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</table>
UNIT 13
s and p- Block Elements

Learning Outcomes:

After Studying this unit Students will be able to:

- Recognize the demarcation of the Periodic Table into s-block, p-block, d-block and f-block.
- Describe how physical properties like atomic radius, ionization energy, electronegativity, electrical conductivity and melting and boiling points of elements change within a group and period in the Periodic Table.
- Describe reactions of 3rd period elements with water, oxygen and chlorine.
- Describe physical properties and acid-base behaviour of oxides, chlorides and hydroxides of period 3 elements.
- Describe reactions of oxides and chlorides of period 3 elements with water.
- Explain the trends in physical properties and oxidation states in group I, II, IV and VII of the Periodic Table.
- Describe reactions of Group I elements with water, oxygen and chlorine.
- Explain effect of heat on nitrates, carbonates and hydrogen carbonates of Group I elements.
- Describe reactions of Group II elements with water, oxygen and nitrogen.
- Discuss the trend in solubility of the hydroxides, sulphates and carbonates of Group II elements.
- Discuss the trends in thermal stability of the nitrates and carbonates of Group II elements.
- Differentiate beryllium from other members of its group.
- Describe reactions of Group IV elements with water.
- Discuss the chlorides and oxides of group IV elements.
- Explain the relative behaviour of halogens as oxidizing agents and reducing agents.
- Compare the acidity of hydrogen halides.
- Distinguish between an oxide and a peroxide.
- Write representative equations for the formation of oxides and sulphides.
- Compare the outermost s and p orbital system of an element with its chemical properties.
- Perform flame tests and explain the appearances of colours in the flame.
- Analyze acidic and basic ions using various tests.
- Describe how the food and beverage industry uses steel, tin, aluminium and glass for canning purposes.
- Explain how certain elements are mined and extracted from the earth.
- Relate the properties of the halogens to their important commercial uses.
- Explain that iodine deficiency leads to goitre.
- Explain the applications of bleaching powder.
- Explain fluoride toxicity and deficiency.
Introduction:

The elements of first and second group constitute the “s” block of the periodic table. The valency electrons in these elements occupy the “s” orbitals. The first group elements are called alkali metals while the second group elements are called alkaline earth metals.

Elements of Group IIIA, IVA, VA, VIA, VIIA and VIIIA (noble gases or zero group) are known as p-block elements. These elements have outer electronic configuration of np\(^1\)-\(^6\). s-block elements consist of only metals, but p-block elements include both metals and non-metals.

13.1 3rd Period (Na to Ar):

13.1.1 Physical and atomic properties of elements of 3\(^{rd}\) period:

Physical and atomic properties of the period 3 elements from sodium to Argon include ionization energy, atomic radius, electronegativity, electrical conductivity, melting and boiling point.

13.1.1.1 Electronic structure:

In third period of the periodic table electrons are successively filled in 3s and 3p orbitals of atoms of elements (Na to Ar). The electronic configurations of these elements are given below where [Ne] represents the electronic configuration of Neon.

\begin{align*}
11 \text{Na} & \[\text{Ne}\] 3s^1 \\
12 \text{Mg} & \[\text{Ne}\] 3s^2 \\
13 \text{Al} & \[\text{Ne}\] 3s^2 3p^1 \\
14 \text{Si} & \[\text{Ne}\] 3s^2 3p^2 \\
15 \text{P} & \[\text{Ne}\] 3s^2 3p^3 \\
16 \text{S} & \[\text{Ne}\] 3s^2 3p^4 \\
17 \text{Cl} & \[\text{Ne}\] 3s^2 3p^5 \\
18 \text{Ar} & \[\text{Ne}\] 3s^2 3p^6
\end{align*}
13.1.1.2 Trends in atomic radius:

The diagram shows how the atomic radius changes as you go across the third period.

The figure is based on
- Metallic radii for Na, Mg and Al
- Covalent radii for Si, P, S and Cl
- The Van der Waals radius for Ar because it does not form any chemical bond.

It is fair to compare metallic and covalent radii because they are both measured in strictly bonded circumstances. It is not suitable to compare these with Van der Waals radius, though, the Van der Waals radius is larger than covalent radii.

13.1.1.3 Trends in first ionization energy:

The first ionization energy is the energy required to remove the most loosely held electron from one mole of gaseous atoms to produce monopositive ion.

\[ X_{(g)} \rightarrow X^+_{(g)} + 1e^- \]

The pattern of first ionization energy of elements of 3rd period is given is figure 13.1.
Notice that general trend is upward, but this is broken by fall between Mg and Al and between P and S.

Explaining the pattern:

First ionization energy depends on

- The charge on the nucleus.
- The distance of the outer electrons from the nucleus.
- The screening effect of inner electrons.
- Electronic configuration of the atom.

The I.E is generally increasing across the period 3 because the electrons are added in the same shell (3rd principal quantum number). So the screening effect remains almost the same for the elements in third period.

The only major difference is the increase in nuclear charge and decrease in atomic radii from Na to Ar. As a result, the greater attraction between the nucleus and the valence electrons gradually increases the I.E.

13.1.1.4 Trends in electronegativity:

Electronegativity is a measure of the tendency of an atom to attract a shared pair of electrons towards itself.

The trend in electronegativity across third period is given as:

<table>
<thead>
<tr>
<th>Elements</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronegativity</td>
<td>0.93</td>
<td>1.31</td>
<td>1.81</td>
<td>2.02</td>
<td>2.19</td>
<td>2.58</td>
<td>3.16</td>
<td>-</td>
</tr>
</tbody>
</table>

Note that EN of Ar is not included. Electronegativity is related to the tendency of an atom to attract the shared pair of electrons. Since Argon does not form covalent bonds, you obviously cannot assign it an electronegativity value.

Moving from one elements to the next across the period, nuclear charge increases by one unit and one electron is added to the outer shell. As the positive charge on the nucleus rises, the atom has increasing electron attracting power and therefore an increasing electronegativity.
13.1.1.5 Trends in electrical conductivity:

- Sodium, magnesium and aluminium are all good conductors of electricity. Conductivity increases as you go from sodium to aluminium.

- Silicon is a semiconductor.

- Phosphorous to Argon are non-conductors.

The metals conduct electricity because the delocalised electrons (in the electron sea) are free to move throughout the solid or liquid metals.

Silicon is a semiconductor, while the rest do not conduct electricity because they are simple molecular substances. These have no mobile electron.

13.1.1.6 Trends in melting and boiling points:

The chart shows how melting and boiling points of element change across the period. The values are plotted in Kelvin instead of ºC to avoid negative values.

![Temperature (K) vs Elements Chart](image)

Fig. 13.2

13.1.2 Reactions of period 3 elements with water, oxygen and chlorine:

13.1.2.1 Reaction with water:

Sodium undergoes exothermic reaction with cold water producing hydrogen and a colourless solution of sodium hydroxide.

$$2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$$
Magnesium reacts slowly with cold water but burns in steam. A very clean coil of magnesium dropped into cold water eventually gets covered with small bubbles of hydrogen which floats it to the surface. Magnesium hydroxide is formed as very thin layer on the surface of magnesium which tends to stop further reaction:

\[
\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2
\]

Magnesium burns in steam with its typical white flame to produce white magnesium oxide and hydrogen.

\[
\text{Mg} + \text{H}_2\text{O} \rightarrow \text{MgO} + \text{H}_2
\]

Aluminium powder when heated in steam produces hydrogen and aluminium oxide. The reaction is relatively slow because of the existing strong aluminium oxide layer on the metal and build up of even more oxide during reaction.

\[
2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2
\]

Silicon will react with steam at red heat to produce silicon dioxide and hydrogen.

\[
\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2
\]

Chlorine dissolves in water to some extent to give a green solution. A reversible reaction takes place to produce a mixture of hydrochloric acid and chloric (I) acid (hypochlorous acid).

\[
\text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCl} + \text{HOCl}
\]

In presence of sunlight, chloric (I) acid slowly decomposes to produce more hydrochloric acid, releasing oxygen gas.
There is no reaction between Argon and water.

**13.1.2.2 Reactions with oxygen**

Sodium burns in oxygen with a yellow flame to produce a white solid mixture of sodium oxide and sodium peroxide.

