FSc / ICS Part-II Chemistry — Punjab Board

## CHAPTER 1

# Periodic Classification of Elements and Periodicity

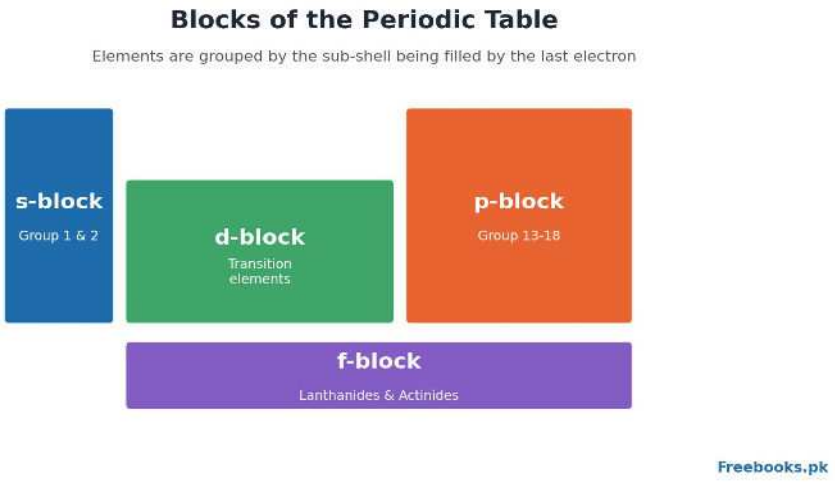


*Figure 1.1 — The four blocks (s, p, d, f) of the periodic table.*

# 1. Chapter Overview

The periodic table is one of the most powerful tools in chemistry. It arranges all known elements in a simple, organised pattern so that elements with similar properties fall together. In this chapter we study how this arrangement developed over time, how the modern periodic table is built, and how the properties of elements change (repeat in a regular way) as we move across a period or down a group. This regular repetition of properties is called periodicity.

Once you understand the pattern behind the periodic table, you no longer need to memorise the behaviour of each element separately. Instead, you can predict the size of an atom, how easily it loses or gains electrons, and whether its oxide is acidic or basic — simply from its position in the table. This makes Chapter 1 the foundation for the whole of Part-II Chemistry.

# 2. Learning Objectives

After studying this chapter, you should be able to:

- Describe the historical development of the periodic table from Dobereiner to Moseley.
- State the modern periodic law and explain why atomic number is the true basis of classification.
- Identify periods, groups, and the s-, p-, d- and f-blocks in the periodic table.
- Define and explain periodicity and the cause behind it.
- Explain the trends in atomic radius, ionic radius, ionization energy, electron affinity and electronegativity across a period and down a group.
- Relate shielding effect and effective nuclear charge to periodic trends.
- Predict the acidic or basic nature of oxides and hydrides of elements.
- Justify the anomalous position of hydrogen in the periodic table.

# 3. Key Concepts

## 3.1 Historical Background

Chemists always wanted to organise elements in a way that reflects their properties. Several attempts led to the modern periodic table:

**Dobereiner's Triads (1829)**

The German chemist Johann Dobereiner grouped elements into sets of three, called triads, having similar chemical properties. He noticed that the atomic mass of the middle element was roughly the average of the other two. For example, in the triad Lithium (7), Sodium (23) and Potassium (39), the average of 7 and 39 is 23 — the mass of sodium. The idea was useful but only a few elements could be arranged this way.

**Newlands' Law of Octaves (1864)**

The English chemist John Newlands arranged elements in order of increasing atomic mass and found that every eighth element repeated the properties of the first — like the notes of a musical

scale. This was called the Law of Octaves. It worked for lighter elements but broke down for heavier ones, so it was not widely accepted at the time.

### Mendeleev's Periodic Table (1869)

The Russian chemist Dmitri Mendeleev arranged the elements in order of increasing atomic mass in horizontal periods and vertical groups. His periodic law stated: 'The properties of elements are a periodic function of their atomic masses.' Mendeleev's great success was that he left gaps for undiscovered elements and even predicted their properties (such as eka-silicon, later found as germanium).

> **Defects of Mendeleev's Table**
>
> Position of hydrogen was not fixed (it resembles both Group IA and Group VIIA).
>
> Isotopes of an element had no separate place, although they have different masses.
>
> Some heavier elements were placed before lighter ones (anomalous pairs) to keep similar elements together, e.g. Argon (40) before Potassium (39).

### Moseley's Work and the Modern Periodic Law (1913)

The English physicist Henry Moseley showed by X-ray studies that the **atomic number** (number of protons), not the atomic mass, is the fundamental property of an element. This corrected the anomalies in Mendeleev's table and gave us the **Modern Periodic Law:** 'The properties of elements are a periodic function of their atomic numbers.'

## 3.2 The Modern Periodic Table

In the modern (long form) periodic table, elements are arranged in order of increasing atomic number. The horizontal rows are called periods and the vertical columns are called groups.

| Feature | Description |
|---|---|
| Periods | 7 horizontal rows. Period number = number of the outermost (valence) shell. |
| Groups | 18 vertical columns. Elements in a group have the same number of valence electrons and similar properties. |
| Representative elements | s-block and p-block elements (Groups IA–VIIA and Group 0). |
| Transition elements | d-block elements, placed in the middle of the table. |
| Inner transition | f-block elements: lanthanides and actinides, placed at the bottom. |

### Important Families (Groups)

**Alkali metals:** Group IA — Li, Na, K, Rb, Cs, Fr. Very reactive, soft metals.

**Alkaline earth metals:** Group IIA — Be, Mg, Ca, Sr, Ba, Ra. Reactive metals, but less than alkali metals.

**Chalcogens:** Group VIA — O, S, Se, Te, Po. The 'ore-forming' family.

**Halogens:** Group VIIA — F, Cl, Br, I, At. Very reactive non-metals.

**Noble (inert) gases:** Group 0 / VIIIA — He, Ne, Ar, Kr, Xe, Rn. Very unreactive due to complete outer shells.

## 3.3 Classification into Blocks

Depending on which sub-shell (orbital) receives the last electron, elements are divided into four blocks:

**s-block:** Last electron enters an s-orbital. Groups IA and IIA. Soft, reactive metals.

**p-block:** Last electron enters a p-orbital. Groups IIIA–VIIA and Group 0. Contains metals, non-metals and metalloids.

**d-block:** Last electron enters a d-orbital. The transition elements. Hard metals, form coloured compounds.

**f-block:** Last electron enters an f-orbital. Lanthanides and actinides (inner transition elements).

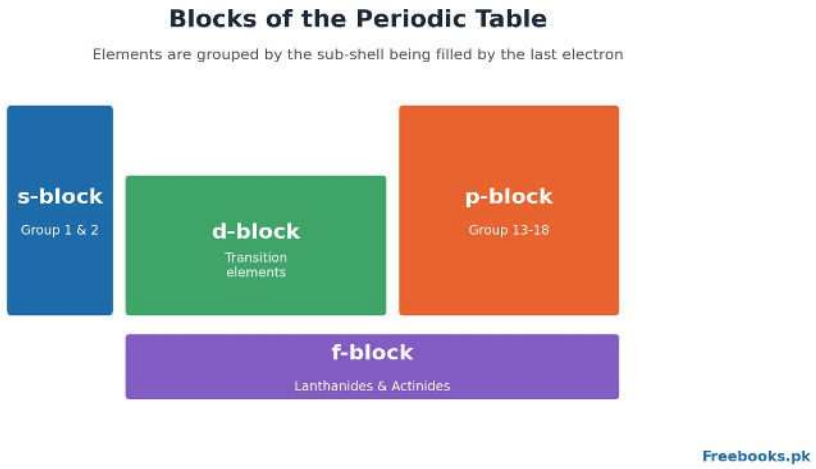


*Figure 1.2 — Position of the s, p, d and f blocks.*

## 3.4 Periodicity and Its Cause

**Periodicity** is the regular repetition of physical and chemical properties of elements after certain regular intervals when they are arranged by increasing atomic number. **Cause of periodicity:** it is due to the periodic repetition of the same outer (valence) electronic configuration. For example, all alkali metals have one electron in their outermost shell ($ns^1$), so they show similar properties.

## 3.5 Periodic Properties and Their Trends

Two ideas explain almost every trend in this chapter:

**Effective nuclear charge (Zeff):** the net positive charge actually felt by the valence electrons after the inner electrons partly cancel the nuclear pull. Higher Zeff pulls electrons in more strongly.

**Shielding (screening) effect:** the inner-shell electrons repel the outer electrons and reduce the nuclear attraction felt by them. More inner shells means more shielding.

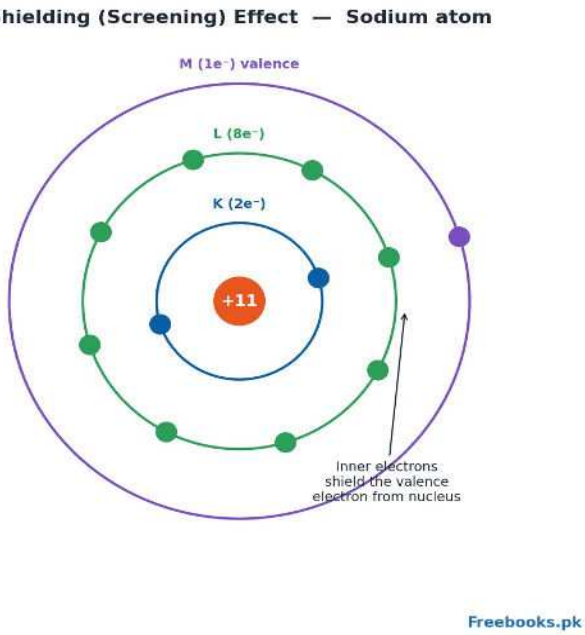


*Figure 1.3 — Shielding of the valence electron in a sodium atom by inner shells.*

### Atomic Radius

The atomic radius is the distance from the nucleus to the outermost shell. Across a period it decreases because the nuclear charge increases while electrons are added to the same shell, pulling the shell inward. Down a group it increases because a new shell is added at each step.

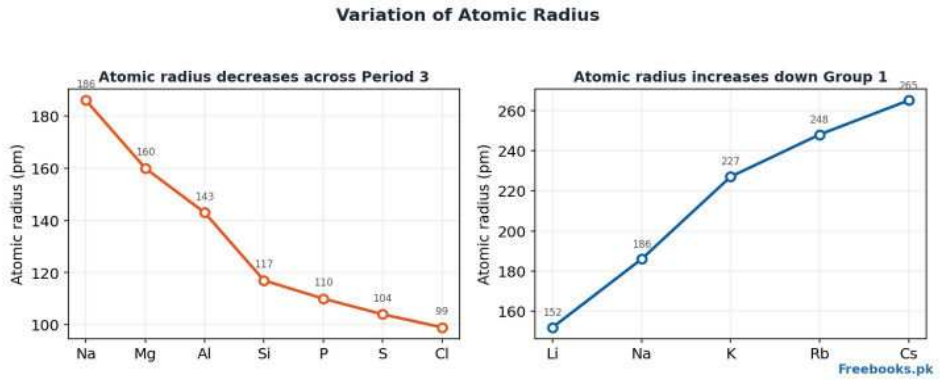


*Figure 1.4 — Atomic radius decreases across a period and increases down a group.*

### Ionic Radius

A cation (positive ion) is always smaller than its parent atom because it has lost electrons and often a whole shell, so the remaining electrons are pulled in more tightly. An anion (negative ion) is always larger than its parent atom because added electrons increase electron–electron repulsion and the same nuclear charge now holds more electrons.

### Ionization Energy

Ionization energy is the minimum energy required to remove the most loosely bound electron from an isolated gaseous atom. Across a period it increases (smaller size + higher Zeff hold electrons tightly). Down a group it decreases (larger size + more shielding make removal easier).

Small dips occur — for example, boron's value is lower than beryllium's because the 2p electron is easier to remove than a 2s electron.

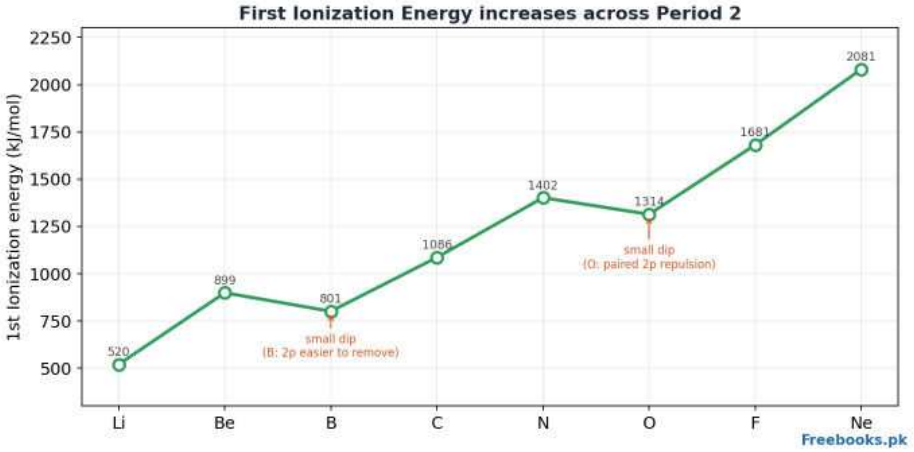


*Figure 1.5 — First ionization energy across Period 2 (note the small dips at B and O).*

### Electron Affinity

Electron affinity is the energy released when an electron is added to an isolated gaseous atom. Generally it increases across a period (atoms more readily accept an electron) and decreases down a group. Halogens have the highest electron affinities, while noble gases have almost zero because their shells are already complete.

### Electronegativity

Electronegativity is the tendency of an atom to attract the shared pair of electrons in a covalent bond towards itself. It increases across a period and decreases down a group. Fluorine is the most electronegative element.

### Nature of Oxides and Hydrides

Across a period the character of oxides changes from basic (metals, e.g. $Na_2O$) through amphoteric (e.g. $Al_2O_3$) to acidic (non-metals, e.g. $SO_3$, $Cl_2O_7$). This mirrors the change from metallic to non-metallic character. Hydrides likewise change from ionic (with reactive metals) to covalent (with non-metals).

## 3.6 Position of Hydrogen

Hydrogen has one electron ($1s^1$). Like Group IA metals it can lose one electron to form $H^+$; like Group VIIA halogens it needs one electron to complete its shell and can form $H^-$. Because it resembles both families but is identical to neither, its position is described as anomalous, and it is usually placed separately at the top of the table.

# 4. Important Definitions

| Term | Definition |
|---|---|
| Periodic table | A table in which elements are arranged in order of increasing atomic number in periods and groups. |

| Term | Definition |
|---|---|
| Modern periodic law | The properties of elements are a periodic function of their atomic numbers. |
| Periodicity | The regular repetition of properties of elements after certain regular intervals. |
| Period | A horizontal row in the periodic table; there are 7 periods. |
| Group | A vertical column in the periodic table; there are 18 groups. |
| Atomic radius | The distance from the nucleus to the outermost electron shell of an atom. |
| Ionization energy | The minimum energy required to remove the outermost electron from an isolated gaseous atom. |
| Electron affinity | The energy released when an electron is added to an isolated gaseous atom. |
| Electronegativity | The tendency of an atom to attract the shared electron pair in a covalent bond. |
| Shielding effect | The reduction in nuclear attraction on valence electrons caused by inner-shell electrons. |
| Effective nuclear charge | The net positive charge experienced by the valence electrons of an atom. |

## 5. Formulas / Rules

### Quick Rules to Remember

**Effective nuclear charge:** Zeff = Z − S (Z = atomic number, S = shielding constant)
**Across a period (left → right):** atomic & ionic radius decrease; IE, EA, EN increase.
**Down a group (top → bottom):** atomic & ionic radius increase; IE, EA, EN decrease.
**Cation < parent atom < anion** (in size).
**Metallic character:** decreases across a period, increases down a group.
**Oxide nature across a period:** basic → amphoteric → acidic.

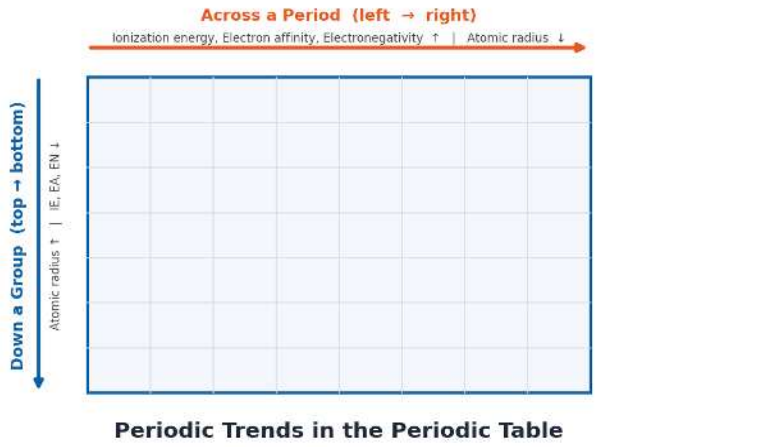


*Figure 1.6 — Summary of periodic trends across a period and down a group.*

## 6. Diagrams / Illustrations

The key diagrams for this chapter are collected here for quick revision. Study each one until you can redraw and label it from memory.

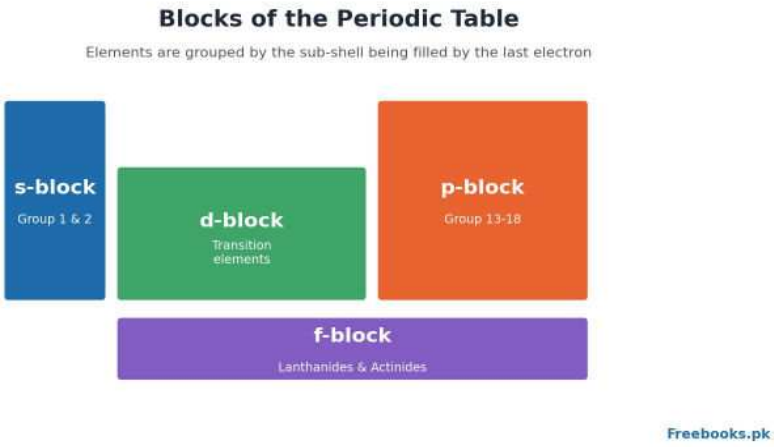


*Diagram 1 — Blocks of the periodic table (s, p, d, f).*

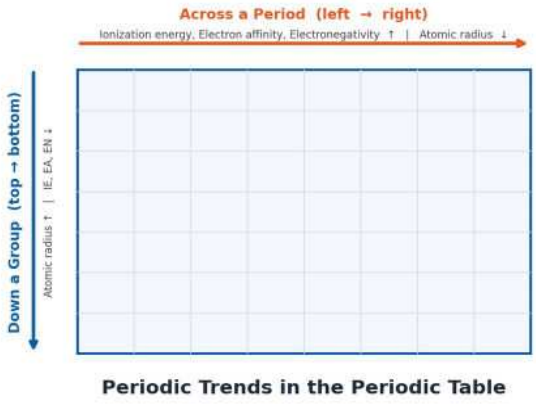


*Diagram 2 — Direction of periodic trends.*

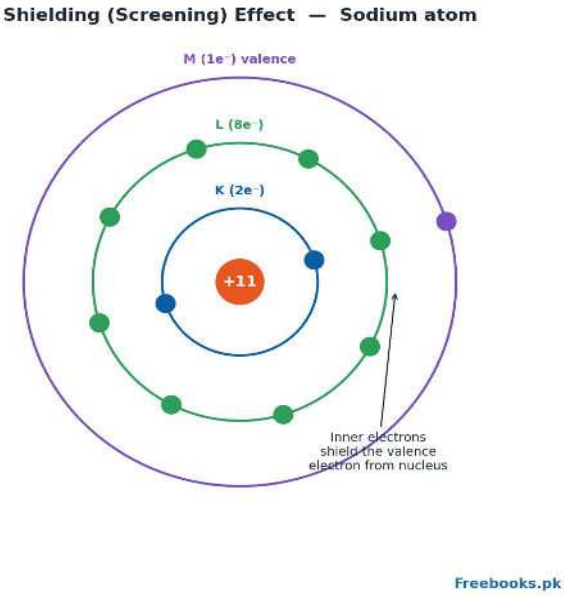


*Diagram 3 — Shielding effect in a sodium atom.*

## 7. Solved Examples

**Example 1 — Comparing atomic size**

**Q:** Which atom is larger, Na or Cl? Give a reason.

**Solution:** Both Na and Cl are in Period 3. Moving from Na to Cl the nuclear charge increases while electrons enter the same third shell, so the shell is pulled in more tightly. Therefore Na is larger than Cl.

**Example 2 — Order of ionization energy**

**Q:** Arrange Li, Na and K in increasing order of first ionization energy.

**Solution:** All three are Group IA metals. Down the group size increases and shielding increases, so the outer electron is removed more easily. Hence: K < Na < Li.

**Example 3 — Nature of an oxide**

**Q:** Predict whether the oxide of magnesium (MgO) is acidic or basic.

**Solution:** Magnesium is a metal (Group IIA). Metals form basic oxides, so MgO is basic — it reacts with acids to form a salt and water.

## 8. Short Questions

**Q1. Define the modern periodic law.**
**Ans.** The properties of elements are a periodic function of their atomic numbers.

**Q2. What is a triad? Give one example.**
**Ans.** A group of three elements with similar properties in which the middle element's atomic mass is the average of the other two, e.g. Li, Na, K.

**Q3. Why does atomic radius decrease across a period?**
**Ans.** Because nuclear charge increases while electrons enter the same shell, pulling it inward.

**Q4. Why does ionization energy increase across a period?**
**Ans.** Smaller size and higher effective nuclear charge hold the outer electron more tightly, so more energy is needed to remove it.

**Q5. Why is a cation smaller than its parent atom?**
**Ans.** It has lost electrons (often a whole shell), so the remaining electrons are held more tightly by the same nucleus.

**Q6. Why do noble gases have almost zero electron affinity?**
**Ans.** Their outermost shells are already complete, so they have no tendency to accept an extra electron.

**Q7. Define shielding effect.**
**Ans.** The decrease in nuclear attraction on valence electrons caused by the repulsion of inner-shell electrons.

**Q8. Why is the position of hydrogen anomalous?**
**Ans.** It resembles both Group IA (loses 1 $e^-$) and Group VIIA (gains 1 $e^-$), but is identical to neither.

## 9. Long Questions

**Q1. Trace the development of the periodic table from Dobereiner to Moseley.**

Dobereiner (1829) grouped elements into triads of three similar elements, where the middle element's atomic mass was the average of the other two. Newlands (1864) proposed the Law of Octaves, noticing that every eighth element repeated the properties of the first when arranged by increasing atomic mass, but this failed for heavier elements. Mendeleev (1869) arranged elements by increasing atomic mass in periods and groups, left gaps for undiscovered elements, and predicted their properties — a major success. However, his table had defects: an uncertain position for hydrogen, no place for isotopes, and a few anomalous pairs. Finally Moseley (1913)

proved that atomic number, not atomic mass, is the true basis of classification, giving the modern periodic law and removing the anomalies.

**Q2. Explain the variation of atomic radius, ionization energy and electronegativity across a period and down a group.**

Across a period the nuclear charge (and effective nuclear charge) increases while electrons are added to the same shell. As a result the atomic radius decreases, and because the outer electrons are held more tightly, both ionization energy and electronegativity increase. Down a group a new shell is added at each step and shielding increases, so the atomic radius increases while ionization energy and electronegativity decrease because the outer electrons are farther from the nucleus and more shielded. These opposite directions are the reason fluorine (top-right region) is small and highly electronegative, whereas caesium (bottom-left) is large and gives up its electron easily.

**Q3. What are effective nuclear charge and shielding effect? How do they control periodic properties?**

Effective nuclear charge (Zeff) is the net positive charge felt by the valence electrons after the inner electrons partly cancel the pull of the nucleus (Zeff = Z − S). The shielding or screening effect is the repulsion of the outer electrons by the inner-shell electrons, which reduces the nuclear attraction they feel. When shielding is large, Zeff is small, the outer electrons are loosely held, the atom is larger, and ionization energy is low. When shielding is small (as across a period, where no new inner shell is added), Zeff is large, electrons are pulled in strongly, the atom is smaller, and ionization energy is high. Thus these two factors together explain nearly every trend in the chapter.

## 10. Multiple Choice Questions (MCQs)

**1. The modern periodic law is based on:**
(A) Atomic mass (B) Atomic number (C) Atomic radius (D) Density

**2. Which scientist arranged elements in triads?**
(A) Newlands (B) Mendeleev (C) Dobereiner (D) Moseley

**3. The most electronegative element is:**
(A) Oxygen (B) Chlorine (C) Fluorine (D) Nitrogen

**4. Down a group, atomic radius:**
(A) Increases (B) Decreases (C) Remains same (D) First increases then decreases

**5. Which of the following is an amphoteric oxide?**
(A) $Na_2O$ (B) MgO (C) $Al_2O_3$ (D) $SO_3$

**6. Elements in which block are called transition elements?**
(A) s-block (B) p-block (C) d-block (D) f-block

**7. Ionization energy across a period generally:**
(A) Increases (B) Decreases (C) Stays constant (D) Becomes zero

**8. A cation is always ___ than its parent atom:**
(A) Larger (B) Smaller (C) Equal (D) Unpredictable

**9. The number of periods in the modern periodic table is:**
(A) 6 (B) 7 (C) 8 (D) 18

**10. Noble gases have electron affinity that is nearly:**
(A) Very high (B) Zero (C) Negative infinite (D) Same as halogens

**MCQ Answer Key**

**1-B 2-C 3-C 4-A 5-C 6-C 7-A 8-B 9-B 10-B**

## 11. Quick Revision / Summary

- Elements are arranged by increasing atomic number (Modern Periodic Law — Moseley).
- 7 periods (rows) and 18 groups (columns); four blocks: s, p, d, f.
- Periodicity = regular repetition of properties due to repeating valence-shell configuration.
- Across a period →: radius ↓, ionization energy ↑, electron affinity ↑, electronegativity ↑.
- Down a group ↓: radius ↑, ionization energy ↓, electron affinity ↓, electronegativity ↓.
- Cation < parent atom < anion (size).
- Oxides across a period: basic → amphoteric → acidic.
- Fluorine = most electronegative; hydrogen has an anomalous position.

## 12. Exam Tips

**Score-Boosting Tips**

Learn the two master ideas — effective nuclear charge and shielding — and you can reason out every trend instead of memorising them.

In trend questions, always mention BOTH the direction (across/down) AND the reason (size + Zeff/shielding).

Remember the small dips: B < Be and O < N in ionization energy — examiners love these exceptions.

Practise drawing and labelling the blocks diagram and the shielding diagram; labelled diagrams earn full marks.

For 'nature of oxide' questions, first decide metal vs non-metal, then say basic vs acidic (amphoteric for Al, Zn, Be).

Common confusion: ionization energy is energy absorbed; electron affinity is energy released — do not mix them.

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## CHAPTER 2

# s-Block Elements

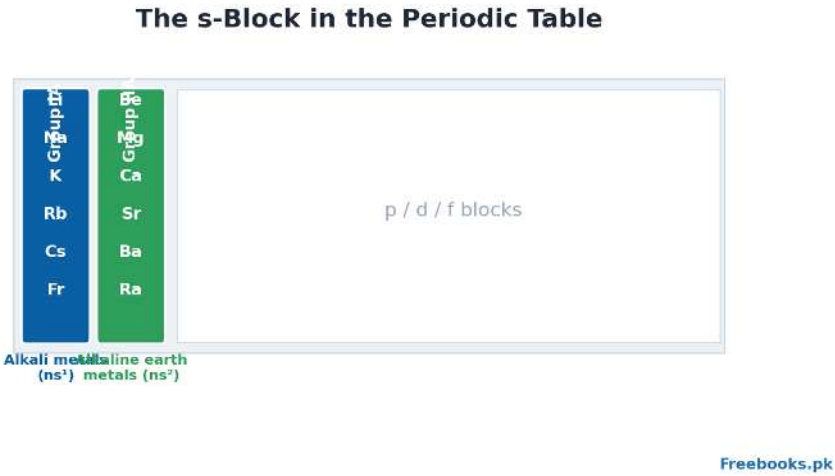


*Figure 2.1 — Group IA (alkali metals) and Group IIA (alkaline earth metals) make up the s-block.*

# 1. Chapter Overview

The s-block contains the elements of Group IA (the alkali metals: Li, Na, K, Rb, Cs, Fr) and Group IIA (the alkaline earth metals: Be, Mg, Ca, Sr, Ba, Ra). They are called s-block elements because their last electron enters an s-orbital. These are the most reactive metals in the whole periodic table — they are shiny, soft, light, and give beautiful colours in a flame. Because they are so reactive, they are never found free in nature; they always occur as compounds such as common salt (NaCl), limestone ($CaCO_3$) and gypsum.

In this chapter we study why these metals behave the way they do, how their properties change down each group, the special (anomalous) behaviour of lithium and beryllium, and the industrially important compounds made from them — including caustic soda, washing soda (Solvay process), plaster of Paris and bleaching powder.

# 2. Learning Objectives

- Identify the members of Group IA and Group IIA and write their general electronic configuration.
- Explain the general physical and chemical properties of s-block elements and their trends down the group.
- Explain why s-block metals are strong reducing agents and very reactive.
- Describe the reactions of these metals with water, oxygen and hydrogen.
- Explain the flame colours of s-block metals and their cause.
- Describe the anomalous behaviour of lithium and beryllium and the diagonal relationship.
- Explain the manufacture of sodium carbonate by the Solvay process.
- State the preparation, properties and uses of important compounds such as NaOH, $Na_2CO_3$, plaster of Paris and bleaching powder.
- Appreciate the biological importance of Na, K, Mg and Ca.

# 3. Key Concepts

## 3.1 The Two Families of the s-Block

| Group | Name | Members |
|---|---|---|
| IA ($ns^1$) | Alkali metals | Li, Na, K, Rb, Cs, Fr |
| IIA ($ns^2$) | Alkaline earth metals | Be, Mg, Ca, Sr, Ba, Ra |

**Why the names?** Group IA metals are called “alkali” metals because they react with water to form strong alkalis (hydroxides). The word alkali comes from the Arabic al-qali, meaning “the ashes” — early alkalis were obtained from plant ash. Group IIA metals are called “alkaline earth” metals because their oxides are alkaline and are found in the earth's crust.

> **Memory Trick**

**“Lithium Never Kisses Rabia's Friend”** → Li, Na, K, Rb, Cs, Fr (Group IA order).
**“Beta Maango Call Serious Baat Rakho”** → Be, Mg, Ca, Sr, Ba, Ra (Group IIA order).

## 3.2 General Properties and Their Trends

Because the s-block metals have only one or two loosely held valence electrons, they share a set of common properties. Understanding the reason behind each one is much easier than memorising a list:

**Large atomic size.** They have the largest atoms in their period, and the size increases down the group as new shells are added.

**Low ionization energy.** The single/double outer electrons are far from the nucleus and well shielded, so little energy is needed to remove them. This is why these metals are so reactive and electropositive. IE decreases further down the group.

**Strong electropositive / metallic character.** They readily lose electrons to form +1 (IA) or +2 (IIA) ions, so they are the most metallic elements.

**Soft and light.** Metallic bonding is weak because only one or two electrons are available, so the metals are soft (sodium and potassium can be cut with a knife) and have low densities (lithium, sodium and potassium even float on water).

**Low melting and boiling points.** Again due to weak metallic bonding; these fall down the group for Group IA.

**Fixed oxidation state.** Group IA always show +1 and Group IIA always show +2 in their compounds.

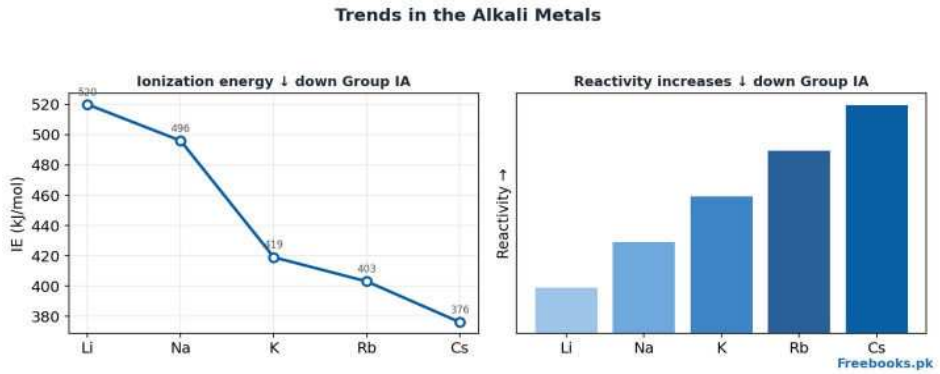


*Figure 2.2 — Down Group IA, ionization energy decreases and reactivity increases.*

### Teacher's Note

Ask students to connect every property back to ONE idea: “one or two loosely-held outer electrons.” Softness, low m.p., low IE, high reactivity and reducing power all flow from this single fact — this stops rote learning.

## 3.3 Reducing Nature

A reducing agent is a substance that loses electrons (and gets oxidised) while reducing something else. Since s-block metals lose their outer electrons very easily, they are powerful reducing agents. The reducing power increases down the group because ionization energy decreases. Lithium is a special case — although it is at the top, its very high hydration energy makes it the strongest reducing agent in aqueous solution.

## 3.4 Important Reactions

**With water:** Alkali metals react vigorously, giving a hydroxide and hydrogen gas: $2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$. The reaction becomes more violent down the group (K, Rb, Cs can catch fire).

**With oxygen:** They burn in air to form oxides. Lithium forms a normal oxide ($Li_2O$), sodium forms a peroxide ($Na_2O_2$), and potassium, rubidium and caesium form superoxides (e.g. $KO_2$). The basic character of the oxides increases down the group.

**With hydrogen:** They form ionic hydrides, e.g. $2Na + H_2 \rightarrow 2NaH$, which contain the $H^-$ ion.

**Nature of hydroxides:** All Group IA hydroxides are strong bases. In Group IIA the basic strength increases down the group; $Be(OH)_2$ is amphoteric (like $Al(OH)_3$), while the others are basic.

**Nitrates on heating:** Most alkali metal nitrates decompose to the nitrite and oxygen (e.g. $2NaNO_3 \rightarrow 2NaNO_2 + O_2$), while $LiNO_3$ (and Group IIA nitrates) give the oxide, $NO_2$ and $O_2$.

## 3.5 Flame Colours

When an s-block metal or its salt is heated in a flame, the heat energy excites its valence electrons to higher energy levels. When these electrons fall back to their original levels, they release the extra energy as visible light of a definite colour. Each metal gives its own characteristic colour, which is used to identify it (flame test).

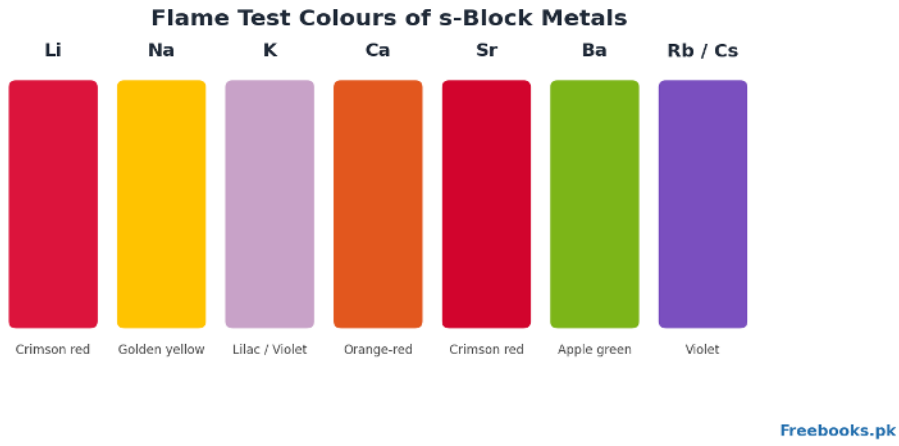


*Figure 2.3 — Characteristic flame-test colours of s-block metals.*

> **Memory Trick**
> **Colours to remember:** Li = crimson red, Na = golden yellow, K = lilac/violet, Ca = orange-red, Sr = crimson red, Ba = apple green, Rb & Cs = violet.

**Tip:** “Na is yellow like the Sun (Na = Sodium = Sooraj).”

**Teacher's Note**

Beryllium and magnesium do NOT give a flame colour because their electrons are too tightly held (small size, high IE) to be excited by an ordinary Bunsen flame — a favourite exam point.

## 3.6 Anomalous Behaviour and the Diagonal Relationship

The first member of each group (lithium in IA and beryllium in IIA) behaves differently from the rest of its family because of its very small size, high charge density and high polarising power. As a result, lithium resembles magnesium (the element diagonally below and to the right of it), and beryllium resembles aluminium. This similarity between an element and the one placed diagonally to it is called the diagonal relationship.

| Diagonal pair | Some common points |
|---|---|
| Li and Mg | Both form normal oxides; nitrates give the oxide on heating; both form covalent, soluble compounds; both react slowly with water. |
| Be and Al | Both are amphoteric; both form covalent halides; both are passivated by concentrated $HNO_3$; oxides are amphoteric. |

**Memory Trick**

**Diagonal pairs:** “Lithium ka dost Magnesium, Beryllium ka dost Aluminium.”

## 3.7 Comparison of Group IA and Group IIA

| Property | Group IA | Group IIA |
|---|---|---|
| Outer configuration | $ns^1$ | $ns^2$ |
| Oxidation state | +1 | +2 |
| Reactivity | Very high | High (less than IA) |
| Ionization energy | Lower | Higher |
| Hardness | Very soft | Comparatively harder |
| Basic nature of oxide | Strongly basic | Basic (Be amphoteric) |

## 3.8 Important Compounds

### (a) Caustic Soda — NaOH

Sodium hydroxide is called caustic soda because it is highly corrosive ('caustic' means 'which corrodes'). It is a white, deliquescent solid, a strong base, and dissolves in water with a lot of heat. It is manufactured by the electrolysis of brine (Nelson's / Castner–Kellner cell). It is used in making soap, paper, artificial silk, and in refining petroleum.

