

**SCHOLAR  
SERIES**

# CHEMISTRY

**For Class**

**Subjective**

**12th**

**Federal Board Edition**

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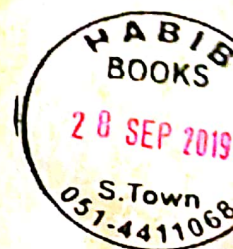
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CHAPTER 13

S AND p-BLOCK ELEMENTS

PERIOD 3 (Na TO Ar)

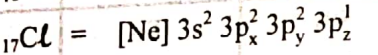
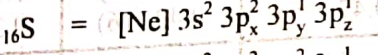
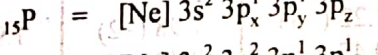
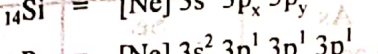
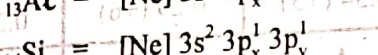
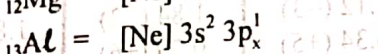
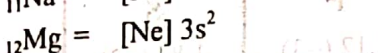
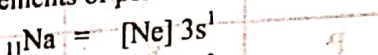
Atomic and Physical Properties of the Period 3 Elements

This period contains Sodium (Na), Magnesium (Mg), Aluminium (Al), Silicon (Si), Phosphorus (P), Sulphur (S), Chlorine (Cl) and Argon (Ar).

(a) Atomic Properties

Electronic Structures

In Period 3 of the periodic table, the 3s and 3p orbitals are filling with electrons. The electronic structures for the eight elements of period 3 are:



In each case, [Ne] represents the complete electronic structure of a neon atom as  $1s^2 2s^2 2p^6$ .



1. The electronic structure of Mg is  $1s^2, 2s^2, 2p^6, 3s^2$ . Write down electronic structure of Al in the same notation.

Ans.  $_{13}\text{Al} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

2. Which of the two elements Mg or Al has the more stable structure?

Ans.  $_{12}\text{Mg} = 1s^2, 2s^2, 2p^6, 3s^2$

$_{13}\text{Al} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

The electronic configuration of Mg shows that it has paired electrons (all) in s-orbital. As a result it has high ionization energy as compared to Al. Therefore Mg is more stable and less reactive as compared to Al.

$$\text{I.E} \propto \text{stability} \propto \frac{1}{\text{Reactivity}}$$

(i) Atomic Radius

"The half of the distance between the centres of two bonded atoms of any element is called atomic radius." or

"The average distance between the nucleus of an atom and its outermost shell is called atomic radius."

Trends in Atomic Radius

As the number of shells in all the elements of a given periods remain the same but the value of effective nuclear charge increases from left to right. The increased effective nuclear charge pulls the electron cloud of the atom nearer to

the nucleus and thus the size of the atoms and ions goes on decreasing from left to right. Thus in going from left to right in a period of s-and p-block elements, atomic and ionic radii decrease with the increase of atomic number. This fact can be illustrated by considering the atomic (covalent) and ionic radii of the elements as shown below.

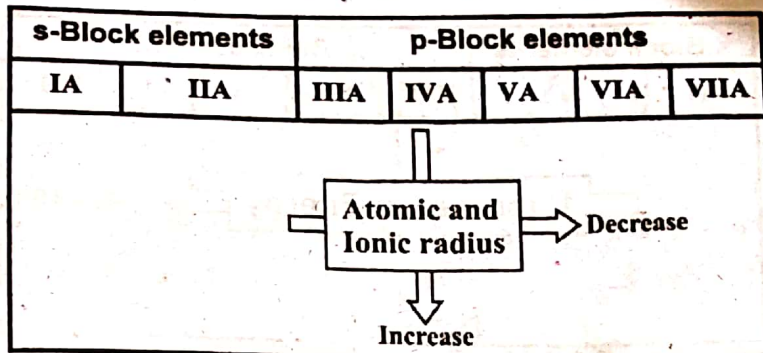
**Ionic radii (in Å) of representative elements (s-and p- block elements). In parenthesis are given the oxidation states of the elements.**

Group → Period ↓	s-block Elements		p-block Elements				
	IA	IIA	IIIA	IVA	VA	VIA	VIIA
1	H 2.08 (-1) 2.09 (+1)						
2	Li 0.60 (+1)	Be 0.31 (+2)	B 0.20 (+3)	C 2.60 (-4) 0.15 (+4)	N 1.71 (-3) 0.11 (+5)	O 1.40 (-2) 0.09 (+6)	F 1.36 (-1) 0.07 (+7)
3	Na 0.95 (+1)	Mg 0.65 (+2)	Al 0.50 (+3)	Si 2.71 (-1) 0.41 (+4)	P 2.12 (-3) 0.34 (+5)	S 1.84 (-2) 0.29 (+6)	Cl 1.81 (-1) 0.26 (+7)
4	K 1.33 (+1)	Ca 0.99 (+2)	Ga 1.13 (+1) 0.62 (+3)	Ge 0.93 (+2) 0.53 (+4)	As 2.22 (-3) 0.47 (+5)	Se 1.98 (-2) 0.42 (+6)	Br 1.95 (-1) 0.39 (+7)
5	Rb 1.48 (+1)	Sr 1.13 (+2)	In 1.32 (+1) 0.81 (+3)	Sn 1.12 (+2) 0.71 (+4)	Sb 0.45 (-3) 0.62 (+5)	Te 2.21 (-2) 0.56 (+6)	I 2.16 (-1) 0.50 (+7)
6	Cs 1.69 (+1)	Ba 1.35 (+2)	Tl 1.40 (+1) 0.95 (+3)	Pb 1.20 (+2) 0.84 (+4)	Bi 1.20 (+3) 0.74 (+5)	Po	At
7	Fr 1.76 (+1)	Ra 1.40 (+2)					

	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic (Covalent) radius (Å)	1.54	1.36	1.18	1.11	1.06	1.02	.99	0.98
	Decreasing →							
Ionic Radius (Å)	0.95	0.65	0.50	0.41	0.34	0.29	0.26	-
	Decreasing →							

Thus in any period the alkali metals (that are present at the extreme left of the periodic table) have the largest size while the halogens (that are present at the extreme right excluding zero group elements) have the smallest size. However the size of the atoms of inert gases is larger than that of the preceding halogen.

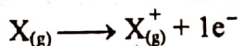
The trends in atomic and ionic radii of representative elements (s- and p-block elements) in a period and a group of the periodic table can be represented as:



Trends in Atomic and ionic radii (s- and p-Block elements)

**(ii) Trends in first ionization energy**

The first ionization energy is the energy required to remove the most loosely held electron from 1 mole of gaseous atoms to produce 1 mole gaseous ion (1+).



First ionization energy depends upon following factors:

- The atomic size
- Nuclear charge
- Shielding / Screening effect
- Nature of orbital

In general, as we move from left to right in a period, the ionization energy of the elements increases due to successive increase in the nuclear charge and decrease in atomic size. However there are certain elements which show irregular trends in period 3. For example ionization energy of Mg (738 kJ mol<sup>-1</sup>) and P (1012 kJ mol<sup>-1</sup>) are higher than those of Al (578 kJ mol<sup>-1</sup>) and S (1000 kJ mol<sup>-1</sup>).

**Q. Why I.E of Mg is higher than Al?**

**Ans:** In case of Mg (1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>) it is more difficult to remove an electron from the completely filled 3s-orbital while in case of Al (1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>1</sup>) it is easier to remove the same from partially filled 3p-orbital. Since to remove an electron from a 3s-orbital of Mg atom requires more energy than to remove the same from a 3p-orbital of Al atom that is why ionization energy of Mg is higher than that of Al.



Similarly higher value of P as compared to S has been explained on the same lines of argument as used in explaining the higher value of Mg compared to Al.

**The values of First Ionization Energy of Period 3**

Period 3 Elements	Na	Mg	Al	Si	P	S	Cl	Ar
First Ionization Energies (kJ/mol)	496	738	578	786	1012	1000	1251	1520

The trends in first ionization energy of period 3 elements (s- and p-Block elements) in a period and in a group of the periodic table can be shown as:

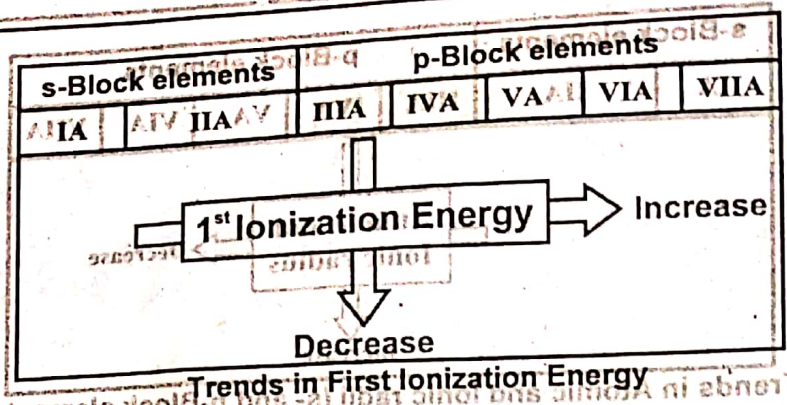
1- Size  
2-

**Do you know?**

*energy required to remove outer electron*

(1) A cation is smaller in size than its parent atom because of effective nuclear charge and lesser shielding effect.  
 $Na \longrightarrow Na^{+1} + 1e^{-}$   
 (154pm)      (95pm)

(2) An anion is bigger in size than its parent atom because of weak effective nuclear charge and strong shielding effect.  
 $Cl + 1e^{-} \longrightarrow Cl^{-}$   
 (99pm)      (181pm)



**(iii) Electronegativity**

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned a value of 4.0 and values range down to caesium and francium which are the least electronegative at 0.7.

**Trend in Electronegativity**

The trend across Period 3 looks like this:  
 In going from left to right in a period of s- and p-block elements, the electronegativity values increase. This increase can be explained on the basis of any of the following facts.

- (i) On moving from left to right in a period, there is a decrease in the size of the atoms. Smaller atoms have greater tendency to attract the electrons towards themselves i.e. smaller atoms have higher electronegativity values.
- (ii) On moving from left to right in a period there is an increase of ionization energy and electron affinity of the elements. The atoms of the elements, which have higher value of ionization energies and electron affinities also have higher electronegativities. The variation of electronegativity in a period and a group of representative elements (s and p-block elements) is shown.

**Note:** Since argon does not form covalent bonds, we obviously can't assign it electronegativity.  
**Explanation**

- As we go across the period, the bonding electrons are always in the same level - the 3-level. They are always being screened by the two inner electrons.
- All that differs is the number of protons in the nucleus. As we go from sodium to chlorine, the number of protons steadily increases and so attracts the bonding pair more closely.

