plants to wilt, and reducing crop yields.

Effects of Extreme Weather Events

Storms can cause physical damage to crops, such as uprooting, branch damage, or lodging (crops that have been flattened). Strong winds can also speed up the loss of moisture from leaves, making drought stress severe. Hail punctures leave, stems and fruits, causing tissue damage, and photosynthetic failure. Severe Hail can cause significant yield loss or complete crop destruction. Sudden and extended heat waves can put crops under extreme heat stress, speeding up the loss of water through transpiration, resulting in leaf burning, reduced flowering, and reduced yields.

Impacts on Food Security and Storage

Crop failures due to adverse weather conditions can disrupt food supply chains. It can lead to food shortages and price increases, especially in areas that rely heavily on local agricultural production. Crop reductions can also affect food supplies such as smaller quantities being available for processing and distribution. This can lead to increased food waste, and threaten food security.

Development of sustainable crop varieties

Climate change requires the development of crop varieties that are more resilient to changing environmental conditions. This means the breeding or genetic modification of crops with traits such as heat tolerance, drought tolerance, disease resistance and water and nutrient use efficiency.

Crop failures due to adverse climate conditions can disrupt food supply chains, leading to food shortages and price spikes, particularly in regions heavily reliant on local agricultural production.

Reduced crop yields may also impact food storage facilities, as lower quantities of produce are available for processing and distribution, potentially leading to increased food wastage and compromised food security.

Development of Resilient Crop Varieties

Climate change necessitates the development of crop varieties that are more resilient to changing environmental conditions. This involves breeding or genetically engineering crops with traits such as drought tolerance, heat tolerance, disease resistance, and improved water and nutrient use efficiency.

KEY POINTS

- Fertilizer, are natural or artificial substances containing elements that improve plant growth and productivity.
- N-fertilizers are especially useful in the middle phases of a plant's life cycle.
- Phosphorus fertilizers serve to reinforce roots and stems, is crucial at all stages of the plant's growth cycle.
- Potassium fertilizers promote root development in plants.
- The chemical substances used in agriculture to control or kill pests including insects, fungi, rodents and weeds are called pesticides.
- Normal rainwater is saturated with carbon dioxide. It has a pH of 5.6
- Acid rain lowers the pH of the soil and makes it more acidic.
- Aluminium ions are poisonous to plants and can kill them. It also makes it difficult for plants to absorb water.
- Genetic engineering also called genetic modification is a technique used to change an organism`s gene using technology.
- Genetically modified crops may result in the development of disease-resistant pests.
- High temperatures affect their photosynthesis, respiration, and water absorption.
- Heavy rainfall can leach essential nutrients from the soil.
- Climate change requires the development of crop varieties that are more resilient to changing environmental conditions.

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EXERCISE

1. Multiple Choice Questions (MCQs)

i. What is the primary cause of acid rain?

a) Carbon dioxide emissions
b) Sulphur dioxide and nitrogen oxides emissions
c) Methane emissions
d) Chlorofluorocarbons emissions

ii. How does acid rain affect soil pH?

a) Increases soil pH
b) Decreases soil pH
c) Does not affect soil pH
d) Depends on the type of soil

iii. Which nutrient leaches away from the soil due to acid rain?

a) Nitrogen
b) Phosphorus
c) Calcium
d) Oxygen

iv. What role do soil microbes play in the context of acid rain?

a) They thrive in acidic soil conditions
b) They help neutralize acid rain
c) They are unaffected by acid rain
d) They play a vital role in nutrient cycling and decomposition

v. Which of the following is NOT a potential benefit of genetic engineering in agriculture?

a) Increased crop yields
b) Reduced biodiversity
c) Pest resistance
d) Enhanced nutritional content

vi. What is the primary purpose of inserting genes into target plants in genetic engineering?

a) To increase crop diversity.
b) To improve crop yield
c) To express desired traits
d) To reduce genetic variation

vii. Which technique is commonly used to transfer genes into target plant cells?

a) CRISPR-Cas9
b) Gene guns (biolistics)
c) Polymerase chain reaction (PCR)
d) Microinjection

viii. Golden rice is genetically modified to address deficiencies in which vitamin?

a) Vitamin C
b) Vitamin D
c) Vitamin A
d) Vitamin E

ix. Which genetically modified crop produces a protein toxic to specific insects, reducing the need for chemical pesticides?

a) Herbicide-tolerant soybeans
b) Bt cotton
c) Disease-resistant tomatoes
d) Golden rice

x. What is one of the primary benefits of using pesticides in agriculture?

a) Decreased crop yields
b) Increased biodiversity
c) Enhanced food quality
d) Reduced global food security

xi. Which of the following is NOT a risk associated with pesticide use?

a) Development of pesticide resistance	b) Loss of biodiversity
c) Enhanced soil fertility	d) Human health concerns

xii. What environmental impact is associated with pesticide runoff from fields?

a) Soil erosion prevention	b) Water contamination
c) Enhanced aquatic ecosystems	d) Increased biodiversity

xiii. What potential risk arises from the development of pesticide resistance in pests?

a) Decreased use of pesticides

b) Increased effectiveness of pesticides

c) Need for stronger or more toxic pesticides

d) Improved pest control methods

xiv. Which change in weather pattern is likely to impact water availability for crops?

a) Increased temperature	b) Altered rainfall patterns
c) Heat stress	d) Enhanced nutrient uptake

xv. How does breeding resilient crop varieties help in adapting to climate change?

a) Reduces pesticide use	b) Enhances nutritional content
c) Improves resistance to stress	d) Increases soil acidification

2. Short Answer Questions

i. Describe the chemical reactions involved in soil acidification due to acid rain.
ii. Explain the role of phosphorus in plant growth and development.
iii. Discuss the potential environmental impacts of excessive nitrogen fertilizer use.
iv. Describe the chemical composition of superphosphate fertilizer and its function in soil fertility
v. How does acid rain affect nutrient uptake by plants?
vi. Explain the impact of acid rain on soil microbial activity.
vii. Discuss the effects of acid rain on crop yield.
viii. Explain the process of genetic engineering in agriculture.
ix. Explain how pesticides contribute to increased crop yields.
x. Discuss one human health concern associated with pesticide exposure.
xi. What is meant by the term "pesticide resistance," and why is it a concern?
xii. How would you determine the appropriate fertilizer to use for a crop with phosphorus deficiency?
xiii. How does the mode of action of insecticides differ from that of herbicides?
xiv. What are the potential environmental risks of excessive pesticide use?
xv. Design a plan to minimize the negative impacts of fertilizer runoff into nearby water bodies.
xvi. How does acid rain affect nutrient availability in the soil?