For normal oxide:

\[ 4\text{Na} + \text{O}_2 \rightarrow 2\text{Na}_2\text{O} \]

For peroxide

\[ 2\text{Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2 \]

Magnesium burns in oxygen with an intense flame to give white solid magnesium oxide.

\[ 2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO} \]

Aluminium will burn in oxygen. If it is powdered, otherwise the strong oxide layer on Aluminium tends to inhibit the reaction. If you sprinkle aluminium powder into a Bunsen flame, white sparkles and white aluminium oxide is formed:

\[ 4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3 \]

Silicon will burn in oxygen if heated strongly enough. Silicon dioxide is produced.

\[ \text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 \]

White phosphorus catches fire spontaneously in air, burning with white flame and producing clouds of white smoke. A mixture of phosphorus (III) oxide and phosphorus (V) oxide is formed.

For phosphorus (III) oxide
For phosphorus (v) oxide

\[ \text{P}_4 + 3\text{O}_2 \rightarrow \text{P}_4\text{O}_6 \]

\[ \text{P}_4 + 5\text{O}_2 \rightarrow \text{P}_4\text{O}_{10} \]

Sulphur burns in air or oxygen on gentle heating with a pale blue flame. It produces colourless sulphur dioxide gas.

\[ \text{S} + \text{O}_2 \rightarrow \text{SO}_2 \]

**13.1.2.3 Reaction with Chlorine:**

Sodium burns in chlorine with a bright orange flame. White, solid sodium chloride is produced.

\[ 2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl} \]

Magnesium burns with its usual intense white flame to give white magnesium chloride.

\[ \text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2 \]

Aluminium reacts with chlorine by passing dry chlorine over aluminium foil heated in a long tube. Aluminium burns in stream of chlorine to produce pale yellow aluminium chloride.

\[ 2\text{Al} + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3 \]

If chlorine is passed over silicon powder heated in a tube, it reacts to produce a colourless liquid silicon tetrachloride.

\[ \text{Si} + 2\text{Cl}_2 \rightarrow \text{SiCl}_4 \]

White phosphorus burns in chlorine to produce a mixture of two chlorides, phosphorus (III) chloride and phosphorus (v) chloride (phosphorus trichloride and phosphorus pentachloride).
Phosphorus (III) chloride is colourless fuming liquid

\[ \text{P}_4 + 6\text{Cl}_2 \longrightarrow 4\text{PCl}_3 \]

Phosphorus (v) chloride is a straw coloured solid.

\[ \text{P}_4 + 10\text{Cl}_2 \longrightarrow 4\text{PCl}_5 \]

If a steam of chlorine is passed over some heated sulphur, it reacts to form an orange, foul smelling liquid disulphur dichloride \( \text{S}_2\text{Cl}_2 \)

\[ 2\text{S} + \text{Cl}_2 \longrightarrow \text{S}_2\text{Cl}_2 \]

It obviously does not make sense to talk about chlorine reacting with itself and Argon.

### 13.1.3 Physical properties of oxides:

This topic is related to physical properties of oxides of period (3) elements (sodium to chlorine) and their structures. Argon is obviously omitted because it does not form any oxide. The oxides and their physical properties are:

<table>
<thead>
<tr>
<th>( \text{Na}_2\text{O} )</th>
<th>( \text{MgO} )</th>
<th>( \text{Al}_2\text{O}_3 )</th>
<th>( \text{SiO}_2 )</th>
<th>( \text{P}<em>4\text{O}</em>{10} )</th>
<th>( \text{P}_4\text{O}_6 )</th>
<th>( \text{SO}_3 )</th>
<th>( \text{SO}_2 )</th>
<th>( \text{Cl}_2\text{O}_7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td></td>
<td></td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The oxides in the top row are the oxides where period 3 elements are in their highest oxidation state. In these oxides, all the outer electrons in period 3 elements are being involved in bonding from just one in sodium to all seven outer electrons of chlorine in \( \text{Cl}_2\text{O}_7 \).

### 13.1.3.1 Structure

The trend in structure is from metallic oxides containing giant structures of ions on the left of the period via a giant covalent oxide (silicon dioxide) in the middle to molecular oxides on right.
13.1.3.2 Melting and boiling points:

The giant structures (the metal oxides and silicon oxide) will have high melting and boiling points because a lot of energy is needed to break the strong bonds (ionic or covalent) operating in these lattices.

The oxides of phosphorus, sulphur and chlorine consist of individual molecules, some small and simple, others polymeric. The attractive forces between these molecules will be dispersion forces and dipole-dipole interactions. These vary in strength depending on the size, shape and polarity of various molecules but are always much weaker than the ionic or covalent bonds required in a giant structure. These oxides are gases, liquids or low-melting solids.

<table>
<thead>
<tr>
<th>Formation of oxide</th>
<th>Melting points (°C)</th>
<th>Boiling points (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>1280</td>
<td>1950</td>
</tr>
<tr>
<td>MgO</td>
<td>2900</td>
<td>3600</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2040</td>
<td>2977</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1610</td>
<td>2230</td>
</tr>
<tr>
<td>P₄O₁₀</td>
<td>340</td>
<td>360</td>
</tr>
<tr>
<td>P₄O₆</td>
<td>23.8</td>
<td>173.1</td>
</tr>
<tr>
<td>SO₃</td>
<td>-17</td>
<td>45</td>
</tr>
<tr>
<td>SO₂</td>
<td>-72</td>
<td>-10</td>
</tr>
<tr>
<td>Cl₂O₇</td>
<td>-92</td>
<td>82</td>
</tr>
<tr>
<td>Cl₂O</td>
<td>-120.6</td>
<td>2</td>
</tr>
</tbody>
</table>

13.1.3.3 Electrical conductivity:

None of these oxides has any free or mobile electrons which means that none of them will conduct electricity when they are solid. The ionic oxides can, however, undergo electrolysis in molten state. They can conduct electricity because of the movement of ions towards the electrodes.
13.1.3.4 Acid Base Behaviour of oxides:

Across the period from left to right there is a steady change in the structure of oxides from ionic through giant molecules to simple molecules. This change in the structure leads to profound difference in the way in which these oxides react with water, acids and alkalis. The ionic oxides contain $O^{2-}$ ions in the crystal lattice. These $O^{2-}$ ions in Na$_2$O react vigorously with H$_2$O to form an alkaline solution.

$$\text{Na}_2\text{O(s) + H}_2\text{O(l)} \rightarrow 2\text{Na}^{+}\text{(aq)} + 2\text{OH}^{-}\text{(aq)}$$

$$\text{Na}_2\text{O(s) + 2HCl(aq)} \rightarrow 2\text{NaCl(aq)} + \text{H}_2\text{O(l)}$$

MgO is slightly soluble in water forming alkaline solution. It reacts with acids to form salt and water.

$$\text{MgO(s) + H}_2\text{O(l)} \rightleftharpoons \text{Mg}^{2+}\text{(aq)} + 2\text{OH}^{-}\text{(aq)}$$

$$\text{MgO(s) + 2HCl(aq)} \rightarrow \text{MgCl}_2\text{(aq)} + \text{H}_2\text{O(l)}$$

Al$_2$O$_3$ is amphoteric oxide. It does not react with water but it will react with both dilute acid (H$^+$) and dilute Alkali (OH$^-$).

$$\text{Al}_2\text{O}_3\text{(s) + 6H}^+\text{(aq)} \rightarrow 2\text{Al}^{3+}\text{(aq)} + 3\text{H}_2\text{O(l)}$$

$$\text{Al}_2\text{O}_3\text{(s) + 2OH}^-\text{(aq)} + 3\text{H}_2\text{O(l)} \rightarrow 2[\text{Al(OH)}_3]^-\text{(aq)}$$

Aluminate ion

SiO$_2$ does not react with water, but it reacts with concentrated alkalis forming silicates (S$_3$O$_5$$^-$)

$$\text{SiO}_2 + 20\text{H}^+\text{(aq)} \rightarrow \text{S}_3\text{O}_5$$^-\text{(aq)} + \text{H}_2\text{O(l)}$$

NO$_2$ reacts with water to form a mixture of two acids HNO$_2$ and HNO$_3$. 
The oxides of phosphorus, sulphur and chlorine except (ClO₂) react readily with water to form a strongly acidic solution.