**(b) Physical Properties**

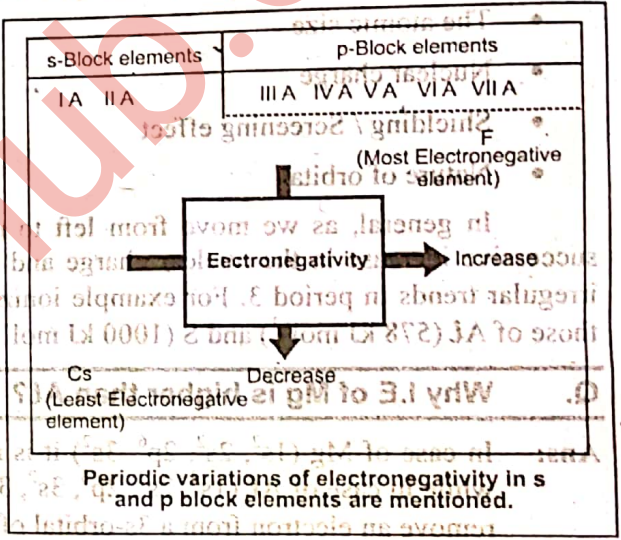
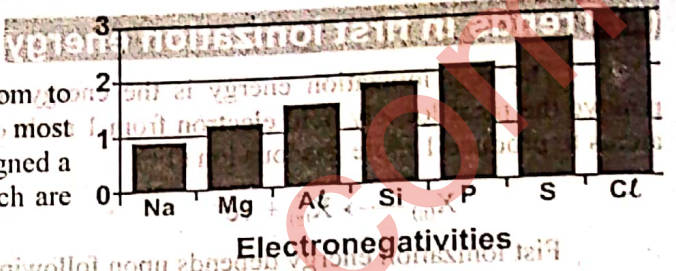
To understand the electrical conductivity and the melting and boiling points of the elements, we have to understand the structure of each of the elements.

**(1) Structures of the Elements**

The structures of the elements change as we go across the period. The first three (i.e. Na, Mg, Al) are metallic, silicon is giant covalent, and the rest (i.e. P, S, Cl, Ar) are simple molecules.

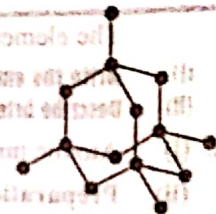
**(i) Three Metallic Structures of Na, Mg and Al**

Sodium, magnesium and aluminium all have metallic structures. In sodium, only one electron per atom is involved in the metallic bond - the single 3s electron. In magnesium, both of its outer electrons are involved, and in



Periodic variations of electronegativity in s and p block elements are mentioned.

aluminium all three. The coordination number of atoms in the metal crystal is also different in these metals. Sodium is 8-co-ordinated - each sodium atom is touched by only 8 other atoms. Both magnesium and aluminium are 12-co-ordinated (although in slightly different ways). This is a more efficient way to pack atoms, leading to less wasted space in the metal structures and to stronger bonding in the metal.



Tiny part of silicon structure

**(ii) A Giant Covalent Structure of Si**

Silicon has a giant covalent structure just like diamond.

**(iii) Four Simple Molecular Structures of P, S, Cl and Ar**

- The structures of phosphorus (i.e. white etc) and sulphur (i.e. rhombic or monoclinic etc) vary depending on the type of phosphorus or sulphur we are talking about.
- The atoms in each of these molecules are held together by covalent bonds and argon is a monoatomic molecule.
- In the liquid or solid state, the molecules are held close to each other by van der Waals dispersion forces.

**(2) Electrical Conductivity**

- Sodium, magnesium and aluminium are all good conductors of electricity. The three metals (Na, Mg and Al) conduct electricity because the delocalized electrons (the "sea of electrons") are free to move throughout the solid or the liquid metal. Conductivity increases as we go from sodium to magnesium to aluminium as they have free electrons.
- Silicon is a semiconductor. With a diamond structure, we might not expect it to conduct electricity, but it does!
- The rest (P, S, Cl and Ar) do not conduct electricity because they are simple molecular substances. There are no electrons free to move around.

**Exercise:** Q.3.i(d) The melting and boiling points of the elements increase from left to right up to the middle in period 3 elements and decrease onward. Why?

**(3) Trends in Melting and Boiling Points**

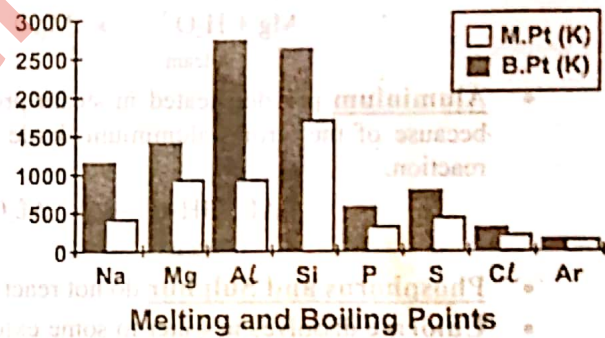
The melting and boiling points tell us about the strength of forces present in atoms, ions and molecules. In the case of elements, the values of melting and boiling points are according to the binding energies present in them.

**Trend:**

As we move from left to the right in a period, the melting and boiling points increase upto middle i.e. group-IVA and then decrease from group V-A to noble gases (Zero group elements)

**Reasons:**

- (1) The melting and boiling points are governed entirely by the sizes of the molecules and intermolecular forces i.e. binding electron present in the outermost shell.
- (2) The melting point and boiling point are high up to middle because these elements contain increasing number of binding electrons from I to IV and also have giant covalent structure.
- (3) The melting point and boiling point are low from P to Ar because these elements exist in the form of diatomic molecules and have orderly least / weak intermolecular forces upto Argon.



**QUICK QUIZ**

**(a) List the symbols of elements present in the third period of the periodic table, in order of increasing atomic number.**  
**Ans.** Elements of 3<sup>rd</sup> Period  
<sub>11</sub>Na, <sub>12</sub>Mg, <sub>13</sub>Al, <sub>14</sub>Si, <sub>15</sub>P, <sub>16</sub>S, <sub>17</sub>Cl, <sub>18</sub>Ar

**(b) Which of the above elements are:**  
 (i) s-block elements (ii) d-block elements

**Ans.** (i) s-block elements (Na and Mg)  
 (ii) d-block elements (None of the 3<sup>rd</sup> period element belongs to d-block)

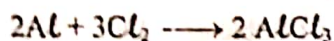
The elements Al, Si, P, S, Cl and Ar of 3<sup>rd</sup> period belong to p-block.

- (c) (i) Write the empirical formula of the chloride formed by the element with atomic number 13.  
 (ii) Describe briefly how can you prepare a sample of this chloride?

Ans. (i) Atomic number of Al is 13 and it forms chloride with empirical formula  $AlCl_3$ .

(ii) Preparation of  $AlCl_3$ :

$AlCl_3$  is prepared by treating aluminium with chlorine. For this, pass the dry chlorine gas over aluminium foil heated in a long tube. The aluminium burns in the stream of chlorine to produce very pale yellow  $AlCl_3$ .



$AlCl_3$  sublimes and collects further down the tube where it is cooled.

## Chemical Reactions of the Period 3 Elements

Exercise: Q.3.1(c) Describe the trends in reaction of period 3 elements with water.

### (a) Reactions with Water

- Sodium** has a very exothermic reaction with cold water producing hydrogen and a colourless solution of sodium hydroxide.



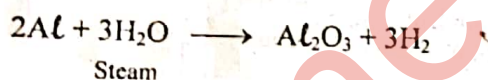
- Magnesium** has a very slight reaction with cold water, but burns in steam. A very clean coil of magnesium dropped into cold water eventually gets covered in small bubbles of hydrogen which float it to the surface. Magnesium hydroxide is formed as a very thin layer on the magnesium and this tends to stop the reaction.



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



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

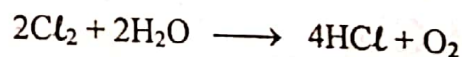
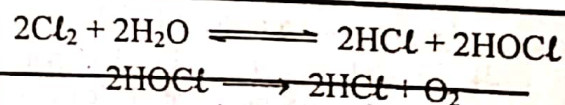
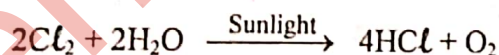


Q. Why does aluminium not corrode in air?

- Phosphorus and Sulphur** do not react with water.
- 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 chlorous (I) acid (hypochlorous acid).



In the presence of sunlight, the chloric(I) acid slowly decomposes to produce more hydrochloric acid, releasing oxygen gas, and we may come across an equation showing the overall change:



- Argon** shows no reaction with water.

### Reactions with Oxygen

- Sodium** burns in oxygen with an orange flame to produce a white solid mixture of sodium oxide and sodium peroxide.

For the simple oxide:



For the peroxide:



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

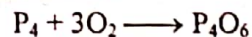


- **Silicon** will burn in oxygen if heated strongly. Silicon dioxide is produced.

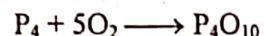


- **White phosphorus** catches fire spontaneously in air, burning with a white flame and producing clouds of white smoke - a mixture of phosphorus (III) oxide and phosphorus (V) oxide. The proportions of these depend on the amount of oxygen available. In an excess of oxygen, the product will be almost entirely phosphorus (V) oxide.

For the phosphorus (III) oxide:



For the phosphorus (V) oxide:



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



- **Chlorine** would not react directly with oxygen although it has several oxides.

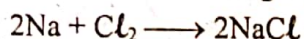
- **Argon** does not react either.

### Properties of the oxides of elements in period 3

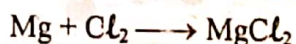
Formula of Oxide	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>4</sub> O <sub>10</sub> (P <sub>4</sub> O <sub>6</sub> )	SO <sub>3</sub> (SO <sub>2</sub> )	Cl <sub>2</sub> O <sub>7</sub> (Cl <sub>2</sub> O)
State of oxide	solid	solid	solid	solid	solid	gas	liquid
Conduction of electricity by molten or liquid oxide	Good	Good	Good	Very poor	Nil	Nil	Nil
Structure of oxide	Giant Structures	-	-	-	Simple molecular structure	-	-
Enthalpy change of formation (kJ mol <sup>-1</sup> ) of oxide at 298K	- 416	- 602	- 1676	- 910	- 2984	- 395	80
Effect of adding oxide to water	reacts to form NaOH (aq) alkaline solution	reacts to form Mg(OH) <sub>2</sub>	does not react with water but it is amphoteric	does not react with water but it is acidic	P <sub>4</sub> O <sub>10</sub> reacts to form H <sub>3</sub> PO <sub>4</sub> acid solution	SO <sub>3</sub> reacts to form H <sub>2</sub> SO <sub>4</sub> acid solution	Cl <sub>2</sub> O <sub>7</sub> reacts to form HClO <sub>4</sub> acid solution
Nature of oxide	Basic (alkaline)	Basic (weakly alkaline)	Amphoteric	Acidic	Acidic	Acidic	Acidic

### (c) Reactions with Chlorine

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

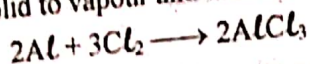


- **Magnesium** burns with its usual intense white flame to give white magnesium chloride.

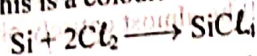




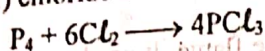
- **Aluminium** is often reacted with chlorine by passing dry chlorine over aluminium foil heated in a long tube. The aluminium burns in the stream of chlorine to produce very pale yellow aluminium chloride. This sublimes (turns straight from solid to vapour and back again) and collects further down the tube where it is cooled.



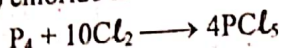
- **With Silicon:** When chlorine is passed over silicon powder heated in a tube, it reacts to produce silicon tetrachloride. This is a colourless liquid which vaporizes and can be condensed further along the apparatus.



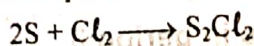
- **White phosphorus** burns in chlorine to produce a mixture of two chlorides, phosphorus (III) chloride ( $PCl_3$ ) and phosphorus (V) chloride ( $PCl_5$ ).  
Phosphorus (III) chloride is a colourless fuming liquid.



Phosphorus (V) chloride is an off-white (going towards yellow) solid.



- **With sulphur:** When a stream of chlorine is passed over some heated sulphur, it reacts to form an orange, evil-smelling liquid, disulphur dichloride,  $S_2Cl_2$ .



- **Argon** doesn't react with chlorine.