### (b) Sodium Carbonate (Washing Soda) — Solvay Process

Sodium carbonate, $Na_2CO_3$, is manufactured on a large scale by the Solvay (ammonia-soda) process. Ammoniacal brine is treated with carbon dioxide in a carbonating tower to precipitate sodium bicarbonate, which is then heated to give sodium carbonate. The great advantage of this process is that ammonia and carbon dioxide are recovered and reused, making it cheap and almost waste-free.

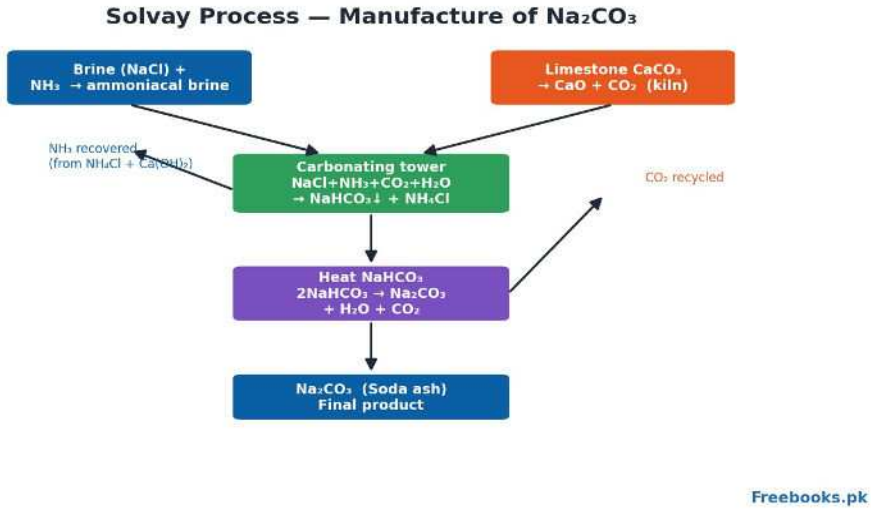


*Figure 2.4 — The Solvay process for manufacturing sodium carbonate.*

**Key Solvay Reactions**

**1.** $CaCO_3 \rightarrow CaO + CO_2$ (heating limestone)

**2.** $NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3\downarrow + NH_4Cl$

**3.** $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$ (heating)

**4.** $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$ (ammonia recovery)

### (c) Plaster of Paris and Gypsum

Gypsum is calcium sulphate dihydrate, $CaSO_4 \cdot 2H_2O$. When gypsum is heated to about 120 °C it loses part of its water and forms plaster of Paris, $CaSO_4 \cdot \frac{1}{2}H_2O$. When plaster of Paris is mixed with water it sets into a hard mass, so it is used for making casts for broken bones, statues and blackboard chalk. Gypsum itself is added (2–5%) to cement to control (slow down) its setting time.

### (d) Bleaching Powder

Bleaching powder, Ca(OCl)Cl, is made by passing chlorine over slaked lime. It is used for bleaching cloth and paper and for disinfecting drinking water.

## 3.9 Biological Importance

The s-block metals are essential for life. Sodium and potassium ions control the water balance and nerve signals in our bodies (the sodium–potassium pump). Calcium is the main mineral in bones and teeth and helps blood to clot, while magnesium is the central metal ion in chlorophyll, the green pigment that lets plants carry out photosynthesis.

## 4. Important Definitions

| Term | Definition |
|---|---|
| s-block elements | Elements in which the last electron enters an s-orbital (Groups IA and IIA). |
| Alkali metals | Group IA metals whose hydroxides are strong alkalis. |
| Alkaline earth metals | Group IIA metals whose oxides are alkaline and found in the earth. |
| Reducing agent | A substance that loses electrons and reduces another species. |
| Flame test | Identification of a metal by the characteristic colour it gives to a flame. |
| Diagonal relationship | The similarity in properties between an element and the one placed diagonally below it (Li–Mg, Be–Al). |
| Deliquescent | A substance that absorbs moisture from air and dissolves in it (e.g. NaOH). |
| Plaster of Paris | Calcium sulphate hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$, which sets hard with water. |

## 5. Formulas / Rules

### Must-Know Formulae and Facts

**Caustic soda** = NaOH | Washing soda = $Na_2CO_3 \cdot 10H_2O$ | Baking soda = $NaHCO_3$

**Gypsum** = $CaSO_4 \cdot 2H_2O$ | Plaster of Paris = $CaSO_4 \cdot \frac{1}{2}H_2O$ | Lime = CaO

**Bleaching powder** = Ca(OCl)Cl | Slaked lime = $Ca(OH)_2$

**Down a group:** size ↑, ionization energy ↓, reactivity ↑, reducing power ↑, basic nature of oxide ↑.

**Oxidation state:** Group IA = +1 always; Group IIA = +2 always.

## 6. Diagrams / Illustrations

The must-know diagrams for this chapter, gathered for quick revision:

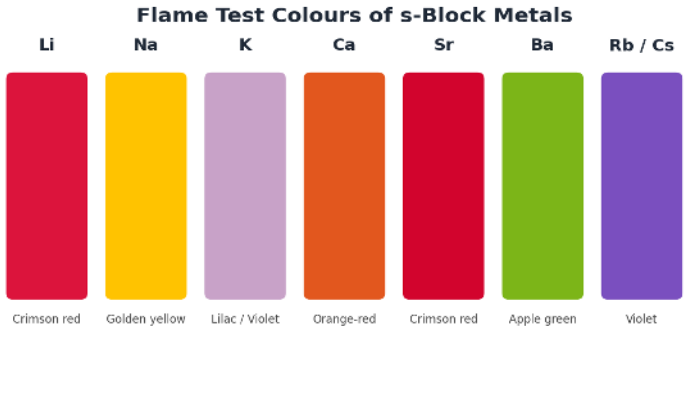


*Diagram 1 — Flame test colours.*

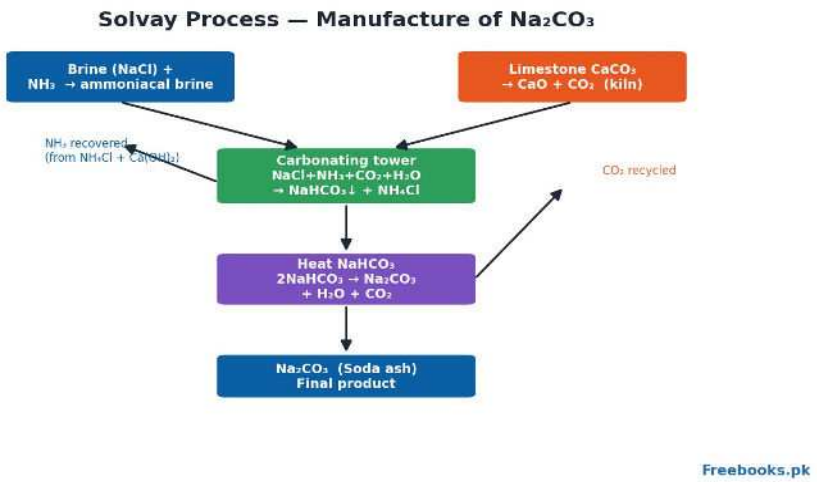


*Diagram 2 — Solvay process flow chart.*

## 7. Solved Examples

**Example 1 — Reactivity order**

**Q:** Which is more reactive, sodium or potassium? Why?

**Solution:** Potassium is more reactive. Going down Group IA the atom becomes larger and its ionization energy decreases, so potassium loses its outer electron more easily than sodium.

**Example 2 — Identifying a metal**

**Q:** An unknown salt gives an apple-green colour in a flame test. Which metal is present?

**Solution:** Apple-green flame colour is characteristic of barium (Ba). So the salt contains barium.

**Example 3 — Products of a reaction**

**Q:** Write the products when sodium reacts with water.

**Solution:** Sodium gives sodium hydroxide and hydrogen gas: $2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$. The solution turns basic (pink with phenolphthalein).

## 8. Short Questions

**Q1. Why are Group IA metals called alkali metals?**
**Ans.** Because they react with water to form strong alkalis (hydroxides); the name comes from Arabic al-qali, 'the ashes'.

**Q2. Why are s-block metals soft?**
**Ans.** Their metallic bonding is weak because only one or two valence electrons are available.

**Q3. Why does reactivity increase down Group IA?**
**Ans.** Atomic size increases and ionization energy decreases, so the outer electron is lost more easily.

**Q4. Why do Be and Mg not give a flame colour?**
**Ans.** Their electrons are held too tightly (small size, high IE) to be excited by an ordinary flame.

**Q5. What is the diagonal relationship?**
**Ans.** The similarity in properties between an element and the one placed diagonally to it, e.g. Li–Mg and Be–Al.

**Q6. Why is $Be(OH)_2$ different from other Group IIA hydroxides?**
**Ans.** It is amphoteric (reacts with both acids and bases), like $Al(OH)_3$, whereas the others are basic.

**Q7. What is caustic soda and why is it called so?**
**Ans.** Sodium hydroxide (NaOH); 'caustic' means corrosive, as it corrodes skin and many materials.

**Q8. Why is gypsum added to cement?**
**Ans.** To slow down (control) the setting time of the cement (about 2–5% is added).

## 9. Long Questions

**Q1. Describe the general characteristics of the s-block elements.**

The s-block elements are the metals of Groups IA and IIA, whose last electron enters an s-orbital. They have one ($ns^1$) or two ($ns^2$) loosely held valence electrons, and almost all their properties follow from this fact. They have large atomic sizes and low ionization energies, so they are strongly electropositive and lose electrons easily to form +1 or +2 ions. Their metallic bonding is weak, which makes them soft, light and low-melting. Because they lose electrons so readily, they are powerful reducing agents and among the most reactive metals known, reacting with water to give hydrogen and a hydroxide, and burning in oxygen to form basic oxides. They give characteristic colours in a flame, and their reactivity increases down each group as size increases and ionization energy falls. Owing to their high reactivity they are never found free in nature.

**Q2. Explain the manufacture of sodium carbonate by the Solvay process.**

In the Solvay (ammonia-soda) process, sodium carbonate is manufactured from cheap raw materials: brine (NaCl), limestone ($CaCO_3$) and ammonia. Limestone is heated in a kiln to give quicklime and carbon dioxide ($CaCO_3 \rightarrow CaO + CO_2$). The carbon dioxide is passed up a carbonating tower through ammoniacal brine, precipitating sparingly soluble sodium bicarbonate: $NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl$. The bicarbonate is filtered off and heated to give sodium carbonate, water and carbon dioxide: $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$. The quicklime is slaked to $Ca(OH)_2$ and used to recover ammonia from ammonium chloride: $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$. Because both the ammonia and the carbon dioxide are recycled, the process is economical and produces little waste (only $CaCl_2$ as a by-product).

**Q3. Discuss the anomalous behaviour of lithium and its diagonal relationship with magnesium.**

Lithium, the first member of Group IA, differs from the other alkali metals because of its very small size and high charge density (high polarising power). Unlike the others, lithium forms a normal oxide ($Li_2O$) rather than a peroxide or superoxide, its nitrate decomposes to the oxide instead of the nitrite, and many of its compounds are covalent and less stable to heat. These features make lithium resemble magnesium, the element placed diagonally to it. Both lithium and magnesium form normal oxides, both have nitrates that give the oxide on heating, both form covalent, hygroscopic compounds, and both react only slowly with water. This close similarity between an

element and the one diagonally placed to it is known as the diagonal relationship, and it arises because the two elements have similar charge-to-size ratios.

## 10. Multiple Choice Questions (MCQs)

**1. The general electronic configuration of alkali metals is:**
(A) $ns^2$ (B) $ns^1$ (C) $ns^2\ np^1$ (D) $ns^2\ np^2$

**2. Which metal gives a golden-yellow flame colour?**
(A) Potassium (B) Calcium (C) Sodium (D) Barium

**3. Washing soda is:**
(A) $NaHCO_3$ (B) $Na_2CO_3 \cdot 10H_2O$ (C) NaOH (D) $Na_2O_2$

**4. Plaster of Paris is:**
(A) $CaSO_4 \cdot 2H_2O$ (B) $CaSO_4 \cdot \frac{1}{2}H_2O$ (C) $CaCO_3$ (D) $Ca(OH)_2$

**5. Which hydroxide is amphoteric?**
(A) NaOH (B) KOH (C) $Be(OH)_2$ (D) $Ca(OH)_2$

**6. The Solvay process is used to manufacture:**
(A) NaOH (B) $Na_2CO_3$ (C) CaO (D) NaCl

**7. Lithium shows a diagonal relationship with:**
(A) Sodium (B) Calcium (C) Magnesium (D) Aluminium

**8. Which of the following is the strongest reducing agent in aqueous solution?**
(A) Na (B) K (C) Cs (D) Li

**9. Caustic soda is:**
(A) $Na_2CO_3$ (B) $NaHCO_3$ (C) NaOH (D) NaCl

**10. Bleaching powder is prepared by passing chlorine over:**
(A) Quicklime (B) Slaked lime (C) Gypsum (D) Limestone

**MCQ Answer Key**

**1-B 2-C 3-B 4-B 5-C 6-B 7-C 8-D 9-C 10-B**

## 11. Quick Revision / Summary

- s-block = Group IA (alkali, $ns^1$, +1) and Group IIA (alkaline earth, $ns^2$, +2).
- Large size, low IE → very reactive, strongly electropositive, powerful reducing agents.
- Soft, light, low melting; reactivity increases down the group.
- Flame colours: Li crimson, Na yellow, K lilac, Ca orange-red, Ba apple-green.
- Anomalous first members: Li (like Mg) and Be (like Al) — diagonal relationship.
- Solvay process makes $Na_2CO_3$; $NH_3$ and $CO_2$ are recycled.
- Caustic soda = NaOH; gypsum = $CaSO_4 \cdot 2H_2O$; plaster of Paris = $CaSO_4 \cdot \frac{1}{2}H_2O$.
- Na, K control nerve signals; Ca in bones; Mg in chlorophyll.

## 12. Exam Tips

**Score-Boosting Tips**

Learn the flame colours cold — they appear almost every year as an MCQ or short question.

For any 'trend down the group' answer, give BOTH the change and the reason (size ↑, IE ↓).

Memorise the four Solvay reactions in order; a labelled flow diagram earns full marks.

Do not confuse washing soda ($Na_2CO_3$), baking soda ($NaHCO_3$) and caustic soda (NaOH).

Remember the exceptions: Li forms a normal oxide, $Be(OH)_2$ is amphoteric, Be & Mg give no flame colour.

Common formulae confusion: gypsum has $2H_2O$, plaster of Paris has $\frac{1}{2}H_2O$ — never mix them up.

FSc / ICS Part-II Chemistry — Punjab Board

## CHAPTER 3

# Group IIIA and Group IVA Elements

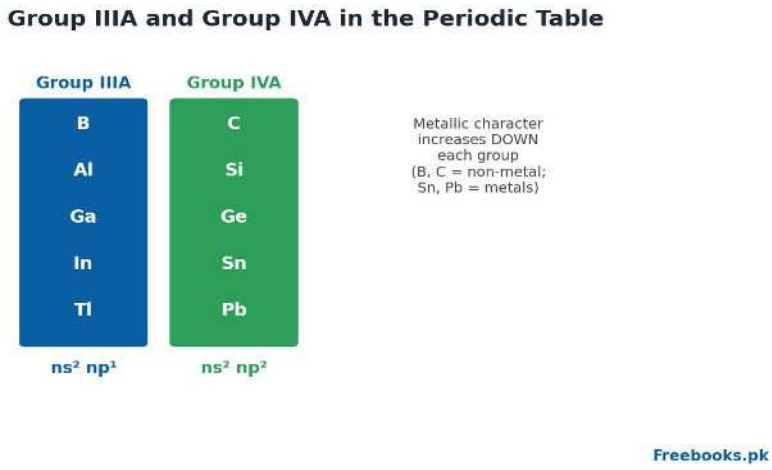


*Figure 3.1 — Group IIIA (boron family) and Group IVA (carbon family).*

# 1. Chapter Overview

This chapter deals with two families of p-block elements. Group IIIA (the boron family: B, Al, Ga, In, Tl) has the outer configuration $ns^2\ np^1$, while Group IVA (the carbon family: C, Si, Ge, Sn, Pb) has $ns^2\ np^2$. These groups are special because they show a clear change from non-metal at the top to metal at the bottom, they display more than one oxidation state, and they include some of the most useful materials on Earth — aluminium, carbon (in diamond, graphite and all of organic chemistry), and silicon (the heart of every computer chip).

A recurring idea in this chapter is the inert pair effect, which explains why the heavier members (thallium and lead) prefer a lower oxidation state. We also study important compounds such as borax, boric acid, aluminium oxide, carbon monoxide and dioxide, silicates and silicones.

# 2. Learning Objectives

- List the members and electronic configurations of Groups IIIA and IVA.
- Explain how metallic character changes down each group.
- Define and apply the inert pair effect to predict stable oxidation states.
- Describe the unusual (anomalous) behaviour of boron and carbon.
- Explain catenation and the allotropy of carbon (diamond and graphite).
- Describe the amphoteric nature and uses of aluminium.
- State the preparation and uses of borax, boric acid, silica, silicates and silicones.
- Explain why silicon and germanium are used as semiconductors.

# 3. Key Concepts

## 3.1 The Two Families

| Group | Name | Members |
|---|---|---|
| IIIA ($ns^2np^1$) | Boron family | B, Al, Ga, In, Tl |
| IVA ($ns^2np^2$) | Carbon family | C, Si, Ge, Sn, Pb |

In both groups the top element is a non-metal (or metalloid) and the character becomes more metallic as we move down. In Group IIIA, boron is a metalloid while aluminium and the rest are metals. In Group IVA, carbon is a non-metal, silicon and germanium are metalloids (semiconductors), and tin and lead are metals.

> **Memory Trick**
> **IIIA order:** “Bara Aluminium Gaya India Thailand” → B, Al, Ga, In, Tl.
> **IVA order:** “Carbon Se Germany Sn Pb” → C, Si, Ge, Sn, Pb.

## 3.2 Oxidation States and the Inert Pair Effect

Group IIIA elements can show a +3 state (using all three outer electrons) and Group IVA a +4 state. However, as we go down each group, the lower oxidation state (+1 for IIIA, +2 for IVA) becomes increasingly stable. This happens because the outer $ns^2$ pair of electrons becomes reluctant to take part in bonding — an idea called the inert pair effect. That is why thallium is most stable as $Tl^+$ and lead as $Pb^{2+}$, whereas aluminium is stable as $Al^{3+}$ and the top of Group IVA prefers +4.

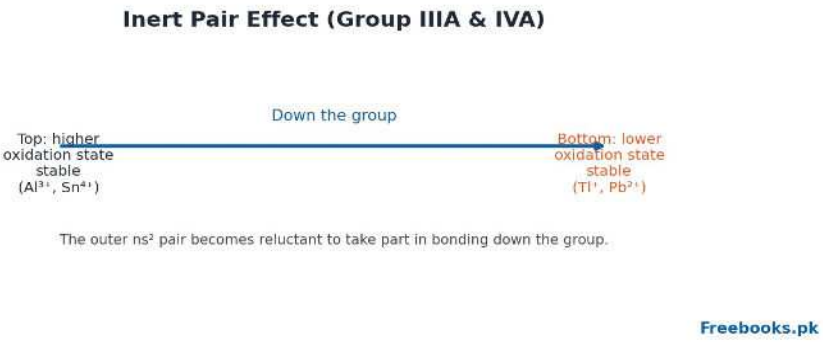


*Figure 3.2 — The inert pair effect stabilises lower oxidation states down the group.*

## 3.3 Anomalous Behaviour of Boron and Carbon

**Boron.** Because it is very small and has a high ionization energy, boron is a non-metal (metalloid), forms only covalent compounds, and its compounds are electron-deficient (e.g. $BF_3$ can accept a lone pair, acting as a Lewis acid). The other members are metals.

**Carbon.** Carbon is unique in its ability to form strong C–C bonds with itself (catenation) and to form multiple bonds (C=C, C≡C). This is the reason carbon forms millions of compounds and is the basis of all organic chemistry. It also shows allotropy.

## 3.4 Catenation and Allotropy of Carbon

Catenation is the self-linking of atoms of the same element to form long chains and rings. Carbon shows catenation to the greatest extent because the C–C bond is very strong. Carbon also exists in different physical forms called allotropes; the two most important crystalline allotropes are diamond and graphite.

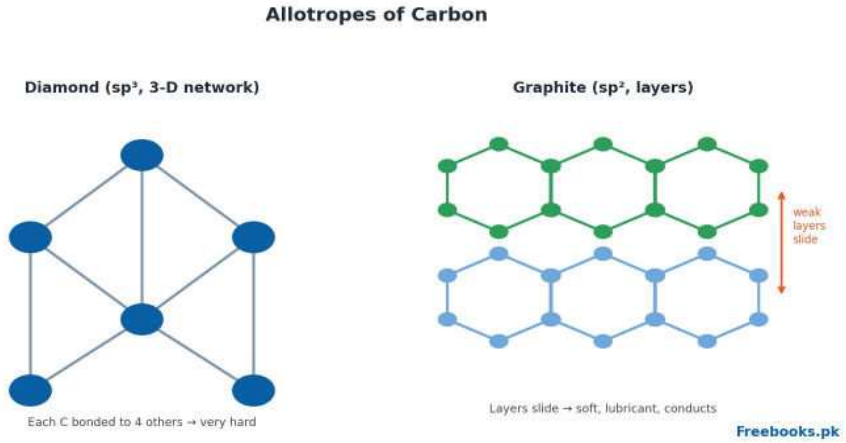

*Figure 3.3 — Diamond (rigid 3-D network) versus graphite (sliding layers).*

| Property | Diamond | Graphite |
|---|---|---|
| Hybridization | $sp^3$ | $sp^2$ |
| Structure | 3-D tetrahedral network | Flat layers of hexagons |
| Hardness | Hardest natural substance | Soft, slippery |
| Electrical conduction | Non-conductor | Good conductor |
| Main use | Cutting/abrasives, jewellery | Lubricant, pencil lead, electrodes |

## 3.5 Aluminium — the Amphoteric Metal

Aluminium is the most abundant metal in the earth's crust. It is light, strong and resists corrosion because a thin oxide layer protects its surface. Aluminium is amphoteric: it reacts with acids to give a salt and hydrogen, and also with strong alkalis to give an aluminate and hydrogen.

> **Amphoteric Aluminium — Key Reactions**
>
> **With acid:** $2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2\uparrow$
>
> **With alkali:** $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2\uparrow$
>
> **Thermite reaction:** $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$ (used for welding rails; strongly exothermic)

Uses of aluminium include electrical cables, aircraft and vehicle bodies, cooking utensils, packaging foil, and the thermite process for welding.

## 3.6 Important Compounds

**Borax ($Na_2B_4O_7 \cdot 10H_2O$).** A white solid used in glass and enamel making, as a water softener, and in the borax-bead test to identify metals.

**Boric acid ($H_3BO_3$).** A weak acid used as a mild antiseptic (eye-wash) and in glazes.

**Oxides of carbon.** Carbon monoxide (CO) is a colourless, poisonous gas and a good reducing agent used in metal extraction; carbon dioxide ($CO_2$) is an acidic oxide, used in fire extinguishers and photosynthesis, and is a greenhouse gas.

**Silica and silicates.** Silicon dioxide ($SiO_2$, sand/quartz) is a giant covalent solid used to make glass. Silicates form rocks, clays and cement; man-made silicones are water-repellent polymers used in sealants, lubricants and medical implants.

## 3.7 Silicon and Germanium as Semiconductors

Silicon and germanium are metalloids whose electrical conductivity lies between that of metals and non-metals and increases with temperature. By adding tiny amounts of other elements (doping), their conductivity can be controlled precisely. This makes them the basic materials of transistors, diodes, solar cells and computer chips.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Inert pair effect | The reluctance of the outer $ns^2$ electron pair to take part in bonding, stabilising the lower oxidation state down a group. |
| Catenation | The self-linking of like atoms to form chains and rings (greatest in carbon). |
| Allotropy | The existence of an element in two or more different physical forms in the same physical state. |
| Amphoteric | A substance that reacts with both acids and bases (e.g. Al, $Al_2O_3$). |
| Metalloid | An element with properties intermediate between metals and non-metals (e.g. B, Si, Ge). |
| Semiconductor | A material whose conductivity is between a conductor and an insulator and rises with temperature. |

## 5. Formulas / Rules

### Must-Know Facts

**Group IIIA:** $ns^2np^1$, main state +3; heavier prefer +1 (inert pair).
**Group IVA:** $ns^2np^2$, main state +4; heavier prefer +2 ($Pb^{2+}$).
**Borax =** $Na_2B_4O_7 \cdot 10H_2O$ | Boric acid = $H_3BO_3$ | Silica = $SiO_2$
**Metallic character** increases down a group; acidic nature of oxides decreases down.
**Diamond =** $sp^3$ (hard, insulator); Graphite = $sp^2$ (soft, conductor).

## 6. Diagrams / Illustrations

Collected diagrams for quick revision:

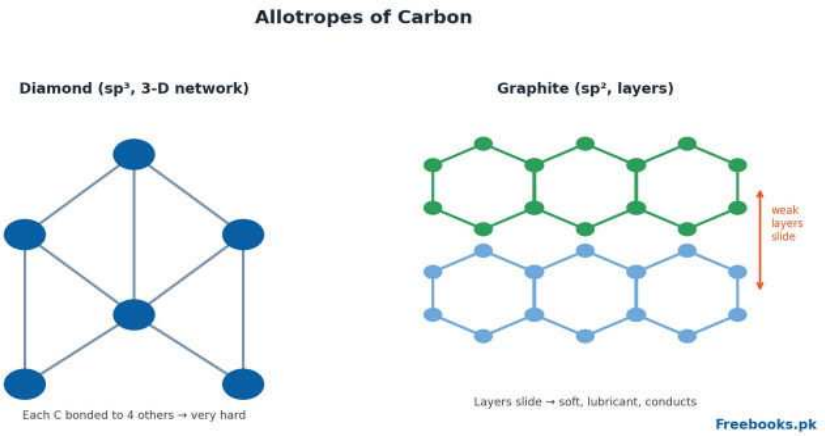


*Diagram 1 — Diamond vs graphite.*

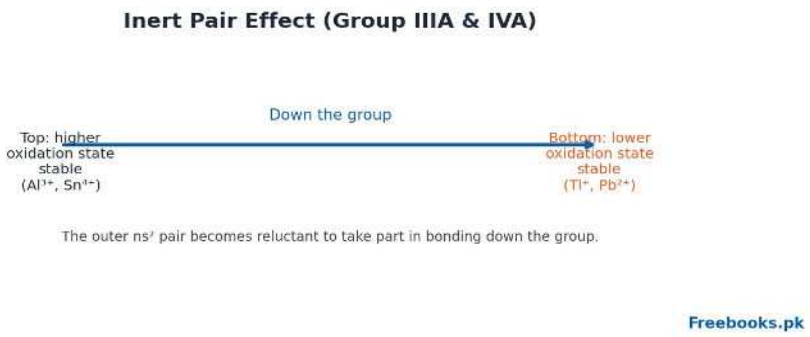


*Diagram 2 — Inert pair effect.*

## 7. Solved Examples

**Example 1 — Predicting oxidation state**

**Q:** Which oxidation state is more stable for lead, +2 or +4? Why?

**Solution:** +2 is more stable. Lead is at the bottom of Group IVA, where the inert pair effect makes the outer $6s^2$ electrons reluctant to bond, so $Pb^{2+}$ is favoured over $Pb^{4+}$.

**Example 2 — Amphoteric behaviour**

**Q:** Show that aluminium is amphoteric.

**Solution:** It reacts with acid ($2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$) and with base ($2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$). Reacting with both acid and base means it is amphoteric.

**Example 3 — Why graphite conducts**

**Q:** Why does graphite conduct electricity but diamond does not?

**Solution:** In graphite each carbon is $sp^2$ and one electron per atom is delocalised between the layers, so it can carry current. In diamond every electron is used in $sp^3$ C–C bonds, leaving none free, so it is an insulator.

## 8. Short Questions

**Q1. What is the inert pair effect?**
**Ans.** The reluctance of the outer $ns^2$ electron pair to bond, which stabilises the lower oxidation state down a group.

**Q2. Why is boron a non-metal while aluminium is a metal?**
**Ans.** Boron is very small with high ionization energy, so it forms only covalent bonds; aluminium is larger and loses electrons to behave as a metal.

**Q3. Define catenation.**
**Ans.** The self-linking of atoms of the same element into chains and rings; carbon shows it most.

**Q4. Why is diamond hard but graphite soft?**
**Ans.** Diamond is a rigid 3-D network of $sp^3$ carbons; graphite has $sp^2$ layers that slide over each other.

**Q5. What is the thermite reaction?**

**Ans.** $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$; a highly exothermic reaction used to weld iron/steel rails.

**Q6. Give two uses of borax.**
**Ans.** Making heat-resistant glass and enamels, and as a flux (borax-bead test).

**Q7. Why are Si and Ge called semiconductors?**
**Ans.** Their conductivity lies between metals and non-metals and increases with temperature and doping.

**Q8. Which is a stronger reducing agent, CO or $CO_2$?**
**Ans.** CO, because it readily takes up oxygen to become $CO_2$, reducing metal oxides.

## 9. Long Questions

**Q1. Discuss the general trends in Groups IIIA and IVA.**

Both groups belong to the p-block, with outer configurations $ns^2np^1$ (IIIA) and $ns^2np^2$ (IVA). Down each group the atomic size increases and ionization energy decreases, so metallic character rises: the top elements (B, C) are non-metals or metalloids, the middle members (Si, Ge, Ga) are metalloids, and the lower members (Sn, Pb, Tl) are true metals. The common higher oxidation state (+3 for IIIA, +4 for IVA) becomes less stable down the group because of the inert pair effect, which favours the lower state (+1, +2) for the heaviest members such as $Tl^+$ and $Pb^{2+}$. The acidic nature of the oxides decreases and their basic nature increases down each group, in line with the growing metallic character.

**Q2. Compare diamond and graphite in terms of structure and properties.**

Diamond and graphite are both allotropes of carbon but differ completely in structure, which gives them opposite properties. In diamond every carbon atom is $sp^3$ hybridised and bonded to four others in a rigid three-dimensional tetrahedral network; there are no free electrons, so diamond is the hardest natural substance, has a very high melting point, and does not conduct electricity. In graphite each carbon is $sp^2$ hybridised and bonded to three others in flat hexagonal layers, with the fourth electron delocalised between the layers; the layers are held only by weak forces, so they slide easily. This makes graphite soft and slippery (a good lubricant and pencil 'lead') and a good conductor of electricity. Thus a single element gives two materials with dramatically different uses.

**Q3. Describe the amphoteric nature and important uses of aluminium.**

Aluminium is described as amphoteric because it reacts with both acids and alkalis. With dilute acids it behaves as a metal, giving a salt and hydrogen: $2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$. With hot concentrated alkalis it dissolves to form an aluminate and hydrogen: $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$. Its oxide, $Al_2O_3$, is likewise amphoteric. In practice aluminium is extremely useful: it is light yet strong, resists corrosion (a protective oxide film), and conducts electricity well, so it is used in overhead power cables, aircraft and car bodies, cooking utensils, packaging foil, and in the thermite reaction ($2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$) to weld railway tracks.

## 10. Multiple Choice Questions (MCQs)

**1. The outer electronic configuration of Group IIIA is:**

(A) $ns^2$ (B) $ns^2np^1$ (C) $ns^2np^2$ (D) $ns^2np^3$

**2. The inert pair effect is most pronounced in:**
(A) B (B) Al (C) Ga (D) Tl

**3. The hardest allotrope of carbon is:**
(A) Graphite (B) Diamond (C) Coke (D) Charcoal

**4. Which element shows the greatest catenation?**
(A) Silicon (B) Carbon (C) Tin (D) Lead

**5. Aluminium reacting with NaOH shows it is:**
(A) Acidic (B) Basic (C) Amphoteric (D) Neutral

**6. Borax formula is:**
(A) $H_3BO_3$ (B) $Na_2B_4O_7 \cdot 10H_2O$ (C) $B_2O_3$ (D) $BF_3$

**7. Which is used as a semiconductor?**
(A) Lead (B) Silicon (C) Boron (D) Thallium

**8. The most stable oxidation state of lead is:**
(A) +4 (B) +3 (C) +2 (D) +1

**9. Graphite conducts electricity because it has:**
(A) $sp^3$ carbons (B) free (delocalised) electrons (C) ionic bonds (D) metallic lattice

**10. Carbon monoxide acts as a:**
(A) Oxidising agent (B) Reducing agent (C) Acid (D) Base

**MCQ Answer Key**

**1-B 2-D 3-B 4-B 5-C 6-B 7-B 8-C 9-B 10-B**

## 11. Quick Revision / Summary

- IIIA (B,Al,Ga,In,Tl) = $ns^2np^1$, state +3; IVA (C,Si,Ge,Sn,Pb) = $ns^2np^2$, state +4.
- Metallic character increases down each group; top members are non-metals/metalloids.
- Inert pair effect → lower state stable at bottom ($Tl^+$, $Pb^{2+}$).
- Carbon: catenation + allotropy (diamond $sp^3$ hard insulator; graphite $sp^2$ soft conductor).
- Aluminium is amphoteric; thermite = $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$.
- Borax = $Na_2B_4O_7 \cdot 10H_2O$; boric acid = $H_3BO_3$; silica = $SiO_2$.
- Si and Ge are semiconductors used in electronics.

## 12. Exam Tips

**Teacher's Note**

Inert pair effect is a favourite exam topic — always link it to 'lower oxidation state stable at the bottom'.

For diamond vs graphite, structure explains every property — always mention hybridisation and free electrons.

Remember amphoteric examples: Al, $Al_2O_3$, Be, Zn, Pb — reacting with BOTH acid and

base.
Learn the three aluminium reactions (acid, alkali, thermite) with balanced equations.
Do not confuse borax ($Na_2B_4O_7 \cdot 10H_2O$) with boric acid ($H_3BO_3$).

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# CHAPTER 4
# Group VA and Group VIA Elements

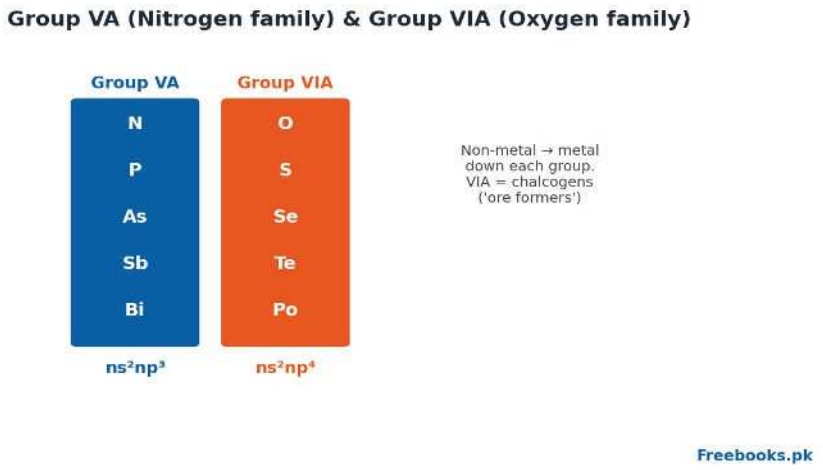


*Figure 4.1 — Group VA (nitrogen family) and Group VIA (oxygen family / chalcogens).*

# 1. Chapter Overview

This chapter covers Group VA — the nitrogen family (N, P, As, Sb, Bi) with outer configuration $ns^2\ np^3$ — and Group VIA — the oxygen family or chalcogens (O, S, Se, Te, Po) with $ns^2\ np^4$. Both groups begin with a typical non-metal at the top and become metallic towards the bottom. They contain elements essential to life and industry: nitrogen and phosphorus are the basis of fertilizers, while oxygen and sulphur are central to breathing, combustion and the manufacture of sulphuric acid — the 'king of chemicals'.

Two of the most important industrial processes in all of chemistry belong to this chapter: the Haber process for making ammonia and the Contact process for making sulphuric acid.

# 2. Learning Objectives

- List the members and configurations of Groups VA and VIA.
- Describe how metallic character and properties change down each group.
- Explain the manufacture of ammonia by the Haber process and its uses.
- Describe the oxides and oxoacids of nitrogen and sulphur.
- Explain the manufacture of sulphuric acid by the Contact process.
- Describe the allotropy of sulphur.
- Appreciate the importance of these elements in fertilizers and industry.

# 3. Key Concepts

## 3.1 The Two Families

| Group | Name | Members |
|---|---|---|
| VA ($ns^2np^3$) | Nitrogen family (pnictogens) | N, P, As, Sb, Bi |
| VIA ($ns^2np^4$) | Oxygen family (chalcogens) | O, S, Se, Te, Po |

In Group VA, nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids, and bismuth is a metal. In Group VIA, oxygen, sulphur and selenium are non-metals, tellurium is a metalloid and polonium is a radioactive metal. In both groups metallic character increases down the group while the acidic strength of the oxides decreases.

> **Memory Trick**
> **VA order:** “Nanhe Papa Aaye Sab Bimar” → N, P, As, Sb, Bi.
> **VIA order:** “Oye Sona Send Tera Polo” → O, S, Se, Te, Po.