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xvii. What are the potential consequences of long-term soil acidification on crop yield?
xviii. How can genetic engineering be used to reduce pesticide use in agriculture?
xix. How would you modify irrigation practices to cope with altered rainfall patterns?
xx. What is the impact of extreme weather events on food storage and supply chains?
xxi. How do different types of pesticides (insecticides, herbicides, fungicides) target pests differently?
xxii. What are the long-term impacts of pesticide use on soil health?

3. Long Answer Questions

i. How do pesticides contribute to the decline of biodiversity?
ii. Name three traits that genetically modified crops may possess and provide an example of each trait.
iii. Critically analyse the role of genetic engineering in addressing global food security challenges.
iv. Compare and contrast the benefits and risks of using genetically modified crops versus traditional breeding methods in agriculture.
v. Evaluate the role of micronutrient fertilizers in crop production. Discuss the symptoms of micronutrient deficiencies in plants and the strategies to address these deficiencies, considering the environmental and economic impacts.
vi. Describe the different types of pesticides used in agriculture, including insecticides, herbicides, fungicides, and rodenticides.
vii. Critically evaluate integrated pest management (IPM) strategies. How do these strategies aim to reduce the negative impacts of pesticide use? Provide examples of successful IPM practices and discuss their long-term sustainability.
viii. Identify and explain the chemical reactions that occur when acid rain falls on crops and soil. Discuss the effects of acid rain on crop growth, nutrient uptake, and crop yield. Propose mitigation strategies to counteract the negative effects of acid rain on agriculture.
ix. Analyse the impact of acid rain on soil chemistry and plant physiology. How does acid rain affect soil pH and nutrient availability? Discuss the long-term implications for crop production and soil health if acid rain continues to be a persistent problem.
x. Critically analyse the role of genetic engineering in developing crops that can withstand biotic and abiotic stresses. Provide examples of genetically modified crops designed for drought tolerance, pest resistance, or enhanced nutritional content. Discuss the challenges and future prospects of genetic engineering in sustainable agriculture.
xi. Analyse the impact of climate change on global agriculture. Discuss how different regions are affected differently by climate change and the adaptive measures being taken. Evaluate the effectiveness of these measures and propose additional strategies to enhance the resilience of agriculture to climate change.

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PROJECT

Create a report or multimedia presentation summarising the research, experiments, findings, and practical solutions for sustainable agriculture.

UNIT 23

INDUSTRY

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Student Learning Outcomes (SLOs)

- Justify the importance and significance of industrial chemistry in various industries such as manufacturing, energy, healthcare, and environmental protection.
- Describe the chemical processes involved in industrial production, including addition and condensation polymerization, and the properties and uses of resulting materials.
- Identify the raw materials and resources used in industrial chemistry, including those readily available in the context of Pakistan.
- Explain the applications of industrial chemistry in industries such as petrochemical, cosmetics, cement, food production and more.
- Elaborate on the safety measures and precautions necessary in industrial chemical processes and facilities.

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The chemical industry is the ultimate fruit of chemical research. The chemical industry provides useful and applied materials to directly consumers or to other industries.

In the large-scale production of chemicals, chemical industry plays a very important role, like in the production of plastics, synthetic fiber, and elastomers. Industrial chemists always look forward to developing new processes for the production of new materials, or improved ones. These processes are adopted due to their energy efficiency, production steps and environmental impacts. Production of fertilizers at large scale and pesticides of great variety has improved crop yields to many folds in recent history. New methods are being developed to increase and improve food and its quality. Synthetic fiber is marvelous advancement used for textiles and insulation. Pharmaceuticals is a big chemical industry. Medicines and drugs have been essential life chemicals throughout the history of mankind. New medicines for the treatment of different diseases are tailored by medicinal chemists with greater efficacy and safety. Personal care products like soaps, shampoos, skin care products, hair dyes and cosmetics are better than ever. Many chemical industries like sulphuric acid, paints, varnish, metallurgy, cement, glass, petrochemicals, ammonia, fertilizers, pesticides, food materials, etc. are inevitable for today's life.

Environmental protection aspect of chemistry known as green chemistry is working for the production of environment-friendly chemicals, development of waste management methods and recycling, biodegradable synthetic fiber etc. It not only takes care of our environment but also works to reduce footprints of environmental pollution.

23.1 Raw Materials and their Resources for Chemical Industry

Raw materials for the chemical industry are obtained from the environment. The environment is composed of the atmosphere, biosphere, hydrosphere and lithosphere.

Raw materials obtained from Atmosphere: The atmosphere is mainly composed of nitrogen, oxygen, hydrogen, carbon dioxide and noble gases. These gases are obtained from the atmosphere to produce useful industrial chemicals for example nitrogen and hydrogen are used to manufacture ammonia gas, which is in turn used for the large-scale production of urea fertilizer. Nitrogen and oxygen are used to produce nitrogen oxides and nitric acid. Oxygen is obtained from the atmosphere which is used in steel industries and in hospitals.

Raw materials obtained from the hydrosphere: Many dissolved minerals like sodium, potassium, magnesium, calcium, sulphates, chlorides and bromides are present in the ocean water and may be obtained for the manufacturing of different chemicals.

Raw materials obtained from the biosphere: Plants produce cellulose, starch, oils, alkaloids, terpenes, and raisins. Cellulose is used for making paper, starch and oils that are not only edible but also work as precursors for many chemicals and synthetic foods. Biomass is used for making biogas, bioplastics and many biochemicals. Microorganisms produce enzymes that are biocatalysts in many in-vitro preparations, such as fermentation and biotechnology. Animal and plant materials are widely used in the medicinal chemical industry.