\[
\begin{align*}
2\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) & \rightarrow \text{HNO}_2(\text{aq}) + \text{HNO}_3(\text{aq}) \\
\text{P}_4\text{O}_{10}(\text{s}) + 6\text{H}_2\text{O}(\text{l}) & \rightarrow 4\text{H}_3\text{PO}_4(\text{aq}) \\
\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) & \rightarrow \text{H}_2\text{SO}_4(\text{aq}) \\
\text{Cl}_2\text{O}_7(\text{g}) + \text{H}_2\text{O}(\text{l}) & \rightarrow 2\text{HClO}_4(\text{aq}) \\
\text{Cl}_2\text{O}_7(\text{l}) + \text{H}_2\text{O}(\text{l}) & \rightarrow 2\text{HClO}_4(\text{aq}) \\
\text{Dichlorine oxide} & \\
\text{Perchloric Acid} &
\end{align*}
\]

13.1.3.5 **Trends in Acid base Behaviours:**

<table>
<thead>
<tr>
<th>Formula of oxide</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₄O₁₀ (P₄O₆)</th>
<th>SO₃ (SO₂)</th>
<th>Cl₂O₇ (Cl₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>State of oxides</strong></td>
<td>Solid</td>
<td>Solid</td>
<td>Solid</td>
<td>Solid</td>
<td>(Solid)</td>
<td>Liquid (gas)</td>
<td>Liquid (gas)</td>
</tr>
<tr>
<td><strong>Electrical conductivity</strong></td>
<td>good</td>
<td>good</td>
<td>good</td>
<td>v.poor</td>
<td>NIl</td>
<td>NIl</td>
<td>NIl</td>
</tr>
<tr>
<td><strong>Structure of oxide</strong></td>
<td>Giant structures</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Nature of oxide</strong></td>
<td>Basic (alkaline)</td>
<td>Basic (weakly alkaline)</td>
<td>Amphoteric</td>
<td>Acidic</td>
<td>Acidic</td>
<td>Acidic</td>
<td>Acidic</td>
</tr>
</tbody>
</table>


The above table shows that there is a change from strongly basic oxide on left side to strongly acidic oxide on right side while amphoteric oxides in the middle of third period.

**13.1.3.6 Reactions of oxides with water, acids and bases:**

The normal oxides of most metals e.g. Na₂O, CaO etc. combine with acids to form salts.

\[ \text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} \]

These usually dissolve in water to give soluble hydroxides.

\[ \text{Na}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \]

Such oxides are called basic oxides.

Acidic oxides are oxides of non-metals e.g. CO₂, SO₂ etc. which react with bases to form salts and combine with water to form acids.

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \]
\[ \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \]

Some oxides like BeO, Al₂O₃ etc. react with both acids and alkalies to form salts. These are called amphoteric oxides which are usually water insoluble.

**13.1.4 Chlorides of the period 3 elements:**

Properties of Chloride of period 3 elements.

<table>
<thead>
<tr>
<th>Formula of chlorides</th>
<th>NaCl</th>
<th>MgCl₂</th>
<th>Al₂Cl₆</th>
<th>SiCl₄</th>
<th>PCl₃</th>
<th>S₂Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>State of chlorides (at 20°C)</td>
<td>solid</td>
<td>solid</td>
<td>solid</td>
<td>liquid</td>
<td>liquid</td>
<td>liquid</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>801</td>
<td>708</td>
<td>192.4</td>
<td>-69</td>
<td>-93.6</td>
<td>-80</td>
</tr>
<tr>
<td>Boiling point of chlorides (°C)</td>
<td>1465</td>
<td>1418</td>
<td>423</td>
<td>57</td>
<td>74</td>
<td>136</td>
</tr>
</tbody>
</table>
NaCl and MgCl₂ are gaint structures composed of oppositely charged ions which attract each other by strong electrostatic forces (ionic bonds). This means that the melting and boiling points of these compound would be high. But the molten substances will conduct electricity because the ions which they contain can move towards the electrodes of opposite charge.

All the other chlorides have simple molecular structure composed of small discrete molecules attracted to each other by relatively weak intermolecular forces. So, the melting & boiling points of these compounds are low and they will not conduct electricity in liquid state.

13.1.5 Hydroxides of period 3 elements:-

The word "Hydroxide" refers to anything which contains either a hydroxide ion (OH⁻) or an –OH group covalently bonded to the element in question. Hydroxides containing OH⁻ ion are basic hydroxides e.g. NaOH, Ca(OH)₂. Aluminium hydroxide (Al (OH)₃) is amphoteric reacting both with acids and bases. The elements Si, P, S and Cl of period 3 form hydroxides in which –OH group is covalently bound to these elements e.g. Si (OH)₄, H₃PO₄, H₂SO₄ and HClO₄. These are all acids.

13.1.5.1 Sodium and magnesium hydroxides:-

These are white solids having soapy touch. Strong solutions of these hydroxides are very corrosive to skin. These are very hygroscopic.

Sodium hydroxide is only slightly soluble in alcohols. It is one of the most soluble substances in water evolving a considerable amount of heat due to the formation of a number of hydrates e.g. NaOH. 2H₂O.
Sodium hydroxide (NaOH) is used in soap industry, petroleum refining and reclaiming of rubber.

Magnesium hydroxide, Mg(OH)\(_2\) is obtained as a white precipitate when caustic potash (KOH) solution is added to a soluble magnesium salt.

\[
\text{MgCl}_2 + 2\text{KOH} \rightarrow \text{Mg(OH)}_2 + 2\text{KCl}
\]

Solubility of Mg(OH)\(_2\) is enhanced tremendously by the addition of NH\(_4\)Cl.

\[
\begin{align*}
2\text{NH}_4\text{Cl} & \rightarrow 2\text{NH}_4^+ + 2\text{Cl}^- \\
\text{Mg(OH)}_2 & \rightarrow 2\text{OH}^- + \text{Mg}^{2+} \\
2\text{NH}_4^+ + 2\text{OH}^- & \rightarrow 2\text{NH}_4\text{OH}
\end{align*}
\]

More Mg(OH)\(_2\) therefore, dissolves to provide a further supply of OH\(^-\) in order to replace those fixed in the form of NH\(_4\)OH.

13.1.5.2 **Aluminium Hydroxide**

When an alkali is added to an aqueous solution of aluminium salt, Aluminium hydroxide Al(OH)\(_3\) gets precipitated.

\[
\text{Al}_2(\text{SO}_4)_3 + 6\text{NH}_4\text{OH} \rightarrow 2\text{Al(OH)}_3 + 3(\text{NH}_4)_2\text{SO}_4.
\]

This hydroxide is soluble in acids and caustic alkalies forming aluminates, in the later.

\[
2\text{Al(OH)}_3 + 2\text{NaOH} \rightarrow 2\text{Na}[\text{Al(OH)}_4]^{-}
\]

The Al(OH)\(_3\) can also be obtained by hydrolysis of AlCl\(_3\) in excess water.

\[
\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{HCl}
\]
The precipitated hydroxide has the capacity of absorbing various dyes forming colouring matter known as “lakes”.

**13.1.5.3 Other Hydroxides:**

Silicon hydroxide is a molecule with formula Si(OH)$_4$. It is produced by the following chemical reaction.

$$\text{SiO}_2 + 2\text{H}_2\text{O} \xrightarrow{800^\circ\text{C}} \text{Si(OH)}_4$$

This compound is unstable and rapidly polymerises.

**13.2 Group I Elements**

The element lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs) and francium (Fr) constitute sub-group IA of the periodic table. These are known as alkali metals since they form oxides and hydroxides which combine with water to produce alkaline solution. Only the first three of these are safe to keep in the school lab. The rest are violently reactive.

The characteristic feature of the sub-group IA is the $s^1$ arrangement in the outermost shell.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic No.</th>
<th>Electronic Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>3</td>
<td>$1s^2, 2s^1$</td>
</tr>
<tr>
<td>Na</td>
<td>11</td>
<td>$1s^2, 2s^2, 2p^6, 3s^1$</td>
</tr>
<tr>
<td>K</td>
<td>19</td>
<td>$1s^2, 2s^2, 2p^6, 3s^2 3p^6, 4s^1$</td>
</tr>
<tr>
<td>Rb</td>
<td>37</td>
<td>$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$</td>
</tr>
<tr>
<td>Cs</td>
<td>55</td>
<td>$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$</td>
</tr>
<tr>
<td>Fr</td>
<td>87</td>
<td>$[\text{k}] 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^1$</td>
</tr>
</tbody>
</table>
Like all metals, they are good conductors of heat and electricity. But they are softer than other metals. You can cut them with knife. They are lighter than other elements and having low melting point, boiling points and density.