## 3.2 Nitrogen and the Haber Process

Nitrogen makes up about 78% of the air but is very unreactive because of the strong triple bond (N≡N) in the $N_2$ molecule. It is 'fixed' into useful compounds mainly as ammonia. Ammonia ($NH_3$)

is manufactured industrially by the Haber process, in which nitrogen and hydrogen combine over an iron catalyst under high pressure and moderate temperature:

### Haber Process

**Reaction:** $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (reversible, exothermic)

**Conditions:** ~200 atm pressure, ~450 °C, finely divided iron catalyst.

**Le Chatelier:** high pressure and moderate temperature favour a good yield; unreacted gases are recycled.

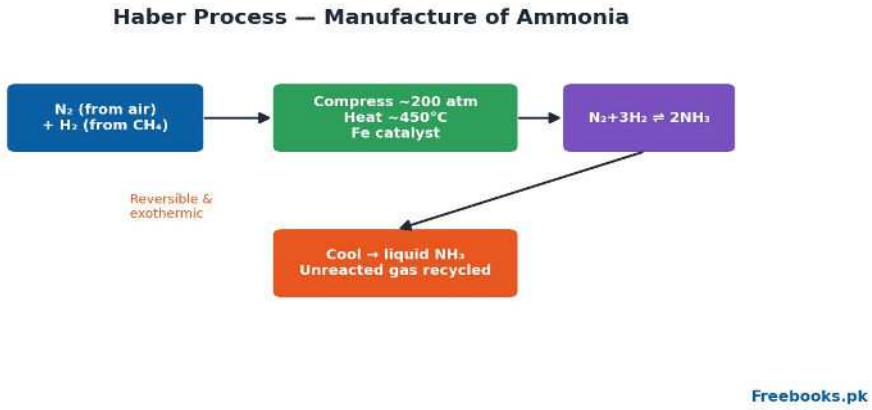


*Figure 4.2 — The Haber process for ammonia.*

Ammonia is used to make nitric acid, urea and ammonium fertilizers, and in the manufacture of nylon and explosives.

### Teacher's Note

Students often ask why not use a very high temperature. Remind them the forward reaction is exothermic, so too high a temperature lowers the yield — 450 °C is a compromise between speed and yield.

## 3.3 Oxides and Oxoacids of Nitrogen

Nitrogen forms several oxides in which it shows oxidation states from +1 to +5, for example nitrous oxide ($N_2O$, 'laughing gas'), nitric oxide (NO) and nitrogen dioxide ($NO_2$, a brown gas). Its most important oxoacid is nitric acid ($HNO_3$), a strong acid and powerful oxidising agent made industrially by the Ostwald process (catalytic oxidation of ammonia).

## 3.4 The Oxygen Family and Allotropy of Sulphur

Oxygen is the most abundant element in the earth's crust and is essential for respiration and combustion. Sulphur is a yellow non-metal that shows allotropy: the two crystalline forms are rhombic (α) sulphur, stable at room temperature, and monoclinic (β) sulphur, stable above 96 °C. Both are made of $S_8$ puckered-ring molecules.

### 3.5 Sulphuric Acid and the Contact Process

Sulphuric acid ($H_2SO_4$) is called the 'king of chemicals' because it is used in so many industries. It is manufactured by the Contact process in three main stages: burning sulphur to sulphur dioxide, oxidising $SO_2$ to $SO_3$ over a vanadium(V) oxide catalyst, and absorbing $SO_3$ in concentrated sulphuric acid to form oleum, which is then diluted.

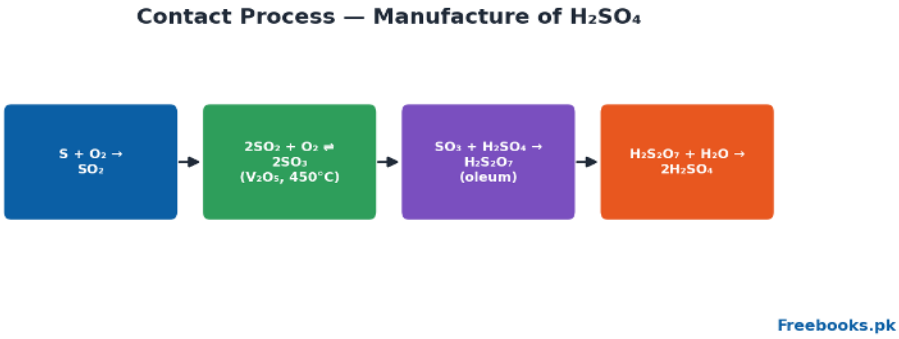


*Figure 4.3 — The Contact process for sulphuric acid.*

**Contact Process — Key Reactions**

**1.** $S + O_2 \rightarrow SO_2$

**2.** $2SO_2 + O_2 \rightleftharpoons 2SO_3$ ($V_2O_5$ catalyst, ~450 °C)

**3.** $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (oleum)

**4.** $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

Concentrated sulphuric acid is a strong acid, a dehydrating agent (it removes water, e.g. it chars sugar) and an oxidising agent. It is used to make fertilizers, detergents, paints, batteries and many other chemicals.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Nitrogen fixation | The conversion of atmospheric $N_2$ into useful nitrogen compounds such as ammonia. |
| Haber process | Industrial manufacture of ammonia from $N_2$ and $H_2$ over an iron catalyst. |
| Contact process | Industrial manufacture of sulphuric acid using a $V_2O_5$ catalyst. |
| Allotropy | Existence of an element in two or more physical forms (e.g. rhombic and monoclinic sulphur). |
| Oleum | Fuming sulphuric acid, $H_2S_2O_7$, formed when $SO_3$ dissolves in $H_2SO_4$. |
| Dehydrating agent | A substance that removes water/hydrogen and oxygen from a compound (e.g. conc. $H_2SO_4$). |

## 5. Formulas / Rules

### Must-Know Facts

**Group VA:** $ns^2np^3$ (N,P,As,Sb,Bi). Group VIA: $ns^2np^4$ (O,S,Se,Te,Po).
**Ammonia:** $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (Haber; Fe, 200 atm, 450 °C).
**Sulphuric acid:** Contact process; catalyst $V_2O_5$.
**Sulphur allotropes:** rhombic (stable <96 °C) and monoclinic (stable >96 °C), both $S_8$.
**Conc. $H_2SO_4$ =** strong acid + dehydrating agent + oxidising agent.

## 6. Diagrams / Illustrations

Key process diagrams for quick revision:

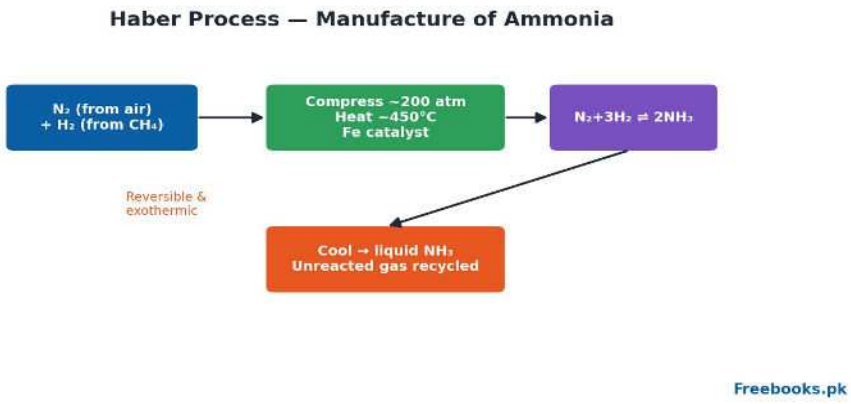


*Diagram 1 — Haber process.*

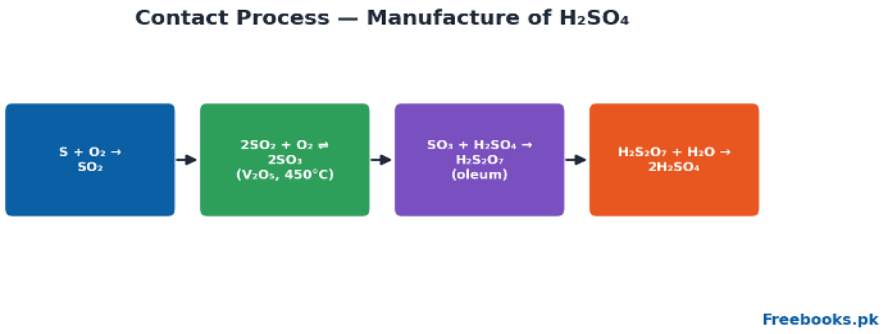


*Diagram 2 — Contact process.*

## 7. Solved Examples

**Example 1 — Le Chatelier in the Haber process**
**Q:** Why is high pressure used in the Haber process?

**Solution:** The forward reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ decreases the number of gas molecules (4 → 2). By Le Chatelier's principle, high pressure shifts the equilibrium toward the side with fewer molecules, increasing the yield of ammonia.

**Example 2 — Role of conc. $H_2SO_4$**

**Q:** What happens when concentrated sulphuric acid is added to sugar?

**Solution:** It acts as a dehydrating agent, removing hydrogen and oxygen (as water) from the sugar and leaving a black mass of carbon. This shows the strong dehydrating property of conc. $H_2SO_4$.

**Example 3 — Identifying a gas**

**Q:** A brown gas is evolved when copper reacts with concentrated nitric acid. Name it.

**Solution:** The brown gas is nitrogen dioxide ($NO_2$), produced because concentrated $HNO_3$ is a strong oxidising agent.

## 8. Short Questions

**Q1. Why is nitrogen gas so unreactive?**
**Ans.** Because the two nitrogen atoms are held by a very strong triple bond (N≡N) that is hard to break.

**Q2. State the conditions for the Haber process.**
**Ans.** About 200 atm pressure, 450 °C, and a finely divided iron catalyst.

**Q3. Why is a moderate (not very high) temperature used in the Haber process?**
**Ans.** The forward reaction is exothermic, so too high a temperature reduces the yield; 450 °C balances rate and yield.

**Q4. What is oleum?**
**Ans.** Fuming sulphuric acid, $H_2S_2O_7$, formed when $SO_3$ dissolves in concentrated $H_2SO_4$.

**Q5. Name the catalyst used in the Contact process.**
**Ans.** Vanadium(V) oxide, $V_2O_5$.

**Q6. What are the two crystalline allotropes of sulphur?**
**Ans.** Rhombic (α) sulphur and monoclinic (β) sulphur.

**Q7. Give three properties of concentrated sulphuric acid.**
**Ans.** It is a strong acid, a dehydrating agent and an oxidising agent.

**Q8. Why is sulphuric acid called the king of chemicals?**
**Ans.** Because it is used in so many industries — fertilizers, detergents, paints, batteries and other chemicals.

## 9. Long Questions

**Q1. Describe the manufacture of ammonia by the Haber process.**

Ammonia is manufactured by combining nitrogen (from the fractional distillation of liquid air) with hydrogen (obtained from natural gas). The purified gases are mixed in a 1:3 ratio, compressed to about 200 atmospheres, and passed over a finely divided iron catalyst at about 450 °C, where

they combine according to the reversible, exothermic reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$. Because the forward reaction reduces the number of gas molecules and gives out heat, a high pressure and a moderate temperature give the best practical yield; a catalyst is used to speed up the reaction without being consumed. The mixture leaving the converter is cooled so that ammonia liquefies and is removed, while the unreacted nitrogen and hydrogen are recycled. Ammonia is then used to make nitric acid, urea and ammonium fertilizers.

**Q2. Describe the manufacture of sulphuric acid by the Contact process.**

In the Contact process, sulphur (or a sulphide ore) is first burned in air to give sulphur dioxide: $S + O_2 \rightarrow SO_2$. The purified, dried sulphur dioxide is then mixed with more air and passed over a vanadium(V) oxide catalyst at about 450 °C, where it is oxidised to sulphur trioxide in a reversible, exothermic reaction: $2SO_2 + O_2 \rightleftharpoons 2SO_3$. Because the reaction gives out heat and reduces the number of gas molecules, a moderate temperature and ordinary pressure are used. The sulphur trioxide is not dissolved directly in water (which would form a dangerous mist) but is absorbed in concentrated sulphuric acid to form oleum, $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$, which is then carefully diluted with water to give sulphuric acid of the required concentration: $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$.

**Q3. Discuss the properties and uses of concentrated sulphuric acid.**

Concentrated sulphuric acid shows three important kinds of behaviour. As a strong acid it reacts with metals, bases and carbonates to form sulphates. As a powerful dehydrating agent it removes the elements of water from other substances — for example it chars sugar and paper to carbon and is used to dry gases. As an oxidising agent, especially when hot and concentrated, it oxidises metals such as copper, itself being reduced to sulphur dioxide. Because of this versatility it is one of the most widely used industrial chemicals, employed in making fertilizers (superphosphate, ammonium sulphate), detergents, dyes, paints, explosives, and in car batteries and metal pickling.

## 10. Multiple Choice Questions (MCQs)

**1. The outer configuration of Group VA elements is:**
(A) $ns^2np^2$ (B) $ns^2np^3$ (C) $ns^2np^4$ (D) $ns^2np^5$

**2. The catalyst used in the Haber process is:**
(A) $V_2O_5$ (B) Fe (C) Pt (D) Ni

**3. The catalyst used in the Contact process is:**
(A) Fe (B) Pt (C) $V_2O_5$ (D) $MnO_2$

**4. Which gas is 'laughing gas'?**
(A) NO (B) $NO_2$ (C) $N_2O$ (D) $N_2O_5$

**5. Oleum is:**
(A) $H_2SO_4$ (B) $H_2SO_3$ (C) $H_2S_2O_7$ (D) $SO_3$

**6. Which is a brown gas?**
(A) $N_2O$ (B) NO (C) $NO_2$ (D) $NH_3$

**7. Sulphur exists mainly as molecules of:**
(A) $S_2$ (B) $S_4$ (C) $S_6$ (D) $S_8$

**8. Chalcogens belong to group:**
(A) IVA (B) VA (C) VIA (D) VIIA

**9. Concentrated $H_2SO_4$ chars sugar because it acts as a:**

(A) Reducing agent (B) Dehydrating agent (C) Base (D) Catalyst

**10. Which element is a radioactive metal of Group VIA?**

(A) Se (B) Te (C) Po (D) S

**MCQ Answer Key**

**1-B 2-B 3-C 4-C 5-C 6-C 7-D 8-C 9-B 10-C**

## 11. Quick Revision / Summary

- VA = $ns^2np^3$ (N,P,As,Sb,Bi); VIA = $ns^2np^4$ (O,S,Se,Te,Po); metallic character increases down.
- Ammonia: Haber process, $N_2+3H_2 \rightleftharpoons 2NH_3$, Fe catalyst, 200 atm, 450 °C.
- Sulphuric acid: Contact process, $V_2O_5$ catalyst; $SO_3$ absorbed as oleum then diluted.
- Sulphur allotropes: rhombic (<96 °C) and monoclinic (>96 °C), both $S_8$.
- Conc. $H_2SO_4$ = strong acid + dehydrating + oxidising agent.
- Nitrogen oxides show states +1 to +5; $NO_2$ is brown.

## 12. Exam Tips

**Teacher's Note**

Learn the Haber and Contact process conditions and equations perfectly — they appear almost every year.

Always justify the chosen conditions with Le Chatelier's principle (pressure, temperature).

Remember the catalysts: Fe for Haber, $V_2O_5$ for Contact — a common MCQ trap.

For conc. $H_2SO_4$, name its three roles: acid, dehydrating, oxidising — with one example each.

Note that $SO_3$ is absorbed in $H_2SO_4$ (not water) to avoid an acid mist.

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# CHAPTER 5
# The Halogens and Noble Gases

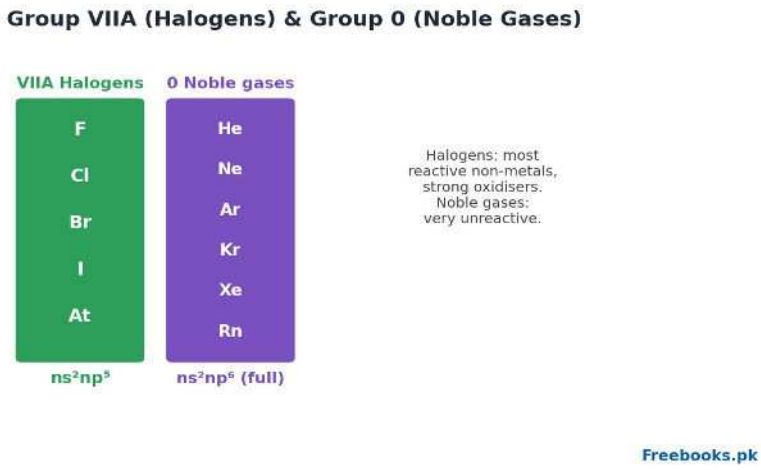


*Figure 5.1 — Group VIIA (halogens) and Group 0 (noble gases).*

# 1. Chapter Overview

This chapter deals with the last two families of the p-block: the halogens of Group VIIA (F, Cl, Br, I, At) and the noble gases of Group 0 / VIIIA (He, Ne, Ar, Kr, Xe, Rn). The two groups are almost opposites. Halogens have the configuration $ns^2\ np^5$ — just one electron short of a full shell — so they are the most reactive non-metals and powerful oxidising agents. Noble gases have completely filled shells ($ns^2\ np^6$, or $1s^2$ for He), which makes them extremely stable and unreactive.

Even so, the very unreactive noble gases surprised chemists when xenon was found to form real compounds. In this chapter we study the properties and trends of the halogens, their important compounds, and the uses and chemistry of the noble gases.

# 2. Learning Objectives

- List the halogens and noble gases with their electronic configurations.
- Explain why halogens are strong oxidising agents and how their reactivity changes down the group.
- Describe the trend in acid strength of the hydrogen halides.
- Explain the bleaching and germicidal action of chlorine.
- Explain why noble gases are unreactive and yet xenon can form compounds.
- State the important uses of the halogens and the noble gases.

# 3. Key Concepts

## 3.1 The Halogens (Group VIIA)

The halogens ('salt-formers') exist as diatomic molecules ($F_2$, $Cl_2$, $Br_2$, $I_2$). At room temperature fluorine and chlorine are gases, bromine is a liquid and iodine is a solid — showing that melting and boiling points increase down the group. Because each atom needs just one more electron to complete its octet, halogens are the most reactive non-metals and strong oxidising agents; they gain an electron to form halide ions ($X^-$) or share one to form a covalent bond.

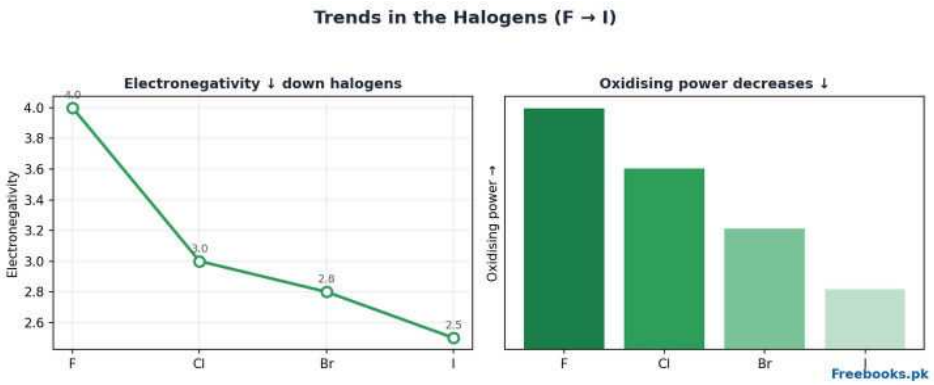


*Figure 5.2 — Down the halogens, electronegativity and oxidising power decrease.*

**Memory Trick**

**Reactivity/oxidising power** decreases down: F > Cl > Br > I. 'Fluorine is the Fiercest.'

**States at room temp:** F, Cl = gas; Br = liquid; I = solid (down the group they get 'heavier').

## 3.2 Oxidising Power and Displacement

Because fluorine and chlorine attract electrons most strongly, a higher halogen can displace a lower one from its salt. For example, chlorine displaces bromine from potassium bromide: $Cl_2$ + 2KBr → 2KCl + $Br_2$. This confirms the order of oxidising power F > Cl > Br > I.

## 3.3 Hydrogen Halides

The halogens form hydrogen halides (HF, HCl, HBr, HI), which dissolve in water to give acids. Their acid strength increases down the group (HF < HCl < HBr < HI) because the H–X bond becomes weaker and easier to break as the halogen gets larger. HF is the weakest because of its strong hydrogen bonding and strong H–F bond, while HI is the strongest acid of the four.

**Teacher's Note**

A common confusion: HF is the weakest ACID but has the strongest bond and hydrogen bonding. Emphasise that acid strength depends on how easily the H–X bond breaks in water, not on electronegativity.

## 3.4 Chlorine — Bleaching and Water Treatment

Chlorine is an important industrial chemical. With water it forms a mixture of hydrochloric and hypochlorous acids; the hypochlorous acid (HOCl) releases nascent oxygen, which bleaches coloured materials and kills germs. This is why chlorine (and bleaching powder) is used to bleach cloth and paper and to disinfect drinking water and swimming pools.

## 3.5 The Noble Gases (Group 0)

The noble gases have completely filled outer shells, giving them very high ionization energies and almost zero electron affinity, so they are chemically very unreactive (inert) and exist as single (monatomic) atoms. For a long time they were thought to form no compounds at all.


*Figure 5.3 — Uses of noble gases and the xenon fluorides.*

### 3.6 Compounds of Xenon

In 1962 it was discovered that xenon — the largest, most easily ionised of the common noble gases — can react with the strongly electronegative fluorine to form real compounds: xenon difluoride ($XeF_2$), xenon tetrafluoride ($XeF_4$) and xenon hexafluoride ($XeF_6$). This is possible because xenon's outer electrons are far from the nucleus and relatively easy to involve in bonding. Helium, neon and argon are still not known to form stable compounds.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Halogens | Group VIIA non-metals (F, Cl, Br, I, At) that form salts with metals. |
| Noble gases | Group 0 elements with completely filled shells and very low reactivity. |
| Oxidising agent | A species that gains electrons and oxidises another substance. |
| Displacement reaction | A reaction in which a more reactive halogen replaces a less reactive one from its salt. |
| Nascent oxygen | Freshly formed, very reactive atomic oxygen responsible for bleaching. |
| Monatomic | Existing as single atoms (as the noble gases do). |

## 5. Formulas / Rules

**Must-Know Facts**

**Halogens:** $ns^2np^5$, diatomic $X_2$, strong oxidisers; power F > Cl > Br > I.

**States:** $F_2$, $Cl_2$ gas; $Br_2$ liquid; $I_2$ solid.

**Acid strength of HX:** HF < HCl < HBr < HI (increases down).

**Displacement:** $Cl_2 + 2KBr \rightarrow 2KCl + Br_2$.

**Xenon compounds:** $XeF_2$, $XeF_4$, $XeF_6$.

## 6. Diagrams / Illustrations

Key diagrams for revision:

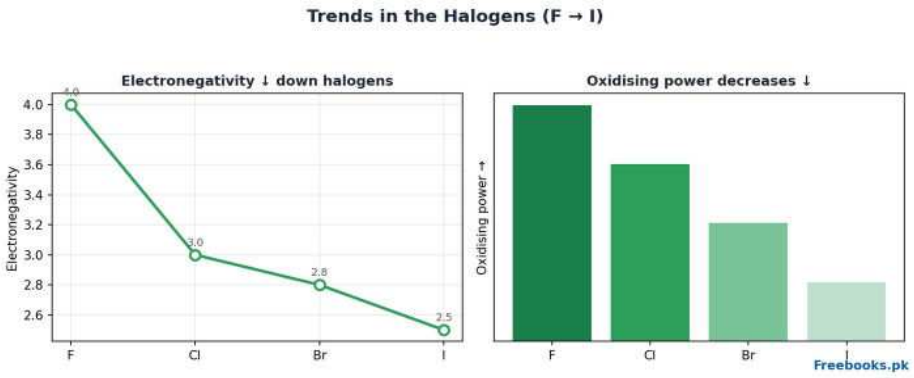

*Diagram 1 — Halogen trends (F → I).*


*Diagram 2 — Noble gas uses and xenon fluorides.*

## 7. Solved Examples

**Example 1 — Displacement**

**Q:** Will bromine displace chlorine from sodium chloride? Explain.

**Solution:** No. Chlorine is a stronger oxidising agent than bromine, so bromine cannot displace it. The reverse happens: chlorine displaces bromine from bromides.

**Example 2 — Acid strength**

**Q:** Arrange HF, HCl, HBr and HI in order of increasing acid strength.

**Solution:** HF < HCl < HBr < HI. Down the group the H–X bond becomes weaker and breaks more easily in water, increasing acid strength.

**Example 3 — Xenon**

**Q:** Why can xenon form compounds while helium cannot?

**Solution:** Xenon is much larger and its outer electrons are far from the nucleus with a low ionization energy, so they can take part in bonding with fluorine. Helium's two electrons are held very tightly, so it stays inert.

## 8. Short Questions

**Q1. Why are halogens strong oxidising agents?**
**Ans.** Each atom needs only one electron to complete its octet, so it strongly attracts and gains electrons, oxidising others.

**Q2. Why does halogen reactivity decrease down the group?**
**Ans.** Atomic size increases and electronegativity decreases, so the tendency to gain an electron falls.

**Q3. Which is the strongest acid: HF or HI?**
**Ans.** HI, because its H–X bond is the weakest and breaks most easily in water.

**Q4. Why is HF a weak acid?**
**Ans.** Because of its strong H–F bond and strong hydrogen bonding, which resist ionization.

**Q5. How does chlorine bleach?**
**Ans.** In water it forms hypochlorous acid, which releases nascent oxygen that oxidises (bleaches) coloured matter.

**Q6. Why are noble gases unreactive?**
**Ans.** They have completely filled outer shells, very high ionization energies and almost zero electron affinity.

**Q7. Name three compounds of xenon.**
**Ans.** $XeF_2$, $XeF_4$ and $XeF_6$.

**Q8. Give one use each of helium and neon.**
**Ans.** Helium fills balloons and is used in diving gas; neon is used in advertising (neon) signs.

## 9. Long Questions

**Q1. Describe the general characteristics and trends of the halogens.**
The halogens are the non-metals of Group VIIA, with the outer configuration $ns^2\ np^5$. They exist as diatomic molecules and, because each atom needs only one more electron to complete its octet, they are the most reactive non-metals and powerful oxidising agents. Going down the group, atomic size increases and electronegativity decreases, so both reactivity and oxidising power fall in the order F > Cl > Br > I; a higher halogen can therefore displace a lower one from its salt. Their physical states change from gases ($F_2$, $Cl_2$) through a liquid ($Br_2$) to a solid ($I_2$) as melting and boiling points rise down the group. The hydrogen halides they form are acids whose strength increases down the group (HF < HCl < HBr < HI) as the H–X bond weakens. Because of their reactivity, halogens are never found free in nature.

**Q2. Why are the noble gases inert, and how does xenon form compounds?**
The noble gases are chemically inert because their outermost shells are completely filled (helium has $1s^2$, the others $ns^2\ np^6$). This stable arrangement gives them very high ionization energies and almost zero electron affinity, so they neither lose, gain nor share electrons easily, and they exist as single atoms. For many years they were believed to form no compounds. However, xenon is the largest of the common noble gases and its outer electrons are far from the nucleus with a comparatively low ionization energy. When combined with the extremely electronegative element fluorine, xenon's electrons can be drawn into bonds, forming real compounds such as $XeF_2$, $XeF_4$ and $XeF_6$. The lighter noble gases (He, Ne, Ar) hold their electrons too tightly and remain inert.

**Q3. Discuss the uses of the halogens and the noble gases.**
The halogens and their compounds are widely used. Fluorine compounds are used in toothpaste (fluoride), non-stick coatings and refrigerants; chlorine is used to bleach cloth and paper, to disinfect drinking water and swimming pools, and to make PVC, solvents and bleaching powder; bromine is used in photographic chemicals and flame retardants; and iodine is used as an antiseptic (tincture of iodine) and in medicines. The noble gases are valued for their inertness and light-giving properties: helium fills balloons and airships and is used in deep-sea diving gas and as a coolant; neon glows in advertising signs; argon provides an inert atmosphere in light bulbs and in welding; and krypton and xenon are used in high-power and flash lamps.

## 10. Multiple Choice Questions (MCQs)

**1. The outer configuration of halogens is:**
(A) $ns^2np^4$ (B) $ns^2np^5$ (C) $ns^2np^6$ (D) $ns^2np^3$

**2. The strongest oxidising agent among halogens is:**
(A) Cl (B) Br (C) I (D) F

**3. Which halogen is a liquid at room temperature?**
(A) $F_2$ (B) $Cl_2$ (C) $Br_2$ (D) $I_2$

**4. The strongest acid is:**
(A) HF (B) HCl (C) HBr (D) HI

**5. Chlorine bleaches by releasing:**
(A) Hydrogen (B) Nascent oxygen (C) Chlorine gas (D) Water

**6. Noble gases are unreactive because they have:**
(A) One valence electron (B) Filled outer shells (C) Empty shells (D) High electron affinity

**7. Which noble gas forms fluorides?**
(A) He (B) Ne (C) Ar (D) Xe

**8. Which gas is used in advertising signs?**
(A) He (B) Ne (C) Ar (D) Kr

**9. $Cl_2 + 2KBr \rightarrow 2KCl + Br_2$ is a:**
(A) Neutralisation (B) Displacement (C) Addition (D) Combustion

**10. Noble gases exist as:**
(A) Diatomic molecules (B) Monatomic atoms (C) Ions (D) Polymers

**MCQ Answer Key**

**1-B 2-D 3-C 4-D 5-B 6-B 7-D 8-B 9-B 10-B**

## 11. Quick Revision / Summary

- Halogens (F,Cl,Br,I,At) = $ns^2np^5$, diatomic, strongest non-metals & oxidisers.
- Oxidising power & electronegativity decrease down: F > Cl > Br > I.
- States: F,Cl gas; Br liquid; I solid. HX acid strength: HF < HCl < HBr < HI.
- Chlorine bleaches/disinfects via nascent oxygen from HOCl.
- Noble gases = filled shells, inert, monatomic; used for their inertness.
- Xenon forms $XeF_2$, $XeF_4$, $XeF_6$; He, Ne, Ar remain inert.

## 12. Exam Tips

**Teacher's Note**

Remember the trend direction: reactivity/oxidising power decrease down halogens but acid strength of HX increases down.

HF weakest acid, HI strongest — a very common MCQ.

Learn one displacement equation ($Cl_2 + 2KBr \rightarrow 2KCl + Br_2$) to prove the oxidising-power order.

Explain noble-gas inertness with 'completely filled shell, high IE'.

Only xenon (large, low IE) forms fluorides — He, Ne, Ar do not.

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# CHAPTER 6
# Transition Elements

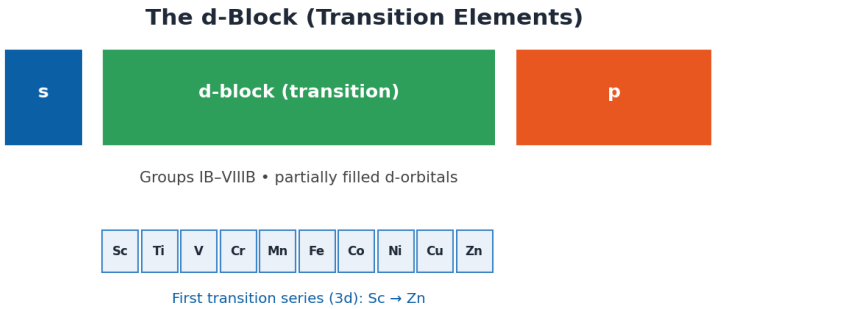


*Figure 6.1 — The d-block transition elements sit between the s- and p-blocks.*

# 1. Chapter Overview

The transition elements are the d-block metals that lie in the middle of the periodic table, between Groups IIA and IIIA. They are defined as elements whose atoms or common ions have partially filled d-orbitals. The first transition series runs from scandium to zinc (Sc → Zn). These metals are the 'workhorses' of chemistry and industry: iron, copper, chromium, nickel and their alloys build our machines, tools and coins, and their compounds give the bright colours seen in gemstones, paints and laboratory solutions.

The transition metals share a set of striking properties — variable oxidation states, coloured ions, catalytic activity, magnetic behaviour and the formation of complex (coordination) compounds — all of which come from their partly filled d-orbitals.

# 2. Learning Objectives

- Define transition elements and give the first transition series.
- Write the electronic configurations of first-series transition metals and their ions.
- Explain why transition metals show variable oxidation states.
- Explain why their ions are coloured and many are paramagnetic.
- Explain their catalytic activity and the formation of complex ions.
- Define ligand, coordination number and complex, with examples.
- State important uses and alloys of transition metals.

# 3. Key Concepts

## 3.1 What Makes an Element a Transition Element?

A transition element is one whose atom or a stable ion has an incompletely filled d-subshell. On this strict definition, zinc is not a true transition metal because its ion $Zn^{2+}$ has a completely filled $3d^{10}$ configuration; it is called a d-block element but not a typical transition metal. The first (3d) series is: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn.

> **Memory Trick**
> **First series:** “Scientist Ti V Cr Mn Fe Co Ni Cu Zinc” — Sc Ti V Cr Mn Fe Co Ni Cu Zn.
> **Odd ones out:** Cr = $[Ar]3d^5 4s^1$ and Cu = $[Ar]3d^{10}4s^1$ (half-filled / filled d is extra stable).

## 3.2 General Characteristics

**Metallic and hard.** They are hard, strong, high-melting metals with high densities because both 3d and 4s electrons take part in strong metallic bonding.

**Variable oxidation states.** Because the 3d and 4s energy levels are very close, a variable number of electrons can be used in bonding, so most transition metals show several oxidation states (e.g. iron as +2 and +3; manganese from +2 up to +7).

**Coloured ions.** Most transition-metal ions are coloured. When light falls on them, electrons jump between split d-orbitals (d–d transitions), absorbing part of the visible light; the colour we see is the remaining light. For example $Cu^{2+}$ is blue and $MnO_4^-$ is purple.

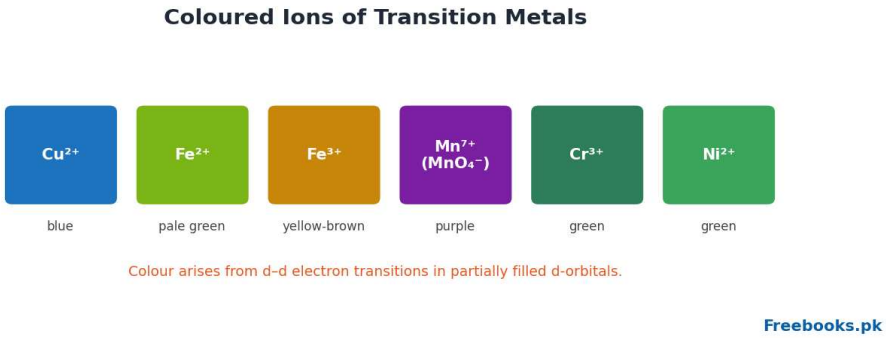


*Figure 6.2 — Characteristic colours of some transition-metal ions.*

**Paramagnetism.** Ions with unpaired d-electrons are attracted by a magnetic field (paramagnetic); the more unpaired electrons, the stronger the effect.

**Catalytic activity.** Transition metals and their compounds are excellent catalysts (e.g. Fe in the Haber process, $V_2O_5$ in the Contact process, Ni in hydrogenation) because they offer variable oxidation states and surfaces on which reactants can adsorb.

## 3.3 Complex (Coordination) Compounds

A special feature of transition metals is their ability to form complex ions, in which a central metal ion is surrounded by a number of molecules or ions called ligands, each donating a lone pair of electrons to the metal (a coordinate/dative bond). The number of ligand atoms directly bonded to the metal is the coordination number.

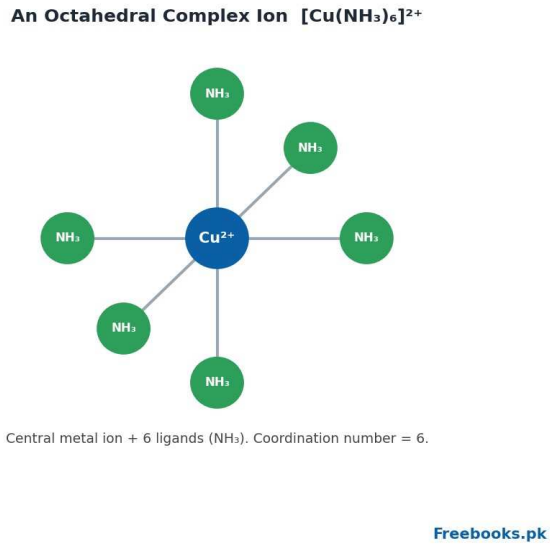


*Figure 6.3 — An octahedral complex ion, $[Cu(NH_3)_6]^{2+}$ (coordination number 6).*

### Complex Ion Vocabulary

**Ligand:** a molecule or ion (e.g. $NH_3$, $H_2O$, $CN^-$, $Cl^-$) that donates a lone pair to the metal.
**Coordination number:** the number of ligand atoms bonded to the central metal ion (commonly 4 or 6).
**Examples:** $[Cu(NH_3)_4]^{2+}$ (deep blue), $[Fe(CN)_6]^{3-}$, $[Ag(NH_3)_2]^+$.

**Teacher's Note**
Ask students to always identify three things in any complex: the central metal, the ligands, and the coordination number. This makes naming and understanding complexes much easier.

### 3.4 Alloys and Uses

Transition metals are widely used both as pure metals and as alloys. Iron is turned into steel (with carbon) and stainless steel (with chromium and nickel); copper is used in wiring and, with zinc, forms brass; chromium and nickel are used for electroplating and corrosion-resistant coatings; and silver, gold and platinum are prized in jewellery, electronics and as catalysts.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Transition element | An element whose atom or stable ion has a partially filled d-subshell. |
| Ligand | A molecule or ion that donates a lone pair to a central metal ion in a complex. |
| Coordination number | The number of ligand atoms directly bonded to the central metal ion. |
| Complex ion | A central metal ion bonded to a definite number of ligands by coordinate bonds. |
| Paramagnetism | Attraction to a magnetic field due to unpaired electrons. |
| Catalyst | A substance that speeds up a reaction without being consumed. |

## 5. Formulas / Rules

**Must-Know Facts**
**First transition series:** Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn (3d).
**Anomalous configs:** Cr = $3d^5 4s^1$, Cu = $3d^{10} 4s^1$.
**Colour cause:** d–d electronic transitions in partly filled d-orbitals.
**Key catalysts:** Fe (Haber), $V_2O_5$ (Contact), Ni (hydrogenation), Pt.
**Common coordination numbers:** 4 (tetrahedral/square planar) and 6 (octahedral).