**Exercise: Q.3.** (ii) Discuss the metallic oxides and silicon dioxide under the following headings:  
(i) Structures (ii) Melting and Boiling points (iii) Electrical conductivity

## Physical Properties of the Oxides

The Oxides of period 3 are as follow:

$Na_2O$	$MgO$	$Al_2O_3$	$SiO_2$	$P_4O_{10}$	$SO_3$	$Cl_2O_7$
				$P_4O_6$	$SO_2$	$Cl_2O$

Those oxides in the top row are known as the **highest oxides** of the various elements. These are the oxides where the Period 3 elements are in their highest oxidation states. In these oxides, all the outer electrons are being involved in the bond formation just as one with sodium, to all seven of chlorine's outer electrons. Argon is obviously omitted because it doesn't form an oxide.

### (1) Structures of oxides

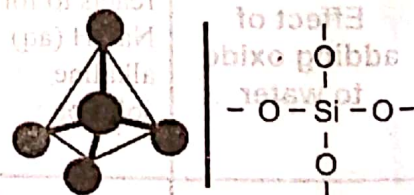
The trend in structure is from the metallic oxides containing giant structures of ions on the left of the period via a giant covalent oxide (silicon dioxide) in the middle to molecular oxides on the right.

#### (i) The Metallic oxides

Sodium, magnesium and aluminium oxides structure/diagram is same as sodium chloride.

#### (ii) Giant Covalent oxides

Crystalline silicon has the same structure as diamond. To turn it into silicon dioxide, each silicon atom is bridged to its neighbours by an oxygen atom.



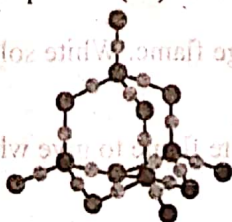
#### (iii) The molecular oxides

##### (a) The Phosphorus oxides

Phosphorus has two common oxides, phosphorus (III) oxide,  $P_4O_6$ , and phosphorus (V) oxide,  $P_4O_{10}$ .



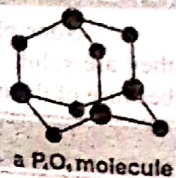
a P<sub>4</sub> molecule



a P<sub>4</sub> molecule

- **Phosphorus (III) oxide** is a white solid, melting at 24°C and boiling at 173°C. The structure of its molecule is best worked out starting from a P<sub>4</sub> molecule, which is a little tetrahedron.

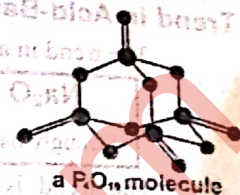
Pull this apart so that we can see the bonds - - - and then replace the bonds by new bonds linking the phosphorus atoms via oxygen atoms. These will be in a V-shape (rather like in water). The phosphorus is using only three of its outer electrons (the 3 unpaired p electrons) to form bonds with the oxygen.



- **Phosphorus (V) oxide** is also a white solid, subliming (turning straight from solid to vapour) at 300°C. In this case, the phosphorus uses all five of its outer electrons in the bonding.

Solid phosphorus (V) oxide exists in several different forms - some of them polymeric. We are going to concentrate on a simple molecular form and this is also present in the vapour.

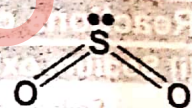
This is most easily drawn starting from P<sub>4</sub>O<sub>6</sub>. The other four oxygen atoms are attached to the four phosphorus atoms via double bonds.



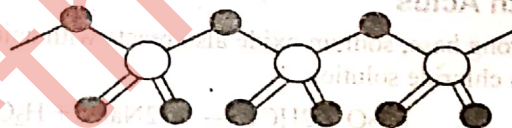
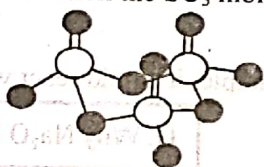
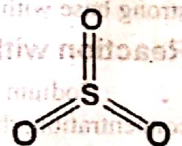
## (b) The Sulphur oxides

Sulphur has two common oxides which are:

- **Sulphur dioxide (SO<sub>2</sub>)** is a colourless gas at room temperature with an easily recognised choking smell. It consists of simple SO<sub>2</sub> molecules. The sulphur uses 4 of its outer electrons to form the double bonds with the oxygen, leaving the other two as a lone pair on the sulphur. The bent shape of SO<sub>2</sub> is due to this lone pair.



- **Pure sulphur trioxide (SO<sub>3</sub>)** is a white solid with a low melting and boiling point. Gaseous sulphur trioxide consists of simple SO<sub>3</sub> molecules in which all six of the sulphur's outer electrons are involved in the bonding. There are various forms of solid sulphur trioxide. The simplest one is a trimer, S<sub>3</sub>O<sub>9</sub>, where three SO<sub>3</sub> molecules are joined up and arranged in a ring. There are also other polymeric forms in which the SO<sub>3</sub> molecules join together in long chains. For example:

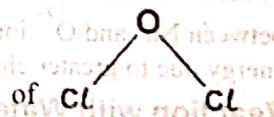


The fact that the simple molecules join up in this way to make bigger structures is what makes the sulphur trioxide a solid rather than a gas.

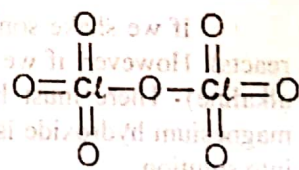
## (c) The Chlorine oxides

Chlorine forms several oxides including the following two:

- **Chlorine (I) oxide (Cl<sub>2</sub>O)** is a yellowish-red gas at room temperature. It consists of simple small molecules. In this structure chlorine uses its one outer electron and bonds with oxygen.



- **Chlorine (VII) oxide (Cl<sub>2</sub>O<sub>7</sub>)** is a colourless oily liquid at room temperature. In chlorine (VII) oxide, the chlorine uses all of its seven outer electrons and bonds with oxygen. This produces a much bigger molecule.



## (2) Melting and Boiling Points

- The giant structures (the metal oxides and silicon dioxide) will have high melting and boiling points because a lot of energy is needed to break the strong bonds (ionic or covalent) operating in three dimensions.
- 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 van der Waals dispersion and dipole-dipole interactions. These vary depending on the size, shape and polarity of the various molecules - but will always be much weaker than the ionic or covalent bonds need to break in a giant structure. These oxides tend to be gases, liquids or low melting point solids.

### (3) Electrical Conductivity

None of these oxides has any free or mobile electrons. That means that none of them will conduct electricity when they are solid. The ionic oxides can, however, undergo electrolysis when they are molten. They can conduct electricity because of the movement of the ions towards the electrodes and the discharge of the ions when they get there.

## ACID-BASE BEHAVIOUR OF THE OXIDES

### Trend in Acid-Base behaviour

The trend in acid-base behaviour is shown in various reactions, but as a simple summary:

$\text{Na}_2\text{O}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{P}_4\text{O}_{10}$	$\text{SO}_3$	$\text{Cl}_2\text{O}_7$
Strongly basic	Basic	Amphoteric	Weakly acidic	Weakly acidic	Acidic	Strongly acidic

The trend is from strongly basic oxides on the left-hand side to strongly acidic ones on the right, via an amphoteric oxide (aluminium oxide) in the middle. An amphoteric oxide is one which shows both acidic and basic properties.

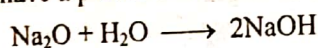
### Reactions of Oxides with Water, Acids and Bases

#### (i) Sodium oxide ( $\text{Na}_2\text{O}$ )

Sodium oxide is a simple strongly basic oxide. It is basic because it contains the oxide ion,  $\text{O}^{2-}$ , which is a very strong base with a high tendency to combine with hydrogen ions.

#### Reaction with Water

Sodium oxide reacts exothermally with cold water to produce sodium hydroxide solution. Depending on its concentration, this will have a pH around 14.



#### Reaction with Acids

As a strong base, sodium oxide also reacts with acids. For example, it would react with dilute hydrochloric acid to produce sodium chloride solution.



Q. Why  $\text{Na}_2\text{O}$  is strongly basic than  $\text{MgO}$ ?

#### (ii) Magnesium oxide ( $\text{MgO}$ )

Magnesium oxide is a simple basic oxide because it also contains oxide ions. However, it is not as strongly basic as sodium oxide because the oxide ions are not so free. In the sodium oxide case, the ions are held together by attractions between  $\text{Na}^+$  and  $\text{O}^{2-}$  ions. In the magnesium oxide case, the attractions are between  $\text{Mg}^{+2}$  and  $\text{O}^{2-}$  ions. It has high lattice energy due to greater charge density of  $\text{Mg}^{+2}$  ion. Thus it takes more energy to break these.

#### Reaction with Water

If we shake some white magnesium oxide powder with water, nothing seems to happen (it doesn't look as if it reacts). However, if we test the pH of the liquid, we find that it is somewhere around pH 9 (showing that it is slightly alkaline). There must have been some slight reaction with the water to produce hydroxide ions in solution. Some magnesium hydroxide is formed in the reaction, but this is almost insoluble and so not many hydroxide ions actually get into solution.



#### Reaction with Acids

Magnesium oxide reacts with warm dilute hydrochloric acid to give magnesium chloride solution.



#### (iii) Aluminium oxide ( $\text{Al}_2\text{O}_3$ )

As it is amphoteric oxide, it has reactions as both a base and an acid.

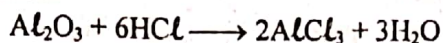
**Milk of Magnesia:** A suspension of  $\text{Mg(OH)}_2$  in water is called Milk of magnesia. It is used for treatment of acidity in stomach.

**Reaction with Water**

Aluminium oxide does not react in a simple way with water and does not dissolve in it. Although it still contains oxide ions, they are held too strongly in the solid lattice to react with the water.

**Reaction with Acids**

Aluminium oxide will react with hot dilute hydrochloric acid to give aluminium chloride solution.

**Reaction with Bases**

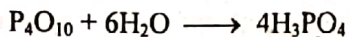
Aluminium oxide has also got an acidic side to its nature, and it shows this by reacting with bases such as sodium hydroxide solution.

Various aluminates are formed (compounds where the aluminium is found in the negative ion). This is possible because aluminium has the ability to form covalent bonds with oxygen.

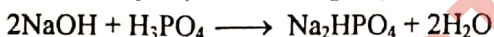
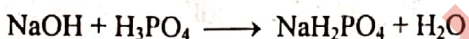
With hot, concentrated sodium hydroxide solution, aluminium oxide reacts to give a colourless solution of sodium tetrahydroaluminate.

**(iv) Phosphorus (V) oxide (P<sub>4</sub>O<sub>10</sub>)****Reaction with Water**

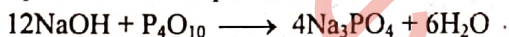
Phosphorus (V) oxide reacts violently with water to give a solution containing a mixture of acids, the nature of which depends on the conditions. We usually just consider one of these, phosphoric (V) acid, H<sub>3</sub>PO<sub>4</sub> (also known just as phosphoric acid or as orthophosphoric acid).

**Reaction with Base:**

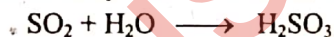
As it is acidic so it reacts with NaOH as follows:



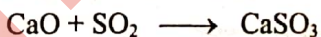
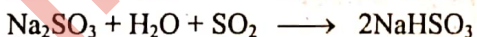
Again, if we were to react phosphorus (V) oxide directly with sodium hydroxide solution rather than making the acid first, we would end up with the same possible salts.

**(v) Sulphur oxides (SO<sub>x</sub>)****(a) Sulphur dioxide (SO<sub>2</sub>)****Reaction with Water**

Sulphur dioxide is fairly soluble in water, reacting with it to give a solution of sulphurous acid, H<sub>2</sub>SO<sub>3</sub>.