13.2.1 Trends in Physical properties:-

The elements in a group behave in similar way, but they also show trends of variations in properties as given below:

13.2.1.1 Trends in Atomic radius:-

As we move from Lithium to Cesium an extra shell of electrons is added to next element. The addition of extra shells increases the atomic radius.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic radius (Å)</td>
<td>1.55</td>
<td>1.90</td>
<td>2.35</td>
<td>2.48</td>
<td>2.67</td>
</tr>
</tbody>
</table>

13.2.1.2 Trend in First ionization energy:-

The ionization energies of these elements are relatively low and first I.E of these elements decreases on moving from Li to Cs. Due to their low I.E, these metals have a greater tendency to lose the valence electron to change into M⁺ ions.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.E (ev)</td>
<td>5.4</td>
<td>5.1</td>
<td>4.3</td>
<td>4.2</td>
<td>3.9</td>
</tr>
</tbody>
</table>

13.2.1.3 Trends in Electronegativity:-

Since these metals are highly electropositive, their electronegativity values are very low.

As their electropositive character increases from Li to Cs, their electronegativities decrease in the same order.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronegativities (Paulings)</td>
<td>1.0</td>
<td>0.9</td>
<td>0.8</td>
<td>0.8</td>
<td>0.7</td>
</tr>
</tbody>
</table>
13.2.1.4 Trends in melting and boiling points:

The forces binding the atoms in crystal lattices of these metals are relatively weak. Consequently these metals are soft and possess low melting and boiling points which decrease down the group.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. pt (°C)</td>
<td>1330</td>
<td>892</td>
<td>760</td>
<td>688</td>
<td>670</td>
</tr>
<tr>
<td>M. pt (°C)</td>
<td>1085</td>
<td>97.8</td>
<td>63.7</td>
<td>38.9</td>
<td>28.7</td>
</tr>
</tbody>
</table>

13.2.1.5 Trends in Density:

Density increase in moving from Li to Cs, Potassium is, however, lighter than sodium.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.534</td>
<td>0.972</td>
<td>0.86</td>
<td>1.53</td>
<td>1.903</td>
</tr>
</tbody>
</table>

13.2.2 Trend in Chemical properties:

13.2.2.1 Reaction with water:

Group-I elements are very good reducing agents. They all react vigorously with water reducing it to hydrogen gas.

\[
\begin{align*}
\text{M}_\text{(s)} & \rightarrow \text{M}^{+}_\text{(aq)} + 1e^- \\
\text{H}_2\text{O}_\text{(l)} + 1e^- & \rightarrow \frac{1}{2}\text{H}_2\text{(g)} + \text{OH}_\text{(aq)} \\
\text{M}_\text{(s)} + \text{H}_2\text{O}_\text{(l)} & \rightarrow \text{MOH}_\text{(aq)} + \frac{1}{2}\text{H}_2
\end{align*}
\]

Excluding Lithium, which reacts slower than all the other elements of group-I. Sodium reacts vigorously, fizzing and skating about on the water surface. Potassium reacts even more vigorously. It cracks and pops as hydrogen explodes. Rb and Cs explode violently in contact with water.

The reactivity of Group-I elements with water closely follows the values of electrode potential.
13.2.2.2 Reactions with Oxygen:

These are all very reactive metals and have to be stored without contact with air to prevent their oxidation. Reactivity increases down the group.

Li, Na and K are stored in oil, Cs and Rb are normally stored in a sealed glass tubes to prevent air contact.

Alkali metals react with air or oxygen to form various types of oxides. Some of the reactions are given below.

\[ 4\text{Li} + \text{O}_2 \rightleftharpoons 2\text{Li}_2\text{O} \]  
(Lithium oxide)

Sometimes “Li” reacts with nitrogen in the air to give Li\(_3\)N.

\[ 6\text{Li} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N} \]

\[ 4\text{Na} + \text{O}_2 \rightarrow 2\text{Na}_2\text{O} \]  
(sodium oxide)

For peroxide, the reaction is

\[ 2\text{Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2 \]  
(sodium peroxide)

\[ 2\text{K} + \text{O}_2 \rightarrow \text{K}_2\text{O}_2 \]  
(potassium peroxide)

For the super oxide, the reaction is

\[ \text{K} + \text{O}_2 \rightarrow \text{KO}_2 \]  
(potassium superoxide)
“Rb” and “Cs” catch fire in air and produce superoxide such as RbO₂ and CsO₂ respectively.

Reactions of oxides with water:

Reaction with water
Oxides of alkali metal may react with water in the following manner.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal oxide</td>
<td>( X_2O + H_2O \rightarrow 2XOH ) (Metal Hydroxide)</td>
</tr>
<tr>
<td>Peroxide</td>
<td>( X_2O_2 + 2H_2O \rightarrow 2XOH + H_2O_2 ) (Hydrogen peroxide)</td>
</tr>
<tr>
<td>Super oxide</td>
<td>( 2XO_2 + 2H_2O \rightarrow 2XOH + H_2O_2 + O_2 )</td>
</tr>
</tbody>
</table>

Reactions of oxides with dilute acids:

Normal oxides react with dilute acids forming salts and water. While peroxides and superoxide also give other products.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal oxide</td>
<td>( X_2O + 2HCl \rightarrow 2XCl + H_2O ) Salt</td>
</tr>
<tr>
<td>Peroxide</td>
<td>( X_2O_2 + 2HCl \rightarrow 2XCl + H_2O_2 ) Salt</td>
</tr>
<tr>
<td>Super oxide</td>
<td>( 2XO_2 + 2HCl \rightarrow 2XCl + H_2O_2 + O_2 )</td>
</tr>
</tbody>
</table>
13.2.2.3 Reaction with Chlorine:-

Sodium burns with an intense orange flame in chlorine in exactly the same way as it does in pure oxygen. Other alkali metals behave similarly. The reactions give white solid chlorides of these metals.

\[
\begin{align*}
2X & + Cl_2 \rightarrow 2 XCl \\
2Na & + Cl_2 \rightarrow 2NaCl \\
2K & + Cl_2 \rightarrow 2KCl
\end{align*}
\]

13.2.2.4 Effect of heat on nitrates, carbonates and hydrogen carbonates explaining the trends in terms of the polarizing ability of the positive ion :-

Compounds of Group-I A Elements are more stable to heat than the corresponding compounds of group-II elements with the exception of Lithium compounds.

Effect of heat on Nitrates:-

Most Nitrates tend to decompose on heating to produce metal oxide, nitrogen dioxide (brown fumes) and oxygen.

Lithium nitrate produces lithium oxide, nitrogen dioxide and oxygen

\[
4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2
\]

Nitrates of the other alkali metals decompose to corresponding nitrites.

\[
2XNO_3 \rightarrow 2XNO_2 + O_2
\]

Effect of heat on Carbonates:

Lithium carbonate decomposes on heating to give litium oxide and carbon dioxide e.g.

\[
Li_2CO_3 \rightarrow Li_2O + CO_2
\]
The rest of group-I carbonates do not decompose even at higher temperature.

**Effect of heat on Hydrogen Carbonates:**

Hydrogen Carbonates of alkali metals are stable enough to be isolated as solids. However, they decompose on heating forming carbonates.

\[ 2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \]

Thermal stability of hydrogen carbonates of group I and group II increases down the group. The reason is increasing size and decreasing charge density of the metal ions. The polarizing power of a cation increases with increasing charge on the ion and decreasing the radius of the ion.

Cation of greater polarizing power distorts the \( \text{HCO}_3^- \) ion more and facilitates its decomposition than a cation of larger size and lesser polarizing power. Due to the same reason, bicarbonates of group-I are more stable than those of group-II.

### 13.2.2.5 Flame Tests:

The alkali metals give characteristic colours to the Bunsen flame because even the small amount of energy of the flame causes an excitation of the outermost electron which on dropping back to its original position gives out the energy so absorbed as visible light. These colours differ from one another as shown in the table.