## 6. Diagrams / Illustrations

Key diagrams for revision:

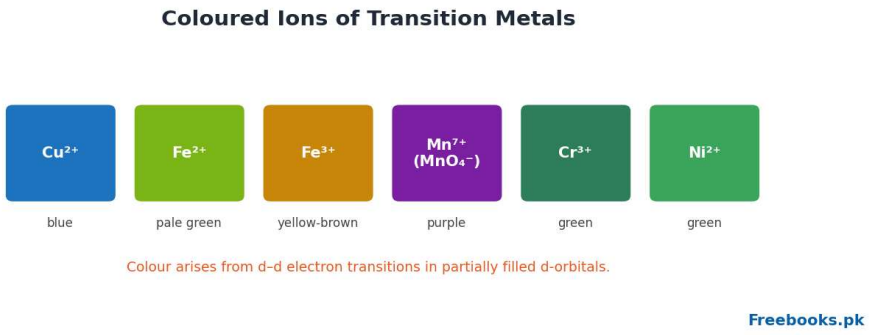


*Diagram 1 — Coloured transition-metal ions.*

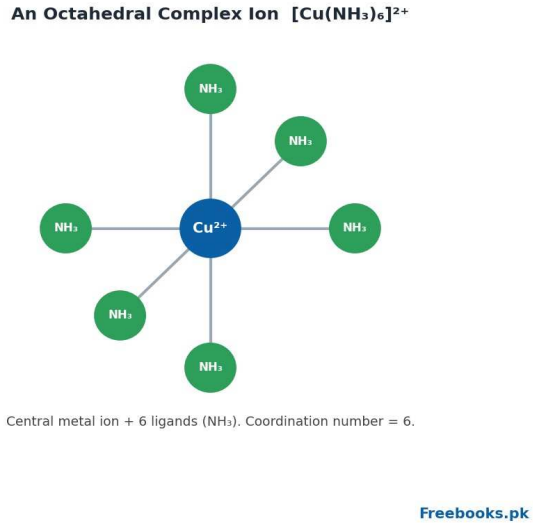


*Diagram 2 — Octahedral complex ion.*

## 7. Solved Examples

### Example 1 — Variable oxidation states

**Q:** Give two oxidation states of iron and one compound of each.

**Solution:** Iron shows +2 (as in $FeSO_4$, iron(II) sulphate) and +3 (as in $FeCl_3$, iron(III) chloride). This is possible because the 3d and 4s electrons have similar energies.

### Example 2 — Identifying a complex

**Q:** In $[Cu(NH_3)_4]^{2+}$, name the central ion, the ligand and the coordination number.

**Solution:** Central ion = $Cu^{2+}$; ligand = $NH_3$ (ammonia); coordination number = 4.

### Example 3 — Colour

**Q:** Why is the $Zn^{2+}$ ion colourless while $Cu^{2+}$ is blue?

**Solution:** $Zn^{2+}$ has a completely filled $3d^{10}$ shell, so no d–d transition is possible and it is colourless. $Cu^{2+}$ has a partly filled d-shell, so d–d transitions absorb light and it appears blue.

## 8. Short Questions

**Q1. Define a transition element.**
**Ans.** An element whose atom or a stable ion has a partially filled d-subshell.

**Q2. Why is zinc not a typical transition metal?**
**Ans.** Its ion $Zn^{2+}$ has a completely filled $3d^{10}$ configuration, so it lacks a partly filled d-shell.

**Q3. Why do transition metals show variable oxidation states?**
**Ans.** Because their 3d and 4s energy levels are close, so different numbers of electrons can be used in bonding.

**Q4. Why are transition-metal ions coloured?**
**Ans.** Because electrons undergo d–d transitions in partly filled d-orbitals, absorbing part of visible light.

**Q5. What is a ligand?**
**Ans.** A molecule or ion that donates a lone pair of electrons to a central metal ion in a complex.

**Q6. Define coordination number.**
**Ans.** The number of ligand atoms directly bonded to the central metal ion.

**Q7. Give two transition metals used as catalysts.**
**Ans.** Iron (Haber process) and nickel (hydrogenation of oils).

**Q8. Why are many transition-metal ions paramagnetic?**
**Ans.** Because they contain unpaired d-electrons that are attracted to a magnetic field.

## 9. Long Questions

**Q1. Describe the general characteristic properties of the transition elements.**

The transition elements are d-block metals with partially filled d-orbitals, and this single feature explains their special properties. They are hard, dense, high-melting metals because both their 3d and 4s electrons take part in strong metallic bonding. Because these two energy levels are very close, a variable number of electrons can be used in bonding, so the metals show several oxidation states (for example iron +2 and +3, manganese +2 to +7). Their ions are usually coloured, because electrons move between split d-orbitals (d–d transitions) and absorb part of the visible light. Ions with unpaired d-electrons are paramagnetic. The metals and their compounds are excellent catalysts, offering variable oxidation states and active surfaces. Finally, their small, highly charged ions readily accept lone pairs from ligands to form stable complex (coordination) compounds.

**Q2. What are complex compounds? Explain with reference to ligands and coordination number.**

A complex (or coordination) compound contains a complex ion, in which a central transition-metal ion is bonded to a definite number of surrounding molecules or ions called ligands. Each ligand possesses at least one lone pair of electrons, which it donates to the metal ion to form a coordinate (dative) bond; common ligands are water, ammonia, chloride ions and cyanide ions. The number of ligand atoms directly attached to the central metal is called the coordination number, which is most often 4 (giving tetrahedral or square-planar shapes) or 6 (giving an octahedral shape). For

example, in $[Cu(NH_3)_6]^{2+}$ the central $Cu^{2+}$ ion is surrounded by six ammonia ligands, giving a coordination number of 6 and an octahedral shape. Transition metals form such complexes readily because their small, highly charged ions with empty d-orbitals can accept the lone pairs of ligands.

**Q3. Explain, with examples, the catalytic activity and important uses of transition metals.**

Transition metals and their compounds are among the best catalysts known. They work well because they can exist in more than one oxidation state (providing an easy path for electron transfer) and because reactant molecules can be adsorbed and activated on their metal surfaces. Familiar examples are iron in the Haber process for ammonia, vanadium(V) oxide in the Contact process for sulphuric acid, nickel in the hydrogenation of vegetable oils into ghee, and platinum in catalytic converters. Beyond catalysis, transition metals are indispensable materials: iron and steel build machinery and structures, stainless steel (iron with chromium and nickel) resists rust, copper carries electricity and forms brass and bronze, and chromium and nickel are used for protective, decorative electroplating.

## 10. Multiple Choice Questions (MCQs)

**1. Transition elements belong to the:**
(A) s-block (B) p-block (C) d-block (D) f-block

**2. Which ion is colourless?**
(A) $Cu^{2+}$ (B) $Fe^{3+}$ (C) $Zn^{2+}$ (D) $Mn^{2+}$

**3. The colour of transition-metal ions is due to:**
(A) s–s transitions (B) d–d transitions (C) nuclear changes (D) ionic bonding

**4. The electronic configuration of chromium is:**
(A) $[Ar]3d^4 4s^2$ (B) $[Ar]3d^5 4s^1$ (C) $[Ar]3d^6$ (D) $[Ar]3d^3 4s^2$

**5. In $[Cu(NH_3)_4]^{2+}$ the coordination number is:**
(A) 2 (B) 4 (C) 6 (D) 8

**6. A ligand is a species that:**
(A) accepts electrons (B) donates a lone pair (C) forms ionic bonds (D) is always neutral

**7. Which is used as a catalyst in the Haber process?**
(A) Ni (B) Fe (C) $V_2O_5$ (D) Pt

**8. Paramagnetism is caused by:**
(A) paired electrons (B) unpaired electrons (C) protons (D) neutrons

**9. Which metal is NOT a typical transition metal?**
(A) Fe (B) Cu (C) Zn (D) Cr

**10. The purple colour of $KMnO_4$ is due to:**
(A) $Mn^{2+}$ (B) $MnO_4^-$ (C) $K^+$ (D) $O^{2-}$

**MCQ Answer Key**

**1-C 2-C 3-B 4-B 5-B 6-B 7-B 8-B 9-C 10-B**

## 11. Quick Revision / Summary

- Transition metals = d-block with partly filled d-orbitals; first series Sc → Zn.
- Zn is not a typical transition metal ($3d^{10}$).
- Key properties: variable oxidation states, coloured ions, paramagnetism, catalysis, complexes.
- Colour = d–d transitions; $Zn^{2+}$ colourless (filled d).
- Complex = central metal + ligands; coordination number = ligand atoms bonded.
- Catalysts: Fe (Haber), $V_2O_5$ (Contact), Ni (hydrogenation).

## 12. Exam Tips

**Teacher's Note**

Link every transition property back to 'partly filled d-orbitals'.

Remember Cr ($3d^5 4s^1$) and Cu ($3d^{10} 4s^1$) exceptions — common MCQ.

For colour questions, always mention d–d transitions; $Zn^{2+}$/$Sc^{3+}$ are colourless (no partly filled d).

In any complex, state central metal + ligand + coordination number.

Know the standard catalysts and the process each is used in.

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## CHAPTER 7

# Fundamental Principles of Organic Chemistry

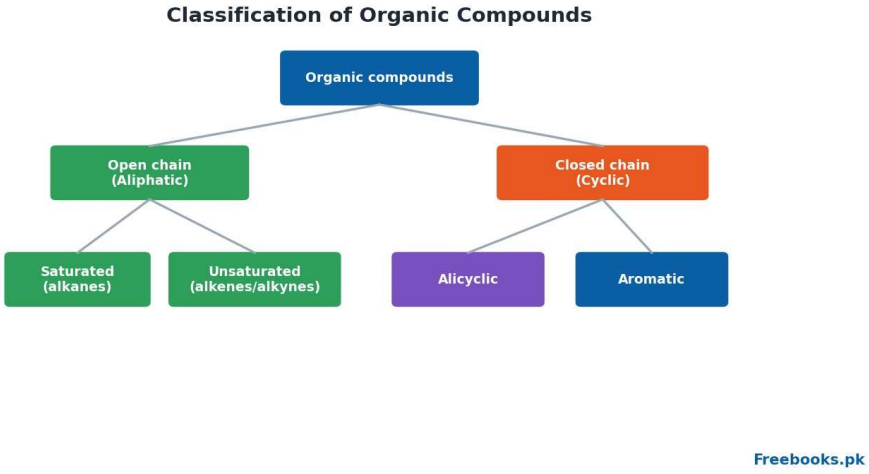


*Figure 7.1 — Classification of organic compounds.*

# 1. Chapter Overview

Organic chemistry is the chemistry of carbon compounds (chiefly hydrocarbons and their derivatives). Carbon is unique because it can bond to itself in long chains and rings (catenation) and form single, double and triple bonds, which is why there are millions of organic compounds — far more than all the compounds of the other elements together. This chapter lays the foundation for the whole organic section: where organic compounds come from, how they are classified, what functional groups and homologous series are, how carbon bonds (hybridization), and the main types of organic reaction.

# 2. Learning Objectives

- Define organic chemistry and explain the special nature of carbon.
- State the main sources of organic compounds.
- Classify organic compounds into aliphatic, alicyclic and aromatic types.
- Define functional group and homologous series with examples.
- Explain $sp^3$, $sp^2$ and sp hybridization of carbon.
- Explain structural isomerism.
- Identify the main types of organic reactions (addition, substitution, elimination).

# 3. Key Concepts

## 3.1 Why Carbon Is Special

Carbon has four valence electrons, so it forms four covalent bonds. It shows catenation (the ability to link with other carbon atoms to form chains and rings) to a greater extent than any other element, and it can form multiple bonds (C=C, C≡C). Because carbon–carbon bonds are strong, the resulting molecules are stable. Together these properties allow an almost unlimited variety of compounds.

## 3.2 Sources of Organic Compounds

The main natural sources of organic compounds are the fossil fuels — coal, petroleum (crude oil) and natural gas — together with plants and animals. Petroleum, separated by fractional distillation, provides fuels (petrol, diesel, kerosene) and the raw materials (from cracking) for plastics, medicines and countless other products.

## 3.3 Classification of Organic Compounds

Organic compounds are broadly divided into open-chain (aliphatic) compounds and closed-chain (cyclic) compounds. Cyclic compounds are further divided into alicyclic (ring compounds that behave like aliphatic ones) and aromatic compounds (those containing the benzene ring). Aliphatic compounds may be saturated (only single bonds, e.g. alkanes) or unsaturated (containing double or triple bonds, e.g. alkenes and alkynes).

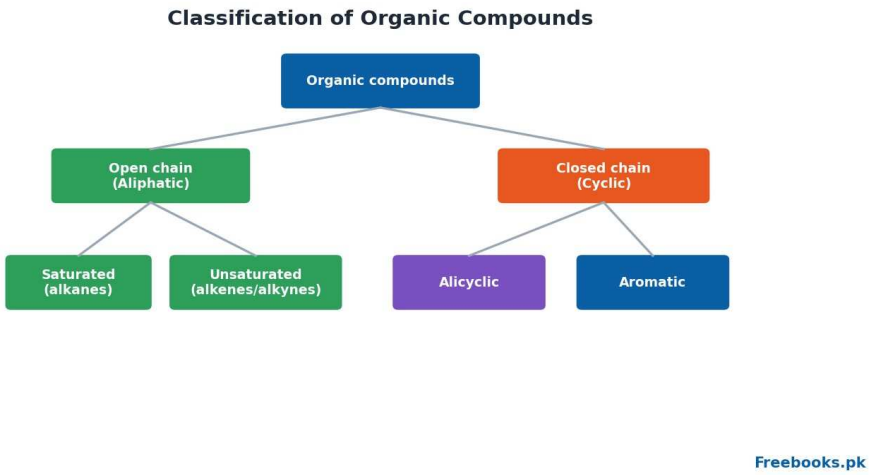


*Figure 7.2 — Classification tree of organic compounds.*

## 3.4 Functional Groups and Homologous Series

A functional group is the atom or group of atoms that gives a molecule its characteristic chemical properties; for example the –OH group makes a compound an alcohol. A homologous series is a family of organic compounds with the same functional group and general formula, in which each member differs from the next by a $–CH_2–$ unit. Members of a homologous series have similar chemical properties and show a gradual change in physical properties (such as boiling point) as the chain grows.

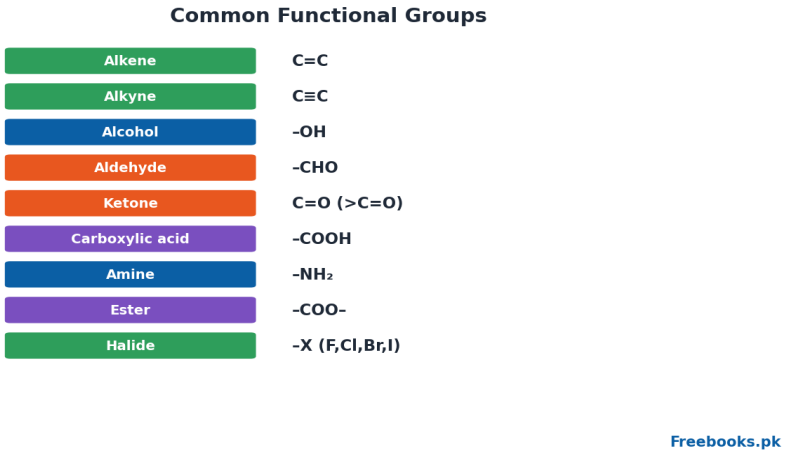


*Figure 7.3 — Some common functional groups.*

> **Memory Trick**
> **Alkane → alkene → alkyne** = single → double → triple bond ('-ane, -ene, -yne').
> **General formulas:** alkane $C_nH_{2n+2}$, alkene $C_nH_{2n}$, alkyne $C_nH_{2n-2}$.

## 3.5 Hybridization of Carbon

The shape and bonding of carbon are explained by hybridization — the mixing of atomic orbitals to give equivalent hybrid orbitals. In $sp^3$ hybridization (as in methane) carbon forms four single bonds arranged tetrahedrally at 109.5°. In $sp^2$ hybridization (as in ethene) carbon forms three σ-

bonds in a plane at 120°, plus one π-bond (a double bond). In sp hybridization (as in ethyne) carbon forms two σ-bonds at 180°, plus two π-bonds (a triple bond).

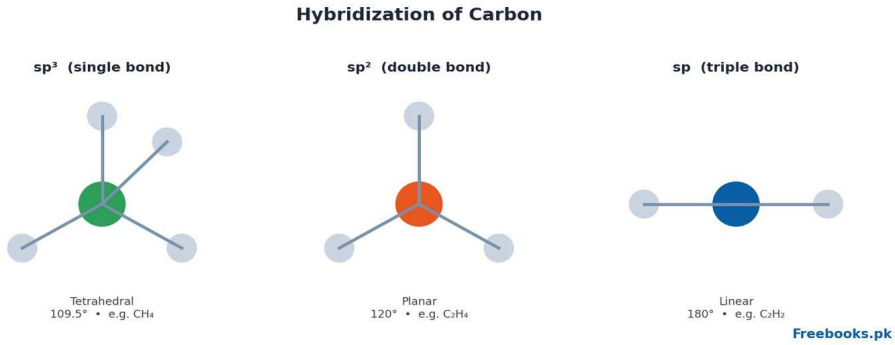


*Figure 7.4 — sp³, sp² and sp hybridization of carbon.*

| Hybridization | Bond type | Shape / angle | Example |
|---|---|---|---|
| $sp^3$ | 4 single bonds | Tetrahedral, 109.5° | $CH_4$ (methane) |
| $sp^2$ | 1 double bond | Planar, 120° | $C_2H_4$ (ethene) |
| sp | 1 triple bond | Linear, 180° | $C_2H_2$ (ethyne) |

### 3.6 Isomerism

Isomers are compounds that have the same molecular formula but different structures. In structural isomerism the atoms are joined in a different order — for example, $C_4H_{10}$ exists as n-butane (a straight chain) and isobutane (a branched chain). Isomerism is another reason organic compounds are so numerous.

### 3.7 Types of Organic Reactions

**Addition.** Atoms are added across a double or triple bond, e.g. ethene + $H_2$ → ethane. Typical of unsaturated compounds.

**Substitution.** One atom or group is replaced by another, e.g. methane + $Cl_2$ → chloromethane + HCl. Typical of saturated compounds.

**Elimination.** A small molecule (such as water or HX) is removed to create a double bond, e.g. dehydration of an alcohol to an alkene.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Organic chemistry | The study of carbon compounds, mainly hydrocarbons and their derivatives. |
| Catenation | The self-linking of carbon atoms into chains and rings. |
| Functional group | The atom or group that gives an organic molecule its characteristic properties. |
| Homologous series | A family of compounds with the same functional group and general |

| Term | Definition |
|---|---|
| | formula, differing by –$CH_2$–. |
| Hybridization | The mixing of atomic orbitals to form equivalent hybrid orbitals. |
| Isomers | Compounds with the same molecular formula but different structures. |

## 5. Formulas / Rules

### Must-Know Facts

**General formulas:** alkane $C_nH_{2n+2}$, alkene $C_nH_{2n}$, alkyne $C_nH_{2n-2}$.

**Hybridization:** $sp^3$ (109.5°, single), $sp^2$ (120°, double), sp (180°, triple).

**Reaction types:** addition (unsaturated), substitution (saturated), elimination (forms double bond).

**Homologues** differ by one –$CH_2$– unit and share chemical properties.

## 6. Diagrams / Illustrations

Key diagrams for revision:

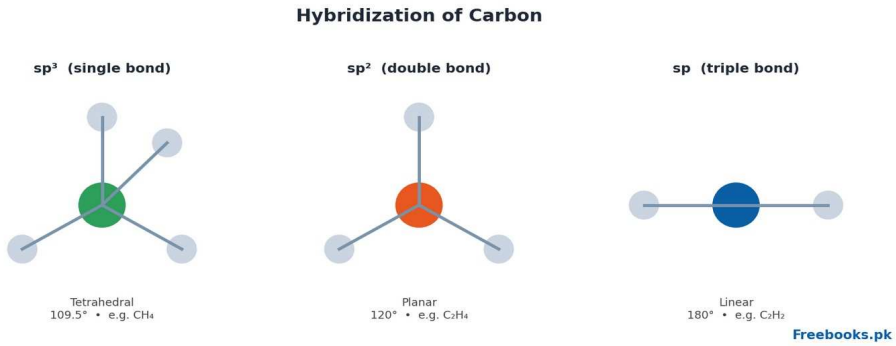


*Diagram 1 — Hybridization of carbon.*

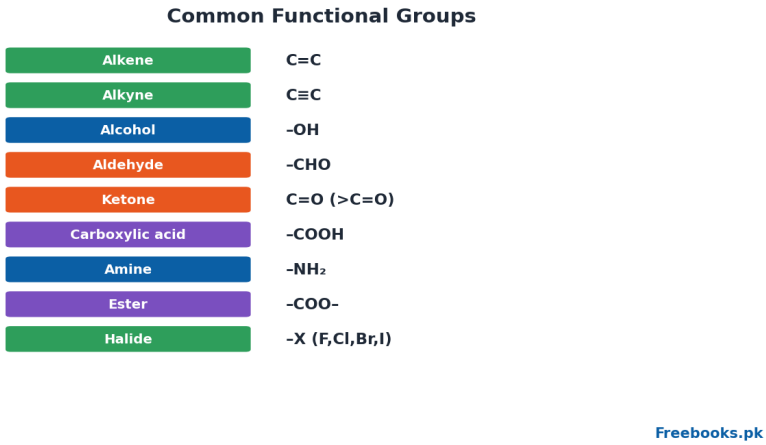


*Diagram 2 — Common functional groups.*

## 7. Solved Examples

**Example 1 — Hybridization**

**Q:** State the hybridization of carbon in ethyne ($C_2H_2$).

**Solution:** Each carbon in ethyne is sp hybridized. It forms two σ-bonds (linear, 180°) and the triple bond includes two π-bonds.

**Example 2 — Isomerism**

**Q:** Draw/describe the structural isomers of $C_4H_{10}$.

**Solution:** There are two: n-butane ($CH_3–CH_2–CH_2–CH_3$, straight chain) and isobutane/2-methylpropane (a branched chain). Same formula, different structure.

**Example 3 — Reaction type**

**Q:** Classify the reaction $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$.

**Solution:** It is a substitution reaction — a hydrogen atom of methane is replaced by a chlorine atom.

## 8. Short Questions

**Q1. Why does carbon form so many compounds?**
**Ans.** Because of catenation (self-linking into chains/rings) and its ability to form single, double and triple bonds.

**Q2. Define functional group.**
**Ans.** The atom or group of atoms that gives an organic compound its characteristic chemical properties.

**Q3. What is a homologous series?**
**Ans.** A family of compounds with the same functional group and general formula, each differing by a $–CH_2–$ unit.

**Q4. Give the hybridization and shape of carbon in methane.**
**Ans.** $sp^3$ hybridized, tetrahedral, bond angle 109.5°.

**Q5. What are structural isomers?**
**Ans.** Compounds with the same molecular formula but a different arrangement of atoms.

**Q6. Differentiate addition and substitution reactions.**
**Ans.** In addition, atoms add across a multiple bond; in substitution, one atom/group replaces another.

**Q7. Name the main sources of organic compounds.**
**Ans.** Coal, petroleum and natural gas (fossil fuels), and plants and animals.

**Q8. Give the general formula of alkenes.**
**Ans.** $C_nH_{2n}$.

## 9. Long Questions

**Q1. Explain the classification of organic compounds.**

Organic compounds are first divided, according to the shape of their carbon skeleton, into open-chain (aliphatic) and closed-chain (cyclic) compounds. Open-chain compounds have carbon atoms joined in straight or branched chains; they may be saturated, containing only single bonds (the alkanes), or unsaturated, containing double or triple bonds (the alkenes and alkynes). Closed-chain (cyclic) compounds have their carbon atoms joined in a ring, and they are further divided into alicyclic compounds, whose rings behave chemically like aliphatic chains, and aromatic compounds, which contain the specially stable benzene ring and its derivatives. This classification, together with the idea of functional groups, allows the millions of organic compounds to be studied in an orderly way.

**Q2. Describe the hybridization of carbon with examples.**

Hybridization is the mixing of a carbon atom's one 2s and some 2p orbitals to give a set of equivalent hybrid orbitals that point in definite directions. In $sp^3$ hybridization the 2s orbital mixes with all three 2p orbitals to give four $sp^3$ orbitals directed to the corners of a tetrahedron at 109.5°; carbon then forms four single (σ) bonds, as in methane, $CH_4$. In $sp^2$ hybridization the 2s orbital mixes with two 2p orbitals to give three $sp^2$ orbitals in a plane at 120°, while the leftover p-orbital forms a π-bond; this gives a carbon–carbon double bond, as in ethene, $C_2H_4$. In sp hybridization the 2s orbital mixes with only one 2p orbital to give two sp orbitals pointing in opposite directions at 180°, while the two leftover p-orbitals form two π-bonds; this gives a triple bond, as in ethyne, $C_2H_2$. Thus the type of hybridization decides the shape of the molecule and the number of multiple bonds.

**Q3. Distinguish between addition, substitution and elimination reactions with examples.**

These are the three most important classes of organic reaction. In an addition reaction, atoms or groups are added across a carbon–carbon double or triple bond, so an unsaturated compound becomes more saturated; for example, ethene reacts with hydrogen to give ethane ($CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_3$). In a substitution reaction, an atom or group in a molecule is replaced by another atom or group; saturated compounds such as alkanes undergo this, as when methane reacts with chlorine to give chloromethane and hydrogen chloride ($CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$). In an elimination reaction, a small molecule such as water or a hydrogen halide is removed from a molecule to create a double bond; for example, the dehydration of ethanol gives ethene. Recognising which class a reaction belongs to helps predict the products.

## 10. Multiple Choice Questions (MCQs)

**1. Organic chemistry is the chemistry of:**
(A) Nitrogen (B) Carbon (C) Silicon (D) Sulphur

**2. The general formula of alkanes is:**
(A) $C_nH_{2n}$ (B) $C_nH_{2n+2}$ (C) $C_nH_{2n-2}$ (D) $C_nH_n$

**3. Carbon in methane is:**
(A) sp (B) $sp^2$ (C) $sp^3$ (D) $dsp^2$

**4. The bond angle in ethene ($sp^2$) is about:**

(A) 109.5° (B) 120° (C) 180° (D) 90°

**5. A group that gives a molecule its characteristic properties is a:**
(A) radical (B) functional group (C) isomer (D) catalyst

**6. Compounds with the same formula but different structures are:**
(A) allotropes (B) isomers (C) homologues (D) polymers

**7. $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ is a:**
(A) addition (B) substitution (C) elimination (D) polymerisation

**8. Members of a homologous series differ by:**
(A) $-CH_3$ (B) $-CH_2-$ (C) –OH (D) –H

**9. The benzene ring is characteristic of ___ compounds:**
(A) aliphatic (B) alicyclic (C) aromatic (D) saturated

**10. Which is unsaturated?**
(A) Ethane (B) Ethene (C) Methane (D) Propane

**MCQ Answer Key**

**1-B 2-B 3-C 4-B 5-B 6-B 7-B 8-B 9-C 10-B**

## 11. Quick Revision / Summary

- Carbon: catenation + multiple bonds → millions of compounds.
- Sources: coal, petroleum, natural gas.
- Classification: aliphatic (open) vs cyclic (alicyclic, aromatic); saturated vs unsaturated.
- Functional group decides properties; homologous series differ by $-CH_2-$.
- Hybridization: $sp^3$ (109.5°, single), $sp^2$ (120°, double), sp (180°, triple).
- Reactions: addition (unsaturated), substitution (saturated), elimination (forms C=C).

## 12. Exam Tips

**Teacher's Note**

Learn the three hybridizations with example, shape and angle — a guaranteed question.
Memorise general formulas: alkane $C_nH_{2n+2}$, alkene $C_nH_{2n}$, alkyne $C_nH_{2n-2}$.
Match reaction type to compound: unsaturated → addition, saturated → substitution.
Give a clear example for functional group and homologous series definitions.
Practise drawing structural isomers of $C_4H_{10}$ and $C_5H_{12}$.

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# CHAPTER 8
# Aliphatic Hydrocarbons

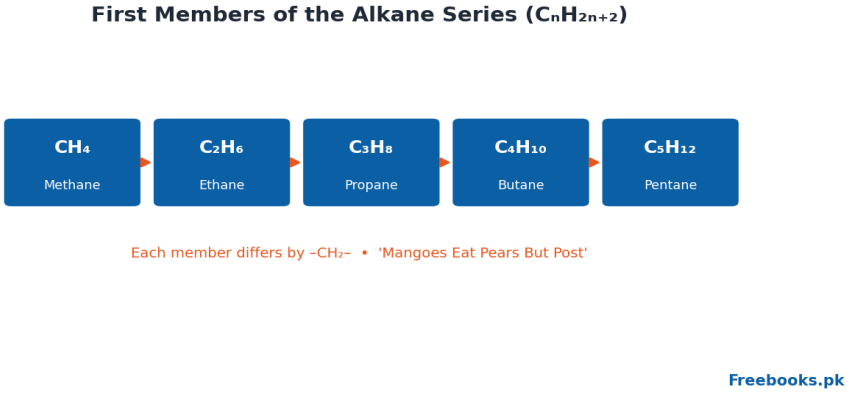


*Figure 8.1 — The first members of the alkane homologous series.*

# 1. Chapter Overview

Hydrocarbons are compounds made of only carbon and hydrogen. The aliphatic (open-chain) hydrocarbons are of three kinds: alkanes (saturated, only single bonds), alkenes (one carbon–carbon double bond) and alkynes (one carbon–carbon triple bond). These are the simplest organic compounds and the starting point for making almost every other organic substance — plastics, alcohols, detergents and fuels. This chapter covers how each type is prepared, how they react, and the key ideas of unsaturation, addition reactions and Markownikoff's rule.

# 2. Learning Objectives

- Distinguish alkanes, alkenes and alkynes and give their general formulas.
- Describe important methods of preparing alkanes, alkenes and alkynes.
- Explain the free-radical substitution (halogenation) of alkanes.
- Describe the addition reactions of alkenes and alkynes.
- State and apply Markownikoff's rule.
- Explain the tests that distinguish saturated from unsaturated hydrocarbons.

# 3. Key Concepts

## 3.1 The Three Families

| Type | Bonding | General formula | Example |
|---|---|---|---|
| Alkanes | All single bonds (saturated) | $C_nH_{2n+2}$ | $CH_4$, $C_2H_6$ |
| Alkenes | One C=C (unsaturated) | $C_nH_{2n}$ | $C_2H_4$ (ethene) |
| Alkynes | One C≡C (unsaturated) | $C_nH_{2n-2}$ | $C_2H_2$ (ethyne) |

**Memory Trick**

**Name endings:** -ane (single), -ene (double), -yne (triple).

**First alkanes:** Methane, Ethane, Propane, Butane, Pentane — 'Monkeys Eat Peanut Butter Perfectly'.

## 3.2 Alkanes — the 'Paraffins'

Alkanes are rather unreactive (the old name 'paraffin' means 'little affinity') because their C–C and C–H single bonds are strong and non-polar. Their most important reactions are combustion (burning in air to give $CO_2$ and water, releasing large amounts of heat — this is why they are used as fuels) and substitution by halogens in the presence of sunlight.

### Free-Radical Halogenation

In sunlight (UV light), methane reacts with chlorine, and a hydrogen atom is replaced step by step by chlorine. The reaction goes by a free-radical chain mechanism with three stages: initiation ($Cl_2$

splits into chlorine radicals), propagation (radicals react to make products and new radicals), and termination (radicals combine).

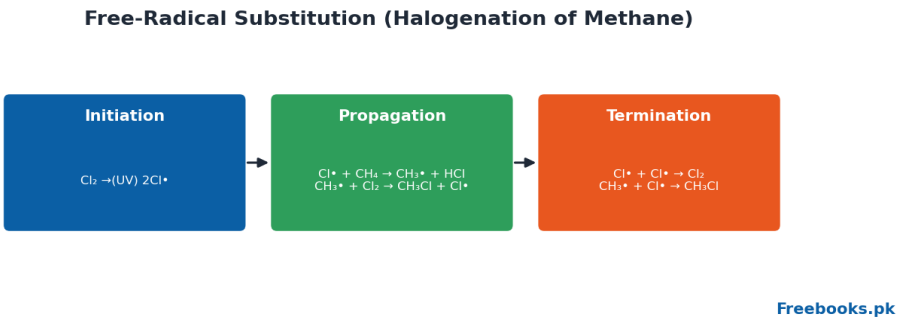


*Figure 8.2 — Free-radical substitution of methane by chlorine.*

## 3.3 Alkenes — Reactive Because of the Double Bond

The carbon–carbon double bond is a region of high electron density, so alkenes are much more reactive than alkanes and readily undergo addition reactions, in which the π-bond breaks and atoms add to the two carbons. Common additions include hydrogenation ($H_2$/Ni → alkane), halogenation ($X_2$ → dihalide), addition of hydrogen halides (HX → haloalkane), hydration ($H_2O/H^+$ → alcohol) and polymerisation (many alkene molecules join to form a polymer such as polythene).

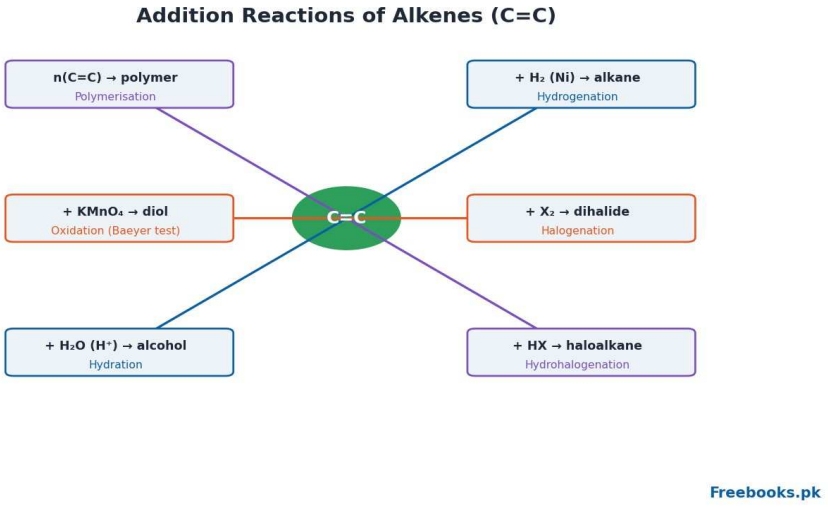


*Figure 8.3 — The main addition reactions of alkenes.*

### Markownikoff's Rule

**Markownikoff's Rule**

When a hydrogen halide (HX) adds to an unsymmetrical alkene, the hydrogen atom goes to the carbon that already has more hydrogen atoms, and the halogen goes to the carbon with fewer hydrogens.

**Example:** $CH_3–CH=CH_2$ + HBr → $CH_3–CHBr–CH_3$ (2-bromopropane, the major product).

**Teacher's Note**

A simple way for students to remember Markownikoff's rule: 'the rich get richer' — the

carbon already rich in hydrogen gets the extra hydrogen.

**Tests for Unsaturation**

Alkenes (and alkynes) decolourise two reagents that alkanes do not: bromine water (turns from orange to colourless) and dilute alkaline $KMnO_4$ (Baeyer's reagent, turns from purple to colourless). These colour changes are simple laboratory tests for a carbon–carbon multiple bond.

### 3.4 Alkynes

Alkynes contain a triple bond and, like alkenes, undergo addition reactions. Ethyne (acetylene, $C_2H_2$) is prepared from calcium carbide and water ($CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$) and is used in oxy-acetylene welding because it burns with a very hot flame. A special feature of terminal alkynes is that the hydrogen on the triple-bonded carbon is weakly acidic, so ethyne reacts with sodium to release hydrogen.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Hydrocarbon | A compound containing only carbon and hydrogen. |
| Saturated hydrocarbon | A hydrocarbon with only single C–C bonds (alkane). |
| Unsaturated hydrocarbon | A hydrocarbon containing a C=C or C≡C bond (alkene/alkyne). |
| Addition reaction | A reaction in which atoms add across a multiple bond. |
| Markownikoff's rule | In HX addition to an unsymmetrical alkene, H goes to the carbon with more H atoms. |
| Free radical | A highly reactive species with an unpaired electron. |

## 5. Formulas / Rules

**Must-Know Facts**

**Formulas:** alkane $C_nH_{2n+2}$, alkene $C_nH_{2n}$, alkyne $C_nH_{2n-2}$.
**Alkanes:** combustion + free-radical substitution (initiation, propagation, termination).
**Alkenes:** addition ($H_2$/Ni, $X_2$, HX, $H_2O/H^+$, polymerisation).
**Markownikoff:** H to the C with more H; example $CH_3CH{=}CH_2 + HBr \rightarrow$ 2-bromopropane.
**Unsaturation tests:** decolourise bromine water and $KMnO_4$.
**Ethyne:** $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$ (used in welding).