Raw materials obtained from Lithosphere: The widest variety and mass of chemical raw materials is found in the lithosphere. Unlike other parts of environment, lithosphere resource of each geographical region is different. It is the source of elements like oxygen, silicon, aluminium, iron, titanium and carbon etc. The most useful raw materials obtained from the Lithosphere are fossil fuels; petroleum, coal and natural gas. Others are metallurgical mineral ores containing iron, aluminium, sulphur, gold, chromium and uranium etc.

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23.2 Chemical Raw Materials in Pakistan:

Among metallic ores, iron ore deposits of Pakistan are estimated to about 1.427 billion tonnes. Pakistan is an exporter of chromite, the ore of chromium. There are large reservoirs of gold and copper in Baluchistan, explored and estimated but unexploited. Pakistan has large reservoirs of natural gas and coal in Sui and Sandak. Estimated reserves of coal are 185 billion tonnes, with high sulphur content. 5.5 billion tonnes of gypsum are present which is mainly used in cement manufacturing. Other minerals include limestone, rock salt, marble and granite.

North Eastern regions of Pakistan are rich in gemstones which sometimes serve as ores for precocious metals. These gemstones include aquamarine, tourmaline, peridot, emerald, ruby, topaz, zircon, rhodochrosite etc.

23.3 Safety Measures and Precautions in Chemical Industry

To avoid accidents and to ensure the protection of workers and the environment, chemical safety is critical. The major purpose is to identify, evaluate and mitigate the adverse situations during the chemical processes. The hazards may include chemical explosive reactions, fire risks and the release of toxic gases or chemicals.

Here are some measures regarding safety in the chemical industry.

1. Adopting the guidelines

By adopting the guidelines and regulations of leading regulatory bodies like OSHA (Occupational Safety and Health Administration) hazards can be avoided or reduced. They provide directions for proper storage, disposal, usage and handling of hazardous chemicals.

2. Safety training

By providing safety training to all workers before they are given a task regarding the process safety needed there. If duty place changes, the process hazard analysis also changes, so continual training sessions of incumbents, so that they can help themselves and others to mitigate any possible accident.

3. Incorporating robust engineering controls

Automatic and efficient ventilation procedures and systems, safety ensuring building *structures*, and automated systems of safety minimise the risks of greater damage.

4. Proper maintenance

The critical chemical processes need mechanical integrity and proper and timely maintenance to prevent failure and accidents.

5. Management of change

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It is inevitable to have a clear policy for changing chemicals, procedures, equipment and personnel. This can ensure a curtailed risk of accidents due to old, expired and torn-out equipment and chemicals.

6. Hazard assessment

Conduction of hazard assessment on a regular basis, reviewing process safety after short intervals, and regular incident investigation can appreciably improve safety degrees.

7. Emergency response

The development of comprehensive and effective emergency response management in a chemical facility is the need of the day to mitigate any possible hazards.

23.4 Important Chemical Processes

Some very important chemical processes are described shortly below.

1. Polymerization

It is included in the modern chemical processes in which small precursors called monomers, are converted into long-chain molecules called polymers. More discussion on polymerization is coming ahead.

2. Calcination

Limestone is converted into calcium oxide and carbon dioxide by strong heating.

3. Reforming

Reforming is usually done with the petroleum fractions in different ways to get different type of products. For example in steam reforming saturated and unsaturated hydrocarbons, hydrogen, ammonia and methanol are prepared. During catalytic reforming, hydrocarbons are heated with the catalyst to obtain high octane gasoline.

4. Smelting

During this process metallic oxides are heated with coke to produce metals.

5. Hall & Heroult Process

Aluminium metal is obtained from its oxide.

6. Bessemer process

It is the major process in the manufacturing of steel.

7. Haber process

During this process, under the influence of catalyst, hydrogen and nitrogen gases are combined to form ammonia which is then used for making urea fertilizer.

8. Bosch process

In this process, steam is passed over red hot coke, to produce hydrogen gas on industrial-scale.

9. Farasch process

Sulphur is extracted from deep wells, with the help of superheated water and this process.

10. Down's methods

Sodium metal is obtained by electrolysis of molten halite.

11. Solvey's process

In this process, sodium carbonate or soda ash is prepared.

12. Burgius process

Lubricants and synthetic fuels are formed from coal by this process.

13. Contact process

In this process, sulphur dioxide gas is converted into sulphur trioxide gas which is further used for making sulphuric acid on the industrial scale.

You may have learned about a few of them, in the previous classes, here we shall only discuss polymerization slightly more.

23.5 Applications of Industrial Chemistry

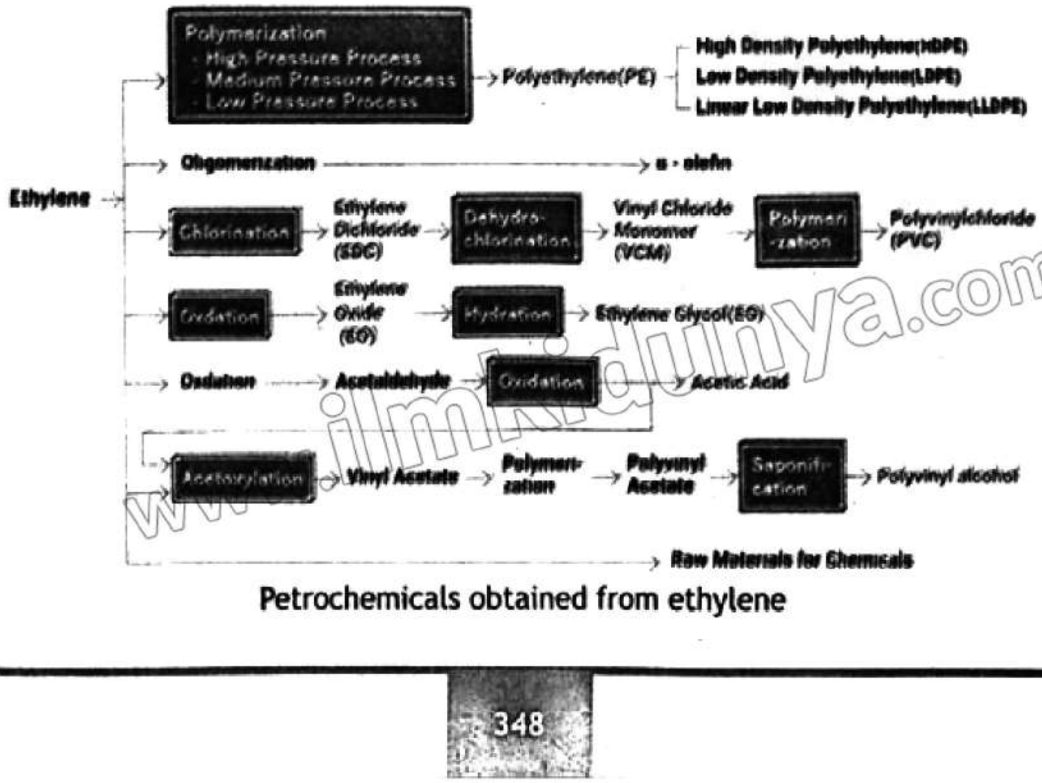
The chemical sector includes the businesses and various groups involved in creating and manufacturing industrial, specialized, and other types of chemicals.