**Reaction with Base**

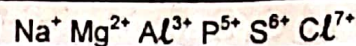
As it is acidic so it reacts with NaOH and CaO as follows:

**(b) Sulphur trioxide (SO<sub>3</sub>)****Reaction with Water**

Sulphur trioxide reacts violently with water to produce a fog of concentrated sulphuric acid droplets.

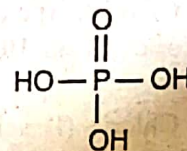
**Reaction with Base**

In principle, we can also get sodium hydrogen sulphate solution by using half as much sodium hydroxide and just reacting with one of the two acidic hydrogens in the acid.



as the oxidation state increases

- Acidic character increases
- Covalent nature increases



Sulphur trioxide itself will also react directly with bases to form sulphates. For example, it will react with calcium oxide to form calcium sulphate.



**(vi) The Chlorine oxides (Cl<sub>2</sub>O<sub>x</sub>)**

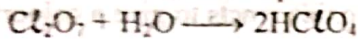
Chlorine forms several oxides but following two are important:

**(a) Chlorine (VII) oxide (Dichlorine heptoxide, Cl<sub>2</sub>O<sub>7</sub>)**

Chlorine (VII) oxide is the highest oxide of chlorine - the chlorine is in its maximum oxidation state of +7. It continues the trend of the highest oxides of the Period 3 elements towards being stronger acids.

**Reaction with Water:**

Chlorine (VII) oxide reacts with water to give the very strong acid, chloric (VII) acid - also known as perchloric acid. The pH of typical solutions will, like sulphuric acid, be around 0.



Chloric (VII) acid reacts with sodium hydroxide solution to form a solution of sodium chlorate (VII).



**Reaction with Base:**

Chlorine (VII) oxide reacts with sodium hydroxide solution to give the sodium chlorate.



**(b) Chlorine (I) oxide (dichlorine monoxide, Cl<sub>2</sub>O)**

**Reaction with water:**

Chlorine (I) oxide is far less acidic than chlorine (VII) oxide. It reacts with water to some extent to give chloric (I) acid, HOCl - also known as hypochlorous acid.



Chloric (I) acid reacts with sodium hydroxide solution to give a solution of sodium chlorate (I) (sodium hypochlorite).



**Reaction with Base**

Chlorine (I) oxide also reacts directly with sodium hydroxide to give sodium hypochlorite.

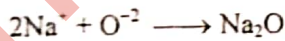
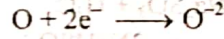


**(a) What is the nature of bonds in the oxides formed when Na, Mg, Al and S react with excess oxygen?**

**Ans. (a) Nature of bonds in oxides of Na, Mg, Al and S**

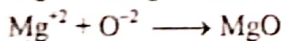
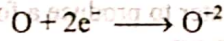
**Sodium Oxide (Na<sub>2</sub>O)**

Ionic bonding is found in Na<sub>2</sub>O



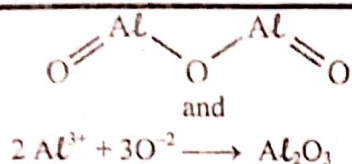
**Magnesium Oxide (MgO)**

Ionic bonding is found in MgO

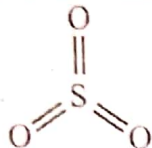


**Aluminium Oxide (Al<sub>2</sub>O<sub>3</sub>)**

Aluminium oxide has intermediate bonding. This basically means that it has a giant lattice structure but also has some covalent bonding too.

**Sulphur Trioxide (SO<sub>3</sub>)**

In SO<sub>3</sub> molecule, sulphur atom is covalently bonded with three oxygen atoms.



(b) How do these oxides react with (I) Water (II) dilute acids, (III) alkali

Ans. (b) **Reactions with Water**

- (i)  $\text{Na}_2\text{O} + \text{H}_2\text{O} \longrightarrow 2\text{NaOH}$
- (ii)  $\text{MgO} + \text{H}_2\text{O} \longrightarrow \text{Mg(OH)}_2$
- (iii)  $\text{Al}_2\text{O}_3$  does not react with water and does not dissolve in it.
- (iv)  $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$

**Reactions with dilute Acids**

- (i)  $\text{Na}_2\text{O} + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O}$
- (ii)  $\text{MgO} + 2\text{HCl} \longrightarrow \text{MgCl}_2 + \text{H}_2\text{O}$
- (iii)  $\text{Al}_2\text{O}_3 + 6\text{HCl} \longrightarrow 2\text{AlCl}_3 + 3\text{H}_2\text{O}$
- (iv)  $\text{SO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{S}_2\text{O}_7$  (Oleum)

**Reactions with Alkalies**

- (i) Being strongly basic oxides, Na<sub>2</sub>O does not react with alkalies.
- (ii) Although MgO is less basic in nature than Na<sub>2</sub>O, yet it does not react with alkalies.
- (iii)  $\text{Al}_2\text{O}_3 + 2\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow 2\text{NaAl(OH)}_4$
- (iv)  $2\text{NaOH} + \text{SO}_3 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$

(c) Magnesium chloride is a high melting point solid, aluminium chloride is a solid which sublimes readily at about 180°C and silicon tetrachloride is a volatile liquid. Explain the nature of the chemical bonding in these chlorides and show how this accounts for the above differences in volatility.

- Ans. • **Magnesium chloride (MgCl<sub>2</sub>)** is an ionic compound consisting of a giant array of magnesium and chloride ions. Strong attraction between these ions need a lot of heat every to break. Therefore MgCl<sub>2</sub> has high melting and boiling points.
- **Solid aluminium chloride** has an ionic lattice with a lot of covalent character. At temperatures around 180 – 190°C, AlCl<sub>3</sub> converts to a molecular form Al<sub>2</sub>Cl<sub>6</sub>. Due to weak intermolecular attractions, it sublimes at this temperature.
- **Silicon tetrachloride (SiCl<sub>4</sub>)** is a simple covalent compound. The only attractions between the molecules are van der Waals dispersion forces. Therefore it is a volatile liquid.

**Chlorides of the Period 3 Elements****Structures of chlorides of period 3**

- Sodium chloride and magnesium chloride are ionic and consist of giant ionic lattices at room temperature.
- Aluminium chloride and phosphorus (V) chloride are tricky! They change their structure from ionic to covalent when the solid turns to a liquid or vapour.
- The others are simple covalent molecules.

## Melting and Boiling Points

- Sodium and magnesium chlorides are solids with high melting and boiling points because of the large amount of heat which is needed to break the strong ionic attractions.
- The rest are liquids or low melting point solids. Leaving aside the aluminium chloride and phosphorus (V) chloride cases where the situation is quite complicated, the attractions in the others will be much weaker intermolecular forces such as van der Waals dispersion forces. These vary depending on the size and shape of the molecule, but will always be far weaker than ionic bonds.

## Electrical Conductivity

- Sodium and magnesium chlorides are ionic and so will undergo electrolysis when they are molten. Electricity is carried by the movement of the ions and their discharge at the electrodes.
- In the aluminium chloride and phosphorus (V) chloride cases, the solid doesn't conduct electricity because the ions aren't free to move. In the liquid (where it exists - both of these sublime at ordinary pressures), they have converted into a covalent form, and so do not conduct either.
- The rest of the chlorides of sulphur do not conduct electricity either solid or molten because they do not have any ions or any mobile electrons.

## Reactions with Water

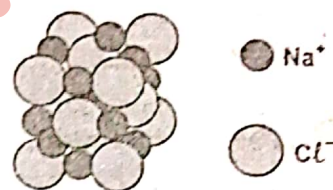
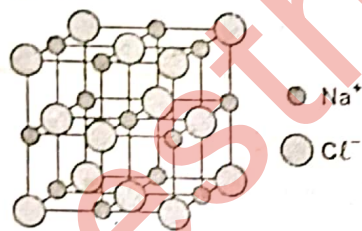
Sodium and magnesium chloride just dissolve in water. The other chlorides all react with water in a variety of ways. The reaction with water is known as hydrolysis.

## The Individual Chlorides

Section D

### Sodium Chloride, NaCl

- Sodium chloride is a simple ionic compound consisting of a giant array of sodium and chloride ions. A small representative bit of a sodium chloride lattice looks like this:  
This is normally drawn in an exploded form as:

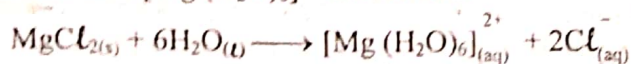


- The strong attractions between the positive and negative ions need a lot of heat energy to break, and so sodium chloride has high melting and boiling points.
- It doesn't conduct electricity in the solid state because it hasn't any mobile electrons and the ions aren't free to move. However, when it melts it undergoes electrolysis.
- Sodium chloride simply dissolves in water to give a neutral solution.

### Magnesium Chloride, MgCl<sub>2</sub>

- Magnesium chloride is an ionic compound, but with a more complicated arrangement of the ions to allow for having twice as many chloride ions as magnesium ions. A lot of heat energy is needed to overcome the attractions between the ions, and so the melting and boiling points are high.
- Solid magnesium chloride is a non-conductor of electricity because the ions aren't free to move. However, it undergoes electrolysis when the ions become free on melting.
- Magnesium chloride dissolves in water to give a faintly acidic solution (pH = approximately 6).
- When magnesium ions are broken off the solid lattice and go into solution, there is enough attraction between the Mg<sup>2+</sup> ions and the water molecules because co-ordinate bonds are formed between the magnesium ions and lone pairs on surrounding water molecules.

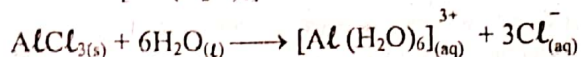
Hexaaquamagnesium ions [Mg(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> are formed:



Ions of this sort are acidic.

**Aluminium Chloride,  $AlCl_3$** 

- Solid aluminium chloride doesn't conduct electricity at room temperature because the ions aren't free to move. Molten aluminium chloride (only possible at increased pressures) doesn't conduct electricity because there aren't any ions any more.
- The reaction of aluminium chloride with water is surprising. If we drop water onto solid aluminium chloride, we get a violent reaction producing clouds of steamy fumes of hydrogen chloride gas.
- The aluminium chloride reacts with the water rather than just dissolving in it. In the first instance, hexaaquaaluminium ions  $[Al(H_2O)_6]^{3+}$  are formed together with chloride ions.

**SUMMARY**

- At room temperature, solid aluminium chloride has an ionic lattice with a lot of covalent character.
- At temperatures around 180 - 190°C (depending on the pressure), aluminium chloride converts to a molecular form,  $Al_2Cl_6$ . This causes it to melt or vaporise because there are now only comparatively weak intermolecular attractions.
- As the temperature increases a bit more, it increasingly breaks up into simple  $AlCl_3$  molecules.

**Silicon Tetrachloride,  $SiCl_4$** 

- Silicon tetrachloride is a simple covalent chloride. There isn't enough electronegativity difference between the silicon and the chlorine for the two to form ionic bonds.
- It fumes in moist air because it reacts with water in the air to produce hydrogen chloride. If we add water to silicon tetrachloride, there is a violent reaction to produce silicon dioxide and fumes of hydrogen chloride. In a large excess of water, the hydrogen chloride will, of course, dissolve to give a strongly acidic solution containing hydrochloric acid.

**Do You Know?**

Silicon tetrachloride is a colourless liquid at room temperature, which fumes in moist air. The only attractions between the molecules are van der Waals dispersion forces. It does not conduct electricity because of the lack of ions or mobile electrons.