## 6. Diagrams / Illustrations

Key diagrams for revision:

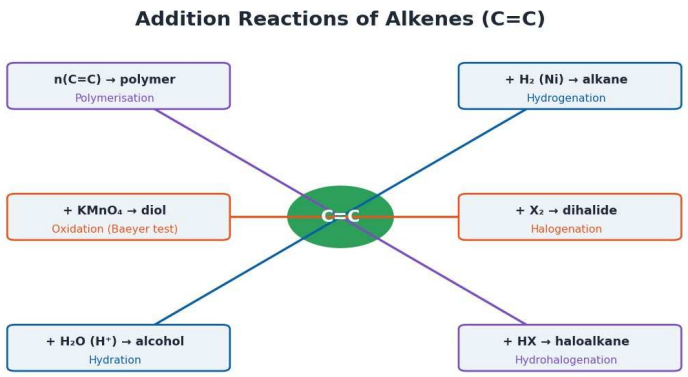


*Diagram 1 — Addition reactions of alkenes.*

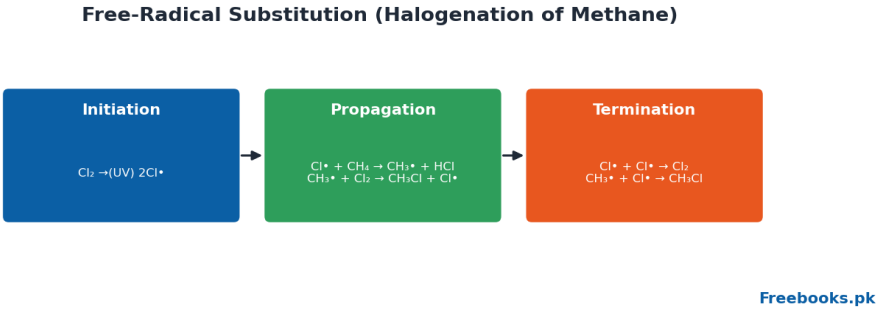


*Diagram 2 — Free-radical substitution.*

## 7. Solved Examples

### Example 1 — Markownikoff's rule

**Q:** Predict the major product of $CH_3–CH=CH_2$ + HCl.

**Solution:** By Markownikoff's rule, H adds to the $CH_2$ (more hydrogens) and Cl to the middle carbon, giving 2-chloropropane, $CH_3–CHCl–CH_3$, as the major product.

### Example 2 — Test for unsaturation

**Q:** How would you distinguish ethane from ethene in the laboratory?

**Solution:** Add bromine water. Ethene (unsaturated) decolourises it quickly; ethane (saturated) does not. Alkaline $KMnO_4$ can be used the same way.

### Example 3 — Preparation

**Q:** How is ethyne prepared from calcium carbide?

**Solution:** Calcium carbide reacts with water: $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$, giving ethyne (acetylene) gas.

## 8. Short Questions

**Q1. Why are alkanes called paraffins?**
**Ans.** 'Paraffin' means 'little affinity'; alkanes are fairly unreactive because of their strong, non-polar single bonds.

**Q2. What are the three steps of free-radical substitution?**
**Ans.** Initiation, propagation and termination.

**Q3. Why are alkenes more reactive than alkanes?**
**Ans.** The C=C double bond is an electron-rich region that readily undergoes addition reactions.

**Q4. State Markownikoff's rule.**
**Ans.** When HX adds to an unsymmetrical alkene, hydrogen goes to the carbon with more hydrogen atoms.

**Q5. Give two tests for unsaturation.**
**Ans.** Decolourisation of bromine water and of alkaline $KMnO_4$ (Baeyer's reagent).

**Q6. How is ethyne prepared?**
**Ans.** From calcium carbide and water: $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$.

**Q7. Why is ethyne used in welding?**
**Ans.** It burns in oxygen with a very hot flame (oxy-acetylene flame).

**Q8. What is produced when ethene is polymerised?**
**Ans.** Polythene (polyethene).

## 9. Long Questions

**Q1. Describe the free-radical halogenation of methane.**

When methane and chlorine are mixed in the presence of sunlight (ultraviolet light), the hydrogen atoms of methane are replaced one by one by chlorine atoms in a substitution reaction that proceeds by a free-radical chain mechanism. In the initiation step, ultraviolet light splits a chlorine molecule homolytically into two very reactive chlorine radicals: $Cl_2 \rightarrow 2Cl\bullet$. In the propagation steps a chlorine radical removes a hydrogen atom from methane to give a methyl radical and hydrogen chloride ($Cl\bullet + CH_4 \rightarrow CH_3\bullet + HCl$), and the methyl radical then reacts with another chlorine molecule to give chloromethane and a new chlorine radical ($CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$); because a radical is regenerated, the chain continues. In the termination steps two radicals combine, ending the chain (for example $Cl\bullet + Cl\bullet \rightarrow Cl_2$, or $CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$). Further substitution can give $CH_2Cl_2$, $CHCl_3$ and $CCl_4$.

**Q2. Discuss the addition reactions of alkenes.**

Because the carbon–carbon double bond is a region of high electron density, alkenes readily undergo addition reactions in which the weaker π-bond breaks and new atoms add to the two carbons, converting the unsaturated compound to a saturated one. With hydrogen and a nickel catalyst an alkene is hydrogenated to the corresponding alkane. With halogens such as bromine it forms a dihalide, and bromine water is decolourised — a test for unsaturation. With hydrogen halides it forms haloalkanes, and for unsymmetrical alkenes the product follows Markownikoff's rule. With water in the presence of an acid catalyst it undergoes hydration to give an alcohol.

Finally, under suitable conditions many alkene molecules add to one another (polymerisation), as when ethene forms polythene. These addition reactions make alkenes valuable building blocks in industry.

**Q3. Compare alkanes, alkenes and alkynes in terms of structure and reactivity.**

Alkanes, alkenes and alkynes are the three families of aliphatic hydrocarbons and differ in the kind of carbon–carbon bond they contain. Alkanes ($C_nH_{2n+2}$) are saturated, having only single bonds; their strong, non-polar bonds make them relatively unreactive, so their main reactions are combustion and free-radical substitution. Alkenes ($C_nH_{2n}$) contain one double bond and alkynes ($C_nH_{2n-2}$) one triple bond; both are unsaturated and therefore much more reactive, undergoing addition reactions across the multiple bond. Alkenes and alkynes decolourise bromine water and $KMnO_4$, whereas alkanes do not, which provides a simple test to tell them apart. A special feature of terminal alkynes is the weak acidity of the ≡C–H hydrogen, which lets ethyne react with sodium to release hydrogen.

## 10. Multiple Choice Questions (MCQs)

**1. The general formula of alkynes is:**
(A) $C_nH_{2n+2}$ (B) $C_nH_{2n}$ (C) $C_nH_{2n-2}$ (D) $C_nH_n$

**2. Halogenation of methane proceeds by a ___ mechanism:**
(A) ionic (B) free-radical (C) addition (D) elimination

**3. Which decolourises bromine water?**
(A) Ethane (B) Ethene (C) Methane (D) Propane

**4. Markownikoff's rule applies to addition of ___ to alkenes:**
(A) $H_2$ (B) $X_2$ (C) HX (D) $H_2O$ only

**5. Ethyne is prepared from:**
(A) $CaCO_3$ (B) $CaC_2$ (C) CaO (D) $CaCl_2$

**6. Polythene is made by polymerising:**
(A) ethyne (B) ethene (C) ethane (D) methane

**7. The catalyst for hydrogenation of alkenes is:**
(A) Fe (B) Ni (C) $V_2O_5$ (D) Pt only

**8. Baeyer's reagent is:**
(A) $Br_2$ water (B) alkaline $KMnO_4$ (C) conc. $H_2SO_4$ (D) NaOH

**9. Which is a saturated hydrocarbon?**
(A) $C_2H_4$ (B) $C_2H_2$ (C) $C_2H_6$ (D) $C_3H_6$

**10. The very hot oxy-acetylene flame uses:**
(A) ethene (B) ethyne (C) ethane (D) methane

**MCQ Answer Key**

**1-C 2-B 3-B 4-C 5-B 6-B 7-B 8-B 9-C 10-B**

## 11. Quick Revision / Summary

- Alkanes $C_nH_{2n+2}$ (single), alkenes $C_nH_{2n}$ (double), alkynes $C_nH_{2n-2}$ (triple).

- Alkanes: unreactive; combustion + free-radical substitution (initiation/propagation/termination).
- Alkenes: reactive; addition ($H_2$/Ni, $X_2$, HX, $H_2O/H^+$, polymerisation).
- Markownikoff: H adds to C with more H atoms.
- Unsaturation tests: decolourise bromine water and $KMnO_4$.
- Ethyne from $CaC_2$ + $H_2O$; used in welding.

## 12. Exam Tips

**Teacher's Note**

Write the free-radical mechanism with all three steps and correct equations — a frequent long question.

Apply Markownikoff's rule carefully to unsymmetrical alkenes; name the major product.

Learn the two unsaturation tests and their colour changes.

Remember the catalyst Ni for hydrogenation and the ethyne preparation from $CaC_2$.

Do not confuse '-ene' (double) with '-yne' (triple) endings.

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## CHAPTER 9

# Aromatic Hydrocarbons

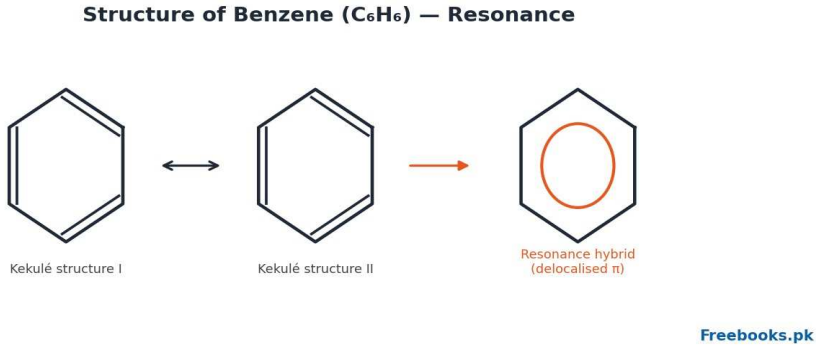


*Figure 9.1 — Benzene: two Kekulé structures and the delocalised resonance hybrid.*

# 1. Chapter Overview

Aromatic hydrocarbons are ring compounds based on benzene ($C_6H_6$). Although benzene is unsaturated, it does not behave like an ordinary alkene: it is unusually stable and prefers substitution reactions to addition. This special stability, called aromaticity, comes from the delocalisation of its six π-electrons around the ring. Benzene and its derivatives are hugely important, being used to make dyes, drugs, explosives, plastics and detergents. This chapter covers the structure of benzene, why it is so stable, and its characteristic reactions.

# 2. Learning Objectives

- Describe the structure of benzene using Kekulé structures and resonance.
- Explain aromaticity and the unusual stability of benzene.
- Explain why benzene undergoes substitution rather than addition.
- Describe the electrophilic substitution reactions of benzene (halogenation, nitration, sulphonation, Friedel–Crafts).
- Describe the addition reactions benzene can undergo under special conditions.
- State the important uses of benzene and its derivatives.

# 3. Key Concepts

## 3.1 Structure of Benzene

Benzene is a flat, six-membered ring of carbon atoms, each bonded to one hydrogen. Kekulé represented it with alternating single and double bonds, but experiments show that all six carbon–carbon bonds are identical, with a length between that of a single and a double bond. This is explained by resonance: the true structure is a resonance hybrid in which the six π-electrons are delocalised evenly around the ring (often drawn as a circle inside the hexagon).

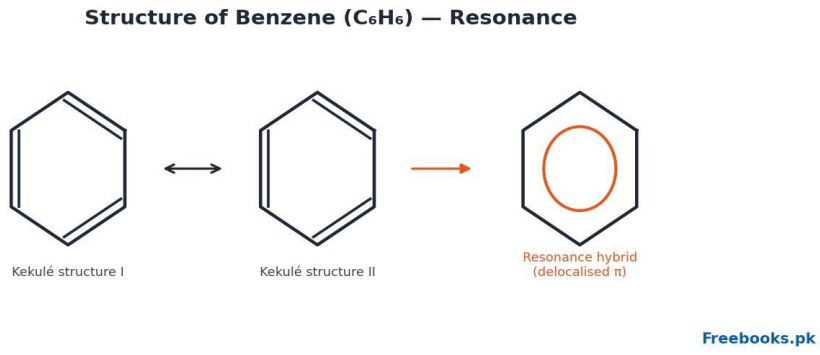


*Figure 9.2 — Resonance in benzene.*

## 3.2 Aromaticity and Stability

The delocalisation of the π-electrons lowers the energy of benzene and makes it much more stable than an imaginary molecule with three fixed double bonds. This extra stability is called

resonance (delocalisation) energy and is the reason benzene is described as aromatic. Because of this stability, benzene resists reactions that would destroy the delocalised ring.

> **Memory Trick**
> **Why substitution, not addition?** Addition would break the stable aromatic ring; substitution keeps it intact, so benzene 'protects' its ring by replacing an H instead.

## 3.3 Electrophilic Substitution Reactions

Benzene's characteristic reactions are electrophilic substitutions, in which an electrophile (an electron-loving species) replaces a hydrogen atom on the ring while the aromatic system is preserved. The main examples are:

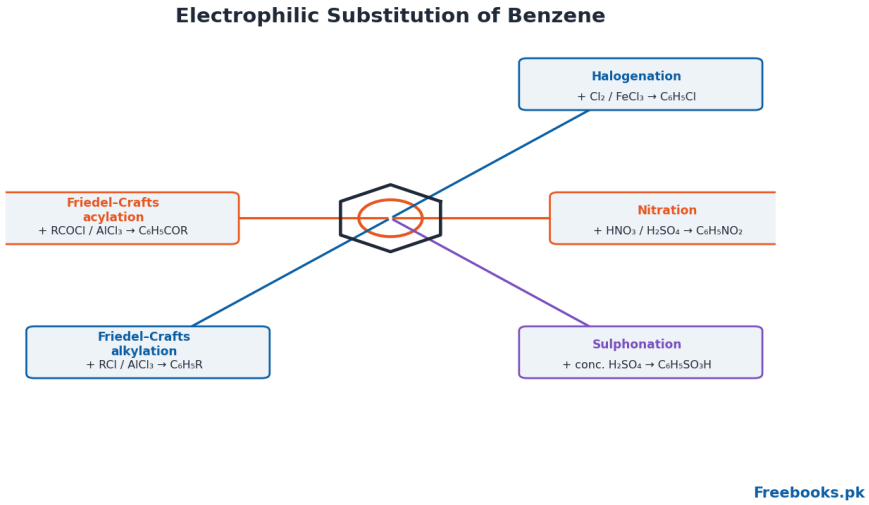


*Figure 9.3 — The main electrophilic substitution reactions of benzene.*

| Reaction | Reagents / conditions | Product |
|---|---|---|
| Halogenation | $Cl_2$ (or $Br_2$) with $FeCl_3$/$FeBr_3$ | Chlorobenzene, $C_6H_5Cl$ |
| Nitration | conc. $HNO_3$ + conc. $H_2SO_4$, ~55 °C | Nitrobenzene, $C_6H_5NO_2$ |
| Sulphonation | conc. (fuming) $H_2SO_4$ | Benzenesulphonic acid, $C_6H_5SO_3H$ |
| Friedel–Crafts alkylation | R–Cl with anhydrous $AlCl_3$ | Alkylbenzene, $C_6H_5R$ |
| Friedel–Crafts acylation | R–COCl with anhydrous $AlCl_3$ | Aryl ketone, $C_6H_5COR$ |

> **Teacher's Note**
> Stress the common pattern: in every case an electrophile replaces one ring hydrogen, and the aromatic ring survives. Students who see the pattern can reproduce all five reactions easily.

## 3.4 Addition Reactions (Special Conditions)

Under forcing conditions benzene can be made to add. With hydrogen under high pressure and a nickel catalyst it forms cyclohexane, and with chlorine in bright sunlight it adds three molecules

to form benzene hexachloride (BHC, an insecticide). These reactions destroy the aromatic ring and so are much harder than substitution.

### 3.5 Uses

Benzene and its derivatives are used to make an enormous range of products: nitrobenzene and aniline for dyes and medicines, phenol for plastics and antiseptics, styrene for polystyrene, and detergents, explosives (TNT) and solvents. (Benzene itself is toxic and carcinogenic, so it must be handled carefully.)

## 4. Important Definitions

| Term | Definition |
|---|---|
| Aromatic compound | A ring compound containing a benzene ring with delocalised π-electrons. |
| Aromaticity | The extra stability of benzene due to delocalisation of its π-electrons. |
| Resonance energy | The energy by which the real (delocalised) molecule is more stable than a single Kekulé structure. |
| Electrophile | An electron-loving species that attacks electron-rich centres. |
| Electrophilic substitution | A reaction in which an electrophile replaces a ring hydrogen of benzene. |
| Friedel–Crafts reaction | Alkylation or acylation of benzene using anhydrous $AlCl_3$. |

## 5. Formulas / Rules

**Must-Know Facts**

**Benzene =** $C_6H_6$, planar ring, delocalised π-electrons (resonance hybrid).

**Prefers** electrophilic substitution (keeps the aromatic ring).

**Nitration:** conc. $HNO_3$ + conc. $H_2SO_4$ → nitrobenzene.

**Friedel–Crafts:** needs anhydrous $AlCl_3$ catalyst.

**Addition (hard):** $H_2$/Ni → cyclohexane; $Cl_2$/sunlight → BHC.

## 6. Diagrams / Illustrations

Key diagrams for revision:

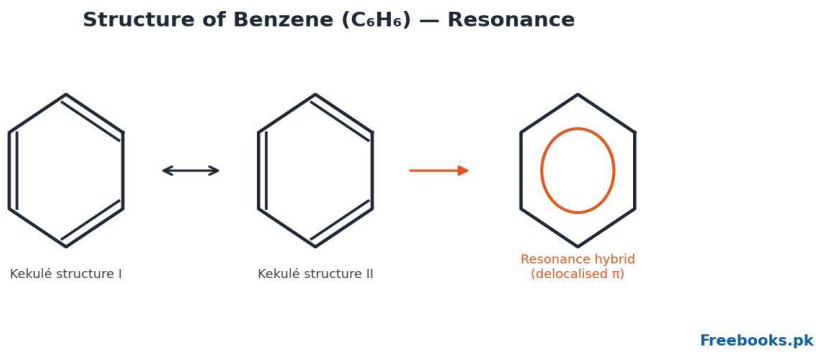


*Diagram 1 — Structure and resonance of benzene.*

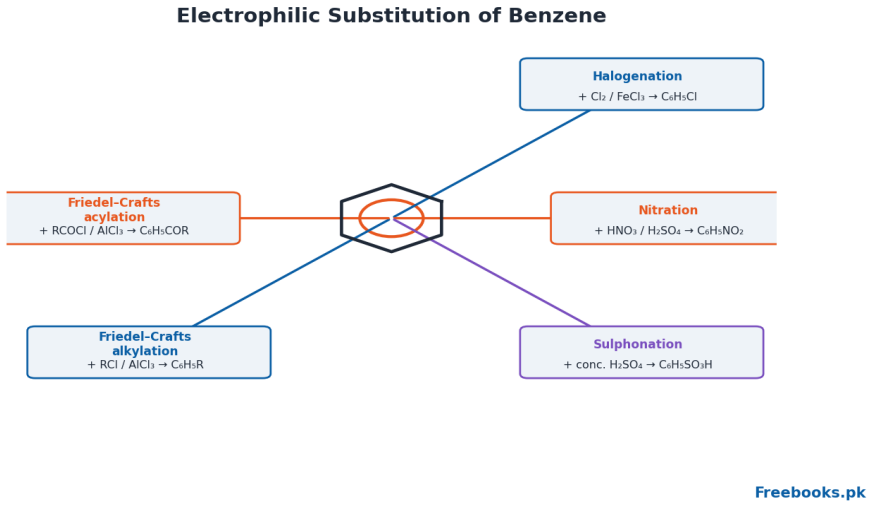


*Diagram 2 — Electrophilic substitution reactions.*

## 7. Solved Examples

### Example 1 — Substitution vs addition

**Q:** Why does benzene undergo substitution rather than addition?

**Solution:** Its six π-electrons are delocalised, giving the ring extra (resonance) stability. Addition would destroy this stable ring, whereas substitution replaces a hydrogen and keeps the aromatic system intact.

### Example 2 — Nitration

**Q:** Give the reagents and product for the nitration of benzene.

**Solution:** Benzene is treated with a mixture of concentrated nitric and sulphuric acids at about 55 °C to give nitrobenzene ($C_6H_5NO_2$) and water.

### Example 3 — Friedel–Crafts

**Q:** What catalyst is required for Friedel–Crafts alkylation, and why must it be anhydrous?

**Solution:** Anhydrous aluminium chloride ($AlCl_3$) is required to generate the electrophile. It must be anhydrous because water destroys (hydrolyses) the catalyst, stopping the reaction.

## 8. Short Questions

**Q1. What is the molecular formula of benzene?**
**Ans.** $C_6H_6$.

**Q2. What is aromaticity?**
**Ans.** The extra stability of benzene arising from the delocalisation of its π-electrons around the ring.

**Q3. Why are all C–C bonds in benzene equal in length?**
**Ans.** Because of resonance; the π-electrons are delocalised, so every bond is identical, between a single and a double bond.

**Q4. Why does benzene prefer substitution to addition?**
**Ans.** Substitution preserves the stable aromatic ring, whereas addition would destroy it.

**Q5. Give reagents for nitration of benzene.**
**Ans.** Concentrated $HNO_3$ with concentrated $H_2SO_4$.

**Q6. Name the catalyst used in Friedel–Crafts reactions.**
**Ans.** Anhydrous aluminium chloride, $AlCl_3$.

**Q7. What is formed when benzene reacts with $H_2$/Ni?**
**Ans.** Cyclohexane.

**Q8. Name two uses of benzene derivatives.**
**Ans.** Making dyes/medicines (from aniline/nitrobenzene) and plastics (from phenol/styrene).

## 9. Long Questions

**Q1. Describe the structure of benzene and explain its stability.**

Benzene, $C_6H_6$, is a flat regular hexagon of six carbon atoms, each carrying one hydrogen. Kekulé first suggested a ring with alternating single and double bonds, but this cannot be the whole truth because measurements show that all six carbon–carbon bonds are exactly the same length, intermediate between a single and a double bond. The modern explanation is resonance: the molecule is best described as a resonance hybrid of the two Kekulé structures, in which each carbon is $sp^2$ hybridised and contributes one electron to a set of π-orbitals that merge into a delocalised π-cloud above and below the ring. This delocalisation spreads the electrons over all six carbons and lowers the energy of the molecule; the difference between this real energy and that of a hypothetical fixed-bond structure is the resonance energy. Because of this large resonance energy, benzene is unusually stable, which is why it resists reactions that would break up the ring.

**Q2. Discuss the electrophilic substitution reactions of benzene.**

Benzene reacts mainly by electrophilic substitution, in which an electron-loving electrophile replaces one hydrogen atom of the ring while the stable aromatic system is preserved. In halogenation, benzene reacts with chlorine or bromine in the presence of a catalyst such as $FeCl_3$ to give chlorobenzene or bromobenzene. In nitration, a mixture of concentrated nitric and sulphuric acids at about 55 °C introduces a nitro group to give nitrobenzene. In sulphonation, hot concentrated (fuming) sulphuric acid gives benzenesulphonic acid. In the Friedel–Crafts

reactions, anhydrous aluminium chloride is used as catalyst: alkylation with an alkyl halide gives an alkylbenzene, and acylation with an acyl chloride gives an aromatic ketone. In every case the pattern is the same — an electrophile replaces a ring hydrogen and the aromatic ring remains intact — which is why these are the characteristic reactions of benzene.

**Q3. Compare the reactivity of benzene with that of an alkene.**

Both benzene and alkenes are unsaturated and contain π-electrons, yet they behave very differently. In an alkene the two π-electrons are localised between two carbons; this exposed double bond is easily attacked, so alkenes readily undergo addition reactions and decolourise bromine water and $KMnO_4$. In benzene the six π-electrons are delocalised over the whole ring, giving a large resonance energy and great stability. As a result benzene does not decolourise bromine water under ordinary conditions and, instead of addition, it undergoes electrophilic substitution, which keeps the aromatic ring intact. Only under forcing conditions ($H_2$/Ni at high pressure, or $Cl_2$ in sunlight) can benzene be made to add. Thus the delocalisation of electrons makes benzene far less reactive, and differently reactive, compared with an ordinary alkene.

## 10. Multiple Choice Questions (MCQs)

**1. The molecular formula of benzene is:**
(A) $C_6H_{12}$ (B) $C_6H_6$ (C) $C_6H_{14}$ (D) $C_5H_6$

**2. Benzene mainly undergoes:**
(A) addition (B) electrophilic substitution (C) elimination (D) free-radical addition

**3. The equal C–C bond lengths in benzene are explained by:**
(A) isomerism (B) resonance (C) hydrogen bonding (D) catenation

**4. Nitration of benzene uses:**
(A) $HNO_3 + H_2SO_4$ (B) $HCl + AlCl_3$ (C) $Br_2 + FeBr_3$ (D) $H_2 + Ni$

**5. The catalyst in Friedel–Crafts reactions is:**
(A) $FeCl_3$ (B) $AlCl_3$ (C) $V_2O_5$ (D) Ni

**6. Benzene + $H_2$/Ni gives:**
(A) cyclohexene (B) cyclohexane (C) toluene (D) phenol

**7. Carbon atoms in benzene are:**
(A) sp (B) $sp^2$ (C) $sp^3$ (D) $dsp^2$

**8. Benzene hexachloride is formed with $Cl_2$ in:**
(A) dark (B) sunlight (C) $AlCl_3$ (D) water

**9. Sulphonation of benzene gives:**
(A) $C_6H_5Cl$ (B) $C_6H_5NO_2$ (C) $C_6H_5SO_3H$ (D) $C_6H_5OH$

**10. The extra stability of benzene is called:**
(A) ionisation energy (B) resonance energy (C) lattice energy (D) bond energy

**MCQ Answer Key**

**1-B 2-B 3-B 4-A 5-B 6-B 7-B 8-B 9-C 10-B**

## 11. Quick Revision / Summary

- Benzene $C_6H_6$: planar ring, $sp^2$ carbons, delocalised π-electrons (resonance hybrid).
- Aromaticity → extra resonance stability → resists ring-breaking reactions.
- Characteristic reaction = electrophilic substitution (keeps the ring).
- Reactions: halogenation ($FeCl_3$), nitration ($HNO_3/H_2SO_4$), sulphonation ($H_2SO_4$), Friedel–Crafts ($AlCl_3$).
- Addition only under force: $H_2$/Ni → cyclohexane; $Cl_2$/sunlight → BHC.
- Derivatives → dyes, drugs, plastics, explosives.

## 12. Exam Tips

**Teacher's Note**

Always explain benzene's behaviour with 'delocalised π-electrons / resonance stability'.
Learn the five substitution reactions with reagents and catalysts in a table.
Remember catalysts: $FeCl_3$ (halogenation), $AlCl_3$ (Friedel–Crafts) — must be anhydrous.
State clearly WHY substitution is preferred over addition (keeps aromatic ring).
Nitration mixture = conc. $HNO_3$ + conc. $H_2SO_4$ — a frequent MCQ.

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## CHAPTER 10

# Alkyl Halides

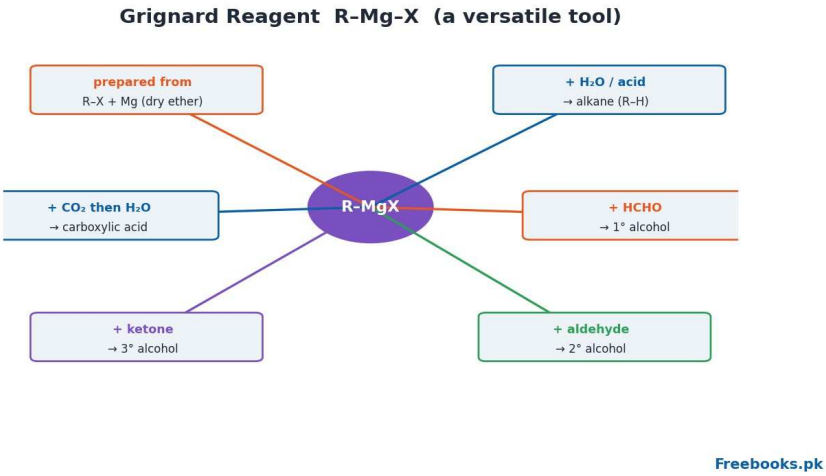


*Figure 10.1 — The Grignard reagent (R–MgX), a versatile synthetic tool made from alkyl halides.*

# 1. Chapter Overview

Alkyl halides (haloalkanes) are compounds in which one or more hydrogen atoms of an alkane have been replaced by a halogen atom, giving the general formula R–X (where X = F, Cl, Br, I). Although they are not usually found in nature, they are extremely useful in the laboratory and industry because the carbon–halogen bond is polar and reactive. This makes alkyl halides ideal starting materials for making alcohols, ethers, amines and, above all, Grignard reagents, which are among the most powerful tools for building larger organic molecules.

# 2. Learning Objectives

- Define alkyl halides and classify them as primary, secondary and tertiary.
- Describe methods of preparing alkyl halides.
- Explain nucleophilic substitution reactions and distinguish SN1 from SN2.
- Describe elimination (dehydrohalogenation) reactions.
- Describe the preparation and synthetic uses of the Grignard reagent.
- State the order of reactivity of alkyl halides.

# 3. Key Concepts

## 3.1 What Are Alkyl Halides?

An alkyl halide has the general formula R–X. The carbon–halogen bond is polar because the halogen is more electronegative than carbon, giving the carbon a small positive charge (δ+). This polarity is the key to the chemistry of alkyl halides: the δ+ carbon is attacked by nucleophiles (electron-rich species).

### Classification

| Type | Carbon bearing the halogen is joined to… | Example |
|---|---|---|
| Primary (1°) | one other carbon | $CH_3CH_2$–Cl |
| Secondary (2°) | two other carbons | $(CH_3)_2CH$–Cl |
| Tertiary (3°) | three other carbons | $(CH_3)_3C$–Cl |

**Memory Trick**

**Reactivity of C–X bond:** R–I > R–Br > R–Cl > R–F (weakest bond breaks most easily → iodide most reactive).

## 3.2 Preparation

Alkyl halides can be prepared by several routes: from alkanes by free-radical halogenation (in sunlight), from alkenes by adding a hydrogen halide (following Markownikoff's rule), and — most usefully in the laboratory — from alcohols by replacing the –OH group using reagents such as HX, $PCl_3$, $PCl_5$ or $SOCl_2$.

## 3.3 Nucleophilic Substitution

The most important reactions of alkyl halides are nucleophilic substitutions, in which a nucleophile replaces the halogen (the leaving group). For example, with aqueous KOH an alkyl halide gives an alcohol, and with alcoholic KCN it gives a nitrile. There are two mechanisms:

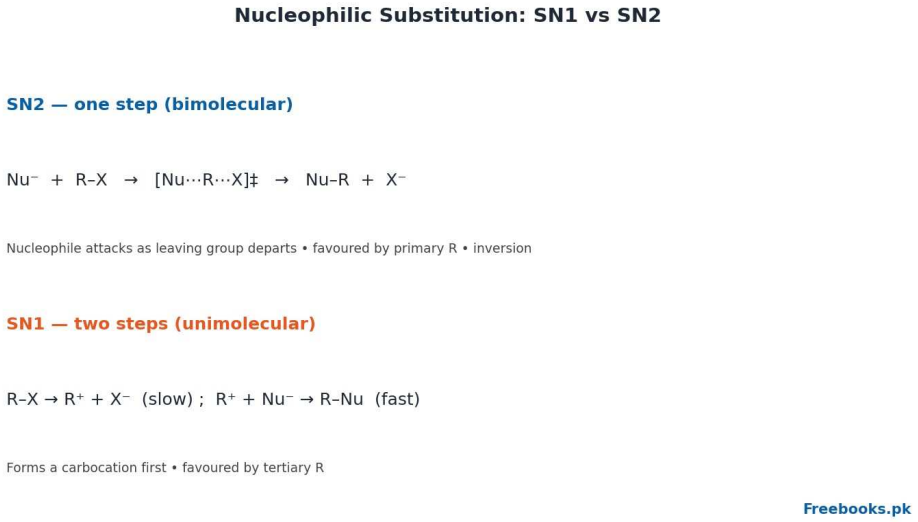


*Figure 10.2 — The SN2 (one-step) and SN1 (two-step) mechanisms.*

> **SN1 vs SN2 at a glance**
>
> **SN2:** one step, the nucleophile attacks as the halide leaves; rate depends on both reactants; favoured by primary halides.
>
> **SN1:** two steps, the halide leaves first to form a carbocation, then the nucleophile attacks; rate depends only on the halide; favoured by tertiary halides.

## 3.4 Elimination (Dehydrohalogenation)

When an alkyl halide is heated with alcoholic KOH, a molecule of hydrogen halide is eliminated and a double bond forms, giving an alkene. This elimination reaction competes with substitution; strong, hot, alcoholic base favours elimination, while aqueous conditions favour substitution.

## 3.5 The Grignard Reagent

One of the most important reasons for studying alkyl halides is the Grignard reagent, formed when an alkyl halide reacts with magnesium in dry ether: R–X + Mg → R–Mg–X. The carbon attached to magnesium is strongly nucleophilic, so Grignard reagents react with many compounds to build larger molecules. They give alkanes with water, primary alcohols with methanal, secondary alcohols with other aldehydes, tertiary alcohols with ketones, and carboxylic acids with carbon dioxide.

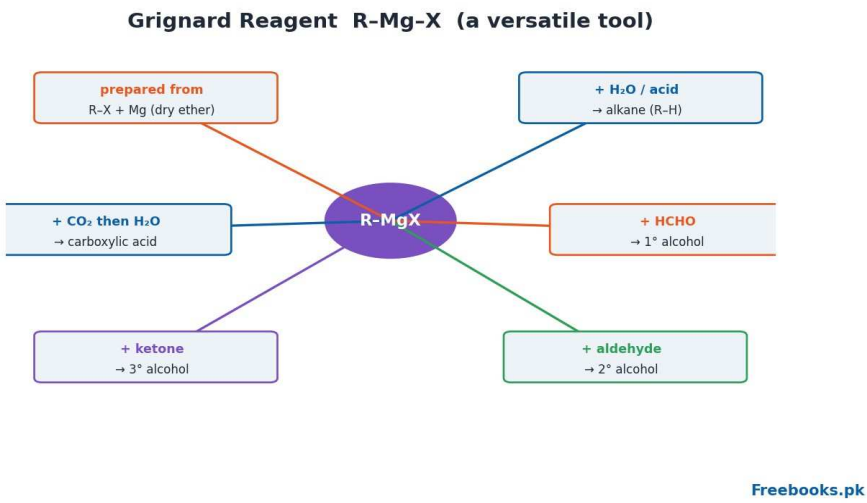


*Figure 10.3 — Some reactions of the Grignard reagent.*

**Teacher's Note**

The Grignard reagent must be made and used in perfectly dry conditions, because even a trace of water destroys it (turning it into an alkane). This 'moisture-sensitivity' is a favourite exam point.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Alkyl halide | A compound R–X in which a halogen replaces a hydrogen of an alkane. |
| Nucleophile | An electron-rich species that attacks a positive (δ+) carbon centre. |
| Nucleophilic substitution | Replacement of a leaving group by a nucleophile. |
| SN1 / SN2 | Two mechanisms of nucleophilic substitution (unimolecular / bimolecular). |
| Elimination | Removal of HX from an alkyl halide to form an alkene. |
| Grignard reagent | An organomagnesium compound R–Mg–X used to build larger molecules. |

## 5. Formulas / Rules

**Must-Know Facts**

**General formula:** R–X; classify as 1°, 2°, 3°.

**Reactivity:** R–I > R–Br > R–Cl > R–F.

**SN2 → primary; SN1 → tertiary** (via carbocation).

**Alc. KOH → elimination (alkene);** aq. KOH → substitution (alcohol).

**Grignard:** R–X + Mg (dry ether) → R–MgX; + $CO_2$ → carboxylic acid.

## 6. Diagrams / Illustrations

Key diagrams for revision:

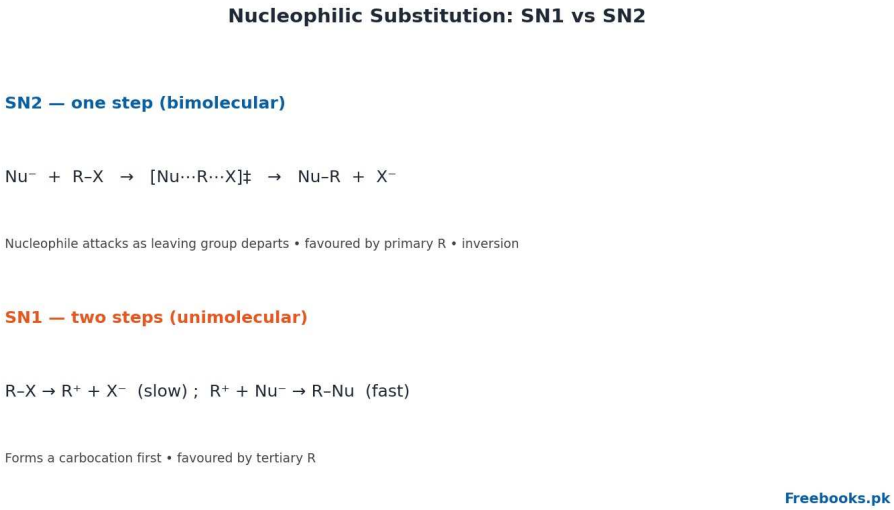


*Diagram 1 — SN1 vs SN2 mechanisms.*

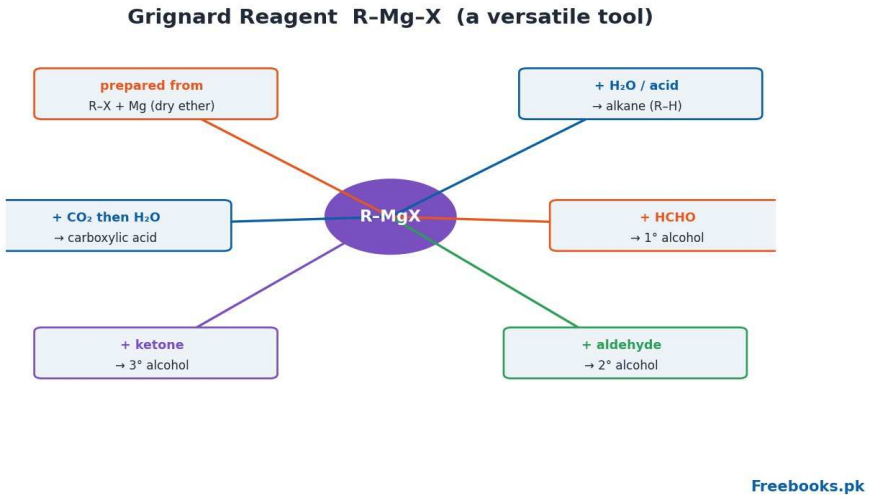


*Diagram 2 — Reactions of the Grignard reagent.*

## 7. Solved Examples

### Example 1 — Substitution product

**Q:** What is formed when ethyl bromide is heated with aqueous KOH?

**Solution:** Nucleophilic substitution occurs: the $OH^-$ replaces $Br^-$, giving ethanol ($C_2H_5OH$) and KBr.

### Example 2 — Substitution vs elimination

**Q:** How can ethyl bromide be converted to ethene?

**Solution:** Heat it with alcoholic KOH. This causes elimination of HBr (dehydrohalogenation) and forms ethene.

**Example 3 — Grignard synthesis**

**Q:** How would you make a carboxylic acid using a Grignard reagent?

**Solution:** React the Grignard reagent (R–MgX) with carbon dioxide, then hydrolyse with dilute acid: R–MgX + $CO_2$ → R–COO–MgX → R–COOH. The product has one more carbon than R.