1. Petrochemicals

Those compounds which are derived from petroleum and it's fractions are called petrochemicals. Examples of petrochemicals are wide spread and highly applied such as insulation, soap, detergents, paints, fertilizers, rubber, coating, cosmetics and textile etc. There are three types of petrochemicals based on starting materials.

a. Olefins

Major olefins are ethene, propene and butadiene. Each one of them is used to prepare lots of petrochemicals.



Petrochemicals obtained from ethylene

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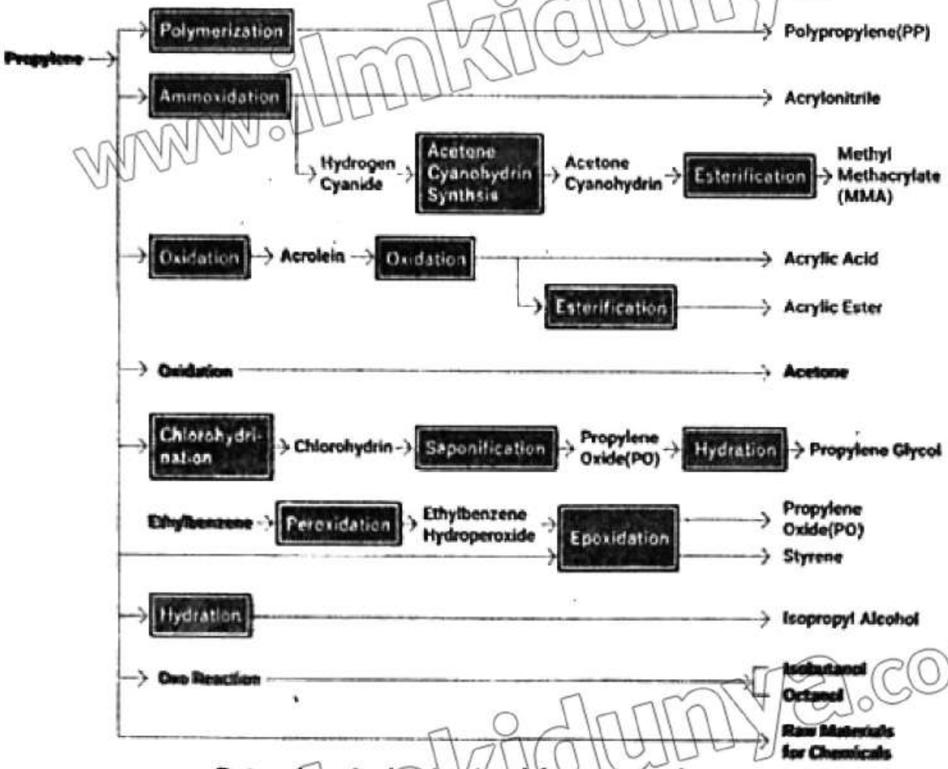
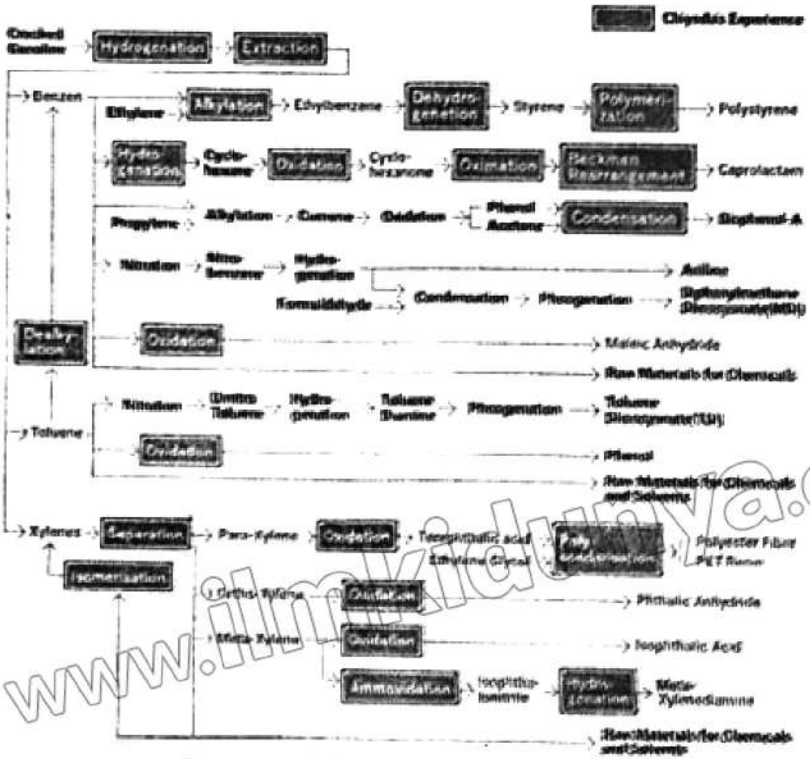


Petrochemicals obtained from propylene

2. Aromatics

Aromatics include benzene, toluene and xylenes etc. These are used to prepare lots of other compounds and polymers, as shown in the flow sheet.