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>red</td>
<td>yellow</td>
<td>Lilac</td>
<td>red</td>
<td>Blue/violet</td>
</tr>
</tbody>
</table>

### 13.3 Groups II - Elements:

Name of elements in group-IIA

Alkaline earth metals do not exist free in nature. They exist in combined form. Magnesium and calcium are very abundant in the rocks of earth's crust.
The chief sources of Mg are sea water, underground brines, the mineral dolomite and magnesite (MgCO₃). Calcium compounds are obtained from sea shell e.g. CaCO₃ and gypsum (CaSO₄·2H₂O) which is one of the important minerals of calcium. Other alkaline earth metals are much less common than magnesium and Calcium.

Elements of group IIA (alkaline earth metals) possess two electrons in the outermost s-orbital. They form dispositive ions by loss of both the electrons. The elements and their atomic numbers etc. are given in table below.

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>At. No.</th>
<th>Electronic configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium</td>
<td>Be</td>
<td>4</td>
<td>1s², 2s²</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>12</td>
<td>1s², 2s², 3s²</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>20</td>
<td>1s², 2s², 2p⁶, 3s², 3p⁶, 4s²</td>
</tr>
<tr>
<td>Strontium</td>
<td>Sr</td>
<td>38</td>
<td>1s², 2s², 2p⁶, 3s², 3p⁶, 4s², 4p⁶, 5s²</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba</td>
<td>56</td>
<td>1s², 2s², 2p⁶, 3s², 3p⁶, 4s², 3d¹⁰, 4p⁶, 5s², 5p⁶, 6s²</td>
</tr>
<tr>
<td>Radium</td>
<td>Ra</td>
<td>88</td>
<td>1s², 2s², 2p⁶, 3s², 3p⁶, 3d¹⁰, 4s², 4p⁶, 4d¹⁰, 5s², 5p⁶, 5d¹⁰, 6s², 6p⁶, 7s²</td>
</tr>
</tbody>
</table>

All alkaline earth metals except Be are white in colour. They are quite reactive and tarnish in air.

The values of their densities, melting points and boiling points are higher than those of alkali metals.

### 13.3.1 Trends in physical properties:-

### 13.3.1.1 Trends in Atomic Radius:-

Due to the successive addition of extra shell of electrons to each element from Be to Ra, the atomic radius increases. While the atomic radii of these elements are smaller than those of alkali metals. These elements harder, have higher densities and higher melting points than the corresponding alkali metals.

<table>
<thead>
<tr>
<th>Elements:</th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Ba</th>
<th>Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Radii (Å):</td>
<td>1.12</td>
<td>1.60</td>
<td>1.97</td>
<td>2.15</td>
<td>2.22</td>
</tr>
</tbody>
</table>
13.3.1.2 Trends in First Ionization energy:-

The first ionization energy of these elements decreases with increase of atomic radii from Be to Ba. However, the value of I.E of Ra is higher than I.E of Ba.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
<th>Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization</td>
<td>9.3</td>
<td>7.6</td>
<td>6.1</td>
<td>5.7</td>
<td>5.2</td>
<td>5.3</td>
</tr>
</tbody>
</table>

13.3.1.3 Trends in Electronegativity:-

The electronegativity values of these elements are small and decrease from Be to Ba.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
<th>Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronegativity</td>
<td>1.5</td>
<td>1.2</td>
<td>1.0</td>
<td>1.0</td>
<td>0.9</td>
<td>0.9</td>
</tr>
</tbody>
</table>

13.3.1.4 Trends in Melting and Boiling Points:-

Melting and boiling points do not show any regular trend. These are, however, higher than those of alkali metals.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
<th>Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.Pt (°C)</td>
<td>1289</td>
<td>651</td>
<td>851</td>
<td>771</td>
<td>727</td>
<td>700</td>
</tr>
<tr>
<td>B.pt (°C)</td>
<td>2500</td>
<td>1105</td>
<td>1494</td>
<td>1381</td>
<td>1850</td>
<td>1700</td>
</tr>
</tbody>
</table>

13.3.2 Trends in chemical properties:-

13.3.2.1 Trends in reactivity with water:-

These metals react slowly with water liberating hydrogen and forming hydroxides. The reaction becomes increasingly vigorous with an increase in atomic number. However, Beryllium does not react with water or steam at red heat. Mg burns in steam to produce white MgO and H₂ gas.

$$\text{Mg}(s) + \text{H}_2\text{O}(g) \rightarrow \text{MgO}(s) + \text{H}_2(g)$$

Group-II elements become more reactive towards water as we go down the group.
13.3.2.2 Reaction with oxygen and Nitrogen:

13.3.2.2.1 Formation of Simple oxide:

All the metals of group II react with oxygen and form simple oxides. It is almost impossible to find any trend in the way the metal react with oxygen. 

\[2\text{Ca}_\text{(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{CaO}_\text{(s)}\]

Be is reluctant to burn unless it is in the form of dust or powder. Be has very strong layer of BeO on its surface which prevents any more oxygen reaching the underlying beryllium to react with it.

13.3.2.2.2 Formation of Peroxide on heating with oxygen:

Be, Mg and Ca do not form peroxide when heated with oxygen. But Sr and Ba react in oxygen to form peroxides SrO$_2$ and BaO$_2$ respectively. The reactions are:

\[\text{Ba}_\text{(s)} + \text{O}_2\text{(g)} \rightarrow \text{BaO}_2\text{(s)}\]
\[\text{Sr}_\text{(s)} + \text{O}_2\text{(g)} \rightarrow \text{SrO}_2\text{(s)}\]

13.3.2.2.3 Formation of Nitrides on heating in air:

The nitrides of alkaline earth metal are ionic and solid in nature except that of Be which is covalent and unpredictable.

The reaction of alkaline earth metals with air rather than oxygen is complicated by the fact that they all react with nitrogen to produce nitrides. In each case we get a mixture of metal oxide and nitride.

\[\text{Mg}_\text{(s)} + \text{N}_2\text{(g)} \xrightarrow{\Delta} \text{Mg}_3\text{N}_2\text{(s)}\]
\[\text{Be}_\text{(s)} + \text{N}_2\text{(g)} \xrightarrow{\Delta} \text{Be}_3\text{N}_2\text{(s)}\]

13.3.2.3 Trends in solubility of Hydroxides, Sulphates and Carbonates.

The solubility of Hydroxides in water increase from Be(OH)$_2$ to Ba(OH)$_2$ as indicated by increasing values of their solubility product.
Be(OH)₂ = 1.6 x 10⁻²⁶  Mg(OH)₂ = 8.6 x 10⁻¹²
Ca(OH)₂ = 1.3 x 10⁻⁴  Sr(OH)₂ = 3.2 x 10⁻⁴
Be(OH)₂ = 5.4 x 10⁻³

The solubility of sulphates decreases as we go down the group. CaSO₄ is sufficiently soluble in water while Strontium and Barium sulphates are almost insoluble.
All carbonates of these elements are insoluble in neutral medium, while all dissolve in acids and decompose at red heat. The stability of carbonates increases down the group as is evident from the temperature at which they decompose.

BeCO₃ < 100 °C  MgCO₃ = 540 °C
CaCO₃ = 900 °C  SrCO₃ = 1290 °C
Ba CO₃ = 1360 °C

13.3.2.4 Trend in Thermal Stability of the Nitrates and Carbonates
Both carbonates and nitrates become more thermally stable as we go down the group. The ones at lower position have to be heated more strongly than those at the top before they decompose.

$$XCO_3(s) \xrightarrow{\Delta} XO(s) + CO_2(g)$$
$$2X(NO_3)_2(s) \rightarrow 2XO(s) + 4NO_2(g) + O_2(g)$$

13.3.3 How Beryllium Differs from other members of its group:
Beryllium differs from other alkaline earth metals in many respects. This is partly due to its small size and partly due to its high electronegativity.
1- Be unlike other alkaline earth metal is not easily affected by dry air, and does not decompose even in boiling water.
2- Oxides, nitrides, sulphides, chlorides etc. of Group II elements are ionic, while those of Be are covalent.
3- Salts of Be do not impart any colour to the flame unlike its family members.
4- Beryllium oxide is insoluble in water unlike oxides of other members of its family.
13.3.4 Why is Beryllium chloride Covalent and not Ionic

The polarizing power of Be\(^{2+}\) ion is high and polarizability of Cl\(^{-}\) ion is also high. So Be\(^{2+}\) essentially pulls the electron cloud from Cl\(^{-}\), such that the electrons are effectively shared. This gives covalent character to BeCl\(_2\).

13.3.5 Amphoteric Beryllium Hydroxide:

Beryllium hydroxide can act both as an acid and as a base because it can neutralize both.