## 8. Short Questions

**Q1. What is an alkyl halide?**
**Ans.** A compound R–X formed when a halogen replaces a hydrogen atom of an alkane.

**Q2. Why is the C–X bond reactive?**
**Ans.** It is polar; the carbon is δ+ and is attacked by nucleophiles, while $X^-$ is a good leaving group.

**Q3. Arrange R–F, R–Cl, R–Br, R–I in order of reactivity.**
**Ans.** R–I > R–Br > R–Cl > R–F (weaker bond, easier to break).

**Q4. Differentiate SN1 and SN2.**
**Ans.** SN2 is a one-step bimolecular reaction (primary halides); SN1 is a two-step unimolecular reaction via a carbocation (tertiary halides).

**Q5. How is an alkene obtained from an alkyl halide?**
**Ans.** By heating it with alcoholic KOH, which eliminates HX (dehydrohalogenation).

**Q6. How is a Grignard reagent prepared?**
**Ans.** By reacting an alkyl halide with magnesium in dry ether: R–X + Mg → R–MgX.

**Q7. Why must Grignard reagents be kept dry?**
**Ans.** Water destroys them, converting them into alkanes.

**Q8. What does a Grignard reagent give with $CO_2$?**
**Ans.** A carboxylic acid (after hydrolysis).

## 9. Long Questions

**Q1. Describe the nucleophilic substitution reactions of alkyl halides (SN1 and SN2).**

Because the carbon–halogen bond is polar, the carbon carries a partial positive charge and is attacked by nucleophiles, which replace the halogen (the leaving group). This replacement can happen by two mechanisms. In the SN2 (bimolecular) mechanism the reaction occurs in a single step: the nucleophile approaches the carbon from the side opposite the halogen and forms a bond at the same time as the carbon–halogen bond breaks, passing through a transition state and giving inversion of configuration. Its rate depends on both the alkyl halide and the nucleophile, and it is favoured by primary halides, which have little steric hindrance. In the SN1 (unimolecular) mechanism the reaction occurs in two steps: first the halide leaves to give a carbocation (the slow, rate-determining step), and then the nucleophile attacks the carbocation. Its rate depends only on the alkyl halide, and it is favoured by tertiary halides, which form the most stable carbocations. Typical products are alcohols (with aqueous KOH) and nitriles (with alcoholic KCN).

**Q2. Explain the preparation and synthetic importance of the Grignard reagent.**

The Grignard reagent is an organomagnesium compound of the form R–Mg–X, prepared by adding an alkyl halide to magnesium turnings in dry ether, where it forms R–X + Mg → R–Mg–X. In this reagent the carbon attached to magnesium is strongly nucleophilic, which makes the Grignard reagent one of the most useful tools in organic synthesis. With water or dilute acid it gives an alkane; with methanal (formaldehyde) it gives a primary alcohol; with other aldehydes it gives secondary alcohols; with ketones it gives tertiary alcohols; and with carbon dioxide, followed by hydrolysis, it gives a carboxylic acid with one more carbon atom than the original halide. Because these reactions form new carbon–carbon bonds, the Grignard reagent allows chemists to build larger and more complex molecules from simple alkyl halides. It must, however, be prepared and used in completely dry conditions, since even a trace of water destroys it.

**Q3. Distinguish between substitution and elimination reactions of alkyl halides.**

Alkyl halides can react in two competing ways, and the conditions decide which one dominates. In a substitution reaction a nucleophile replaces the halogen while the carbon skeleton stays the same; for example, ethyl bromide with aqueous KOH gives ethanol. In an elimination reaction a molecule of hydrogen halide is removed from two adjacent carbons to create a carbon–carbon double bond; for example, ethyl bromide with hot alcoholic KOH gives ethene. Thus the same reagent (KOH) can give different products depending on the solvent: aqueous conditions favour substitution (forming an alcohol), while hot, concentrated, alcoholic conditions favour elimination (forming an alkene). Tertiary halides and strong, bulky bases also favour elimination, whereas primary halides favour substitution.

## 10. Multiple Choice Questions (MCQs)

**1. The general formula of alkyl halides is:**
(A) R–OH (B) R–X (C) R–CHO (D) R–COOH

**2. Which alkyl halide is most reactive?**
(A) R–F (B) R–Cl (C) R–Br (D) R–I

**3. SN2 reactions are favoured by ___ halides:**
(A) primary (B) secondary (C) tertiary (D) aromatic

**4. SN1 reactions proceed through a:**
(A) free radical (B) carbocation (C) carbanion (D) transition metal

**5. Alkyl halide + aqueous KOH gives:**
(A) alkene (B) alcohol (C) alkane (D) ether

**6. Alkyl halide + alcoholic KOH gives:**
(A) alcohol (B) alkene (C) acid (D) amine

**7. A Grignard reagent is:**
(A) R–OH (B) R–MgX (C) R–ONa (D) $R–NH_2$

**8. Grignard reagent + $CO_2$ (then $H_2O$) gives:**
(A) alkane (B) alcohol (C) carboxylic acid (D) ketone

**9. Grignard reagents are prepared in:**
(A) water (B) dry ether (C) dilute acid (D) alcohol

**10. Grignard reagent + ketone gives a:**
(A) 1° alcohol (B) 2° alcohol (C) 3° alcohol (D) carboxylic acid

**MCQ Answer Key**

**1-B 2-D 3-A 4-B 5-B 6-B 7-B 8-C 9-B 10-C**

## 11. Quick Revision / Summary

- Alkyl halide R–X; classify 1°, 2°, 3°; C–X bond polar and reactive.
- Reactivity: R–I > R–Br > R–Cl > R–F.
- Nucleophilic substitution: SN2 (one step, primary) and SN1 (carbocation, tertiary).
- Aq. KOH → substitution (alcohol); alc. KOH → elimination (alkene).
- Grignard R–MgX from R–X + Mg (dry ether); builds C–C bonds.
- Grignard + $CO_2$ → carboxylic acid; + aldehyde/ketone → alcohols.

## 12. Exam Tips

**Teacher's Note**

Contrast SN1 and SN2 in a small table: steps, molecularity, which halide is favoured.
Remember: aqueous KOH → alcohol (substitution), alcoholic KOH → alkene (elimination).
Learn the full set of Grignard reactions — a very common long question.
Always mention that Grignard reagents need dry conditions.
Reactivity order R–I > R–Br > R–Cl > R–F is a frequent MCQ.

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# CHAPTER 11
# Alcohols, Phenols and Ethers

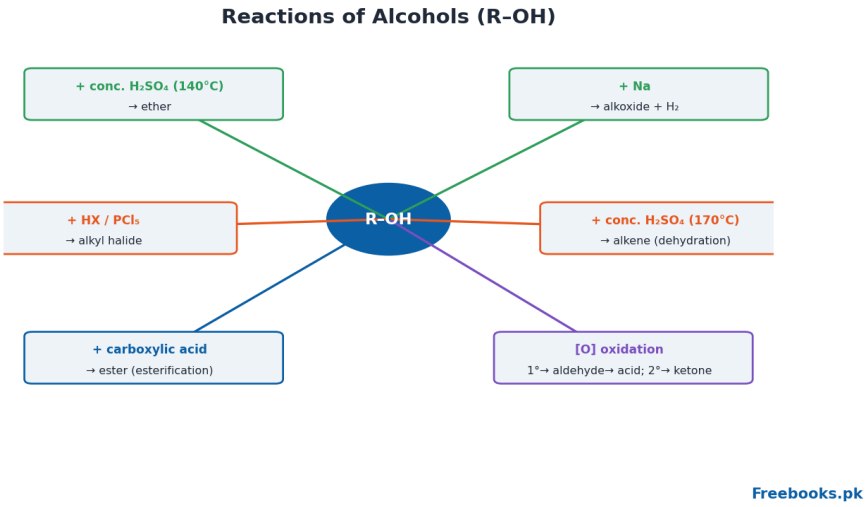


*Figure 11.1 — The versatile reactions of alcohols (R–OH).*

# 1. Chapter Overview

This chapter deals with three related families of oxygen-containing organic compounds. Alcohols (R–OH) have a hydroxyl group attached to a carbon chain; phenols ($C_6H_5$–OH) have a hydroxyl group attached directly to a benzene ring; and ethers (R–O–R′) have an oxygen atom joining two carbon groups. Alcohols such as ethanol are among the most useful of all organic compounds — as solvents, fuels, antiseptics and starting materials — so most of the chapter focuses on their preparation, properties and reactions, followed by the special behaviour of phenols and ethers.

# 2. Learning Objectives

- Define and classify alcohols as primary, secondary and tertiary.
- Describe the preparation of alcohols, including fermentation.
- Describe the important reactions of alcohols.
- Distinguish 1°, 2° and 3° alcohols by oxidation and the Lucas test.
- Explain why phenol is acidic and describe its reactions.
- Describe the preparation (Williamson synthesis) and properties of ethers.

# 3. Key Concepts

## 3.1 Alcohols and Their Classification

An alcohol contains the hydroxyl (–OH) functional group. Alcohols are classified by the carbon that carries the –OH group: in a primary (1°) alcohol that carbon is joined to one other carbon, in a secondary (2°) alcohol to two, and in a tertiary (3°) alcohol to three. This classification controls how the alcohol behaves on oxidation and in the Lucas test.

## 3.2 Preparation — Including Fermentation

Alcohols can be prepared by hydration of alkenes ($H_2O/H^+$), by reduction of aldehydes and ketones, and by the hydrolysis of alkyl halides. Ethanol is also made on a large scale by fermentation, in which enzymes (zymase) in yeast convert sugars into ethanol and carbon dioxide: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$. This is the basis of the alcoholic-drinks industry and of bio-ethanol fuel.

## 3.3 Reactions of Alcohols

The –OH group makes alcohols react in several ways. With sodium they release hydrogen and form alkoxides. With concentrated sulphuric acid they undergo dehydration — at about 170 °C to give an alkene, or at about 140 °C to give an ether. With hydrogen halides or $PCl_5$ the –OH is replaced by a halogen to give an alkyl halide. With carboxylic acids they form sweet-smelling esters (esterification). And they can be oxidised, which distinguishes the three classes.

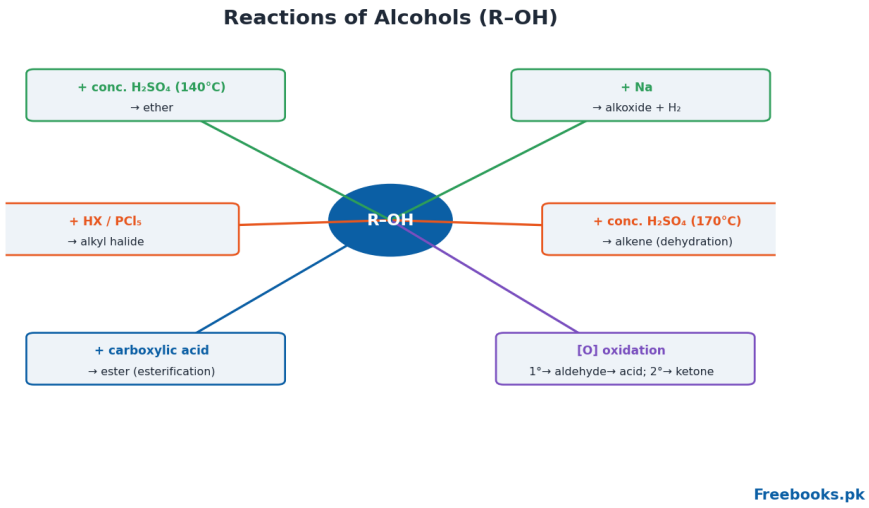


*Figure 11.2 — Summary of alcohol reactions.*

### Distinguishing 1°, 2° and 3° Alcohols

On oxidation, a primary alcohol first gives an aldehyde and then a carboxylic acid; a secondary alcohol gives a ketone; and a tertiary alcohol is not easily oxidised, because the carbon bearing the –OH has no hydrogen to remove. The Lucas test (with anhydrous $ZnCl_2$ and concentrated HCl) also distinguishes them: tertiary alcohols react at once (immediate turbidity), secondary alcohols react within a few minutes, and primary alcohols do not react at room temperature.

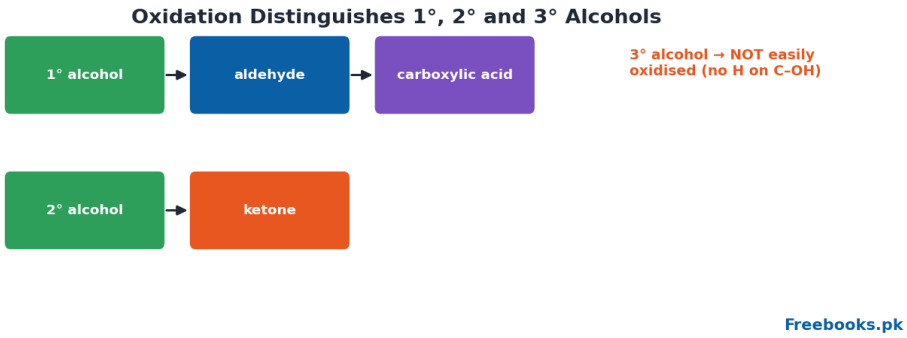


*Figure 11.3 — Oxidation products distinguish 1°, 2° and 3° alcohols.*

> **Memory Trick**
> **Oxidation shortcut:** 1° → aldehyde → acid; 2° → ketone; 3° → no reaction (no H on the C–OH).

## 3.4 Phenols

In phenol ($C_6H_5OH$) the –OH group is attached directly to the benzene ring. Unlike ordinary alcohols, phenol is weakly acidic: it reacts with sodium hydroxide to form sodium phenoxide and water, because the ring stabilises the phenoxide ion by delocalising its negative charge. Phenol also undergoes electrophilic substitution on the ring very readily (for example bromination), and it is used to make plastics (Bakelite), antiseptics and dyes.

**Teacher's Note**

A key comparison for exams: ordinary alcohols are neutral, but phenol is weakly acidic because the benzene ring delocalises the negative charge of the phenoxide ion. Emphasise this difference.

### 3.5 Ethers

Ethers have the general formula R–O–R′. They are fairly unreactive and are widely used as solvents (for example diethyl ether). A common laboratory method of making them is the Williamson synthesis, in which a sodium alkoxide reacts with an alkyl halide: R–ONa + R′–X → R–O–R′ + NaX.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Alcohol | An organic compound containing the –OH group attached to a carbon chain. |
| Phenol | A compound with –OH attached directly to a benzene ring. |
| Ether | A compound of the type R–O–R′ with oxygen joining two carbon groups. |
| Fermentation | Enzyme-catalysed conversion of sugars into ethanol and $CO_2$. |
| Esterification | Reaction of an alcohol with a carboxylic acid to form an ester and water. |
| Williamson synthesis | Preparation of an ether from a sodium alkoxide and an alkyl halide. |

## 5. Formulas / Rules

**Must-Know Facts**

**Classes:** 1°, 2°, 3° alcohols by the carbon bearing –OH.
**Dehydration:** conc. $H_2SO_4$ at 170 °C → alkene; at 140 °C → ether.
**Oxidation:** 1° → aldehyde → acid; 2° → ketone; 3° → no easy oxidation.
**Lucas test:** 3° immediate, 2° in minutes, 1° no reaction (cold).
**Fermentation:** $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ (zymase).
**Phenol** is weakly acidic; reacts with NaOH → sodium phenoxide.

## 6. Diagrams / Illustrations

Key diagrams for revision:

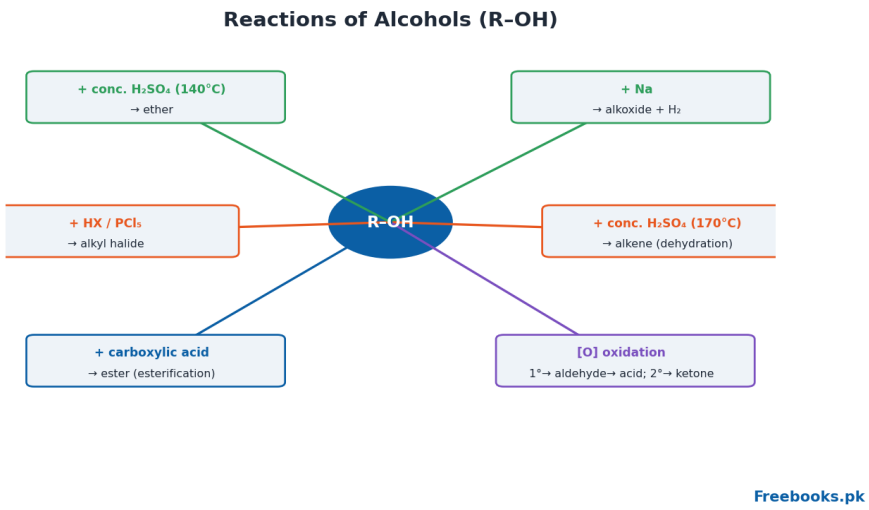


*Diagram 1 — Reactions of alcohols.*

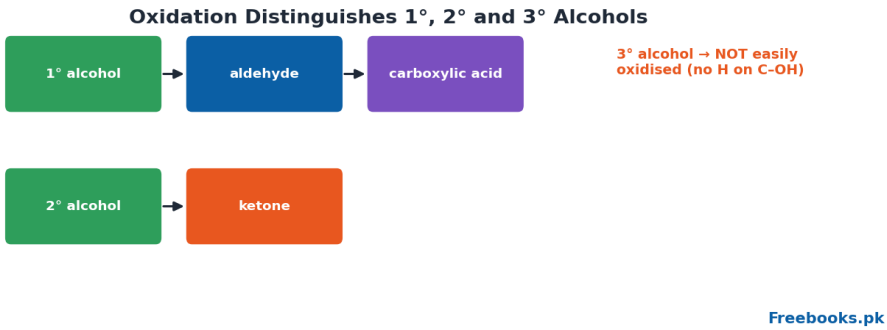


*Diagram 2 — Oxidation distinguishes alcohol classes.*

## 7. Solved Examples

### Example 1 — Oxidation

**Q:** What is formed when ethanol (a 1° alcohol) is oxidised?

**Solution:** It is first oxidised to ethanal (an aldehyde) and then to ethanoic acid (a carboxylic acid).

### Example 2 — Distinguishing alcohols

**Q:** How can you distinguish a tertiary alcohol from a primary alcohol?

**Solution:** Use the Lucas test ($ZnCl_2$ + conc. HCl). A tertiary alcohol gives immediate turbidity; a primary alcohol does not react at room temperature. Alternatively, on oxidation the tertiary alcohol resists oxidation while the primary gives an aldehyde/acid.

### Example 3 — Acidity of phenol

**Q:** Why is phenol acidic while ethanol is neutral?

**Solution:** When phenol loses $H^+$, the benzene ring delocalises the negative charge of the phenoxide ion, stabilising it. Ethanol's alkoxide has no such stabilisation, so ethanol is neutral.

## 8. Short Questions

**Q1. What is the functional group of alcohols?**
**Ans.** The hydroxyl group, –OH.

**Q2. How are alcohols classified?**
**Ans.** As primary, secondary or tertiary, depending on the number of carbons attached to the carbon bearing –OH.

**Q3. What is fermentation?**
**Ans.** The enzyme-catalysed conversion of sugars into ethanol and $CO_2$ by yeast.

**Q4. What forms when a 2° alcohol is oxidised?**
**Ans.** A ketone.

**Q5. Why can a tertiary alcohol not be easily oxidised?**
**Ans.** The carbon bearing –OH has no hydrogen atom to be removed during oxidation.

**Q6. What is the Lucas test used for?**
**Ans.** To distinguish 1°, 2° and 3° alcohols by how fast they react with $ZnCl_2$/conc. HCl.

**Q7. Why is phenol acidic?**
**Ans.** The phenoxide ion is stabilised by delocalisation of its charge over the benzene ring.

**Q8. Name a method to prepare ethers.**
**Ans.** The Williamson synthesis (sodium alkoxide + alkyl halide).

## 9. Long Questions

**Q1. Describe the important reactions of alcohols.**

The hydroxyl group makes alcohols react in several characteristic ways. With active metals such as sodium they release hydrogen gas and form alkoxides, showing that the O–H bond is weakly acidic. With concentrated sulphuric acid they undergo dehydration: at about 170 °C an alcohol loses water to form an alkene, while at about 140 °C two molecules combine with loss of water to give an ether. With hydrogen halides, $PCl_5$ or $PCl_3$ the –OH group is replaced by a halogen atom to give an alkyl halide. With carboxylic acids, in the presence of a little acid catalyst, alcohols form sweet-smelling esters (esterification), the reverse being hydrolysis. Finally, alcohols can be oxidised: a primary alcohol gives first an aldehyde and then a carboxylic acid, a secondary alcohol gives a ketone, and a tertiary alcohol resists oxidation. These reactions make alcohols central to organic synthesis.

**Q2. How are primary, secondary and tertiary alcohols distinguished?**

Primary, secondary and tertiary alcohols can be told apart by two simple methods. The first is oxidation: when treated with an oxidising agent such as acidified potassium dichromate, a primary alcohol is oxidised first to an aldehyde and then to a carboxylic acid, a secondary alcohol is oxidised to a ketone, and a tertiary alcohol is not oxidised under ordinary conditions because the carbon carrying the –OH group has no hydrogen atom to be removed. The second method is the Lucas test, in which the alcohol is shaken with the Lucas reagent (anhydrous zinc chloride dissolved in concentrated hydrochloric acid): a tertiary alcohol produces cloudiness (turbidity) immediately, a secondary alcohol produces it within about five minutes, and a primary alcohol

produces no turbidity at room temperature. Together these tests give a reliable way of classifying an unknown alcohol.

**Q3. Compare alcohols and phenols.**

Alcohols and phenols both contain the hydroxyl group, but they differ in where it is attached and in how it behaves. In an alcohol the –OH is joined to a saturated carbon of a chain, whereas in a phenol it is joined directly to a benzene ring. This difference gives them different acidity: ordinary alcohols are essentially neutral and do not react with sodium hydroxide, while phenol is weakly acidic and does react with sodium hydroxide to form sodium phenoxide, because the benzene ring can delocalise and stabilise the negative charge of the phenoxide ion. Phenols also undergo electrophilic substitution on the ring much more readily than benzene itself, and they give a characteristic violet colour with neutral ferric chloride, a test that alcohols do not give. Thus, although related, alcohols and phenols show clearly different chemistry.

## 10. Multiple Choice Questions (MCQs)

**1. The functional group of alcohols is:**
(A) –CHO (B) –OH (C) –COOH (D) –O–

**2. Oxidation of a primary alcohol first gives:**
(A) ketone (B) aldehyde (C) ether (D) ester

**3. Oxidation of a secondary alcohol gives:**
(A) aldehyde (B) ketone (C) acid (D) alkene

**4. Which alcohol resists easy oxidation?**
(A) primary (B) secondary (C) tertiary (D) all equally

**5. Fermentation of glucose gives ethanol and:**
(A) $O_2$ (B) $CO_2$ (C) $H_2$ (D) $CH_4$

**6. Dehydration of ethanol at 170 °C gives:**
(A) ether (B) ethene (C) ethane (D) ethanal

**7. The Lucas test distinguishes:**
(A) acids (B) alcohols (1°,2°,3°) (C) ethers (D) esters

**8. Phenol reacting with NaOH shows it is:**
(A) basic (B) neutral (C) weakly acidic (D) amphoteric

**9. Ethers are prepared by the:**
(A) Wurtz reaction (B) Williamson synthesis (C) Kolbe reaction (D) Cannizzaro reaction

**10. Alcohol + carboxylic acid gives:**
(A) ether (B) ester (C) ketone (D) amide

**MCQ Answer Key**

**1-B 2-B 3-B 4-C 5-B 6-B 7-B 8-C 9-B 10-B**

## 11. Quick Revision / Summary

- Alcohol R–OH; classify 1°, 2°, 3° by carbon bearing –OH.
- Prepared by hydration of alkenes, reduction, and fermentation (sugar → ethanol + $CO_2$).

- Reactions: with Na ($H_2$), dehydration (alkene/ether), with HX/$PCl_5$ (halide), esterification, oxidation.
- Oxidation: 1° → aldehyde → acid; 2° → ketone; 3° → resists.
- Lucas test: 3° immediate, 2° minutes, 1° no reaction cold.
- Phenol is weakly acidic; ethers (R–O–R′) made by Williamson synthesis.

## 12. Exam Tips

**Teacher's Note**

Draw the alcohol-reactions map and label conditions (140 °C vs 170 °C for $H_2SO_4$).

Learn oxidation products for each class — 1°→aldehyde→acid, 2°→ketone, 3°→no reaction.

Lucas test order (3° > 2° > 1°) is a favourite short question.

Explain phenol's acidity via delocalisation of the phenoxide charge.

Remember fermentation equation and the enzyme (zymase in yeast).

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# CHAPTER 12
# Aldehydes and Ketones

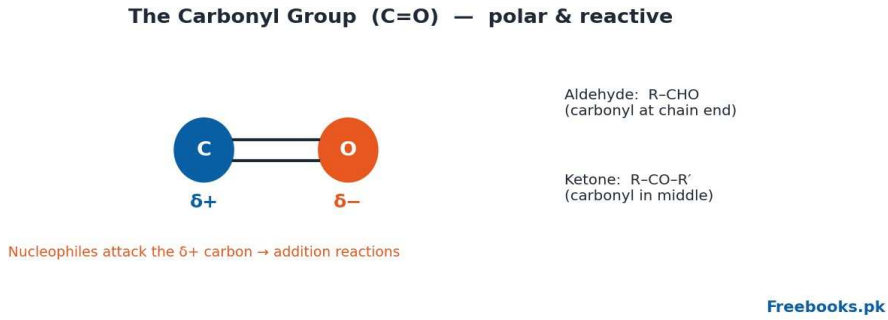


*Figure 12.1 — The polar carbonyl group (C=O) is the reactive centre of aldehydes and ketones.*

# 1. Chapter Overview

Aldehydes and ketones both contain the carbonyl group (C=O). In an aldehyde the carbonyl carbon is at the end of the chain and carries a hydrogen (R–CHO), while in a ketone it is in the middle, joined to two carbon groups (R–CO–R′). The carbonyl group is polar, with a δ+ carbon and a δ− oxygen, which makes these compounds react readily with nucleophiles. Aldehydes and ketones are important in the manufacture of plastics, perfumes, medicines and solvents (for example methanal in Bakelite and acetone as a solvent). A central theme of this chapter is how to tell aldehydes and ketones apart.

# 2. Learning Objectives

- Identify the carbonyl group and distinguish aldehydes from ketones.
- Describe methods of preparing aldehydes and ketones.
- Explain nucleophilic addition reactions of the carbonyl group.
- Describe the oxidation and reduction of aldehydes and ketones.
- Use Tollens', Fehling's, Benedict's and the iodoform tests to distinguish them.
- State the important uses of methanal and acetone.

# 3. Key Concepts

## 3.1 The Carbonyl Group

The carbonyl group, C=O, is the functional group of both aldehydes and ketones. Because oxygen is more electronegative than carbon, the group is polar: the carbon carries a partial positive charge (δ+) and the oxygen a partial negative charge (δ−). The δ+ carbon is therefore open to attack by nucleophiles, which is why nucleophilic addition is the characteristic reaction of these compounds.

## 3.2 Preparation

Aldehydes and ketones are most simply prepared by the controlled oxidation of alcohols: oxidising a primary alcohol gives an aldehyde, and oxidising a secondary alcohol gives a ketone. They can also be made by the ozonolysis of alkenes and by other routes. Methanal and ethanal are made industrially from methanol and ethene.

## 3.3 Nucleophilic Addition Reactions

The typical reaction of the carbonyl group is nucleophilic addition, in which a nucleophile adds to the δ+ carbon and the π-bond of C=O opens. Important examples include addition of hydrogen cyanide (HCN) to give cyanohydrins, addition of sodium hydrogen sulphite ($NaHSO_3$) to give crystalline bisulphite compounds (useful for purification), and addition of Grignard reagents (which, after hydrolysis, give alcohols). Aldehydes are generally more reactive towards these additions than ketones, because ketones have two bulky groups that hinder the approach of the nucleophile.

## 3.4 Oxidation and Reduction

Aldehydes and ketones behave very differently towards oxidation. Aldehydes are easily oxidised to carboxylic acids (because the carbonyl carbon carries a hydrogen that can be removed), whereas ketones are not oxidised under mild conditions. This difference is the basis of the tests that distinguish them. On reduction (for example with hydrogen and a catalyst, or with $LiAlH_4$) aldehydes give primary alcohols and ketones give secondary alcohols.

## 3.5 Distinguishing Tests

Several simple tests tell aldehydes and ketones apart, all relying on the fact that aldehydes are easily oxidised while ketones are not:

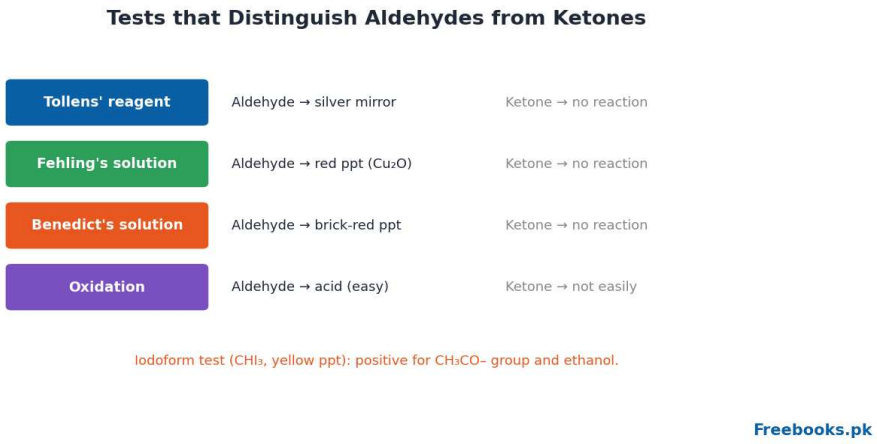


*Figure 12.2 — Tests that distinguish aldehydes from ketones.*

### Key Tests

**Tollens' reagent (ammoniacal $AgNO_3$):** aldehydes give a bright silver mirror; ketones do not.

**Fehling's / Benedict's solution:** aldehydes give a red precipitate of $Cu_2O$; ketones give no reaction.

**Iodoform test ($I_2$/NaOH):** a yellow precipitate of iodoform ($CHI_3$) forms with compounds containing the $CH_3CO–$ group (e.g. acetaldehyde, acetone) and with ethanol.

### Teacher's Note

A clean way to explain the tests: they are all mild oxidations. Aldehydes have a hydrogen on the carbonyl carbon and are easily oxidised (positive result); ketones do not, so they are negative — except the iodoform test, which detects the $CH_3CO–$ group in both.

## 3.6 Uses

Methanal (formaldehyde) is used as a preservative (formalin) and to make Bakelite and other plastics; ethanal is used to make ethanoic acid and other chemicals; and acetone (propanone) is a very common solvent, for example in nail-polish remover and in industry.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Carbonyl group | The C=O group present in aldehydes and ketones. |
| Aldehyde | A compound R–CHO with the carbonyl group at the end of the chain. |
| Ketone | A compound R–CO–R′ with the carbonyl group between two carbons. |
| Nucleophilic addition | Addition of a nucleophile across the polar C=O bond. |
| Tollens' test | Silver-mirror test that is positive for aldehydes. |
| Iodoform test | A test giving $CHI_3$ with $CH_3CO–$ compounds and ethanol. |

## 5. Formulas / Rules

### Must-Know Facts

**Aldehyde R–CHO; ketone R–CO–R′;** both contain C=O.

**Reactivity:** aldehydes > ketones in nucleophilic addition.

**Oxidation:** aldehyde → carboxylic acid (easy); ketone → not easily.

**Reduction:** aldehyde → 1° alcohol; ketone → 2° alcohol.

**Tests:** Tollens' (silver mirror) and Fehling's (red ppt) positive for aldehydes; iodoform for $CH_3CO–$.

## 6. Diagrams / Illustrations

Key diagrams for revision:

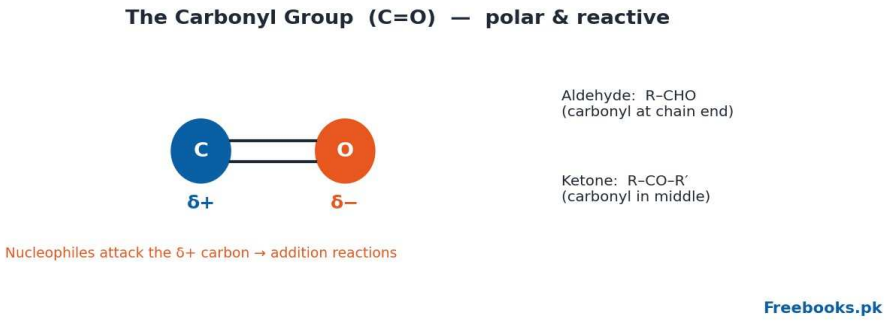


*Diagram 1 — The carbonyl group.*

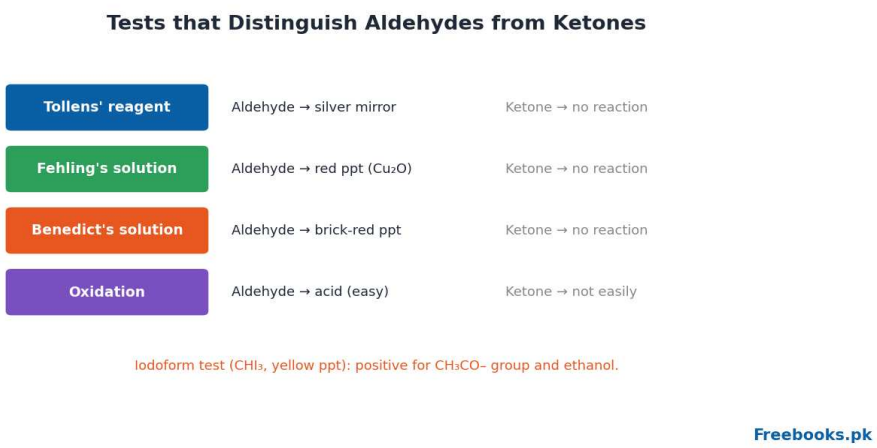


*Diagram 2 — Distinguishing tests.*

## 7. Solved Examples

**Example 1 — Distinguishing test**

**Q:** How would you distinguish ethanal from propanone?

**Solution:** Use Tollens' reagent. Ethanal (an aldehyde) gives a silver mirror; propanone (a ketone) does not. Fehling's solution can be used the same way (red precipitate with the aldehyde only).

**Example 2 — Reduction**

**Q:** What is formed when propanone is reduced?

**Solution:** Propanone (a ketone) is reduced to propan-2-ol, a secondary alcohol.

**Example 3 — Iodoform test**

**Q:** Which of ethanal and benzaldehyde gives a positive iodoform test?

**Solution:** Ethanal ($CH_3CHO$) gives a positive iodoform test because it contains the $CH_3CO–$ group; benzaldehyde ($C_6H_5CHO$) does not, as it lacks that group.

## 8. Short Questions

**Q1. What is the carbonyl group?**
**Ans.** The C=O group, the functional group of aldehydes and ketones.

**Q2. Differentiate an aldehyde from a ketone structurally.**
**Ans.** In an aldehyde the C=O is at the chain end (R–CHO); in a ketone it is between two carbons (R–CO–R′).

**Q3. Why is the carbonyl carbon attacked by nucleophiles?**
**Ans.** It is δ+ because oxygen pulls electrons away, so nucleophiles attack it.

**Q4. Why are aldehydes more reactive than ketones in addition?**
**Ans.** Ketones have two bulky groups that hinder the nucleophile's approach and stabilise the carbonyl.

**Q5. What does Tollens' reagent give with an aldehyde?**

**Ans.** A bright silver mirror.

**Q6. What is formed when a ketone is reduced?**
**Ans.** A secondary alcohol.

**Q7. Which functional group gives a positive iodoform test?**
**Ans.** The $CH_3CO–$ (methyl ketone) group, and ethanol.