Compound obtained from benzene

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3. Synthesis gas

It is usually known as syn gas, actually a mixture of carbon monoxide, hydrogen gas, nitrogen, *hydrocarbons* etc. It's is used to prepare many useful compounds like acetic acid, ammonia,urea, SNG, biofuels like methanol and ethanol. It is also used to capture carbon dioxide to reduce greenhouse effect to avoid global warming. Synthesis gas is used to generate electricity and heat through combined heat and power (CHP) systems.

Cosmetics

Cosmetics are mixtures of chemical compounds derived from natural and synthetic both. Cosmetics have many purposes, including personal and skin care, conceal spots and enhance natural looks. Makeup can also add colour to face, or change the appearance of the face completely. Few examples include lipstick, mascara, nail polish, creams, colours and dyes etc.

1. Nail polish

There is no fixed single formula of nail polish. However, there are a number of ingredients that may be used. The basic components include;

a. **Film forming agent:** Nitrocellulose, cellulose acetate, cellulose acetate butyrate, vinyl polymers, acrylates, maliec acid, monobutyl ester, and zein(protein) etc. depending on brand.
b. **Resins and plasticizers:** castor oil, amyl and butyl stearate and mixes of fatty acids and glycerol etc
c. **Solvents:** Ethyl acetate, butyl acetate, acetone, toluene and isopropyl alcohol etc.
d. **Colouring agents:** Iron oxides, colour lakes, mica, titanium dioxide, carmine, ultramarine, manganese violet etc.

Manufacturing method

i. Pigments like nitrocellulose and plasticizer are mixed and ground in a "two-roll" differential speed mill to produced fine dispersion of the color.
ii. When properly and fully milled, the mixture is removed from the mill in the form of sheets and then broken down into small chips for mixing with the solvent.
iii. The mixture is cooled slightly before the addition of such other materials as perfumes, moisturizers and cooling agents.
iv. The mixture is then pumped into smaller drums, and then trucked to a production line. The finished nail polish is pumped into explosion proof pumps, and then into smaller bottles suitable for the consumer market.

2. Lipstick

Raw materials

Waxes: bees wax, carnauba wax, candlila wax

Oils: linolin oil, castor oil, and vegetable oils

Natural ingredients: butter, natural pigments, fruit based chemicals

Pigments: both natural and synthetic

Alcohols: *isopropyl* alcohol

Preservatives: antioxidants

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Manufacturing

The raw materials firstly are melted and mixed separately due to heterogeneous ingredients. Initially three mixtures are prepared separately. One contains solvents, the other contains oils in the third one contains fats and waxy materials.Secondly the solvent mixture and oils are mixed with the colour pigments. After the pigment mass ground and mixed, it is added to the hot wax mass untill a uniform colour is obtained. The lipstick mass is made free from air. The melted mass is transferred into a mould "upside down". The lipstick is cooled, separated from mould and sealed from the bottom.Then the lipsticks are passed through the flame to seal pinholes and improve the finish. Lastly the lipstick is caped now it is ready for labelling and packaging.

3. CEMENT

Cement is a very useful material used to glue bricks and stones together in construction after mixing with water, sand and crush etc. It is a dirty green coloured powder.

Raw materials:

1. Lime stone(almost 65% of cement)
2. Gypsum (2-3%)
3. Clay or shale(20-30%)
4. Supplementary ingredients (fly ash, silica fumes, iron ore or mill scale, bauxite etc. in minor amounts according to typeof cement and its applications)

Process

Step 1: Mining: Usually cement industry is installed where the raw materials are nearby and there is no need for large expenses on the transport. Raw materials are dug, extracted,and transported to the factory by trucks.

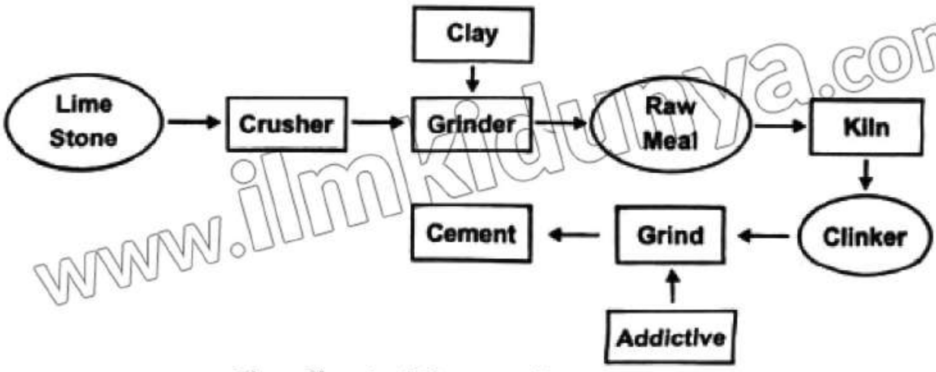
Step 2: Crushing: These raw materials reach in the factory in the form of big stones. They are crushed to small pebbles and then ground to fine powder.

Step 3: Homogenisation: Raw materials are mixed in proper percentages, mixed thoroughly to get a homogeneous powder.

Step 4: Clinkerization: In this process, calcium oxide reacts with silica, alumina, and iron oxide to form the aluminates, silicates and ferrites in a rotary kiln, whitch operates at a temeperature around 1400 °C to 1450 °C. These are the main components of the clinker(small semi round pebbles).

Step 5: Cement grinding: These clinkers are then ground in the ball mill together with gypsum(for the increase in setting time) and other additives to produce cement.

Step 6: Packing: Usually 50 kg bags are made. But open trucking is also done based on demand.



Flow Sheet of Cement Manufacture

23.7 Industrial Chemistry in Food Production

1. Food additives and preservatives

- Anti-caking agents are used to stop ingredients from becoming lumpy.
- Antioxidants prevent foods from oxidising, or becoming rancid.
- Artificial sweeteners sweetens with out sugar.
- Food acids maintain the correct acid level.
- Synthetic colours enhance food colour.
- Sodium benzoate is usually used as food preservative.