As a base: (neutralizing acid)

\[
\text{Be(OH)}_2 + 2\text{HCl} \rightarrow \text{BeCl}_2 + 2\text{H}_2\text{O}
\]

As an Acid: (neutralizing base)

\[
\text{Be(OH)}_2 + 2\text{NaOH} \rightarrow \text{Na}_2 \left[\text{Be(OH)}_4\right]
\]

13.4 Group-IV elements:

The Group-IV A of the periodic table consists of five elements C, Si, Ge, Sn and Pb. This group is present in the middle of periodic table forming a link between more electropositive elements of groups IA to IIIA and more electronegative elements of group VA-VIIA. The elements of group IVA evidently exhibit an intermediate character.

13.4.1 Physical properties:

13.4.1.1 Melting and boiling point:

The decrease in melting point from silicon downwards is due to the presence of weak bonds which become weaker due to increase in atomic size. Moreover, Tin and Lead do not use all the four electrons for metallic bond. The extremely high boiling points of Carbon and Silicon are due to very stable arrangement of diamond type lattice.
<table>
<thead>
<tr>
<th>Elements</th>
<th>Melting point (°C)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3600</td>
<td>4827</td>
</tr>
<tr>
<td>Si</td>
<td>1420</td>
<td>2355</td>
</tr>
<tr>
<td>Ge</td>
<td>937</td>
<td>2830</td>
</tr>
<tr>
<td>Sn</td>
<td>232</td>
<td>2560</td>
</tr>
<tr>
<td>Pb</td>
<td>328</td>
<td>1744</td>
</tr>
</tbody>
</table>

13.4.1.2 Trend from non-metal to metal:

The change from non-metallic to metallic character with the increase of atomic number is best illustrated in this group e.g. C and Si are non-metals. Ge is metalloid and Sn and Pb exhibit metallic character.

13.4.1.3 Oxidation state:

Oxidation state is defined as the apparent charge positive or negative on an atom of an element in a molecule or ion.

Carbon and Silicon show +4 oxidation state in carbonates and silicates. The remaining members can show +2 as well as +4 oxidation states. Since, the electronegativity of these elements is low, they do not have such a high tendency to form negative ions. However, carbon forms C^-4 and C_2^-2 ions in certain compounds.

Be_2C (C=-4, Be=+2), Na_2C_2 (C_2 = -2, Na = +1)

Oxidation state of group-IV elements may be positive or negative depending upon the nature of the compounds. The typical oxidation state shown by elements of group-IV is +4, found in compounds like CCl_4, SiCl_4 and SnO_2. However, down the group there are more and more examples where the oxidation state is +2, such as SnCl_2 and PbCl_2.

13.4.1.2 Inert pair effect in formation of ionic bond:

All the elements in group-IV have valence electronic structure of ns^2, np^2, where 'n' varies from 2 (for carbon) to 6 (for lead). The oxidation state of +4 is found where all these outer electrons are involved in bonding. But
at the bottom of the group there is tendency for the $s^2$ pair not to be used in bonding. This is called inert pair effect which dominates in lead.

If the elements of group-IV form M($^+$2) ions they will lose the ‘p’ electrons, leaving the $s^2$ pair unused e.g. In the formation Pb$^{+2}$ ions, Pb will lose the two ‘6p’ electrons, but the ‘6s’ electrons will be left unchanged (inert pair effect). Therefore, the compounds of Pb$^{+2}$ are ionic in nature.

### 13.4.1.3 Inert pair effect and the formation of covalent bonds:

Although the most stable electronic configuration of a carbon atom requires it to be divalent, but carbon is tetravalent in majority of compounds. In order to explain this apparent anomaly, it is assumed that electron from ‘2s’ orbital is promoted to an empty ‘2p’ orbital.

![Diagram of electron promotion](image)

It is obvious from the electronic configuration ($C^+$) that it can form four covalent bonds due to its C($^+$4) oxidation state. While the other members of the same group show +2 as well as +4 oxidation state. Therefore, these members can form both ionic and covalent compounds depending upon the size of cation. The nature of compounds M$^{+2}$ and M$^{+4}$ cations can be predicted by Fajan’s rule e.g. Sn$^{+4}$ is smaller than Sn$^{+2}$ so the compounds of Sn$^{+4}$ are covalent, while those of Sn$^{+2}$ are ionic.

### 13.4.2 Chemical properties

### 13.4.2.1 Chlorides of carbon, silicon and lead:

All these elements give tetrachlorides (MCl$_4$) which are covalent and tetra-hedral due to sp$^3$ hybrid orbitals. MCl$_4$ are fuming liquids at room temperature. The stability of MCl$_4$ decreases from CCl$_4$ to PbCl$_4$. PbCl$_4$ decomposes to give PbCl$_2$ and Cl$_2$ gas.

\[ \text{PbCl}_4 \rightarrow \text{PbCl}_2 + \text{Cl}_2 \]
13.4.2.1.1 Structure and stability:-

At the top of group-IV A the most stable oxidation state shown by an element is +4. This oxidation state is shown by carbon and silicon in CCl₄ and SiCl₄. These have no tendency to form dichloride. However, the relative stability of +4 oxidation state falls down the group and +2 oxidation state becomes the most stable at lead.

13.4.2.1.2 Reaction with water:-

CCl₄ does not react with water. This is due to bulky nature of chlorine atoms around small carbon atom. As a result oxygen of water cannot penetrate to reach carbon atom. SiCl₄ to PbCl₄ react violently with water to produce their respective oxides and fumes of HCl.

\[
\begin{align*}
\text{SiCl}_4 + 2\text{H}_2\text{O} & \rightarrow \text{SiO}_2 + 4\text{HCl} \\
\text{White} & \\
\text{PbCl}_4 + 2\text{H}_2\text{O} & \rightarrow \text{PbO}_2 + 4\text{HCl} \\
\text{Brown} &
\end{align*}
\]

PbCl₂ is ionic in nature and sparingly soluble in cold water but more soluble in hot water. The solubility in water involves break up of the ionic lattice and the hydration of Pb⁺² and Cl⁻ ions:

\[
\begin{align*}
\text{PbCl}_2 \quad (s) & \quad \text{H}_2\text{O} (l) \quad \rightarrow \quad \text{Pb}^{+2} (aq) + 2\text{Cl}^- (aq)
\end{align*}
\]

13.4.2.2 Oxides:-

The elements of group-IV form two types of oxides i.e. monoxide and dioxide in which these exist in +2 and +4 oxidation states.

Monoxides include CO, SnO and PbO while the dioxides include CO₂, SiO₂, SnO₂ and PbO₂. The oxides of carbon and silicon are non-metal oxides and are covalent in nature, whereas, oxides of tin and lead are metal oxides and are ionic in nature.
13.4.2.2.1 Structure of Carbon dioxide and Silicon dioxide

Carbon dioxide and silicon dioxides are formed by the direct combination of these elements with oxygen. However, CO$_2$ is a gas whereas SiO$_2$ is a hard, high melting solid. The other oxides of group-IV are also solids. The fact that CO$_2$ is a gas suggests that it must consist of simple discrete molecules, with double bonds between carbon and oxygen atoms.

$$O = C = O$$

The molecule has linear shape and hence the carbon atom is supposed to be 'sp' hybridized in it. The two 'sp' hybrid orbitals of carbon atom form two sigma bonds with 'p' orbitals of each oxygen atom. Half filled 'p' orbitals on carbon atom which do not participate in hybridization process form two "\( \equiv \)" bonds with two oxygen atoms.

![Diagram of hybridization](image)

Silicon atoms are bigger than carbon atoms, which means that silicon-oxygen bond will be long as compared to carbon-oxygen bond. The 'p' orbital on the silicon and the oxygen are not quite close enough together to allow enough side wise overlap to give us a stable "\( \equiv \)" bond. Thus silicon-oxygen bond is a single sigma bond. The SiO$_2$ molecule is a giant covalent structure in which each silicon atom is bonded to four oxygen atoms through single covalent bonds whereas each oxygen atom is bonded to two silicon atoms.
The geometry of the SiO$_2$ is tetrahedral (diamond like)

### 13.4.2.2.2 Acid Base Behaviour of Group IV oxides

The acidity of group-IV oxides decreases as we move down the group. Thus CO$_2$ and SiO$_2$ are acidic and GeO$_2$, SnO$_2$ and PbO$_2$ are amphoteric. Among the mono oxides of these elements CO is neutral while SnO and PbO are amphoteric. Acid base reactions of these oxides are given below.