**Q8. Give one use of acetone.**
**Ans.** As a solvent (e.g. nail-polish remover).

## 9. Long Questions

**Q1. Explain the nucleophilic addition reactions of aldehydes and ketones.**
Aldehydes and ketones react mainly by nucleophilic addition because their carbonyl group is polar: the carbon is δ+ and the oxygen δ−. A nucleophile attacks the electron-poor carbon, the π-bond of C=O breaks, and the electrons move onto the oxygen to give an alkoxide, which then picks up a proton. In this way hydrogen cyanide adds to give a cyanohydrin, which has one more carbon than the starting compound; sodium hydrogen sulphite adds to give a crystalline bisulphite addition compound that is useful for purifying and identifying aldehydes and some ketones; and a Grignard reagent adds and, after hydrolysis, gives an alcohol (a primary alcohol from methanal, a secondary alcohol from other aldehydes, and a tertiary alcohol from ketones). Aldehydes generally undergo these additions more readily than ketones, because the two carbon groups of a ketone hinder the approaching nucleophile and reduce the positive charge on the carbon.

**Q2. Describe the tests used to distinguish aldehydes from ketones.**
The key chemical difference between aldehydes and ketones is that aldehydes are easily oxidised while ketones are not, and the distinguishing tests are based on this. In the Tollens' test the compound is warmed with Tollens' reagent (an ammoniacal solution of silver nitrate); an aldehyde reduces the silver ions to metallic silver, which deposits as a bright silver mirror on the tube, whereas a ketone gives no mirror. In the Fehling's test (and the similar Benedict's test) the compound is warmed with a blue copper(II) solution; an aldehyde reduces the copper(II) to a brick-red precipitate of copper(I) oxide, whereas a ketone gives no precipitate. A further useful test is the iodoform test: when a compound containing the $CH_3CO–$ group (such as ethanal or acetone), or ethanol, is warmed with iodine and sodium hydroxide, a yellow precipitate of iodoform ($CHI_3$) with a characteristic smell is formed. Together these tests allow aldehydes, methyl ketones and other ketones to be identified.

**Q3. Compare the reactivity of aldehydes and ketones and explain the difference.**
Both aldehydes and ketones react through their carbonyl group, but aldehydes are generally the more reactive of the two, both in nucleophilic addition and in oxidation. There are two main reasons. First, a ketone has two alkyl (or aryl) groups attached to the carbonyl carbon, and these bulky groups get in the way of an approaching nucleophile (a steric effect), whereas an aldehyde has only one such group and a small hydrogen atom. Second, the alkyl groups of a ketone push electron density towards the carbonyl carbon, reducing its δ+ charge and making it less attractive to nucleophiles (an electronic effect). In oxidation the difference is even clearer: the aldehyde's carbonyl carbon carries a hydrogen atom that can be removed, so aldehydes are easily oxidised

to carboxylic acids, whereas ketones have no such hydrogen and resist mild oxidation. These differences explain why aldehydes give positive Tollens' and Fehling's tests while ketones do not.

## 10. Multiple Choice Questions (MCQs)

**1. The functional group of aldehydes and ketones is:**
(A) –OH (B) C=O (C) –COOH (D) –O–

**2. An aldehyde has the general formula:**
(A) R–CO–R′ (B) R–CHO (C) R–OH (D) R–COOH

**3. Tollens' reagent gives a silver mirror with:**
(A) ketones (B) aldehydes (C) alcohols (D) ethers

**4. Fehling's solution gives a red precipitate of:**
(A) Ag (B) $Cu_2O$ (C) CuO (D) $Fe_2O_3$

**5. On reduction a ketone gives a:**
(A) 1° alcohol (B) 2° alcohol (C) 3° alcohol (D) acid

**6. Aldehydes are more reactive than ketones due to:**
(A) resonance only (B) steric and electronic effects (C) hydrogen bonding (D) ionic character

**7. A positive iodoform test indicates the group:**
(A) –CHO (B) $CH_3CO$– (C) –COOH (D) –OH only

**8. Oxidation of an aldehyde gives a:**
(A) ketone (B) carboxylic acid (C) alcohol (D) ester

**9. Acetone is commonly used as a:**
(A) fuel (B) solvent (C) catalyst (D) fertilizer

**10. Which does NOT react with Tollens' reagent?**
(A) ethanal (B) methanal (C) propanone (D) benzaldehyde

**MCQ Answer Key**

**1-B 2-B 3-B 4-B 5-B 6-B 7-B 8-B 9-B 10-C**

## 11. Quick Revision / Summary

- Carbonyl C=O: aldehyde R–CHO (end), ketone R–CO–R′ (middle); polar (δ+ C, δ− O).
- Characteristic reaction = nucleophilic addition (HCN, $NaHSO_3$, Grignard).
- Aldehydes more reactive than ketones (steric + electronic).
- Oxidation: aldehyde → acid (easy); ketone → resists.
- Reduction: aldehyde → 1° alcohol; ketone → 2° alcohol.
- Tests: Tollens' (silver mirror), Fehling's (red ppt) for aldehydes; iodoform for $CH_3CO$–.

## 12. Exam Tips

**Teacher's Note**

Learn the three distinguishing tests and their exact positive results (silver mirror, red ppt, yellow ppt).

State clearly WHY aldehydes are more reactive/easily oxidised (H on carbonyl carbon; steric+electronic).

Know which compounds give the iodoform test ($CH_3CO$– group and ethanol).

Reduction products: aldehyde → 1° alcohol, ketone → 2° alcohol.

Remember uses: formalin/Bakelite (methanal), solvent (acetone).

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# CHAPTER 13
# Carboxylic Acids

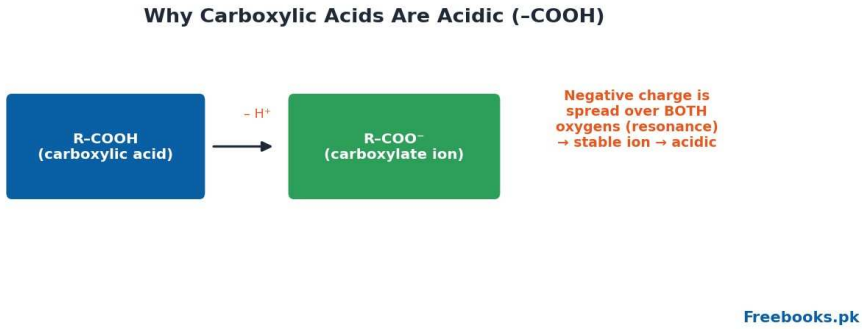


*Figure 13.1 — Why carboxylic acids are acidic: the carboxylate ion is stabilised by resonance.*

# 1. Chapter Overview

Carboxylic acids contain the carboxyl group (–COOH), which is really a combination of a carbonyl (C=O) and a hydroxyl (–OH) group on the same carbon. They are the most acidic of the common organic compounds, and are found everywhere in daily life — vinegar (ethanoic acid), citrus fruits (citric acid), sour milk (lactic acid) and ants (formic/methanoic acid). This chapter explains why carboxylic acids are acidic, how they are prepared, and their reactions, many of which produce important derivatives such as esters, acid chlorides and amides.

# 2. Learning Objectives

- Identify the carboxyl group and name simple carboxylic acids.
- Explain why carboxylic acids are acidic using resonance.
- Describe methods of preparing carboxylic acids.
- Describe the reactions of carboxylic acids and their derivatives.
- Explain esterification and its reverse, hydrolysis.
- State the important uses of carboxylic acids.

# 3. Key Concepts

## 3.1 The Carboxyl Group and Acidity

The carboxyl group –COOH is the functional group of carboxylic acids. These compounds are acidic because, when the O–H bond breaks and a proton is lost, the resulting carboxylate ion ($–COO^-$) is stabilised by resonance: the negative charge is shared equally between the two oxygen atoms, and the two C–O bonds become identical. This spreading of the charge makes the ion stable and the loss of the proton favourable, so carboxylic acids are far more acidic than alcohols or phenols (though still weak acids).

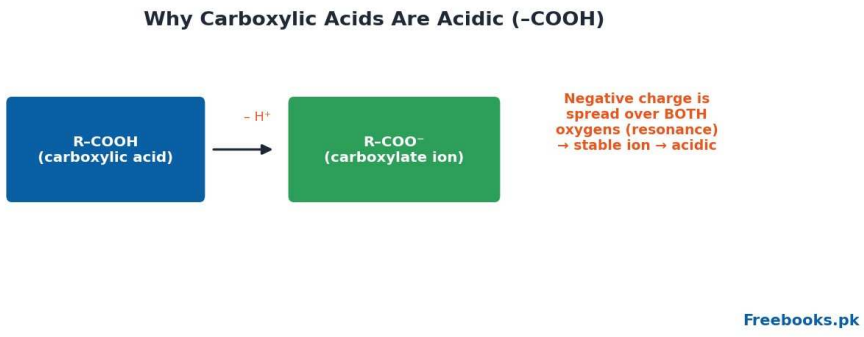


*Figure 13.2 — Resonance stabilisation of the carboxylate ion.*

> **Memory Trick**
> **Acidity order:** carboxylic acid > phenol > water > alcohol. 'Acids beat phenols beat alcohols.'

## 3.2 Preparation

Carboxylic acids can be prepared in several ways: by the oxidation of primary alcohols or aldehydes, by the hydrolysis of nitriles ($R–CN + 2H_2O \rightarrow R–COOH + NH_3$), and by treating a Grignard reagent with carbon dioxide followed by hydrolysis ($R–MgX + CO_2 \rightarrow R–COOH$), which adds one carbon to the chain. Ethanoic acid is made industrially from ethanol or ethene.

## 3.3 Reactions of Carboxylic Acids

The reactions of carboxylic acids fall into two groups: those of the acidic O–H, and those that replace the –OH of the carboxyl group to form derivatives.

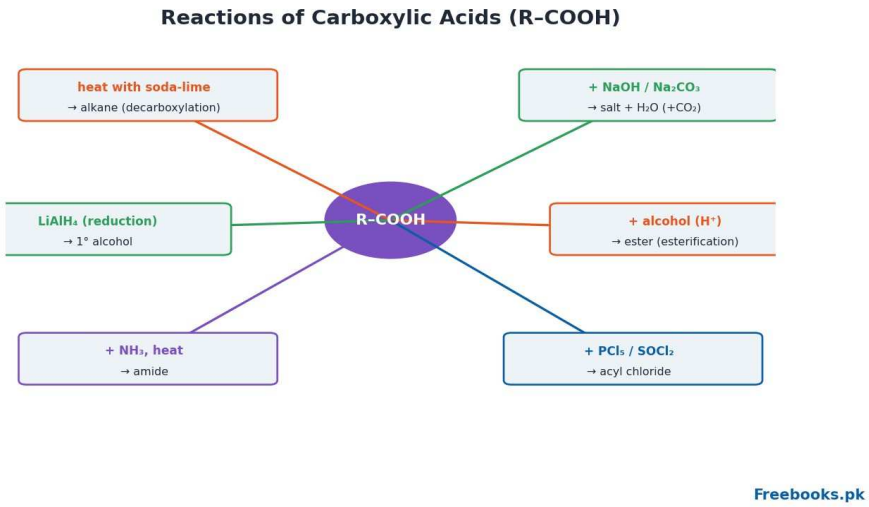


*Figure 13.3 — Reactions of carboxylic acids and their derivatives.*

**Salt formation.** As acids they react with metals, bases and carbonates to form salts; the reaction with sodium carbonate releases carbon dioxide (effervescence), a useful test.

**Esterification.** With an alcohol and a trace of acid catalyst they form a sweet-smelling ester and water; this reaction is reversible, and the reverse (with water) is hydrolysis.

**Formation of acyl chlorides.** With $PCl_5$, $PCl_3$ or $SOCl_2$ the –OH is replaced by –Cl to give a reactive acyl chloride.

**Formation of amides.** With ammonia (via the ammonium salt, on heating) they give amides ($R–CONH_2$).

**Reduction.** Strong reducing agents such as $LiAlH_4$ reduce carboxylic acids to primary alcohols.

**Decarboxylation.** On heating their sodium salts with soda-lime, carboxylic acids lose $CO_2$ to give an alkane with one fewer carbon.

> **Teacher's Note**
>
> Point out that all the 'derivative' reactions (ester, acyl chloride, amide) replace the –OH of –COOH with a different group. Seeing this pattern helps students remember the whole set.

### 3.4 Uses

Carboxylic acids and their derivatives are widely used: ethanoic acid (vinegar) as a food preservative and to make esters and other chemicals; methanoic acid in leather and rubber processing; benzoic acid and its salts as food preservatives; and long-chain fatty acids to make soaps. Esters of carboxylic acids are used as flavourings and perfumes.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Carboxylic acid | An organic compound containing the –COOH (carboxyl) group. |
| Carboxylate ion | The $–COO^-$ ion formed when a carboxylic acid loses a proton; stabilised by resonance. |
| Esterification | Reaction of a carboxylic acid with an alcohol to form an ester and water. |
| Hydrolysis | The breaking of a bond by water; the reverse of esterification. |
| Acyl chloride | A reactive derivative R–COCl formed by replacing –OH of –COOH with –Cl. |
| Decarboxylation | Loss of $CO_2$ from a carboxylic acid (or its salt) to give an alkane. |

## 5. Formulas / Rules

**Must-Know Facts**

**Functional group:** –COOH (carbonyl + hydroxyl).

**Acidic because** the carboxylate ion is resonance-stabilised.

**Acidity order:** carboxylic acid > phenol > water > alcohol.

**Test:** with $Na_2CO_3$ gives $CO_2$ effervescence (distinguishes acids from phenols/alcohols).

**Derivatives:** ester (with alcohol), acyl chloride ($PCl_5$), amide ($NH_3$).

**Grignard + $CO_2$** → carboxylic acid (adds one carbon).

## 6. Diagrams / Illustrations

Key diagrams for revision:

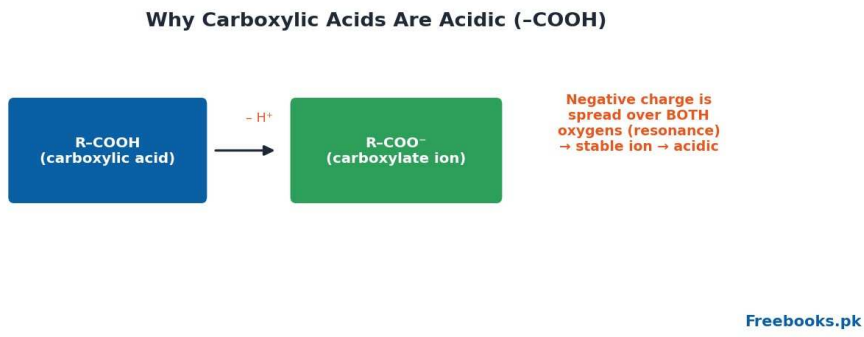

*Diagram 1 — Acidity and resonance.*

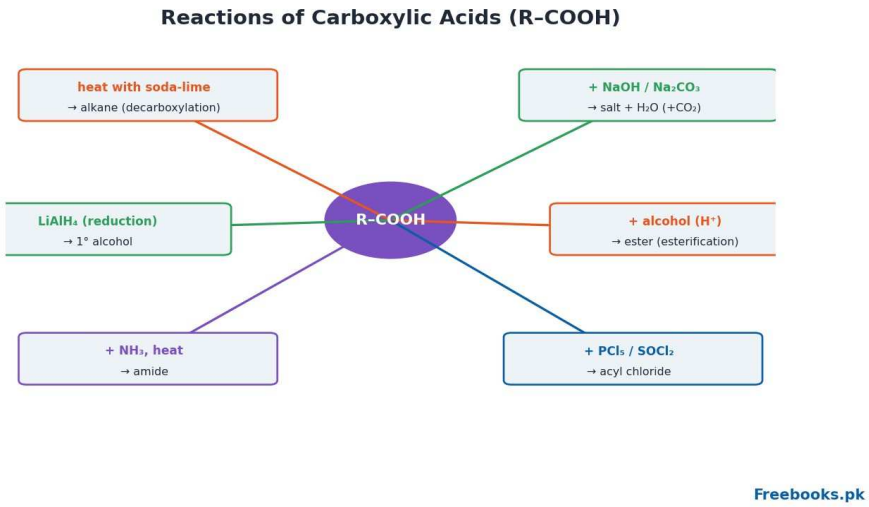


*Diagram 2 — Reactions and derivatives.*

## 7. Solved Examples

**Example 1 — Why acidic**

**Q:** Why is ethanoic acid more acidic than ethanol?

**Solution:** When ethanoic acid loses $H^+$, the carboxylate ion is stabilised by resonance (charge shared over two oxygens). Ethanol's alkoxide ion has no such stabilisation, so ethanoic acid is much more acidic.

**Example 2 — Distinguishing test**

**Q:** How can you distinguish a carboxylic acid from a phenol?

**Solution:** Add sodium carbonate (or sodium bicarbonate). A carboxylic acid gives brisk effervescence of $CO_2$; a phenol, being a weaker acid, does not react with sodium carbonate.

**Example 3 — Esterification**

**Q:** Write the product when ethanoic acid reacts with ethanol.

**Solution:** With a little concentrated $H_2SO_4$ they form the ester ethyl ethanoate (ethyl acetate) and water: $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$.

## 8. Short Questions

**Q1. What is the functional group of carboxylic acids?**
**Ans.** The carboxyl group, –COOH.

**Q2. Why are carboxylic acids acidic?**
**Ans.** Because the carboxylate ion left after losing $H^+$ is stabilised by resonance.

**Q3. Arrange alcohol, phenol and carboxylic acid in order of acidity.**
**Ans.** Carboxylic acid > phenol > alcohol.

**Q4. How can a carboxylic acid be distinguished from a phenol?**
**Ans.** A carboxylic acid gives $CO_2$ effervescence with sodium carbonate; a phenol does not.

**Q5. What is esterification?**
**Ans.** The reaction of a carboxylic acid with an alcohol to form an ester and water.

**Q6. What is formed when a carboxylic acid reacts with $PCl_5$?**
**Ans.** An acyl (acid) chloride, R–COCl.

**Q7. What is decarboxylation?**
**Ans.** Loss of $CO_2$ from a carboxylic acid (or its salt) to give an alkane, e.g. on heating with soda-lime.

**Q8. How is a carboxylic acid made from a Grignard reagent?**
**Ans.** By reacting R–MgX with $CO_2$ and then hydrolysing; this adds one carbon.

## 9. Long Questions

**Q1. Explain why carboxylic acids are acidic.**

Carboxylic acids are acidic because they readily give up the hydrogen of their –OH group as a proton, and the ion that is left behind is unusually stable. When a carboxylic acid loses $H^+$, it forms a carboxylate ion, $R–COO^-$. In this ion the negative charge is not fixed on one oxygen; instead it is delocalised by resonance so that both oxygen atoms share it equally, and the two carbon–oxygen bonds become identical in length. This spreading out of the charge lowers the energy of the ion and makes it stable, so the acid loses its proton easily. In contrast, when an alcohol loses a proton the resulting alkoxide ion has its charge fixed on a single oxygen with no resonance stabilisation, which is why alcohols are essentially neutral. Phenols lie in between, because their charge is delocalised into the ring but not as effectively. This is why the order of acidity is carboxylic acid > phenol > water > alcohol. Even so, carboxylic acids are still weak acids and only partly ionise in water.

**Q2. Describe the important reactions of carboxylic acids.**

Carboxylic acids react both as acids and by forming derivatives. As acids they turn blue litmus red and react with reactive metals, with bases and with carbonates to form salts; the reaction with sodium carbonate releases carbon dioxide, which is used as a test. The rest of their reactions replace the –OH of the carboxyl group with another group to give a derivative. With an alcohol and an acid catalyst they undergo esterification to form a sweet-smelling ester and water, a reversible reaction whose reverse is hydrolysis. With phosphorus pentachloride, phosphorus trichloride or thionyl chloride they form reactive acyl chlorides. With ammonia, through the ammonium salt on heating, they form amides. Strong reducing agents such as lithium aluminium hydride reduce them to primary alcohols. Finally, heating their sodium salts with soda-lime causes decarboxylation, removing carbon dioxide to leave an alkane with one fewer carbon. These reactions make carboxylic acids a gateway to many other organic compounds.

**Q3. What is esterification? Discuss the reaction and its importance.**

Esterification is the reaction in which a carboxylic acid combines with an alcohol, in the presence of a small amount of a strong acid catalyst such as concentrated sulphuric acid, to form an ester and water. For example, ethanoic acid and ethanol give ethyl ethanoate: $CH_3COOH + C_2H_5OH$

⇌ $CH_3COOC_2H_5$ + $H_2O$. The reaction is reversible, so it never goes fully to completion under ordinary conditions; the yield can be improved by using an excess of one reactant or by removing the water or ester as it forms. The reverse reaction, in which an ester is split by water back into an acid and an alcohol, is called hydrolysis (and when it is carried out with alkali it is called saponification, the basis of soap-making). Esterification is important because esters have pleasant, fruity smells and are widely used as artificial flavourings and perfumes, as solvents, and as the basis of fats, oils and many polymers.

## 10. Multiple Choice Questions (MCQs)

**1. The functional group of carboxylic acids is:**
(A) –OH (B) –CHO (C) –COOH (D) C=O

**2. Carboxylic acids are acidic because the carboxylate ion is stabilised by:**
(A) hydrogen bonding (B) resonance (C) ionic bonding (D) catenation

**3. Which is the most acidic?**
(A) ethanol (B) phenol (C) ethanoic acid (D) water

**4. A carboxylic acid + $Na_2CO_3$ gives:**
(A) $H_2$ (B) $CO_2$ (C) $O_2$ (D) $NH_3$

**5. Acid + alcohol ($H^+$) gives:**
(A) amide (B) ester (C) acyl chloride (D) alkane

**6. Acid + $PCl_5$ gives:**
(A) ester (B) amide (C) acyl chloride (D) alcohol

**7. Reduction of a carboxylic acid ($LiAlH_4$) gives:**
(A) aldehyde (B) 1° alcohol (C) ketone (D) ester

**8. Grignard reagent + $CO_2$ (then $H_2O$) gives:**
(A) alcohol (B) carboxylic acid (C) ketone (D) amide

**9. Heating a sodium carboxylate with soda-lime gives:**
(A) alkene (B) alkane (C) alcohol (D) ester

**10. The reverse of esterification is:**
(A) oxidation (B) hydrolysis (C) reduction (D) decarboxylation

**MCQ Answer Key**

**1-C 2-B 3-C 4-B 5-B 6-C 7-B 8-B 9-B 10-B**

## 11. Quick Revision / Summary

- –COOH group; acidic because carboxylate ion is resonance-stabilised.
- Acidity: carboxylic acid > phenol > water > alcohol.
- Preparation: oxidise 1° alcohol/aldehyde; hydrolyse nitrile; Grignard + $CO_2$.
- Reactions: salts ($CO_2$ with $Na_2CO_3$), esterification, acyl chloride ($PCl_5$), amide ($NH_3$), reduction, decarboxylation.
- Esterification is reversible; reverse = hydrolysis (with alkali = saponification).

- Uses: vinegar, preservatives, soaps, flavours/perfumes (esters).

## 12. Exam Tips

**Teacher's Note**

Explain acidity with the resonance of the carboxylate ion — a guaranteed question.
$Na_2CO_3$ effervescence distinguishes acids from phenols/alcohols — remember this test.
Learn the derivative reactions as 'replacing –OH': ester, acyl chloride, amide.
Esterification is reversible; know both directions and the catalyst (conc. $H_2SO_4$).
Grignard + $CO_2$ adds one carbon to give an acid — a common synthesis question.

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# CHAPTER 14
# Macromolecules

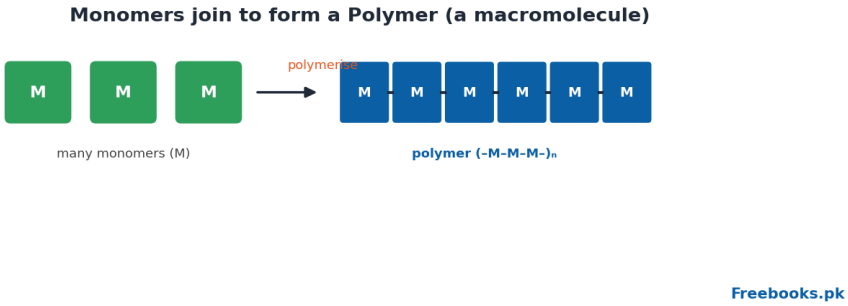


*Figure 14.1 — Many small monomers join to form a giant polymer molecule.*

# 1. Chapter Overview

Macromolecules are very large molecules built by joining together many small repeating units. The most important macromolecules are polymers, formed when hundreds or thousands of small molecules called monomers link together. Polymers are all around us: natural polymers such as starch, cellulose, proteins and natural rubber, and synthetic polymers such as polythene, PVC, nylon and polyester. This chapter explains how polymers form, the two main types of polymerisation, the difference between thermoplastics and thermosetting plastics, and the uses and environmental effects of these materials.

# 2. Learning Objectives

- Define macromolecule, polymer and monomer.
- Distinguish addition and condensation polymerisation.
- Give examples of natural and synthetic polymers.
- Distinguish thermoplastic and thermosetting plastics.
- Describe important polymers such as polythene, PVC, nylon and Bakelite.
- Discuss the uses and environmental impact of plastics.

# 3. Key Concepts

## 3.1 Polymers and Monomers

A polymer is a large molecule made of many repeating units joined together; the small molecules that join up are called monomers, and the process is called polymerisation. For example, thousands of ethene molecules (the monomer) join to form polythene (the polymer). Because polymers are so large, they are also called macromolecules or 'giant molecules'.

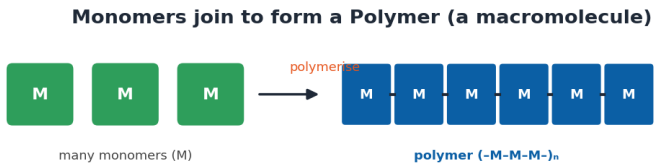


*Figure 14.2 — Polymerisation: monomers → polymer.*

> **Memory Trick**
>
> **Remember:** 'Poly' = many, 'mono' = one, 'mer' = part. A polymer is 'many parts'; a monomer is 'one part'.

## 3.2 Two Types of Polymerisation

There are two main ways in which monomers join together:

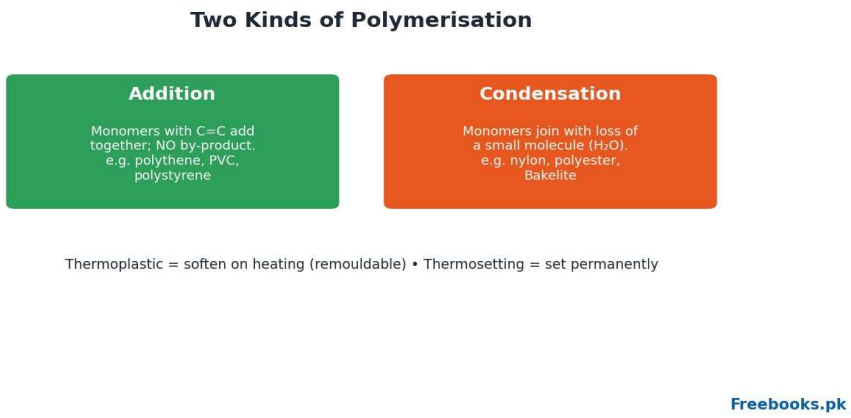


*Figure 14.3 — Addition versus condensation polymerisation.*

**Addition polymerisation.** Monomers that contain a carbon–carbon double bond simply add to one another, with no other product formed. Examples are polythene (from ethene), PVC (from vinyl chloride) and polystyrene (from styrene).

**Condensation polymerisation.** Monomers join with the loss of a small molecule (usually water) at each link. Examples are nylon and polyester (both from two different monomers) and Bakelite.

## 3.3 Natural and Synthetic Polymers

Natural polymers are made by living things: examples are starch and cellulose (polymers of glucose), proteins (polymers of amino acids), natural rubber and DNA. Synthetic polymers are made in industry from petroleum products: examples are polythene, PVC, nylon, polyester, Bakelite and synthetic rubber. Synthetic polymers can be designed to have almost any property — flexible or rigid, transparent or opaque, insulating or tough.

## 3.4 Thermoplastic and Thermosetting Plastics

Plastics are synthetic polymers that can be moulded into shape. They are of two kinds. Thermoplastics (such as polythene and PVC) soften on heating and can be melted and remoulded again and again, because their chains are only weakly held together. Thermosetting plastics (such as Bakelite) set permanently on first heating and cannot be softened again, because their chains become joined by strong cross-links into a rigid network.

| Feature | Thermoplastic | Thermosetting |
|---|---|---|
| On heating | Softens, can be remoulded | Sets permanently, chars |
| Structure | Long chains, weak forces | Cross-linked network |
| Reusable | Yes (can be recycled) | No |
| Examples | Polythene, PVC, polystyrene | Bakelite, melamine, epoxy |

**Teacher's Note**

A neat memory hook: 'thermoPLASTIC stays plastic (can be reshaped); thermoSET is set

| Feature | Thermoplastic | Thermosetting |
|---|---|---|
| forever.' | | |

### 3.5 Some Important Polymers

| Polymer | Monomer / type | Main uses |
|---|---|---|
| Polythene | ethene (addition) | Bags, bottles, sheets, insulation |
| PVC | vinyl chloride (addition) | Pipes, cable covering, floor tiles |
| Polystyrene | styrene (addition) | Packaging, disposable cups |
| Nylon | condensation (2 monomers) | Fibres, ropes, fabrics |
| Polyester | condensation (2 monomers) | Clothing fibres, bottles (PET) |
| Bakelite | phenol + methanal (condensation) | Electrical fittings, handles |

### 3.6 Uses and Environmental Impact

Polymers are cheap, light, strong, and resistant to water and corrosion, which is why they have replaced many traditional materials in packaging, clothing, building and electronics. However, most synthetic plastics are non-biodegradable, so they persist in the environment and cause pollution. Careful use, recycling of thermoplastics and the development of biodegradable plastics are important ways to reduce this problem.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Macromolecule | A very large molecule built from many repeating units. |
| Polymer | A large molecule made of many repeating monomer units. |
| Monomer | The small molecule that joins to form a polymer. |
| Addition polymerisation | Joining of unsaturated monomers with no by-product. |
| Condensation polymerisation | Joining of monomers with loss of a small molecule (e.g. water). |
| Thermoplastic | A plastic that softens on heating and can be remoulded. |

## 5. Formulas / Rules

**Must-Know Facts**

**Polymer =** many monomers; polymerisation is the joining process.
**Addition:** unsaturated monomers, no by-product (polythene, PVC, polystyrene).
**Condensation:** loss of a small molecule (nylon, polyester, Bakelite).
**Thermoplastic** = remouldable; thermosetting = set permanently.
**Natural:** starch, cellulose, protein, rubber, DNA; Synthetic: plastics/fibres.

## 6. Diagrams / Illustrations

Key diagrams for revision:

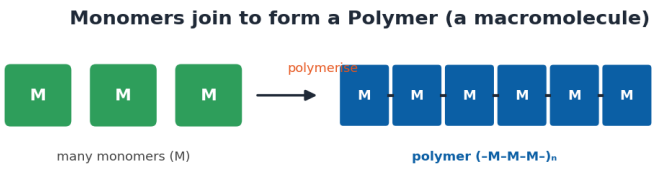


*Diagram 1 — Monomer to polymer.*

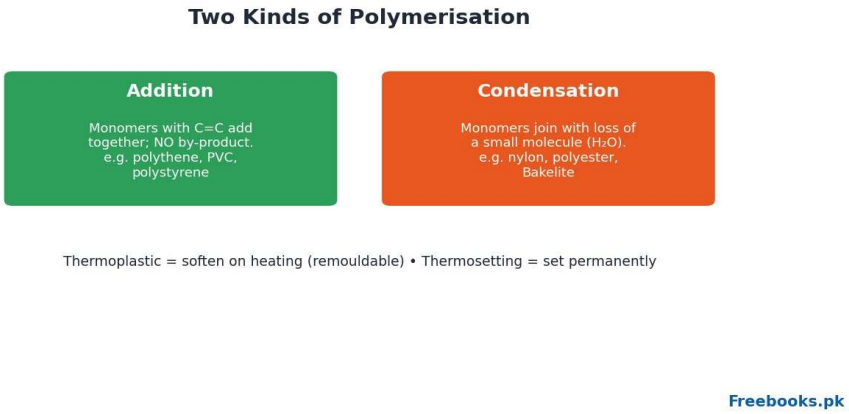


*Diagram 2 — Addition vs condensation.*

## 7. Solved Examples

### Example 1 — Type of polymerisation

**Q:** Is the formation of polythene addition or condensation polymerisation?

**Solution:** It is addition polymerisation. Ethene molecules (which contain C=C) simply add to one another with no small molecule being lost.

### Example 2 — Classifying a plastic

**Q:** Why can polythene be recycled but Bakelite cannot?

**Solution:** Polythene is a thermoplastic; its chains are weakly held, so it softens on heating and can be remoulded. Bakelite is thermosetting; its chains are cross-linked into a rigid network that does not soften, so it cannot be reshaped.

### Example 3 — Natural polymer

**Q:** Name the monomer of starch and of protein.

**Solution:** Starch is a polymer of glucose; proteins are polymers of amino acids.

## 8. Short Questions

**Q1. Define a polymer.**
**Ans.** A large molecule made of many repeating monomer units.

**Q2. What is a monomer?**
**Ans.** The small molecule that joins with others to form a polymer.

**Q3. Differentiate addition and condensation polymerisation.**
**Ans.** In addition, unsaturated monomers join with no by-product; in condensation, monomers join with loss of a small molecule such as water.

**Q4. Give two natural polymers.**
**Ans.** Starch and protein (also cellulose, rubber, DNA).

**Q5. Give two synthetic polymers.**
**Ans.** Polythene and nylon (also PVC, polyester, Bakelite).

**Q6. Differentiate thermoplastic and thermosetting plastics.**
**Ans.** Thermoplastics soften on heating and can be remoulded; thermosetting plastics set permanently and cannot.

**Q7. Name the monomer of PVC.**
**Ans.** Vinyl chloride.

**Q8. Why are plastics an environmental problem?**
**Ans.** Most are non-biodegradable, so they persist and cause pollution.

## 9. Long Questions

**Q1. Distinguish between addition and condensation polymerisation with examples.**

Polymers are formed by joining many monomers, and this can happen in two different ways. In addition polymerisation the monomers contain a carbon–carbon double bond, and they simply add to one another when the double bond opens; no other molecule is produced, so the polymer has exactly the same empirical formula as the monomer. Common examples are polythene (from ethene), PVC (from vinyl chloride) and polystyrene (from styrene). In condensation polymerisation the monomers usually contain two reactive groups, and they join with the elimination of a small molecule — most often water — at every link. Because a small molecule is lost, the polymer does not have the same formula as the monomers. Common examples are nylon and polyester, each made from two different monomers, and Bakelite, made from phenol and methanal. Thus the key difference is whether or not a small molecule is given off during polymerisation.

**Q2. Compare thermoplastic and thermosetting plastics.**

Plastics are moulded synthetic polymers, and they fall into two classes that behave very differently on heating. Thermoplastics are made of long polymer chains held together only by weak forces; when heated they soften and can be melted and remoulded into a new shape, and this can be repeated many times, which also makes them easy to recycle. Familiar thermoplastics are polythene, PVC and polystyrene. Thermosetting plastics, by contrast, form strong chemical cross-links between their chains during their first heating and moulding, so they set into a hard, rigid, three-dimensional network; once set they cannot be softened or remoulded, and on strong heating

they simply char. Familiar thermosetting plastics are Bakelite, melamine and epoxy resins. Because of these differences, thermoplastics are used where reshaping and recycling are useful, while thermosetting plastics are used where permanent hardness and heat resistance are needed, such as in electrical fittings.

**Q3. Discuss the importance and environmental impact of polymers.**

Polymers have become some of the most important materials in modern life because they are cheap to make, light in weight, strong, easily shaped, and resistant to water and corrosion. They are used in packaging (polythene bags and bottles), building (PVC pipes and fittings), clothing (nylon and polyester fibres), electrical insulation, medical equipment and countless everyday objects, often replacing heavier or more expensive materials such as metal, wood and glass. However, this usefulness comes with a serious drawback: most synthetic polymers are non-biodegradable, meaning that micro-organisms cannot break them down, so discarded plastics remain in the environment for a very long time, litter the land and oceans, and harm wildlife. Burning them can release toxic gases. The impact can be reduced by using plastics responsibly, by recycling thermoplastics, and by developing biodegradable and plant-based plastics. Balancing the great benefits of polymers against their environmental cost is one of the important challenges of chemistry today.

## 10. Multiple Choice Questions (MCQs)

**1. A polymer is made of many:**
(A) atoms (B) monomers (C) ions (D) isotopes

**2. Polythene is formed by ___ polymerisation:**
(A) condensation (B) addition (C) substitution (D) elimination

**3. Which is a condensation polymer?**
(A) polythene (B) PVC (C) nylon (D) polystyrene

**4. The monomer of PVC is:**
(A) ethene (B) vinyl chloride (C) styrene (D) glucose

**5. Which is a natural polymer?**
(A) nylon (B) starch (C) PVC (D) Bakelite

**6. A plastic that can be remoulded on heating is:**
(A) thermosetting (B) thermoplastic (C) cross-linked (D) elastomer

**7. Bakelite is a ___ plastic:**
(A) thermoplastic (B) thermosetting (C) natural (D) biodegradable

**8. Proteins are polymers of:**
(A) glucose (B) amino acids (C) nucleotides (D) fatty acids

**9. In condensation polymerisation, the small molecule usually lost is:**
(A) $CO_2$ (B) $H_2O$ (C) $O_2$ (D) $NH_3$

**10. Most synthetic plastics harm the environment because they are:**
(A) biodegradable (B) non-biodegradable (C) soluble (D) volatile

**MCQ Answer Key**

**1-B 2-B 3-C 4-B 5-B 6-B 7-B 8-B 9-B 10-B**

## 11. Quick Revision / Summary

- Polymer = many monomers joined; macromolecule = giant molecule.
- Addition polymerisation: unsaturated monomers, no by-product (polythene, PVC).
- Condensation polymerisation: loses a small molecule (nylon, polyester, Bakelite).
- Natural polymers: starch, cellulose, protein, rubber; synthetic: plastics/fibres.
- Thermoplastic = remouldable; thermosetting = set permanently.
- Plastics are useful but mostly non-biodegradable → pollution.