**Phosphorus Chlorides**

There are two phosphorus chlorides which are as follow:

**(i) Phosphorus (III) Chloride (phosphorus Trichloride,  $PCl_3$ )**

This is simple covalent chloride and is a fuming liquid at room temperature. Phosphorus (III) chloride reacts violently with water. We get phosphorous acid,  $H_3PO_3$ , and fumes of hydrogen chloride (or a solution containing hydrochloric acid if lots of water is used).

**Do You Know?**

Phosphorus trichloride is a liquid because there are only van der Waals dispersion forces and dipole dipole attractions between the molecules. It does not conduct electricity because of the lack of ions or mobile electrons.

**(ii) Phosphorus (V) Chloride (Phosphorus pentachloride), ( $PCl_5$ )**

Unfortunately, phosphorus (V) chloride is structurally more complicated.

Phosphorus (V) chloride has a violent reaction with water producing fumes of hydrogen chloride. As with the other covalent chlorides, if there is enough water present, these will dissolve to give a solution containing hydrochloric acid. The reaction happens in two stages.

- In the first, with cold water, phosphorus oxychloride,  $POCl_3$ , is produced along with  $HCl$ .





- If the water is boiling, the phosphorus (V) chloride reacts further to give phosphoric (V) acid and more HCl. Phosphoric (V) acid is also known just as phosphoric acid or as orthophosphoric acid.

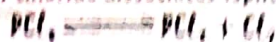


- The overall equation in boiling water is just a combination of these:



### Do You Know?

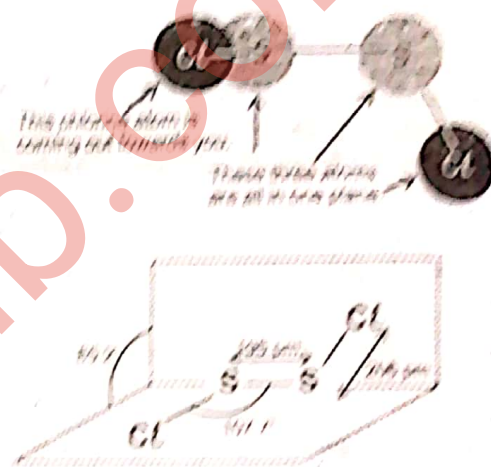
Phosphorus (V) chloride is a white solid which sublimes at 163°C. The higher the temperature goes above that, the more the phosphorus (V) chloride dissociates (falls up reversibly) to give phosphorus (III) chloride and chlorine:



Solid phosphorus (V) chloride contains ions - that is why it is a solid at room temperature. The formation of the ions involves two molecules of  $PCl_5$ .

### Disulphur dichloride, $S_2Cl_2$

- Disulphur dichloride is formed when chlorine reacts with hot sulphur.
- Disulphur dichloride is a simple covalent liquid (orange and smelly).
- The shape is difficult to draw convincingly. The atoms are all joined up in a line but twisted. The reason for drawing the shape is to give a hint about what sort of intermolecular attractions are possible. There is no plane of symmetry in the molecule and that means that it will have an overall permanent dipole.
- Disulphur dichloride reacts slowly with water to produce a complex mixture of things including hydrochloric acid, sulphur, hydrogen sulphide and various sulphur containing acids and anions (negative ions).



### Do You Know?

Disulphur dichloride ( $S_2Cl_2$ ) has van der Waals dispersion forces and dipole-dipole attractions. There are no ions in disulphur dichloride and no mobile electrons - so it never conducts electricity.

### Properties of the chlorides of elements in period 2

Formula of chloride	NaCl	MgCl <sub>2</sub>	Al <sub>2</sub> Cl <sub>6</sub>	SiCl <sub>4</sub>	PCl <sub>3</sub> (PCl <sub>5</sub> )	S <sub>2</sub> Cl <sub>2</sub>	Cl <sub>2</sub>
State of chloride (at 20°C)	s	s	s	l	l	l	g
b.pt. of chloride /°C	1465	1418	423	57	76	136	-35
Conduction of electricity by molten or liquid chloride	Good	Good	Very poor	Nil	Nil	Nil	Nil
Structure of chloride	Giant structures			Simple molecular structures			
Enthalpy change of formation of chloride at 298 K/ kJmol <sup>-1</sup>	-411	-642	-1498	-640	-320	-61	0

Enthalpy change of formation of chloride at 298 K per mole of Cl atoms / KJ	-411	-321	-235	-160	-107	-30	0
Effect of adding chloride to water	Solid dissolves readily		Chloride reacts with water, HCl fumes are produced				Some Cl <sub>2</sub> reacts with water
pH of aqueous solution of chloride	7	6.5	3	2	2	2	2



### QUICK QUIZ

1. How do the states of the chlorides at 20°C vary across the third period?

Ans. When we move across the period the states of chloride change from solid to liquid to gas

- Solid (NaCl, MgCl<sub>2</sub>, Al<sub>2</sub>Cl<sub>6</sub>)
- Liquid (SiCl<sub>4</sub>, PCl<sub>3</sub>, S<sub>2</sub>Cl<sub>2</sub>)
- Gas (Cl<sub>2</sub>)

2. How do the boiling points of the chlorides vary across the period?

Ans. Across the period 3 boiling point decreases from group I to IV then increases a little bit. But at the end Cl<sub>2</sub> has least boiling point in the period

3. How do the conductivities of the molten chlorides vary across the period?

Ans. The chlorides of IA and IIA group (NaCl, MgCl<sub>2</sub>) are good conductor in molten state. Al<sub>2</sub>Cl<sub>6</sub> is a very poor conductor. The remaining chlorides of period 3 are non-conductor.



### QUICK QUIZ

1. Which of the following give acidic solution with water: MgCl<sub>2</sub>, AlCl<sub>3</sub>, SiCl<sub>4</sub>, NaCl?

Ans. • Sodium chloride (NaCl) dissolves in water to give a neutral solution.

• Magnesium chloride (MgCl<sub>2</sub>) dissolves in water to give a faintly acidic solution.

• Aluminium chloride (AlCl<sub>3</sub>) reacts with water to produce clouds of steamy fumes of HCl gas.

• SiCl<sub>4</sub> reacts with water in air to produce hydrogen chloride gas which dissolves in large excess of water to give a strongly acidic solution containing hydrochloric acid.



2. Why NaCl has high melting and boiling point?

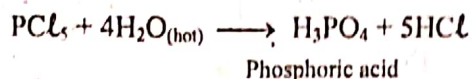
Ans. Sodium chloride is an ionic compound consisting of a giant array of sodium and chloride ions. The strong attractions between these ions need a lot of heat energy to break. Therefore NaCl has high melting and boiling points.

3. Write equations for reactions of PCl<sub>3</sub> with hot and cold water.

Ans. Reaction of PCl<sub>3</sub> with cold water



Phosphorous oxychloride

**Reaction of  $\text{PCl}_5$  with hot water****4. What products are obtained on reaction of disulphur dichloride with water?**

**Ans.** Disulphur dichloride reacts slowly with water to produce a complex mixture of things including hydrochloric acid, sulphur, hydrogen sulphide and various sulphur containing acids and anions (negative ions).

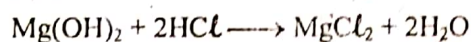
**5. Why  $\text{AlCl}_3$  is non-conductor in solid as well as in liquid state but  $\text{NaCl}$  and  $\text{MgCl}_2$  are conductor in liquid state and non-conductor in solid state?**

**Ans.**

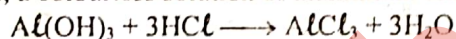
- Solid  $\text{AlCl}_3$  does not conduct electricity because the ions are not free to move. In molten state,  $\text{AlCl}_3$  has converted into covalent form and so do not conduct electricity due to unavailability of free electrons.
- Solid  $\text{MgCl}_2$  and  $\text{NaCl}$  are non-conductor of electricity because the ions are not free to move. However in molten state, their ions become free and are available to conduct electricity.

**Hydroxides of the Period 3 Elements**

- **Sodium and magnesium hydroxides** are ionic compounds and are simple basic hydroxides. Both react with acids to form salts. For example, with dilute hydrochloric acid, colourless solution of sodium chloride or magnesium chloride are formed.



- **Aluminium hydroxide**, like aluminium oxide, is amphoteric - it has both basic and acidic properties. With dilute hydrochloric acid, a colourless solution of aluminium chloride is formed.

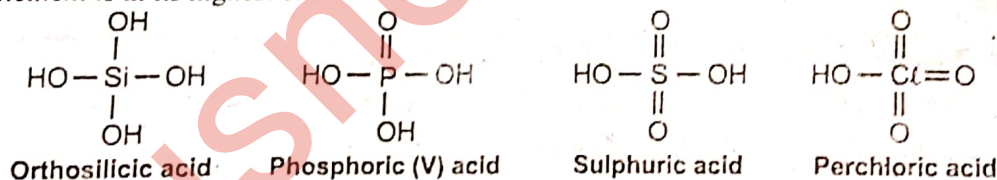


But aluminium hydroxide also has an acidic side to its nature. It will react with sodium hydroxide solution to give a colourless solution of sodium tetrahydroxoaluminate.



- **Silicon, phosphorus and sulphur hydroxides** have  $-\text{OH}$  (hydroxide) groups covalently bounded to the atoms. These compounds are all acidic-ranging from the very weakly acidic silicic acids to the very strong sulphuric or perchloric acids.

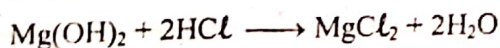
There are other acids (also containing  $-\text{OH}$  groups) formed by these elements, but these are the ones where the Period 3 element is in its highest oxidation state.

**Summary**

- Aluminium hydroxide is amphoteric. Like sodium or magnesium hydroxides, it will react with acids. This is showing the basic side of its nature.
- Orthosilicic acid is very weak.
- Phosphoric(V) acid is a weak acid - although somewhat stronger than simple organic acids like ethanoic acid.
- Sulphuric acid and perchloric (VII) acids ( $\text{HClO}_4$ ) are both very strong acids.

**1. Justify that  $\text{NaOH}$  and  $\text{Mg}(\text{OH})_2$  are basic in nature.**

**Ans.** Sodium and magnesium hydroxides react with acids to form salts. It shows their basic nature.



2. Justify that  $Al(OH)_3$  is an amphoteric compound.

Ans.  $Al(OH)_3$  is an amphoteric compound. It has both acidic and basic properties.

- As a base, it reacts with dilute  $HCl$  to form a colourless solution of  $AlCl_3$ .



- With sodium hydroxide it reacts as an acid to form sodium tetrahydroxoaluminate.



## GROUP 1 ELEMENTS

### Atomic and Physical Properties of the Group 1 Elements (Alkali Metals)

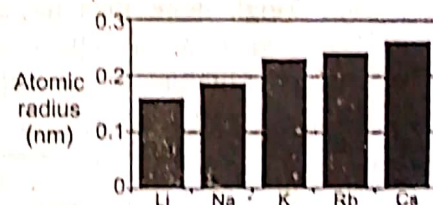
The elements of group 1 are called alkali metals. They include lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr).