- **Acidic**
  - CO$_2$ + H$_2$O $\rightarrow$ H$_2$CO$_3$
  - SiO$_2$ + NaOH $\rightarrow$ 2Na$_2$SiO$_3$ + H$_2$O

- **Amphoteric**
  - SnO + NaOH + H$_2$O $\rightarrow$ Na$_2$Sn(OH)$_4$ (Acidic)
  - SnO + HCl $\rightarrow$ SnCl$_2$ + H$_2$O (Basic)
  - PbO + 2NaOH + H$_2$O $\rightarrow$ Na$_2$Pb(OH)$_4$ (Acidic)

### 13.5 Group VII A Elements: halogens

Group VIIA comprises the elements fluorine, chlorine, bromine, iodine and astatine. The elements are collectively known as halogens due to their salt forming tendency. These are non-metals.
13.5.1 Physical properties:

The electronic configuration of the atoms of these elements is shown in table below, the characteristics feature being $s^2p^5$ in the outer most shell.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Atomic No</th>
<th>Complete electronic configuration</th>
<th>Valence shell configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>9</td>
<td>2,7</td>
<td>$2s^22p^5$</td>
</tr>
<tr>
<td>Cl</td>
<td>17</td>
<td>2,8,7</td>
<td>$3s^23p^5$</td>
</tr>
<tr>
<td>Br</td>
<td>35</td>
<td>2,8,18,7</td>
<td>$4s^24p^5$</td>
</tr>
<tr>
<td>I</td>
<td>53</td>
<td>2,8,18,18,7</td>
<td>$5s^25p^5$</td>
</tr>
</tbody>
</table>

Halogens in the uncombined state exist as diatomic covalent molecules ($F_2$, $Cl_2$, etc). These discrete molecules are held together by weak Van der Waals forces which explain the volatile nature of these elements. These elements are also poisonous in nature.

13.5.1.1 Trends in Atomic Radius:

Atomic radius of Group VII elements, in the periodic table increases down the group as shown in the fig 13.4.
13.5.1.2 Trends in Electronegativity :-

It is usually measured on Pauling scale, on which Flourine is the most electronegative element having E.N value of 4.0. These values decrease gradually from F to I.

<table>
<thead>
<tr>
<th>Elements</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronegativity</td>
<td>4.0</td>
<td>3.0</td>
<td>2.8</td>
<td>2.5</td>
</tr>
</tbody>
</table>

13.5.1.3 Trends in Electron Affinity :-

The trend down the group is not regular. The electron affinity of halogens decreases down the group with the exception of fluorine (F).

The electron affinity is the measure of the attraction between the incoming electrons and the nucleus. The higher the attraction the higher the electron affinity.

<table>
<thead>
<tr>
<th>Elements</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron affinity (ev)</td>
<td>-3.7</td>
<td>-4.0</td>
<td>-3.8</td>
<td>-3.4</td>
</tr>
</tbody>
</table>

13.5.1.4 Trends in melting and boiling points :-

The melting and boiling points increase down the group in group VII A of the periodic table. This trend is given below.

<table>
<thead>
<tr>
<th>Elements</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.pt (°C)</td>
<td>-219.6</td>
<td>-101.0</td>
<td>-7.2</td>
<td>+113.7</td>
</tr>
<tr>
<td>B.pt (°C)</td>
<td>-188.2</td>
<td>-34.7</td>
<td>+59</td>
<td>+184</td>
</tr>
</tbody>
</table>

13.5.1.5 Bond Enthalpies:-

Bond enthalpy is the amount of heat needed to break one mole of covalent bonds to form individual atoms. It begins with the original substance in a gaseous state and ending with gaseous atoms.

$$\text{Cl} \longrightarrow \text{Cl}_2(g) \quad \Delta \quad 2\text{Cl}_2(g)$$
13.5.1.5.1 Bond Enthalpy in halogens:-

Bond enthalpy is the energy required to break a chemical bond. The exact bond enthalpy of a particular chemical bond depends upon the molecular environment in which the bond exists. Bond breaking is an endothermic process and bond enthalpy involved is given +ive sign.

The following table illustrates the Halogen-Halogen bond enthalpies.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length (nm)</th>
<th>Bond enthalpy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F – F</td>
<td>0.142</td>
<td>158</td>
</tr>
<tr>
<td>Cl – Cl</td>
<td>0.199</td>
<td>242</td>
</tr>
<tr>
<td>Br – Br</td>
<td>0.228</td>
<td>193</td>
</tr>
<tr>
<td>I – I</td>
<td>0.267</td>
<td>151</td>
</tr>
</tbody>
</table>

The abnormal behaviour in F – F bond is due to its smaller size and high repulsion between nuclei of fluorine atoms.

13.5.1.5.2 Bond Enthalpies in Hydrogen Halides:-

As the halogen atoms get bigger down the group, the bonding pair electrons get more and more distant from the nucleus, so attraction becomes less and the bond becomes weaker. The bond enthalpy is important in the thermal stability of Hydrogen halides.

H – I is easily decomposed into its components by plunging a red hot wire into a test tube of the gas. H – Br may or may not decompose depending on the exact temperature of the wire.

H – F and H – Cl are very stable to heat and they do not decompose.

Bond enthalpies of halides are given in table.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond enthalpies (kJ/moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H – F</td>
<td>568</td>
</tr>
<tr>
<td>H – Cl</td>
<td>432</td>
</tr>
<tr>
<td>H – Br</td>
<td>366</td>
</tr>
<tr>
<td>H – I</td>
<td>298</td>
</tr>
</tbody>
</table>
13.5.2 **Strength of Halogens as oxidizing agents:**

When halogens combine with a metal or non-metal they normally act as oxidizing agents. The element with which they react has +ive oxidation number in resultant compounds e.g. when halogens combine with a metal to form ionic compounds, they gain electron from metal to form −ive halide ions.

\[ 2\text{Na}_\text{(s)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{Na}^+\text{Cl}^-\text{(s)} \]

The halogen accepts electron during the above reaction and acts as oxidizing agent. Fluorine is the most reactive halogen and most powerful oxidizing agent.

The order of decreasing power as oxidizing agent is \( \text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2 \)

The electrode potential of halogens become less positive from \( \text{F} \) to \( \text{I} \) which reflects decreasing oxidizing power.

“\( \text{F} \)” and “\( \text{Cl} \)” are such powerful oxidizing agents that they can oxidize coloured dyes to colourless substances acting as oxidizing agents for bleaching.

When chlorine water is added to KI solution, the solution becomes brown. This is due to formation of iodine.

\[ 2\text{I}^-\text{(aq)} \rightarrow \text{I}_2\text{(s)} + 2e^- \]

The “\( \text{Cl}_2 \)” acts as oxidizing agent accepting electrons from “\( \text{I}_2 \)” forming \( \text{Cl}^- \) ions.

\[ \text{Cl}_2\text{(g)} + 2e^- \rightarrow 2\text{Cl}^-\text{(aq)} \]

Chlorine can oxidize \( \text{I}^- \) to \( \text{I}_2 \) and \( \text{Br}^- \) to \( \text{Br}_2 \).
The Acidity of Hydrogen Halides:

According to Bronsted and Lowery definition acid is a proton donor. HCl is an acid because it gives proton to other substances HCl, HBr and HI are strong acids, while HF is a weaker acid. HCl is soluble in water and produce $\text{H}_3\text{O}^+$ and $\text{Cl}^-$ ions.

$$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$$

This reaction shows that HCl completely dissociates in water and is a strong acid.

HBr and HI dissolve in water in exactly the same way as HCl. By contrast although HF dissolves freely in water yet it is a weak acid.