## 12. Exam Tips

**Teacher's Note**

Define monomer and polymer precisely, with one example each.
Contrast addition vs condensation by whether a small molecule is lost.
Learn the thermoplastic vs thermosetting table — a common question.
Know monomers of polythene (ethene) and PVC (vinyl chloride).
Mention 'non-biodegradable' when discussing environmental impact.

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## CHAPTER 15

# Common Chemical Industries in Pakistan

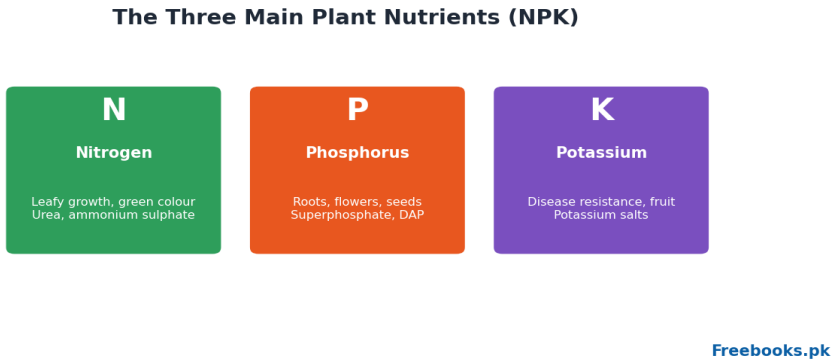


*Figure 15.1 — The three main plant nutrients supplied by fertilizers (N, P, K).*

# 1. Chapter Overview

Chemical industries turn raw materials into the products a country needs, and they are a major part of Pakistan's economy. This chapter looks at three of the most important chemical industries in Pakistan — the fertilizer industry, the cement industry and the paper industry. Because Pakistan is an agricultural country, the fertilizer industry is especially important: it supplies the nutrients that keep our soils fertile and our crops productive. We study the raw materials, the manufacturing steps and the uses of the products of each industry.

# 2. Learning Objectives

- Explain the importance of the fertilizer industry for Pakistan.
- Name the three main plant nutrients and the fertilizers that supply them.
- Describe the manufacture of important fertilizers such as urea.
- Describe the raw materials and manufacture of cement.
- Describe the raw materials and manufacture of paper.
- Appreciate the role of these industries in the national economy.

# 3. Key Concepts

## 3.1 The Fertilizer Industry

Fertilizers are substances added to the soil to supply the nutrients that plants need for healthy growth. The three most important nutrients are nitrogen (N), phosphorus (P) and potassium (K), together called NPK. Nitrogen promotes leafy, green growth; phosphorus helps the roots, flowers and seeds; and potassium improves disease resistance and the quality of fruit. Because Pakistani soils are often short of these nutrients, fertilizers are essential for good crop yields.

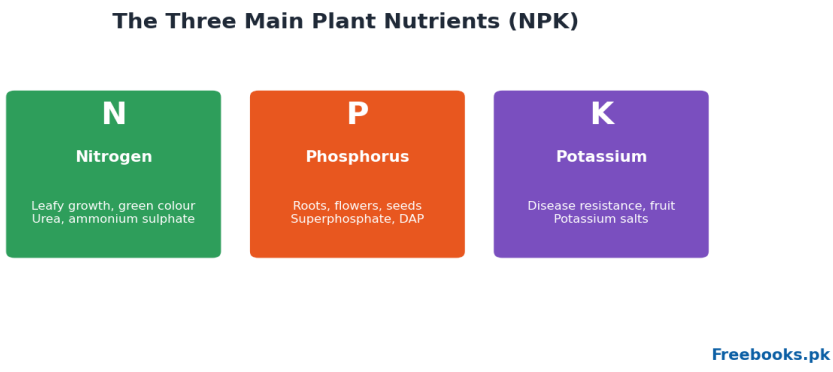


*Figure 15.2 — Roles of the NPK nutrients.*

| Fertilizer | Nutrient supplied | Formula |
|---|---|---|
| Urea | Nitrogen (highest N%) | $CO(NH_2)_2$ |
| Ammonium sulphate | Nitrogen | $(NH_4)_2SO_4$ |
| Ammonium nitrate | Nitrogen | $NH_4NO_3$ |

| Fertilizer | Nutrient supplied | Formula |
|---|---|---|
| Superphosphate | Phosphorus | $Ca(H_2PO_4)_2 + CaSO_4$ |
| Diammonium phosphate (DAP) | Nitrogen + phosphorus | $(NH_4)_2HPO_4$ |

### Manufacture of Urea

Urea is the most widely used nitrogen fertilizer in Pakistan because it has the highest nitrogen content (about 46%). It is made from ammonia (from the Haber process) and carbon dioxide in two steps: the two gases first combine to form ammonium carbamate, which is then decomposed by heat to give urea and water. The overall reaction is $2NH_3 + CO_2 \rightarrow CO(NH_2)_2 + H_2O$. Pakistan has several large urea plants that use natural gas as the source of hydrogen for the ammonia.

> **Memory Trick**
> **NPK roles:** N = 'Naya patta' (leaves), P = 'Phal-phool & roots', K = 'Kamzori se bachao' (disease resistance).

## 3.2 The Cement Industry

Cement is the grey powder that, when mixed with water, sand and gravel, sets into concrete — the basis of nearly all modern building. Its main raw materials are limestone (which provides calcium) and clay (which provides silica, alumina and iron). The manufacture has four main steps: the raw materials are crushed and mixed, the mixture is heated in a rotary kiln at about 1450–1500 °C to form small lumps called clinker, the clinker is ground to a fine powder, and a small amount of gypsum (about 2–5%) is added to control the setting time.

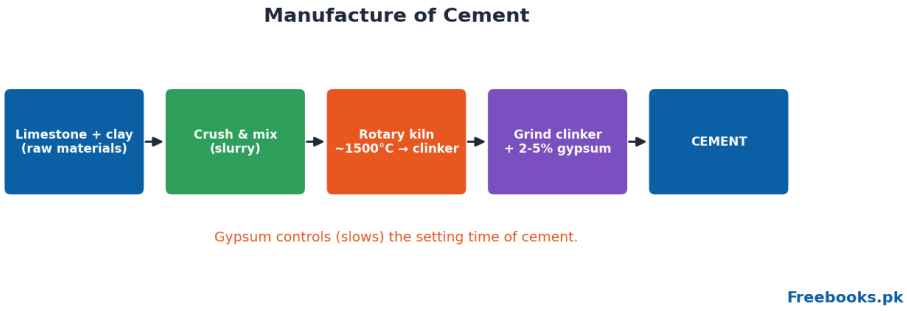


*Figure 15.3 — The manufacture of cement.*

> **Teacher's Note**
> Link this back to Chapter 2: gypsum ($CaSO_4 \cdot 2H_2O$) is added to cement to SLOW its setting so it can be worked before it hardens — a point that connects two chapters.

## 3.3 The Paper Industry

Paper is made mainly from cellulose fibres obtained from wood or, in Pakistan, from bagasse (the fibrous residue left after crushing sugar cane). The process has several steps: the raw material is digested (pulped) with chemicals to separate the cellulose fibres, the pulp is bleached and beaten

to the right texture, and it is then spread out, pressed and dried into thin sheets of paper. The paper industry is closely linked to Pakistan's large sugar industry, which supplies the bagasse.

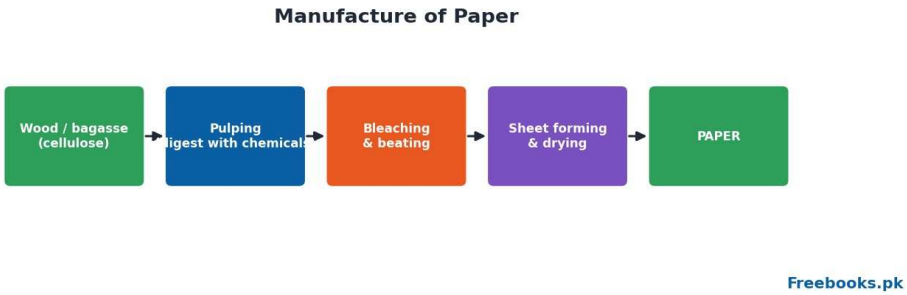


*Figure 15.4 — The manufacture of paper.*

### 3.4 Importance for Pakistan

These industries are vital to the national economy. The fertilizer industry supports agriculture, which employs a large part of the population and provides food and raw materials. The cement industry supplies the construction and infrastructure sector. The paper industry supports education, printing and packaging. Together they create jobs, reduce imports and add to the country's wealth.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Fertilizer | A substance added to soil to supply nutrients for plant growth. |
| NPK | The three main plant nutrients: nitrogen, phosphorus and potassium. |
| Urea | A nitrogen fertilizer, $CO(NH_2)_2$, with the highest nitrogen content. |
| Clinker | The lumps formed when the cement raw mixture is heated in the kiln. |
| Bagasse | The fibrous residue of sugar cane, used to make paper. |
| Pulping | Digesting raw material with chemicals to free the cellulose fibres for paper. |

## 5. Formulas / Rules

**Must-Know Facts**

**NPK:** N (leaves), P (roots/flowers/seeds), K (disease resistance/fruit).

**Urea:** $2NH_3 + CO_2 \rightarrow CO(NH_2)_2 + H_2O$; ~46% N (highest).

**Cement raw materials:** limestone + clay; heated in kiln → clinker; + gypsum.

**Gypsum** (2–5%) controls the setting time of cement.

**Paper:** cellulose from wood/bagasse → pulp → bleach → sheet.

## 6. Diagrams / Illustrations

Key diagrams for revision:

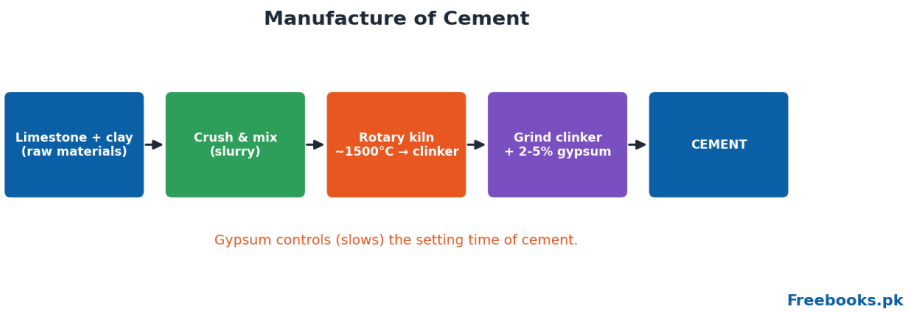


*Diagram 1 — Cement manufacture.*

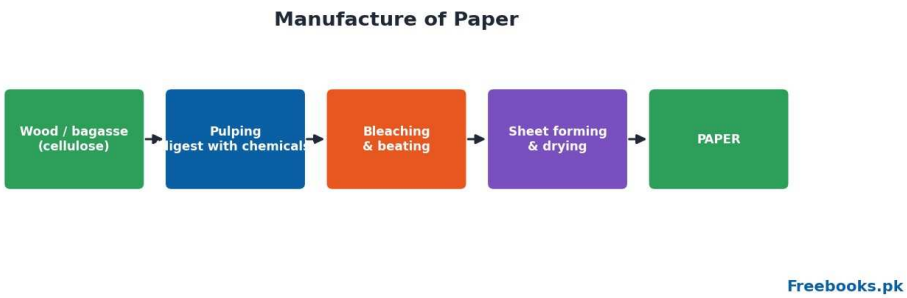


*Diagram 2 — Paper manufacture.*

## 7. Solved Examples

### Example 1 — Choosing a fertilizer

**Q:** A farmer's crop has pale, poor leafy growth. Which nutrient is likely deficient and which fertilizer would help?

**Solution:** Pale, poor leafy growth suggests a nitrogen deficiency. A nitrogen fertilizer such as urea, $CO(NH_2)_2$, would help.

### Example 2 — Cement

**Q:** Why is gypsum added to cement?

**Solution:** A small amount of gypsum (2–5%) is added to slow down (control) the setting time of the cement, so that it can be mixed and used before it hardens.

### Example 3 — Paper

**Q:** Which by-product of the sugar industry is used to make paper?

**Solution:** Bagasse — the fibrous residue left after the juice is crushed out of sugar cane — is used as a source of cellulose for paper.

## 8. Short Questions

**Q1. Why is the fertilizer industry important for Pakistan?**
**Ans.** Because Pakistan is an agricultural country, and fertilizers supply the nutrients needed for good crop yields.

**Q2. What are the three main plant nutrients?**
**Ans.** Nitrogen (N), phosphorus (P) and potassium (K).

**Q3. Which fertilizer has the highest nitrogen content?**
**Ans.** Urea, $CO(NH_2)_2$ (about 46% nitrogen).

**Q4. Write the reaction for the manufacture of urea.**
**Ans.** $2NH_3 + CO_2 \rightarrow CO(NH_2)_2 + H_2O$.

**Q5. Name the raw materials for cement.**
**Ans.** Limestone (calcium) and clay (silica, alumina, iron).

**Q6. What is clinker?**
**Ans.** The lumps formed when the cement raw mixture is strongly heated in the rotary kiln.

**Q7. Why is gypsum added to cement?**
**Ans.** To control (slow down) the setting time of the cement.

**Q8. What is bagasse used for?**
**Ans.** As a source of cellulose fibres to make paper.

## 9. Long Questions

**Q1. Describe the fertilizer industry and the manufacture of urea.**

Because Pakistan's economy depends heavily on agriculture, the fertilizer industry is one of its most important chemical industries. Fertilizers replace the nutrients that crops take out of the soil, the three most important being nitrogen, phosphorus and potassium (NPK): nitrogen encourages green, leafy growth, phosphorus develops the roots, flowers and seeds, and potassium improves disease resistance and fruit quality. Different fertilizers supply these nutrients, for example urea and ammonium sulphate for nitrogen, superphosphate for phosphorus, and diammonium phosphate (DAP) for both nitrogen and phosphorus. Of these, urea is the most widely used in Pakistan because it has the highest nitrogen content, about 46%. Urea is manufactured from ammonia (made by the Haber process using hydrogen from natural gas) and carbon dioxide. The two gases first combine to form ammonium carbamate, which is then decomposed by heat to give urea and water; overall, $2NH_3 + CO_2 \rightarrow CO(NH_2)_2 + H_2O$. Pakistan has several large urea plants, which help the country grow enough food and reduce its dependence on imports.

**Q2. Describe the raw materials and manufacture of cement.**

Cement is the essential building material that sets hard with water to bind sand and gravel into concrete. Its two main raw materials are limestone, which provides calcium oxide, and clay, which provides silica, alumina and iron oxide; a small amount of gypsum is also needed at the end. The manufacture takes place in four main steps. First, the limestone and clay are crushed and mixed together in the correct proportions, sometimes with water to make a slurry. Second, the mixture is fed into a large sloping rotary kiln and heated to about 1450–1500 °C, where chemical reactions

convert it into hard, marble-sized lumps called clinker. Third, the cooled clinker is ground to a very fine grey powder. Fourth, a small amount of gypsum (about 2–5%) is added and ground in with the clinker; the gypsum controls (slows) the setting time so that the cement can be mixed and placed before it hardens. The finished cement is then packed and sold. Pakistan has a large cement industry that supports its construction sector and exports.

**Q3. Describe how paper is manufactured, and the link with the sugar industry.**

Paper is made from cellulose fibres, which come from wood and, in Pakistan especially, from bagasse — the fibrous material left after the juice has been pressed out of sugar cane. The manufacture has several stages. First the raw material is cut up and digested (pulped) with chemicals, which dissolve away the substances that hold the fibres together and free the cellulose as a soft pulp. The pulp is then bleached to make it white and beaten to give the fibres the right texture. Next the watery pulp is spread out evenly on a moving wire screen, where the water drains away and the fibres mat together into a thin, wet sheet. Finally the sheet is pressed and dried over heated rollers to give finished paper. Because bagasse is a by-product of sugar making, the paper industry is closely linked to Pakistan's large sugar industry, which turns what would otherwise be waste into a valuable raw material. The paper industry supports education, printing, newspapers and packaging.

## 10. Multiple Choice Questions (MCQs)

**1. The three main plant nutrients are:**
(A) C, H, O (B) N, P, K (C) Na, Ca, Mg (D) Fe, Cu, Zn

**2. Which fertilizer has the highest nitrogen content?**
(A) ammonium sulphate (B) urea (C) DAP (D) superphosphate

**3. The formula of urea is:**
(A) $NH_4NO_3$ (B) $CO(NH_2)_2$ (C) $(NH_4)_2SO_4$ (D) $(NH_4)_2HPO_4$

**4. Urea is made from ammonia and:**
(A) $O_2$ (B) $CO_2$ (C) $N_2$ (D) $H_2O$

**5. The main raw materials for cement are:**
(A) sand and gravel (B) limestone and clay (C) gypsum and coal (D) clay and salt

**6. The lumps formed in the cement kiln are called:**
(A) slurry (B) clinker (C) slag (D) pulp

**7. Gypsum is added to cement to:**
(A) increase strength (B) control setting time (C) give colour (D) reduce cost

**8. Paper is mainly made of:**
(A) protein (B) cellulose (C) starch (D) nylon

**9. Bagasse is a by-product of the ___ industry:**
(A) cement (B) sugar (C) fertilizer (D) paper

**10. DAP supplies:**
(A) only nitrogen (B) only phosphorus (C) nitrogen and phosphorus (D) potassium

**MCQ Answer Key**

**1-B 2-B 3-B 4-B 5-B 6-B 7-B 8-B 9-B 10-C**

## 11. Quick Revision / Summary

- Fertilizers supply NPK: N (leaves), P (roots/flowers), K (disease resistance).
- Urea $CO(NH_2)_2$ = highest N (~46%); $2NH_3 + CO_2 \rightarrow$ urea + $H_2O$.
- Cement: limestone + clay → kiln (clinker) → grind + gypsum.
- Gypsum controls cement setting time.
- Paper: cellulose from wood/bagasse → pulp → bleach → sheet.
- These industries are vital to Pakistan's agriculture, construction and economy.

## 12. Exam Tips

**Teacher's Note**

Learn the NPK roles and match each nutrient to its fertilizer.
Remember urea has the highest nitrogen content and its manufacturing equation.
Know the four steps of cement manufacture and why gypsum is added.
Link bagasse to the sugar industry for the paper question.
Mention the economic importance for Pakistan in long answers.

FSc / ICS Part-II Chemistry — Punjab Board

## CHAPTER 16

# Environmental Chemistry

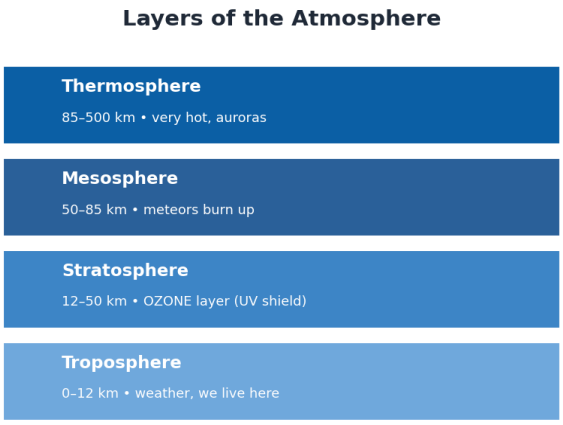


*Figure 16.1 — The layers of the atmosphere; the ozone layer in the stratosphere shields us from UV light.*

# 1. Chapter Overview

Environmental chemistry studies the chemical processes that take place in our surroundings — the air, water and soil — and how human activities affect them. As populations and industries grow, pollution has become a serious threat to health and to the planet. This chapter looks at the structure of the atmosphere, the main air and water pollutants, and the major environmental problems of our time: acid rain, ozone depletion and the greenhouse effect (global warming). It also introduces the idea of controlling pollution and practising 'green' chemistry.

# 2. Learning Objectives

- Describe the main layers of the atmosphere and their importance.
- Identify the major air pollutants and their sources.
- Explain the causes and effects of acid rain.
- Explain ozone depletion and the role of CFCs.
- Explain the greenhouse effect and global warming.
- Describe water pollution and simple ways to control pollution.

# 3. Key Concepts

## 3.1 The Atmosphere

The atmosphere is the blanket of gases surrounding the Earth. It is divided into layers. The lowest is the troposphere, where we live and where weather occurs. Above it is the stratosphere, which contains the vital ozone layer that absorbs most of the Sun's harmful ultraviolet (UV) radiation. Higher still are the mesosphere and the thermosphere. The atmosphere protects life, provides the gases we breathe, and keeps the Earth warm enough to live on.

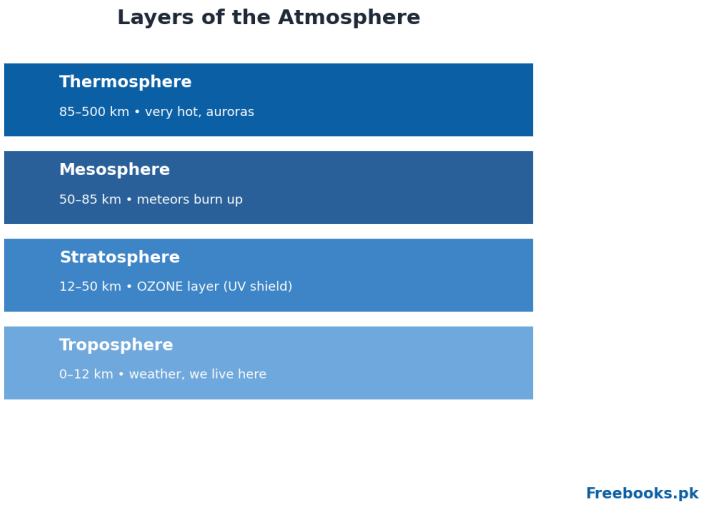


*Figure 16.2 — Layers of the atmosphere.*

## 3.2 Air Pollution

Air pollution is the presence of harmful substances in the air. The main pollutants and their chief sources are shown below; most come from burning fossil fuels in vehicles, factories and power stations.

| Pollutant | Main source | Harmful effect |
|---|---|---|
| Carbon monoxide (CO) | Incomplete burning of fuel | Poisonous; reduces oxygen in blood |
| Sulphur dioxide ($SO_2$) | Burning coal and oil | Acid rain, breathing problems |
| Oxides of nitrogen ($NO_x$) | Vehicle and factory exhaust | Acid rain, smog |
| Carbon dioxide ($CO_2$) | Burning all fossil fuels | Greenhouse gas → global warming |
| CFCs | Old aerosols, refrigerants | Destroy the ozone layer |
| Particulates (smoke, dust) | Combustion, industry | Lung and breathing diseases |

## 3.3 Acid Rain

When fuels containing sulphur and nitrogen are burned, they release sulphur dioxide and oxides of nitrogen into the air. These gases react with oxygen and water vapour to form sulphuric acid and nitric acid, which fall to the ground dissolved in rain — this is acid rain. Acid rain damages plants and soil, corrodes buildings and statues (especially those made of marble/limestone), and kills fish by making lakes and rivers too acidic.


*Figure 16.3 — Formation of acid rain.*

> **Memory Trick**
> **Acid rain culprits:** $SO_2$ and $NO_x$ → $H_2SO_4$ and $HNO_3$. 'Sulphur and Nitrogen make the rain sour.'

## 3.4 Ozone Depletion

The ozone layer in the stratosphere absorbs harmful UV radiation from the Sun. Certain man-made gases, especially chlorofluorocarbons (CFCs) once used in refrigerators, air-conditioners and aerosol sprays, rise into the stratosphere where UV light breaks them down to release chlorine atoms. These chlorine atoms destroy ozone molecules, thinning the ozone layer (the 'ozone hole'). A thinner ozone layer lets more UV reach the Earth, increasing skin cancer, eye

cataracts and crop damage. For this reason CFCs have been banned under international agreements.

> **Teacher's Note**
> Clarify a common confusion: ozone in the stratosphere is 'good' (it shields us from UV), but ozone at ground level is a harmful pollutant. The problem in this section is the LOSS of the good, high-level ozone.

### 3.5 The Greenhouse Effect and Global Warming

Certain gases in the atmosphere — mainly carbon dioxide, methane, water vapour and CFCs — let the Sun's light through to warm the Earth but trap much of the heat that the Earth radiates back. This natural warming, called the greenhouse effect, keeps the planet warm enough for life. However, burning huge amounts of fossil fuels has raised the level of carbon dioxide, so more heat is trapped and the Earth's average temperature is slowly rising — this is global warming. Its effects include melting glaciers, rising sea levels, and changes in weather and climate.

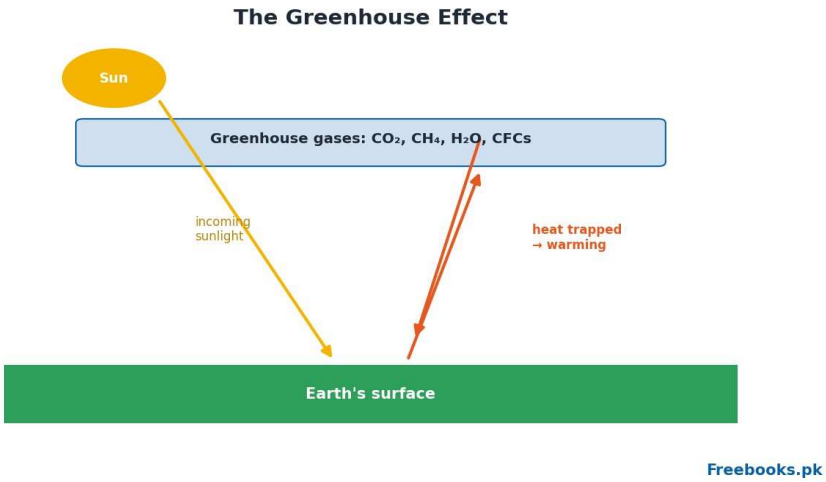


*Figure 16.4 — The greenhouse effect.*

### 3.6 Water Pollution and Its Control

Water pollution is caused by sewage, industrial waste, fertilizers and pesticides washing into rivers and lakes. It spreads disease and kills aquatic life. Pollution can be reduced by treating sewage and industrial waste before it is released, using cleaner fuels and catalytic converters in vehicles, controlling the use of fertilizers and pesticides, recycling waste, and planting trees. Practising 'green chemistry' — designing processes that make less waste and use safer chemicals — is an important long-term solution.

## 4. Important Definitions

| Term | Definition |
|---|---|
| Environmental chemistry | The study of chemical processes and pollution in the air, water and soil. |
| Air pollution | The presence of harmful substances in the air. |

| Term | Definition |
|---|---|
| Acid rain | Rain made acidic by dissolved sulphuric and nitric acids from $SO_2$ and $NO_x$. |
| Ozone depletion | Thinning of the stratospheric ozone layer, mainly by CFCs. |
| Greenhouse effect | The trapping of heat in the atmosphere by gases such as $CO_2$. |
| Global warming | The gradual rise in Earth's average temperature due to increased greenhouse gases. |

## 5. Formulas / Rules

### Must-Know Facts

**Atmosphere layers:** troposphere, stratosphere (ozone), mesosphere, thermosphere.
**Acid rain:** $SO_2$ and $NO_x$ → $H_2SO_4$ and $HNO_3$.
**Ozone depletion:** caused by CFCs releasing chlorine atoms.
**Greenhouse gases:** $CO_2$, $CH_4$, $H_2O$ vapour, CFCs → global warming.
**Control:** treat waste, cleaner fuels, catalytic converters, recycling, tree planting.

## 6. Diagrams / Illustrations

Key diagrams for revision:

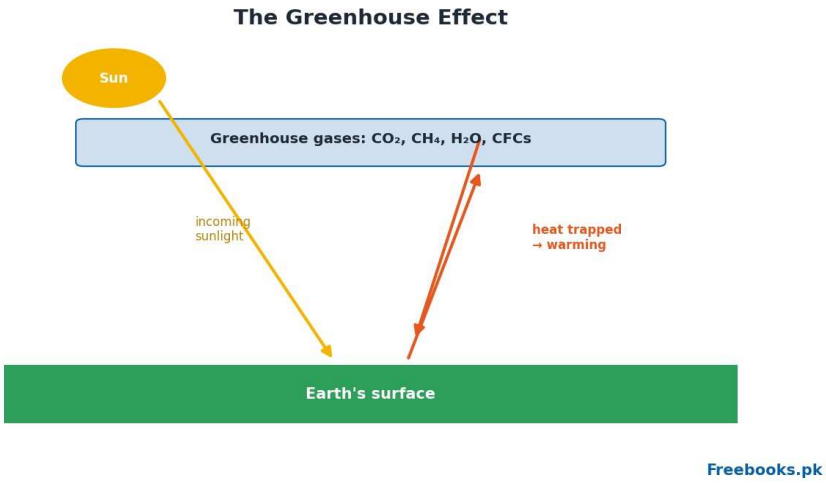


*Diagram 1 — The greenhouse effect.*

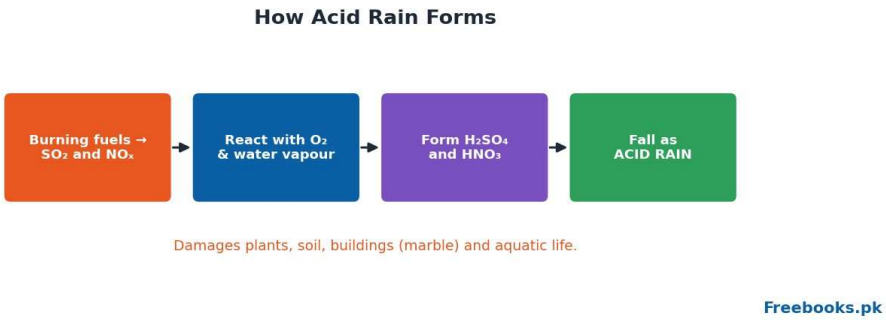


*Diagram 2 — Acid rain formation.*

## 7. Solved Examples

**Example 1 — Acid rain**

**Q:** Which gases are mainly responsible for acid rain, and what acids do they form?

**Solution:** Sulphur dioxide ($SO_2$) and oxides of nitrogen ($NO_x$). They react with oxygen and water in the air to form sulphuric acid ($H_2SO_4$) and nitric acid ($HNO_3$), which fall as acid rain.

**Example 2 — Ozone layer**

**Q:** Why are CFCs harmful to the ozone layer?

**Solution:** In the stratosphere, UV light breaks CFCs to release chlorine atoms, which destroy ozone molecules. This thins the ozone layer and lets more harmful UV reach the Earth.

**Example 3 — Greenhouse gas**

**Q:** Name the main greenhouse gas and its chief source.

**Solution:** Carbon dioxide ($CO_2$); its chief source is the burning of fossil fuels in vehicles, factories and power stations.

## 8. Short Questions

**Q1. What is environmental chemistry?**
**Ans.** The study of chemical processes and pollution in the air, water and soil.

**Q2. Name the layer of the atmosphere that contains the ozone layer.**
**Ans.** The stratosphere.

**Q3. Why is carbon monoxide dangerous?**
**Ans.** It is poisonous; it combines with haemoglobin and reduces the oxygen carried by the blood.

**Q4. What causes acid rain?**
**Ans.** Sulphur dioxide and oxides of nitrogen, which form sulphuric and nitric acids in the air.

**Q5. What are CFCs and why are they harmful?**
**Ans.** Chlorofluorocarbons; they release chlorine in the stratosphere that destroys the ozone layer.

**Q6. What is the greenhouse effect?**

**Ans.** The trapping of the Earth's heat by gases such as $CO_2$, which keeps the planet warm.

**Q7. Name two greenhouse gases.**
**Ans.** Carbon dioxide and methane (also water vapour and CFCs).

**Q8. Give two ways to control air pollution.**
**Ans.** Use cleaner fuels and fit catalytic converters to vehicles; also plant trees and treat waste gases.

## 9. Long Questions

**Q1. Explain the causes and effects of acid rain.**
Acid rain is rain that has become acidic because of pollutant gases in the air. Its main causes are the burning of fossil fuels that contain sulphur and nitrogen in power stations, factories and vehicles, which release sulphur dioxide and oxides of nitrogen into the atmosphere. High in the air these gases react with oxygen and with water vapour to form sulphuric acid and nitric acid, which dissolve in the rain and fall to the ground. The effects of acid rain are serious and wide-ranging. It makes soils and lakes acidic, which damages plants, kills fish and other aquatic life, and upsets whole ecosystems. It strips nutrients from the soil and harms forests. It also attacks buildings, bridges and statues, especially those made of marble and limestone, which are dissolved by the acid. Acid rain can be reduced by removing sulphur from fuels, by fitting equipment to trap $SO_2$ before it escapes, and by using cleaner sources of energy.

**Q2. Explain ozone depletion and the greenhouse effect.**
The ozone layer, high up in the stratosphere, is vital because it absorbs most of the Sun's harmful ultraviolet radiation. Ozone depletion is the thinning of this layer, caused mainly by man-made chlorofluorocarbons (CFCs) that were once used in refrigerators, air-conditioners and aerosol sprays. When CFCs drift up into the stratosphere, ultraviolet light breaks them apart to release chlorine atoms, and each chlorine atom can destroy many ozone molecules, creating thin areas known as 'ozone holes'. A thinner ozone layer lets more ultraviolet radiation reach the surface, increasing skin cancer, eye damage and harm to crops, which is why CFCs have been banned. The greenhouse effect is a separate problem, in the lower atmosphere. Gases such as carbon dioxide, methane and water vapour let sunlight through to warm the Earth but trap much of the heat that the Earth radiates back into space, keeping the planet warm. However, the huge amounts of carbon dioxide released by burning fossil fuels have strengthened this effect, trapping more heat and causing global warming — a slow rise in the Earth's temperature that is melting glaciers, raising sea levels and changing the climate.

**Q3. Discuss the sources of air pollution and how it can be controlled.**
Air pollution is the presence of harmful substances in the atmosphere, and most of it comes from burning fossil fuels. Vehicles release carbon monoxide (from incomplete combustion), oxides of nitrogen and unburnt hydrocarbons; power stations and factories that burn coal and oil release sulphur dioxide and carbon dioxide; and various industries release smoke and dust particles. Household and agricultural activities add further pollutants such as CFCs and smoke. These pollutants cause breathing diseases, acid rain, smog, ozone depletion and global warming. Air pollution can be controlled in several ways: by using cleaner fuels (such as natural gas) and removing sulphur from fuels; by fitting catalytic converters to vehicles to convert harmful gases

into less harmful ones; by trapping smoke and gases from factory chimneys before release; by banning harmful chemicals such as CFCs; by recycling waste to reduce burning; and by planting trees, which absorb carbon dioxide and release oxygen. Practising green chemistry — designing industrial processes that produce less waste and use safer materials — is an important long-term solution.

## 10. Multiple Choice Questions (MCQs)

**1. The ozone layer is found in the:**
(A) troposphere (B) stratosphere (C) mesosphere (D) thermosphere

**2. Which gas is responsible for acid rain?**
(A) $CO_2$ (B) $SO_2$ (C) $O_2$ (D) $N_2$

**3. Acid rain contains mainly:**
(A) HCl and HF (B) $H_2SO_4$ and $HNO_3$ (C) $H_2CO_3$ only (D) NaOH

**4. The ozone layer is destroyed mainly by:**
(A) $CO_2$ (B) CFCs (C) $SO_2$ (D) $O_2$

**5. The main greenhouse gas is:**
(A) $O_2$ (B) $N_2$ (C) $CO_2$ (D) $H_2$

**6. Carbon monoxide is dangerous because it:**
(A) causes acid rain (B) reduces oxygen in blood (C) destroys ozone (D) forms smog

**7. Global warming is caused by an increase in:**
(A) oxygen (B) greenhouse gases (C) ozone (D) nitrogen

**8. The ozone layer protects us from:**
(A) visible light (B) UV radiation (C) infrared (D) radio waves

**9. Which device reduces vehicle pollution?**
(A) condenser (B) catalytic converter (C) transformer (D) carburettor only

**10. Bagasse burning and fossil-fuel burning add ___ to the air:**
(A) oxygen (B) $CO_2$ (C) ozone (D) helium

**MCQ Answer Key**

**1-B 2-B 3-B 4-B 5-C 6-B 7-B 8-B 9-B 10-B**

## 11. Quick Revision / Summary

- Atmosphere: troposphere, stratosphere (ozone), mesosphere, thermosphere.
- Main pollutants: CO, $SO_2$, $NO_x$, $CO_2$, CFCs, particulates — mostly from burning fuels.
- Acid rain: $SO_2 + NO_x \rightarrow H_2SO_4 + HNO_3$; harms plants, water, buildings.
- Ozone depletion: CFCs release chlorine that destroys ozone → more UV.
- Greenhouse effect: $CO_2$/$CH_4$ trap heat → global warming.
- Control: cleaner fuels, catalytic converters, treat waste, ban CFCs, plant trees.

## 12. Exam Tips

**Teacher's Note**

Match each pollutant to its source and harmful effect — a common table question.

For acid rain, name the gases ($SO_2$, $NO_x$) AND the acids ($H_2SO_4$, $HNO_3$).

Distinguish ozone depletion (CFCs, UV) from the greenhouse effect ($CO_2$, heat) — do not mix them.

Remember the ozone layer is in the stratosphere and blocks UV.

List concrete control measures in pollution questions (catalytic converters, cleaner fuel, trees).