#### Some Physical Properties of Alkali Metals

Property	Li	Na	K	Rb	Cs
Atomic weight	6.94	22.99	39.1	85.47	132.91
Atomic volume	12.97	23.63	45.36	55.8	69.95
Atomic (i.e. metallic radius for coordination number 12)	1.55	1.9	2.35	2.46	2.6
covalent radius	1.23	1.54	2.03	2.16	2.36
Ionic radius of $M^{+1}$ ion	0.6	0.95	1.33	1.48	1.69
Melting point ( $^{\circ}C$ )	180.5	97.8	63.7	38.9	28.7
Boiling point ( $^{\circ}C$ )	1330	892	760	688	670
1 <sup>st</sup> ionization energies(kJ/mol) ( $I_1$ )	520.3	495.8	418.9	403.0	375.7
2 <sup>nd</sup> ionization energies(kJ/mol) ( $I_2$ )	7298.1	4562.4	3051.4	2633.0	2230.0
Standard oxidation potential	3.04	2.71	2.99	2.99	2.99
Sublimation energy (eV/ion)	1.7472	1.2432	1.032	0.984	0.9024
Hydration energy (eV/ion)	5.904	3.792	3.6955	3.36	0.624
Electronegativity	1	0.9	0.8	0.8	0.7
Colour of the flame	Crimson red	Golden yellow	Violet	Violet	Violet
Heat of atomization at $25^{\circ}C$ (eV/atm)	1.7472	1.2432	1.032	0.984	0.9024
Ionic conduction of $M^{+1}$ ion	33.5	43.5	64.6	67.5	63

#### Trends in Atomic Radius

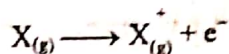
As we move from lithium to caesium, an extra shell of electrons is added to each element. The addition of an extra shell increases the atomic volume. We find therefore, that there is an increase of atomic and ionic radii (of  $M^{+1}$  ions) as we move from lithium to caesium.



Atomic Radii of the Group 1 Elements

#### Trends in First Ionization Energy

First ionization energy is the energy needed to remove the most loosely held electron from each of one mole of gaseous atoms to make one mole of singly charged gaseous ions - in other words, for 1 mole of this process:



- The first ionization energy decreases as we go down the group. We know that alkali metals have only one electron in their outermost shells ( $ns^1$  electron). This  $ns^1$  electron is so weakly held with the nucleus that it can be removed very easily. Alkali metals therefore have low ionization energies.
- As the distance of  $ns^1$  electron from the nucleus increases on moving from Li to Cs its removal becomes more and more easy. As a result, the I.E<sub>1</sub> of alkali metals go on decreasing from Li to Cs.
- The second ionization energies are fairly high, since the loss of the second electron from  $M^{+}$  cation (which has a noble gas configuration) is quite difficult.

### Electronegativity

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is given an electronegativity of 4.0 and least electronegativity is given to Cs (0.7).

### Trends in Electronegativity

When we move down the group, the electronegativity of alkali metals decreases.

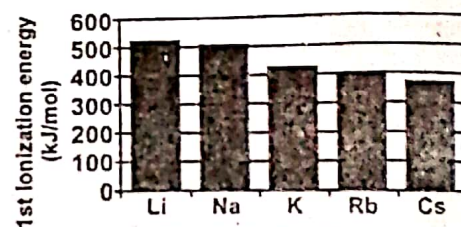
### Trends in Melting and Boiling Points

The melting points and boiling points of group-I fall as we go down the group. The melting and boiling points are very low because of the presence of weak inner atomic bonds in the solid state of the alkali metals. These bonds are due to their atomic radii and mainly due to their electronic configuration having single valence electrons as compared to large number of available vacant orbitals. As the size of the metal atoms increases, the repulsion of the non-bonding electrons also increases. This increase in the repulsion of nonbonding electron decreases the melting and boiling points of alkali metals when we move from Li to Cs.

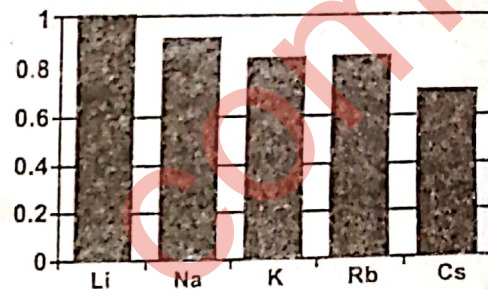
### Trends in Density

- The densities of the Group 1 elements increase down the group (except for a downward fluctuation at potassium).
- The metals in this series are relatively light—lithium, sodium, and potassium are less dense than water (less than  $1 \text{ g cm}^{-3}$ ).
- Atomic radius increases down a group, so the volume of the atoms also increases.
- Fewer sodium atoms than lithium atoms, therefore, can be packed into a given volume. However, as the atoms become larger, their masses increase. A given number of sodium atoms will weigh more than the same number of lithium atoms. Therefore,  $1 \text{ cm}^3$  of sodium contains fewer atoms than the same volume of lithium, but each atom weighs more.
- Mathematical calculations are required to determine the densities.

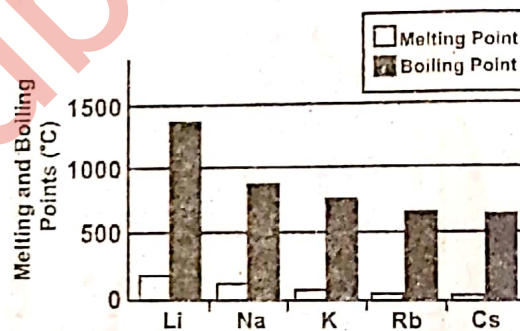
Elements	Li	Na	K	Rb	Cs
Densities at $0^{\circ}\text{C}$ (g/c.c)	0.534	0.972	0.859	1.525	1.903



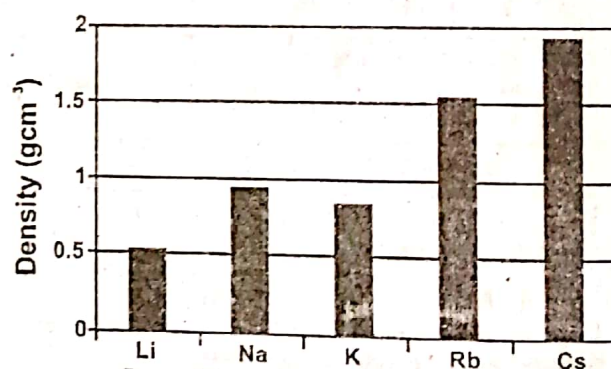
First Ionization Energy of the Group 1 elements



Electronegativities of the Group 1 elements



Melting and Boiling Points of the Group-1 Elements



Densities of the Group 1 elements



### 1. Different element imparts different colours in flame?

**Ans.** Flame test is given by elements in which valence electrons of atoms are loosely held with the nucleus. When heat energy is provided, the electrons absorb some energy and get excited. When these excited electrons come back to their original position, they give out absorbed energy in the form of light. Since the amount of energy absorbed during excitation process is different in different atoms, so different colours are imparted by the atoms to the flame.

### 2. Explain that 2<sup>nd</sup> ionization energy of alkali metals is greater than 1<sup>st</sup> ionization energy.

**Ans.** After the loss of one valence electron, the alkali metal atom becomes unipositive ( $M^+$ ) ion which

- (i) has complete octet.
- (ii) Small ionic radius than parent atom.
- (iii) imbalance proton to electron ratio.

Due to these reasons it becomes difficult to remove second electron from  $M^+$  ion. Therefore alkali metals have greater 2<sup>nd</sup> I.E than 1<sup>st</sup> I.E.

$$I.E_1 \text{ of Na} = 496 \text{ kJ mol}^{-1}$$

$$I.E_2 \text{ of Na} = 4562 \text{ kJ mol}^{-1}$$

### 3. Why melting points of alkali metals are low as compared to alkaline earth metals?

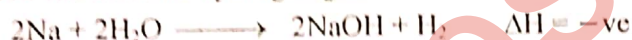
**Ans.** The melting and boiling points of alkaline earth metals are higher than alkali metals. The reason is that alkaline earth metals have 2 electrons in the outermost orbital. So the number of bonds which have been formed are greater. Therefore the melting points of alkali metals are low as compared to alkaline earth metals. e.g.

$$\text{Melting point of Na} = 98^\circ\text{C}$$

$$\text{Melting point of Mg} = 648^\circ\text{C}$$

## Reactivity with Water

The reaction of alkali metals with water is very fast. A small piece of Li, Na and K floats on water. They react vigorously and liberate hydrogen. They produce metal hydroxide. These reactions are highly exothermic. The energy which is produced can burn the hydrogen gas.



The reactivity of alkali metals with water becomes more and more vigorous as we move down the group. K, Rb and Cs are so reactive with water that they react with ice at  $-100^\circ\text{C}$ .

## Reactions with Oxygen

Alkali metals react with  $\text{O}_2$  or air rapidly and thus get tarnished due to the formation of their oxides on the surface of the metals. It is for this reason that alkali metals are stored in kerosene or paraffin oil.

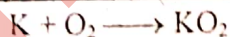
- **Lithium (Li)** when burnt in  $\text{O}_2$  gives mainly lithium monoxide, (normal oxide)  $\text{Li}_2\text{O}$ .



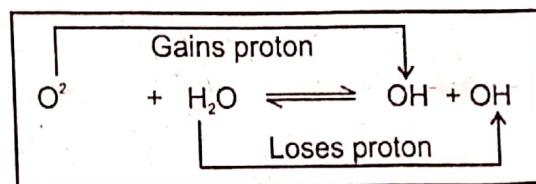
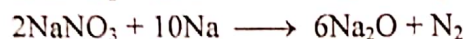
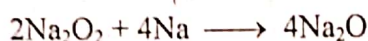
- **Sodium (Na)** when burnt in  $\text{O}_2$  forms sodium peroxide,  $\text{Na}_2\text{O}_2$



- **Potassium (K), Rubidium (Rb) & Caesium (Cs)** react with  $\text{O}_2$  to form super oxide of  $\text{MO}_2$  type.



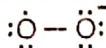
Since the normal oxides of alkali metals other than that of Li ( $\text{Li}_2\text{O}$ ) are not formed by the direct reaction between the metals and  $\text{O}_2$ , they are formed by indirect methods, e.g. by reducing peroxides, nitrite and nitrates with the metals itself.



**Properties:**

- Normal oxides ( $O^{2-}$ ) react with  $H_2O$  to form hydroxides by proton exchange.
- The peroxides ( $O_2^{2-}$ ) and super oxides ( $O_2^{-1}$ ) are strong oxidizing agents and react with  $H_2O$  to give  $H_2O_2$  and  $O_2$ .  

$$2O_2^{1-} + 2H_2O \longrightarrow 2H_2O_2 + O_2$$
- Normal oxides have anti-fluorite structure and are ionic in nature since they contain monoxide ion, ( $O^{2-}$ ).
- Peroxides contain peroxide ion,  $O_2^{2-}$  or  $[O - O]^{2-}$ .
- The superoxide ion has a three electron bond as shown below:



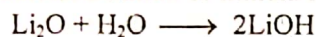
The presence of one unpaired electron in it makes this paramagnetic and coloured.

**Antifluorite Structure:**

$M_2X$ , including  $Li_2O$ ,  $Na_2O$  and  $K_2O$  simple the inverse of the fluorite structure with the X ions at the FCC positions and the M ions filling all of the tetrahedral positions.

**Reactions of the Oxides with Water and Dilute Acids****(i) The normal oxides,  $X_2O$** **Reaction with Water**

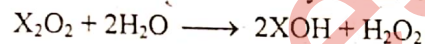
These are simple basic oxides, reacting with water to give the metal hydroxide. For example, lithium oxide reacts with water to give a colourless solution of lithium hydroxide.

**Reaction with dilute acids**

These simple oxides react with an acid to give a salt and water. For example, sodium oxide will react with dilute hydrochloric acid to give colourless sodium chloride solution and water.

**(ii) The peroxides,  $X_2O_2$** **Reaction with Water**

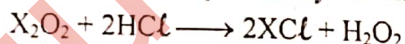
If the reaction is done in ice cold (and the temperature controlled so that it doesn't rise even though these reactions are strongly exothermic), a solution of the metal hydroxide and hydrogen peroxide is formed.