2. Fermentation

A process which makes use of microorganisms and their enzymes for converting raw materials into finished edible products such as vinager, wine etc.

3. Food processing

Food Processing is the technique of transforming food items into a form that can be consumed. It can cover the processing of raw materials into food through different physical and chemical steps.

4. Purification

Many food or beverage products use a purification step to remove colourful contaminants, unwanted taste and odour.

5. Food packaging

Food packaging is the crucial step and uses specialized techniques to avoid biological and chemical attacks and contamination.

6. Food waste management

The chemical treatment of waste refers to reducing its hazardous nature by using some specific chemicals such as acids, bases, oxidizers, reducers, etc.

KEY POINTS

1. In the large scale production of chemicals chemical industry plays a very important role, like in the production of plastics, synthetic fibre, and elastomers etc.
2. Raw materials for the chemical industry is obtained from atmosphere, biosphere, hydrosphere and lithosphere.
3. To avoid accidents and to ensure protection of workers and environment, chemical safety is critical.
4. Polymerization is a process in which small molecules like ethene, propylene, butadiene, vinyl alcohol, vinyl chloride, styrene etc. Under a set of conditions link together to form long chain, high molecular weight compounds, called polymers.
5. There are two types of polymerization reactions ; addition polymerization and condensation Polymerization.
6. Those compounds which are derived from petroleum and it's fractions are called petrochemicals. They have thee major classes; olefin based, aromatics and synthesis gas based.
7. Cosmetics have many purposes, including personal and skin care, conceal spots and enhance natural looks.
8. Cement is a very useful material used to glue bricks and stones together in construction after mixing with water, sand and crush etc.
9. Industrial chemistry has got its applications in food industry.

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References:

1. Ullmann's Encyclopedia of Industrial Chemistry
2. Principles of Industrial Chemistry by Chris A. Clausen

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Industrial chemistry is very important in the field of:
a) Medicines b) Cement c) Glass d) All of them
ii. Halite (rock salt) in Pakistan is obtained from:
a) Lithosphere b) Hydrosphere c) Biosphere d) Atmosphere
iii. The methods and applications to avoid accidents in chemical industry is termed as:
a) Security b) Hazard analysis c) Chemical safety d) Protection
iv. Butadiene is included in the class:
a) Olefins b) Aromatics c) Petroleum d) Syn gas
v. Polyvinyl chloride (PVC) is a polymer:
a) Addition b) Substitution c) Reduction d) Condensation
vi. Nylon 6'6 preparation needs:
a) Adipic acid b) Hexamethylene diamine
c) Citric acid d) Both a and b
vii. The percentage of gypsum in cement is :
a) 2-3% b) 1-5% c) 20% d) 65%
viii. Vinegar is made by:
a) Addition Polymerization b) Condensation Polymerization
c) Fermentation d) Pasteurization

2. Short Answer Questions

i. What are the petrochemicals? Explain their classes.
ii. What useful products are obtained from ethylene?
iii. Enlist useful products obtained from benzene and it's derivatives.
iv. How does chemical industry get raw materials for production of useful stuff?
v. Explain the addition polymerization with an example.
vi. Explain condensation Polymerization with an example.
vii. How is the Kevlar prepared? What are it's uses?
viii. Write the raw materials used in nail polish.
ix. Enlist of raw materials used for making lipstick.
x. Write down the method for the preparation of lipstick.

3. Long Answer Questions

i. Write a detailed note on cement.
ii. Write the involvement of industrial chemistry in food production and preservation.
iii. Write a detailed account of petrochemicals.

PROJECT

Prepare a report on the Impact of Artificial Intelligence (AI) on Various Industries.

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Glossary

Acid dissociation constant: K_a is termed as the acid dissociation constant. It is a measure of the extent to which an acid is ionized or dissociated at the equilibrium state.

Acid strength: The degree to which different Bronsted acids give off protons is called acid strength.

Acylation: The reaction in which the acyl group is introduced in the benzene ring when acyl chloride (ethanoyl chloride) is reacted with benzene in the presence of a catalyst, aluminium chloride, is called acylation.

Addition polymers: Addition polymers are formed by combining alkene monomers, resulting in just one huge molecule.

Alkaline earth metals: The elements in Group 2 of the Periodic Table are referred to as the alkaline earth metals.

Alloying: Alloying is the process of combining a metal with one or more other elements to enhance its properties such as strength, ductility, corrosion resistance, and hardness.

Ampere: The SI Unit of current is the ampere, which is the amount of current flowing when one coulomb passes a given point in one second.

Anode: The electrode at which oxidation occurs is called the anode.

Antiviral drugs: Antiviral drugs are a class of medicines particularly used to treat viral infections.

Artificial organ: An artificial organ is a biological device or tissue created by scientists to replace, replicate, or augment a functional naturally occurring organ.

Assumptions : Assumptions are the basic convictions or declarations accepted without evidence.

Atomic absorption spectrum: An atomic absorption spectrum is observed when free atoms in the ground state absorb specific wavelengths of light and get excited to higher energy levels.

Atomic emission spectroscopy: Atomic emission spectroscopy is a powerful technique to quantify the elements by the measurement of the specific wavelength of light emitted from a pre-excited sample.

Begging the Question: Asking a question that begs an answer is referred to as "begging the question,"

Biodegradable polymers: The polymers which can be decomposed by the action of microorganisms are called biodegradable polymers.

BOD: *The* biological oxygen demand (BOD) is the amount of oxygen used to decompose the organic matter in a sample of water over a specified time period, usually 5 days, at a specified temperature.

Buffer solution: A buffer solution is a solution, the pH of which does not change significantly when a small amount of acid or base is added to it.

C-13 NMR: C-13 NMR is based on the magnetic properties of the C-13 nuclei.

Carbocation: A carbon atom which is attached with three atoms or a group of atoms and possesses a unit positive charge is known as carbocation.

Carbohydrates: *Carbohydrates* have the general formula $C_x(H_2O)_y$

Carbonyl compounds: Carbonyl compounds are a class of organic substances characterized by the presence of a carbonyl group (C=O).