13.5.4 Halide Ions as Reducing Agents and Trends in Reducing Strength of Halide Ions:

As reducing agents halide ions show the following trend in reducing strength:

$$\Gamma > \text{Br}^- > \text{Cl}^- > \text{F}^-$$

Larger the size of the halide ion, the stronger, it is as reducing agent. For example, Br$^-$ reduces sulphuric acid to SO$_2$. There is a decrease of oxidation state of sulphur from “+6” in H$_2$SO$_4$ to “+4” in SO$_2$.

$$\text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{Br}^- \rightarrow \text{Br}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$$

‘$\Gamma$’ is stronger reducing agent than “$\text{Br}^-$”.

$$\text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{I}^- \rightarrow 4\text{I}_2 + \text{H}_2\text{S}_2^2 + 4\text{H}_2\text{O}$$
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Bleaching powder is white amorphous powder which smells strongly like chlorine. Bleaching powder is frequently called “Bleach”. It is oxidizing agent. This property is due to the hypochlorite ion, which takes up two electrons from the substance undergoing oxidation.

\[
\text{CaOCl}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaCl}_2 + \text{CaSO}_4 + 2\text{HClO}
\]

\[
\text{HClO} \rightarrow \text{HCl} + [\text{O}]
\]

Coloured matter [O] \rightarrow Colourless product.

The formation of nascent oxygen gives the oxidizing or bleaching properties. Bleaching powder is used for bleaching cotton, linen and wood pulp. It is used as disinfectant and germicide. It is also used for manufacture of chloroform.

Severe iodine deficiency results in impaired thyroid hormone synthesis or thyroid gland enlargement (goiter).

Iodine is chemical element. It is found in traces amounts in the human body, in which its only function is the synthesis of thyroid hormone.

Worldwide, the soil in large geographic areas is deficient in iodine. Twenty-nine percent of the world population, living in approximately 130 countries is estimated to live in the areas of deficiency. This occurs primarily in mountainous regions such as Himalayas, the European Alps and Andes.

Poor nutrition enhances the toxicity of fluorides. As discussed below, nutrient deficiencies have been specifically linked to increased susceptibility to fluoride induced tooth damage, bone damage. Fluoride deficiency may lead to increased cavities, weak bones and teeth.

Halogenes are commercially used in halogen lamps formation, glass etching, Tincture of iodine, water fluorination, fluorides in toothpaste, dry cleaning, refrigerants, agriculture fumigant.

Aluminium is used in coming because it is light, non-toxic, resistant to corrosion. Steel is wonderfully hydene and durable alloy, which is the material of choice in industries as diverse as processing of milk and dairy products confectionary and cooked meat etc.
Key Points:

- group IA and group IIA elements belong to s-block.
- group IIIA – VIIIA element belong to p-block.
- atomic radius of group II A increases down the group.
- atomic radius in third period decreases across the period but Ar does not follow the trend.
- electrical conductivity increases from Na to Al.
- phosphorus and sulphur do not react with water.
- Phosphorous react with oxygen and produces mixture of phosphorous (III) oxide and phosphorous (V) oxide.
- Oxides of Na and Mg are basic, while those of Al are amphoteric and oxides of rest of the elements in third period are acidic oxide.
- All the oxides of groups I A react with water to produce hydroxide, peroxide and superoxide.
- Most of the nitrates of group I elements decompose on heating and produce metal oxides, nitrogen dioxide and oxygen.
- Group I-A bicarbonates are solid which easily decompose on heating.
- The electronegativity of group II-A elements decrease from Be to Ba.
- Group II-A metals react slowly with water liberating hydrogen and forming hydroxides.
- All the metals of group II-A react with oxygen and form simple oxide.
- The solubility of hydroxide in water increase from Be(OH)₂ to Ba(OH)₂.
Exercise

Q.1 Choose the correct answer from the given choices in each case.

(i) Electronegativity of Be is approximately equal to that of
(a) Al  (b) Mg
(c) B  (d) Na

(ii) The word Alkali means
(a) Base  (b) Basic salt
(c) Ashes  (d) spirit

(iii) The elements which are most abundant in earth crust.
(a) Si & Al  (b) Ca & Mg
(c) B & Ar  (d) All

(iv) Carbonates of Li are not stable like that of sodium due to
(a) Low electronegativity
(b) Low electropositivity
(c) High charge density of Li⁺
(d) All of the above

(v) Which one of the following is not an alkali metal?
(a) Fr  (b) Cs
(c) Rb  (d) Ra

(vi) Which one of the following metal sulphates is not soluble in water?
(a) Na₂SO₄  (b) K₂SO₄
(b) BaSO₄  (d) ZnSO₄
(vii) Which one of following alkali metal forms only normal oxide with $O_2$?
   (a) Li  (b) K  (c) Na  (d) Rb

(viii) Strongest reducing agent among the halogens is
   (a) Cl₂  (b) F₂  (c) Br₂  (d) I₂

(ix) Which one of the following has lowest electron affinity?
   (a) F  (b) I  (c) Cl  (d) Br

(x) Which is the highest melting halide?
   (a) NaCl  (b) NaBr  (c) NaF  (d) NaI

(xi) The highest boiling point of HF amongst the hydrogen halides is due to
   (a) Lowest electronegativity of F  (b) Highest electronegativity of F
   (c) Lowest atomic weight of F  (d) Lowest atomic radius of F

(xii) The dry ice is
   (a) Solid ice without water  (b) Solid CO₂
   (c) Solid SO₂  (d) Solid C₆H₆

(xiii) Which one of the following is acidic in nature?
   (a) Al₂O₃  (b) CO₂
   (c) CO  (d) CaO
(xiv) Third period element that initially reacts rapidly with oxygen to form a protective oxide coating that prevents further reaction is.
(a) Na  
(c) Si
(b) Al  
(d) Mg

(xv) The yellow flame shown by sodium in Bunsen flame is due to excitation of electron.
(a) 2p to 3s  
(c) 4p to 4s
(b) 3p to 1s  
(d) 5p to 4s

(xvi) When sodium is heated with excess of O₂, which of the following is formed?
(a) NaO  
(c) Na₂O
(b) NaO₂  
(d) None of these

(xvii) Which of the following has a greater affinity for oxygen?
(a) B  
(c) K
(b) Na  
(d) Mg

(xviii) Which of the following is the strongest base?
(a) Si(OH)₄  
(c) Mg (OH)₂
(b) Be(OH)₂  
(d) Al(OH)₃

(xix) The inert pair effect dominates in
(a) Pb  
(c) C
(b) Sn  
(d) Si

(xx) Those elements of group IV-A which have no tendency to form a dichloride are
(a) C and Si  
(c) Ga and C
(b) P and Sn  
(d) Sn and Si
Q2- Short questions:
(i) Explain reaction of magnesium with H₂O
(ii) Why the NaCl does not conduct electricity in solid state?
(iii) Rubidium is below potassium in Group I-A. Predict how it will react with.
   (a) Water
   (b) Chlorine
   And describe the products.
(iv) Why halogens are so reactive?
(v) What is flame test?
(vi) Write down any four characteristics of group II-A elements.
(vii) Explain the thermal stability of nitrates and carbonates of group II-A elements.
(viii) Why carbonates of group I-A elements are more thermally stable than those of group II-A?
(ix) Why Beryllium is differs from the members of its group?
(x) Explain the structure and stability of chlorides of group IV-A elements.
(xi) Why Fluorine is stronger oxidizing agent than chlorine?
(xii) Why BeCl₂ is covalent and not ionic?
(xiii) Explain the amphoteric nature of Be (OH)₂.
(xiv) Why the atomic radius of Argon is larger than all the member of third period?
(xv) Why fall in ionization energy occurs at Al and S in same period?
(xvi) Why the compounds of Sn⁴⁺ are covalent in nature while those of Sn²⁺ are ionic?

Q3 Long Questions
(i) Explain halide ions as reducing agents and discuss their trends in reducing strength.
(ii) Discuss the atomic and physical properties of halogens.
(iii) What is meant by bond enthalpy? Explain the bond enthalpies in halogens and hydrogen halides.
(iv) Discuss physical properties of Group-IVA elements.
(v) Discuss oxides of carbon family and explain inert pair effect in formation of ionic and covalent bond.
(vi) Discuss in detail acid base behavior of Group IV-A oxides.
(vii) What are the trends in thermal stability of nitrates and carbonates of Group II-A elements?
(viii) Write down atomic and physical properties of group I-A and group II-A elements.
(ix) How peroxides, simple acids and nitrates of Group II-A elements are formed?
(x) Explain the reaction of Group II-A elements with oxygen.
(xi) Explain trends in reactivity of Group I-A elements with water.
(xii) Explain the properties of Hydroxide of third period elements.
(xiii) Explain the acid base behavior of oxides of third period elements.
(xiv) What is meant by inert pair effect? Explain inert pair effect in formation of ionic and covalent bond.