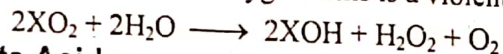
If the temperature increases (as it inevitably will unless the peroxide is added to water very slowly), the hydrogen peroxide produced decomposes into water and oxygen. The reaction can be very violent overall.

**Reaction with dilute Acids**

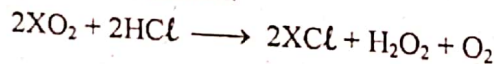
These reactions are even more exothermic than the ones with water. A solution containing a salt and hydrogen peroxide is formed. The hydrogen peroxide will decompose to give water and oxygen if the temperature rises again, it is almost impossible to avoid this. Another potentially violent reaction!

**(iii) The Superoxides,  $XO_2$** **Reaction with Water**

Superoxides react with water to form a solution of the metal hydroxide and hydrogen peroxide, but oxygen gas is given off as well. Once again, these are strongly exothermic reactions and the heat produced will inevitably decompose the hydrogen peroxide to water and more oxygen. This is a violent reaction.

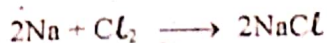
**Reaction with dilute Acids**

These reactions are even more exothermic than the ones with water. A solution containing a salt and hydrogen peroxide is formed together with oxygen gas. The hydrogen peroxide will decompose to give water and oxygen as temperature rises. This is a violent reaction.



### Reactions of the Elements with Chlorine

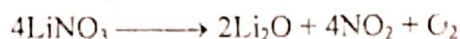
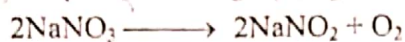
Alkali metals react with halogens (chlorine) to give halides (chlorides). Li and Na react slowly with chlorine at room temperature to give LiCl and NaCl. Molten Na burns with a brilliant yellow flame in the atmosphere of chlorine to form NaCl.



K, Rb and Cs react vigorously with all the halogens to form metal halides.

### Effect of heat on Nitrates, Carbonates and Hydrogen carbonates

- Group 1 compounds are more stable to heat than the corresponding compounds in Group 2.
- It is observed that the lithium compounds behave similarly to Group 2 compounds, but the rest of Group 1 are in some way different.
- The carbonates ( $\text{M}_2\text{CO}_3$ ) and bicarbonates ( $\text{MHCO}_3$ ) are highly stable to heat. With increase of electropositive character from Li to Cs, the stability of these salts increases.
- Their nitrates decompose on strong heating to the corresponding nitrite and  $\text{O}_2$ . (Exception is  $\text{LiNO}_3$ ).



### Explaining the trend in terms of the polarizing ability of the positive ion

When alkali metal cations approach near an anion, attracts the outer most electrons of the anion and repels the nucleus. Thus the distortion or polarization of the anion takes place. This distortion results in the sharing of electrons between two oppositely charged ions, i.e. the bond between the cation and anion becomes partly covalent in character. In general the smaller cations polarize the anions more effectively than bigger one. Therefore, the lithium salts are slightly covalent while other alkali metal salts are ionic.

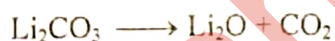


1. Why lithium salts are more covalent in nature while salts of other alkali metals are ionic.

Ans. Greater the charge density of a cation, greater will be its polarizing power and more covalent character it will induce. Among alkali metals,  $\text{Li}^+$  has greater polarizing power. Thus its salts are more covalent in nature, than other alkali metals.

2. Give trend of stability of carbonates of alkali and alkaline earth metals along group.

Ans. • All alkali metals carbonates are stable towards heat except  $\text{Li}_2\text{CO}_3$  which decomposes on heating.



- Alkaline earth metals decompose on heating and the ease of decomposition decreases down the group.

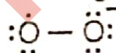


The ease of decomposition can be related to the size of the metal ion. The smaller the ion, the more is the lattice energy of the resulting oxide and hence higher the stability of the product.

3. Show bonding in superoxide ion.

Ans. Bonding in superoxide

The Lewis electron configuration of superoxide is:



and the bonding in super oxide ion is  $:\ddot{\text{O}} = \ddot{\text{O}}:$

4. Why alkali metals stores in kerosene / paraffin oil.

Ans. Due to low ionization energy alkali metals highly reactive. When exposed to air, they immediately form their respective oxides. Similarly with water, they form bases and hydrogen gas. Kerosene oil is a mixture of alkanes which are least reactive compounds. So, alkali metals in kerosene oil remain inert and kerosene oil can be a useful medium for their storage.



# FLAME TESTS

## Objective

- Flame tests are used to identify the presence of a relatively small number of metal ions in a compound. Not all metal ions give flame colours.
- For Group 1 compounds, flame tests are usually by far the easiest way of identifying which metal we have got.
- For other metals, there are usually other easy methods which are more reliable - but the flame test can give a useful hint as to where to look.

## Procedure

- Clean a platinum or nichrome (a nickel-chromium alloy) wire by dipping it into concentrated hydrochloric acid and then holding it in a hot Bunsen flame. Repeat this until the wire doesn't produce any colour in the flame.
- When the wire is clean, moisten it again with some of the acid and then dip it into a small amount of the solid we are testing so that some sticks to the wire.
- Place the wire back in the flame again. If the flame colour is weak, it is often worthwhile to dip the wire back in the acid again and put it back into the flame as if we were cleaning it.
- We often get a very short but intense flash of colour by doing that.

## Flame colour observation

Different flame colours shown by different elements are given below:

Elements	Flame colour	Elements	Flame colour
Li	red	Ca	orange-red
Na	golden yellow	Sr	Red
K	lilac (pink)	Ba	pale green
Rb	red (reddish-violet)	Cu	blue-green (often with white flashes)
Cs	Blue	Pb	greyish-white

## The Origin of Flame Colours

We have seen that the outer electron (i.e.  $ns^1$  electron) of atom of alkali metals is loosely held with the nucleus and hence it can be easily excited to the higher energy levels even by a small amount of heat energy (e.g. by heating the metals or their salts into Bunsen burner). During the excitation process the electron absorbs some energy and when this excited electron comes back to its original position, it gives out absorbed energy in the form of light in visible region of the electromagnetic spectrum and hence the colour is imparted by the atoms to the flame. Since the amount of energy absorbed during the excitation process is different in different atoms, different colours are imparted by the atoms to the flame. The property of alkali metals to give coloration in the Bunsen flame has been used to detect their presence in salts by a test known as flame test.

**Q. What do you do if you have a red flame colour for an unknown compound and do not know which of the various reds it is?**

**Ans.** Get samples of known lithium, strontium (etc) compounds and repeat the flame test, comparing the colours produced by one of the known compounds and the unknown compound side by side until you have a good match.



**1. Ion of which element among the alkali metals has the greatest polarizing power?**

**Ans.** Polarizing power  $\propto$  charge density =  $\frac{\text{charge}}{\text{size}}$

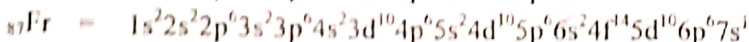
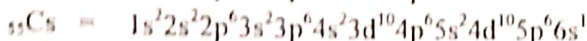
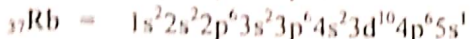
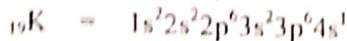
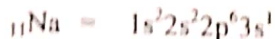
Since cationic radius of  $\text{Li}^{+1}$  is smaller, therefore it has greatest charged density among alkali metals hence it has greatest polarizing power.

2. Justify the placing of Li, Na, K, Rb, and Cs in the same group of the periodic table.

Ans. The classification of elements in a group is based on their valence shell electronic configuration. Since alkali metals have same valence shell electronic configuration i.e.,  $ns^1$ , so they are placed in same group 1 or IA.

3. Write the electronic configuration for alkali metal atoms. Explain the periodicity in ionization energy, electronegativity and atomic radii on passing from Li to Rb.

Ans. Electronic configuration of alkali metals (group 1).



- The ionization energy of alkali metals decreases down the group from Li to Rb. It is due to;
  - (i) Increase in atomic size due to successive addition of extra shells.
  - (ii) Increase in shielding effect.
- The electronegativity also decreases from top to bottom in alkali metals.
- As we move from lithium to Caesium, an extra shell of electrons is added to each element. Therefore there is an increase of atomic size from Li to Rb.

4. Explain the periodicity in ionization energy, electronegativity and atomic radii on passing from Li to Rb.

Ans. Down the group ionization energy and electronegativity decrease while, atomic radii increase.

5. Among alkali metals atoms which has the largest ionization potential?

Ans. Ionization energy decreases down the group in alkali metals due to increase in atomic radius and shielding effect. Thus Li has largest IE among alkali metals that is  $520.3 \text{ kJ mol}^{-1}$ .

6. Explain the following:

(a) Alkali metals show an oxidation state +1 only

Ans. Alkali metals have only one valence electron. On losing that electron, alkali metals achieve noble gas configuration and thus become stable. Therefore they show +1 oxidation state.

(b) Alkali metals are univalent.

Ans. An alkali metal can easily lose its valence electron to form the univalent cation. Hence it is univalent in nature.

(c) Alkali metals are good reducing agents.

Ans. Reducing property of an element depends upon the ionization energy value. Elements with low ionization energy value are good reducing agents. In periodic table alkali metals are the elements with lowest ionization energy. Therefore they are good reducing agents.

(d) Alkali metals have low melting points.

Ans. The melting points of alkali metals are very low because of the presence of weak inner atomic bonds in their solid state. These bonds are due to their atomic radii and mainly due to their electronic configuration having a single valence electrons as compared to large number of available vacant orbitals.

(e) Alkali metals give characteristic colour to the Bunsen flame.

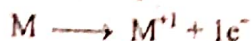
Ans. The valence electron ( $ns^1$ ) of alkali metals atom is loosely held with nucleus and hence it can be easily excited even by small amount of energy. During de excitation it gives out energy in the form of light in the visible region of electromagnetic spectrum. In this way different colours are imparted by atoms to the Bunsen flame.

(f) Na is stored under kerosene.

Ans. Sodium is an alkali metal. Due to low ionization energy it is highly reactive metal. When exposed to air, it immediately forms  $\text{Na}_2\text{O}_2$ . Similarly with water, it forms NaOH and hydrogen gas. Kerosene oil is a mixture of alkanes which are least reactive compounds. So, sodium in kerosene oil remains inert and kerosene oil can be a useful medium for its storage.

(g) Alkali metal form  $M^+$  cations instead of  $M^{2+}$  cations

Ans. Alkali metals have only one valence electron. On losing that electron,  $M^+$  cations are formed



Due to stability of this cation, 2<sup>nd</sup> I.E of alkali metals is very high. So formation of  $M^{2+}$  cations is ruled out.

(h) Alkali metals have low ionization potentials.

Ans. Alkali metals have only one electron in their outer most shell ( $ns^1$ ). This  $ns^1$  electron is so weakly held with the nucleus that it can be removed very easily. Therefore alkali metals have low ionization energies.

7. Hydroxides of 1<sup>st</sup> group are strong bases. Explain why?

Ans. The basic character of hydroxide depends upon:

(i) Polarity of M – OH bond.

(ii) Inter nuclear distance between oxygen of – OH.

Alkali metal cation ( $M^+$ ) has large size due to which it has greater polarity of M – OH bond and the Inter nuclear distance between oxygen of – OH. As a result there is greater ionization of MOH and hence alkali metal hydroxides are strong bases.

8. Explain the following:  $Li_2CO_3$ , is unstable while other alkali metals carbonates are relatively more stable.

Ans. The carbonates of alkali metals are all stable towards heat except  $Li_2CO_3$  which decomposes on heating to lithium oxide.