Cathode: The electrode at which reduction occurs is called the cathode.

Cement: Cement is a very useful material used to glue bricks and stones together in construction after mixing with water, sand crush etc.

Ceramics: Ceramics include materials like cement, glass, and clay minerals such as porcelain.

Chiral molecules: Chiral molecules are those having carbon atoms bonded to four different atoms or groups of atoms.

Chiral: All objects that are non-super imposable on their mirror images are called chiral.

Claims: A claim is a declaration or proposition that represents the central idea or stance of a debate.

Common ion effect: The phenomenon in which the degree of ionization or solubility of an electrolyte is suppressed by the addition of a highly soluble electrolyte containing a common ion is called the common ion effect.

Competitive inhibitor: A competitive inhibitor is a molecule that is similar to the substrate and competes with it for the active site on the enzyme.

Complex compound: A complex compound or coordination compound is formed between transition metals and ligand(s).

Conclusion: The conclusion is the final statement that naturally follows from the initial statements. It represents the ultimate goal of the argument.

Condensation polymers: Condensation polymers are formed by the combination of monomers with the elimination of simple molecules such as H_2O.

Confirmation bias: The tendency of people to process information by searching for or interpreting information that is consistent with their existing beliefs.

Coordination number: The number of coordinate covalent bonds formed by metal ions with ligands is called coordination number.

Coordination sphere: The central atom or ion with ligand(s) is. called coordination sphere.

Coulomb: The SI unit of charge is the coulomb (C).

Counterclaims: A counterclaim is a statement that opposes the main claim.

Dependant variable: The variable that is affected by changes in the independent variable and this is usually plotted on the y-axis.

Disproportionation reaction: A redox reaction in which the same element is oxidized and reduced simultaneously.

Drug action: Drug action refers to certain biochemical or physiological effects that the drug produces in the body to produce a therapeutic response.

electrochemical cells: Devices, which convert electrical energy into chemical energy and vice versa, are known as electrochemical cells.

Electrochemical series; A list of arrangement of elements in the order of their standard electrode potential with reference to standard hydrogen electrode is called electrochemical series.

Electrolysis: Electrolysis is the process by which chemical reactions are stimulated by an external electrical current.

Electrolytic cell: Electrolytic cell is a device that converts electrical energy to chemical energy by electrolysis.

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Electromotive force: The force with which electrons are pushed to flow through the wire from the anode to the cathode is called the electromotive force or emf.

Enzymes: Enzymes are biocatalysts which alter the speed of metabolic activities in the living bodies.

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Equivalence point: The equivalence point is the point at which indicator changes its colour and the point at which neutralisation takes place.

Error: Error is the difference between the value or quantity obtained in an experiment and the value accepted in the experiment or in the literature.

Falling Occam's Razor: If there are two possible explanations for the same event, you should choose the more straightforward one.

Faraday (F). It corresponds to the charge carried by one mole of electrons and amounts to 96487 C.

Fertilizers: Fertilizers, are natural or artificial substances containing elements that improve plant growth and productivity.

Fibrous proteins: Proteins that are made up of elongated or fibrous polypeptide chains are called fibrous proteins.

Fridel-Craft acylation: The introduction of the acyl group in the benzene ring when it is heated with chloroalkane in the presence of aluminium chloride (Lewis acid) is called Fridel-Craft acylation.

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Fridel-Craft alkylation: The introduction of an alkyl group in a benzene ring when it is heated with chloroalkane in the presence of aluminium chloride (Lewis acid) is called Fridel-Craft alkylation.

Fungicides: Fungicides are pesticides that kill or prevent the growth of fungi and their spores.

Galvanic or voltaic cell: An electrochemical cell in which a spontaneous redox reaction produces an electric current is known as a galvanic or voltaic cell.

Genetic engineering: Genetic engineering also called genetic modification is a technique used to change an organism's genes using technology.

Geometric isomerism: Geometric isomerism is also called cis-trans isomerism

Globular proteins: Proteins that are water-soluble and possess a shape like a sphere or a globe upon folding are called globular proteins.

Glycogen: Glycogen is a type of stored glucose molecule made up of a large number of connected glucose molecules.

Halogenoalkanes: Halogenoalkanes also known as alkyl halides are compounds in which one hydrogen atom of alkanes has been replaced by a halogen atom.

Hasty Generalizations: A hasty generalization fallacy is a claim made on the basis of insufficient evidence.

Herbicides: Herbicides are chemicals used to control unwanted plants also called weeds.

Independent variable: It is manipulated or controlled by the individual who is doing an experiment. It is plotted on the x-axis.

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Insecticides: Insecticides are chemicals used to control insects.

Ionic product of water: The product of the concentration of H^+ and OH^- ions in pure water at room temperature (298 k) is called an ionic product of water.

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IR spectroscopy: The spectroscopy that makes use of the interaction of infrared radiations with organic molecules.

Isomerism: The phenomenon which gives different structural formulae to organic compounds with the same molecular formulae is called isomerism.

Ligand: A ligand is an atom or group of atoms which are electron-rich and have the ability to donate lone pairs of electrons to the transition metal ions, making dative covalent bonds with them.

Lipids: Lipids are naturally occurring heterogeneous groups of organic compounds of animals and plants origin, which are soluble in organic solvents.

Material: A material is a substance or mixture that makes up an object.

Metabolite: A metabolite is a biologically active form of a drug or substance produced by the body's metabolic processes.

Metallurgy: The process of separating materials from ores and alloying them is known as metallurgy.

Naphthols: Naphthols are derivatives of naphthalene and consist of a naphthalene ring system bonded to a hydroxyl group.

Nematicide: A nematicide is a type of pesticide used to kill plant-parasitic nematodes.

Nernst equation: The Nernst equation is a mathematical expression that relates the standard electrode potential (E°) to the actual electrode potential (E) under non-standard conditions, taking into account the concentrations of the reactants and products.

**Nernst`s law:** Nernst`s law states that a solute is distributed between two layers of immiscible solvents so that the ratio of its concentration in each solvent is equal to its solubility.

NMR spectroscopy: NMR spectroscopy or magnetic resonance spectroscopy (MRS), is a spectroscopic technique based on re-orientation of atomic nuclei with non-zero nuclear spins in an external magnetic field.

Non-specific reactions: The reactions that occur without specificity to a particular substrate are called non-specific reactions.

Nuclear spin flipping: Nuclear spin flipping is a quantum mechanical phenomenon where certain atomic nuclei absorb energy from an external magnetic field, leading to a change in their spin state.

Nucleic acids: Naturally occurring biomolecules that serve as the primary information-carrying molecules in cells are called nucleic acids.

Nucleophilic substitution reaction: The reaction in which the halogen atom of an alkyl halide is substituted or replaced by a strong nucleophile is known as a nucleophilic substitution reaction.

Oligosaccharides: Carbohydrates which upon hydrolysis form 2 to 10 molecules of monosaccharides or simple sugars are called oligosaccharides.

Opiates: Opiates, also called opioids are a class of drugs that include the illegal drug heroin, synthetic opioids such as fentanyl, and legal prescription pain relievers such as oxycodone, hydrocodone, codeine, morphine, and many others.

Optical isomers: Optical isomers rotate the plane of polarized light either clockwise or anticlockwise.

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Oxidation half-cell: Half-cell, in which oxidation occurs is called an oxidation half-cell or anode half-cell.

Oxidation: A reaction in which a substance loses electrons is called oxidation.

oxidizing agent: *An oxidizing* agent is a substance that accepts electrons and causes oxidation, therefore, its oxidation state decreases.

Partition coefficient: The partition coefficient (K_{pc}) is defined as the ratio of the concentrations of a solute in two different immiscible solvents in contact with each other when equilibrium has been established at a particular temperature.

Pesticides: The chemical substances used in agriculture to control or kill pests including insects, fungi, rodents and weeds are called pesticides.

Petrochemicals: The compounds which are derived from petroleum and its fractions are called petrochemicals.

pH scale: the pH scale is a numerical scale that shows the acidic or alkaline strength of a solution.

pH: The pH of a solution is the logarithm to base 10 of the reciprocals of the numerical value of the hydrogen ion concentration.

Phenols: Phenols are compounds that contain a hydroxyl group (-OH) attached to an aromatic ring (benzene ring).

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Polyamide: A polyamide is produced by the condensation of diamines and dicarboxylic acids.

Polyesters: Polyesters are produced by the condensation of diols and dicarboxylic acids.

Polymerization: The reaction by which monomers are converted into polymers is known as polymerization.

Polymers: Polymers are high molecular weight compounds whose structures are made up of a large number of simple repeating units.

Polysaccharides: The Carbohydrates upon hydrolysis form hundreds to thousands of units of simple sugars are called polysaccharides.

Premises: Premises are the statements or reasons that provide the foundation for the claim.

Proteins: Proteins are complex nitrogenous substances that produce amino acids on complete hydrolysis.

Qualitative data: Qualitative data in chemistry refers to non-numeric information derived from observations about chemical characteristics and reactions.

Quantitative data: Quantitative data refers to numerical measurements that are obtained from experiments.

Random error: Random error is the random difference between the observed value and the true value.

Rebuttals: A rebuttal challenges and opposes an opposing viewpoint, offering proof or logic to undermine or disprove it.

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Recycling: Recycling is the process of collecting, and processing materials that would otherwise be discarded as waste, converting them into new products.

Reducing agent: A reducing agent is a substance that causes reduction through the loss of electrons.

Reduction half-cell: Half-cell, in which reduction occurs is called a reduction half-cell or *cathode half-cell*.

Reduction: A reaction in which a substance gains electrons is called reduction.

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Retention time: Retention time is the time taken for a sample molecule to travel through the column, from the time it is inserted into the machine to the time it is detected.

Rf (retardation factor) value: Rf value of a compound is the ratio of the distance travelled by the solute to the distance travelled by the solvent.

Roasting: The concentrated ore is heated in air below its melting point and converted into oxide. This process is called roasting.

Smelting: The method to reduce metal ions to free metal is called smelting.

SN_1: SN_1 is a unimolecular nucleophilic substitution reaction that occurs in two steps.

SN_2: SN_2 is a bimolecular nucleophilic substitution reaction which occurs in a single step.

Solubility Product: It is defined as the product of the equilibrium concentrations of ions, each raised to a power which is equal to the coefficient of the ion in the balanced chemical equation.

Spectroscopy is a technique used for structural elucidation of the molecule. It is based on the interaction of atoms or molecules and light.

Standard electrode potential: The standard electrode potential is defined as the tendency of a half-cell reaction to undergo reduction relative to the standard hydrogen electrode.

Stereoisomers: Stereoisomers are those molecules which have the same chemical formulae, same structural formulae but different arrangements of atoms in space. The phenomenon of the existence of such molecules is called stereoisomerism.

Steroids: Steroids are organic compounds with a typical molecular structure containing four fused rings of carbon atoms (three six-membered and one five-membered).

Straw Man Fallacy: The straw man fallacy occurs when someone distorts or exaggerates another's claim and then attacks the distorted version of the claim instead of refuting the original claim.

Substrate molecule: The alkyl halide molecule on which nucleophile attacks is called a substrate molecule.

Systematic error: Systematic error is a consistent or proportional difference between the observed and true values of something.

Terpenes: Lipids containing isoprene units (five-carbon units) are called terpenes or isoprenoids.

Therapeutic window: The therapeutic window, also known as the therapeutic range or therapeutic index, indicates the range of drug concentrations in the body that bring about the desired therapeutic effects with minimum adverse effects.

Titration: Titration is a technique used in neutralisation reactions between acids and alkalis to determine the concentration of the unknown solution.

TLC: Thin-layer chromatography (TLC) separates substances based on how they interact with different surfaces. In TLC, substances move across a thin layer on a plate.

UV-spectroscopy: UV-spectroscopy is the technique in which the UV and visible light absorption by any compound is measured. Its typical range of wavelength is from 200 nm-800nm.

X-ray crystallography: It is a method that uses X-rays to find out the detailed structure of a crystal, including the arrangement of its atoms and molecules.

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