The decomposition is made easy because the electrostatic attraction in converting from carbonate to oxide is considerable.

In case of other alkali metals carbonates like  $K_2CO_3$  (pearl ash), due to large cation ( $K^+$ ), the gain in electrostatic attraction is relatively much less and the decomposition is difficult.

## GROUP 2 ELEMENTS

### Atomic and Physical Properties

The Group 2 consists of Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra)

Some physical properties of alkaline earth metals

Property	Be	Mg	Ca	Sr	Ba	Ra
Atomic weight	9.01	24.31	40.08	87.62	137.34	226
Abundance (% of earth's crust)	$6.4 \times 10.4$	2.0	3.45	0.915	0.040	$1.3 \times 10.10$
Density ( $g/cm^3$ )	1.84	1.74	1.55	2.54	3.75	6.00
Melting point ( $^{\circ}C$ )	1277	650	838	763	714	700
Boiling point ( $^{\circ}C$ )	2770	1107	1440	1380	1610	--
Atomic volume (c.c)	4.90	13.97	25.9	34.54	63.7	38.0
Atomic radius ( $\overset{\circ}{A}$ ) (i.e. metallic radius for coordination number 12)	1.12	1.60	1.97	2.15	2.22	--
Covalent radius ( $\overset{\circ}{A}$ )	0.90	1.36	1.74	1.91	1.98	--
Ionic radius ( $\overset{\circ}{A}$ ) (crystal radius of $M^{2+}$ ion for coordination number 12)	0.31	0.65	0.99	1.13	1.35	1.40
Ionization energies (kJ/mole) $I_1$	899.5	737.7	590.0	547.5	502.9	509.4
$I_2$	1757.1	1450.7	1145.4	1064.3	965.2	979.06
$I_1 + I_2$	2656.6	2188.4	1735.2	1613.8	1468.1	1488.46

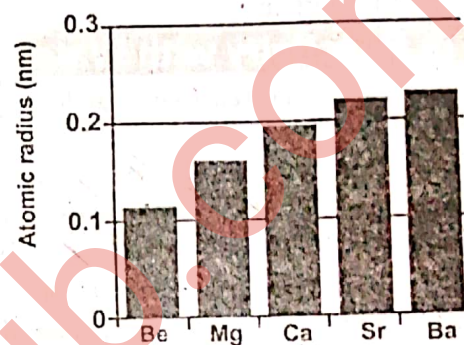
Oxidation state	+2	+2	+2	+2	+2	+2
Electronegativity	1.57	1.31	1.00	0.95	0.89	0.90
Flame colouration	None	None	Brick red	Crimson	Apple green	Red
Oxidation potentials (volts) for $M(s)$ $M(s) \longrightarrow M^{2+}_{(aq)} + 2e^{-}$	1.70 1.70	1.37	2.87	2.89 163.21	2.90 175.77	2.92 --
Heat of atomization (kJ/mole) at 25°C and 1atm pressure	327.26	146.89	181.21	164	180	--
Heat of hydration (kJ/mole)	2385.45	1925.1	1653.07	1458.67	1276.42	--
Ionic potential of $M^{2+}$ ion (i.e., charge/radius ratio)	6.66	3.08	2.12	1.82	1.55	1.33

### Trends in Atomic Radius

The atomic radii of group 2 elements increases down the Group. Notice that beryllium has a particularly small atomic radius compared with the rest of the group.

#### Reason:

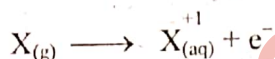
Because of the addition of an extra shell of electrons to each element from Be to Ra, the atomic volume increases from Be to Ra. With the increase of atomic volume, the atomic and ionic radii (of  $M^{2+}$  ions) also increase from Be to Ra. The atomic radii of these elements are however, smaller than those of alkali metals in the same period. This is due to the fact that the alkaline earth metals have higher nuclear charge which tends to draw the orbit electrons towards the nucleus. The smaller values of atomic radii result in that the alkaline earth metals are harder, have higher densities and higher melting points than alkali metals.



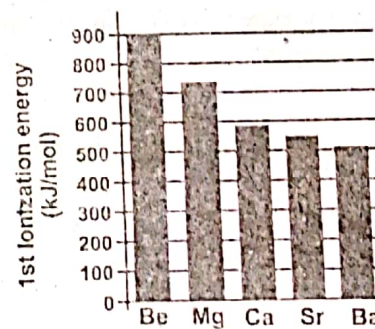
Atomic Radii of the Group 2 Elements

### Trends in First Ionization Energy

First ionization energy is the energy needed to remove the most loosely held electron from each of one mole of gaseous atoms to make one mole of singly charged gaseous ions. In other words, for 1 mole of this process:



Notice that first ionization energy falls as we go down the group.



First Ionization Energy of the Group 2 Elements

#### Reason:

The first and second ionization energies of these elements decrease with the increase of atomic radii from Be to Ba. However, the value for Ra is slightly higher than those of Ba.

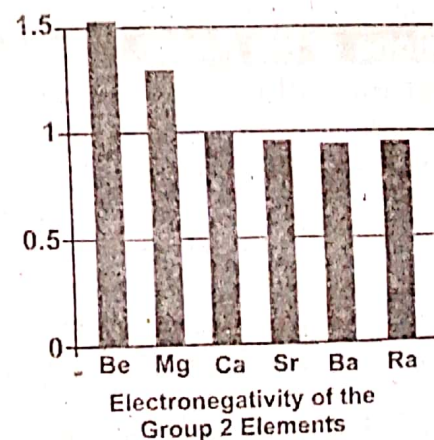
### Trend in Electronegativity

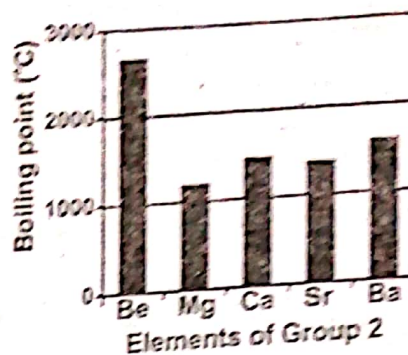
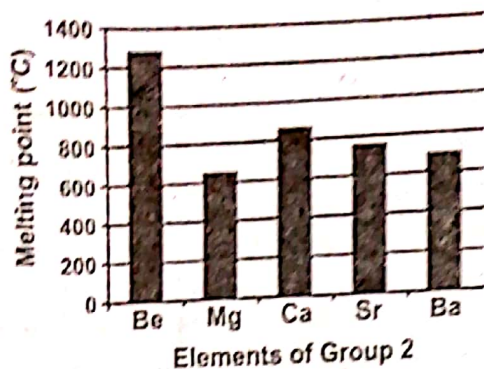
Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is given an electronegativity of 4.0.

Notice that electronegativity values fall as we go down the group.

### Trends in Melting Points and Boiling Points

The melting and boiling points of group 2 elements are higher than group 1 elements. The reason is that the group 2 elements have 2 electrons in the outermost orbital. So the number of bonds which have been formed are greater. Anyhow there is no regular trend is present which can be observed.





- It shows that (apart from where smooth trend is broken by magnesium) the melting point falls as we go down the Group.

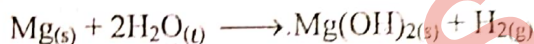
- It shows that there is no obvious pattern in boiling points. It would be quite wrong to suggest that there is any trend here whatsoever.

## Trends in Reactivity with Water

- Beryllium** has no reaction with water or steam even at red heat.
- Magnesium** burns in steam to produce white magnesium oxide and hydrogen gas.



Very clean magnesium ribbon has a very slight reaction with cold water. After several minutes, some bubbles of hydrogen form on its surface, and the coil of magnesium ribbon usually floats to the surface. However, the reaction soon stops because the magnesium hydroxide formed, is almost insoluble in water and forms a barrier on the magnesium preventing further reaction.



- Calcium, strontium and barium** react with cold water with increasing vigour to give the metal hydroxide and hydrogen. Strontium (Sr) and barium (Ba) have reactivities similar to lithium in Group 1 of the periodic table. Calcium, for example, reacts fairly vigorously with cold water in an exothermic reaction. Bubbles of hydrogen gas are given off, and a white precipitate (of calcium hydroxide) is formed, together with an alkaline solution. The equation for the reactions of any of these metals would be:



The hydroxides aren't very soluble, but they get more soluble as we go down the group. The calcium hydroxide  $\text{Ca}(\text{OH})_2$  formed mainly as a white precipitate (although some does dissolve). We get less precipitate as we go down the group because more of the hydroxide dissolves in the water.

## Summarising the trend down the Group

As the metal atoms get bigger, any bonding pair gets further and further away from the metal nucleus, and so is less strongly attracted towards it. In other words, as we go down the Group, the elements become less electronegative. As we go down the Group, the bonds formed between these elements and other things such as chlorine become more and more ionic. The bonding pair is increasingly attracted away from the Group 2 element towards the chlorine (or whatever).

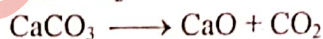
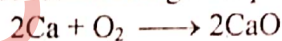
## Summary of the trend in reactivity

The Group 2 metals become more reactive towards water as you go down the Group.

## 1) Reactions of the Group 2 Elements with Air or Oxygen

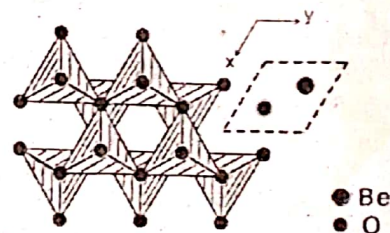
### a) Preparation of normal oxides:

The alkaline earth metals form the normal oxides of MO type which are obtained by heating the metal in  $\text{O}_2$  or by heating their carbonates at high temperature e.g.



### Properties:

- These oxides are extremely stable due to their high crystal lattice energies obtained by packing doubly charged ions ( $\text{M}^{2+}$ ) in a sodium chloride type of lattice.
- $\text{BeO}$  and  $\text{MgO}$  are quite insoluble in  $\text{H}_2\text{O}$  while  $\text{CaO}$ ,  $\text{SrO}$  and  $\text{BaO}$  react with  $\text{H}_2\text{O}$  to give soluble hydroxides,  $\text{M}(\text{OH})_2$  which are strong bases.
- $\text{BeO}$  is not at all basic in nature; in fact it is amphoteric since it reacts with acids to form salts and with alkalis to give beryllate. The oxides of other metals are

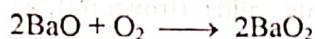


basic in character. Their basic character increases on moving down the group

- (iv) Due to small size of  $\text{Be}^{2+}$  ion,  $\text{BeO}$  is covalent while other oxides are ionic. Although  $\text{BeO}$  is covalent yet it has a higher melting point and is harder than the oxides of other metals as it is polymeric. Each  $\text{Be}$  atom is tetrahedrally coordinated by four oxygen atoms.
- (v) These oxides exist as white crystalline solids.

### (b) Preparation of peroxides:

The peroxides of heavier metals ( $\text{Ca}$ ,  $\text{Sr}$ ,  $\text{Ba}$  etc.) can be obtained on heating the normal oxides with  $\text{O}_2$  at high temperature.



#### Properties:

- The peroxides are white, ionic solids having peroxide anion,  $[\text{O} - \text{O}]^{2-}$ .
- They react with acids to produce  $\text{H}_2\text{O}_2$ .

### (2) Formation of nitrides on heating in air

All the elements of group 2 burn in nitrogen to form nitrides,  $\text{M}_3\text{N}_2$ , e.g.



These nitrides react with  $\text{H}_2\text{O}$  to liberate  $\text{NH}_3$  e.g.  $\text{Be}_3\text{N}_2$  is volatile while other nitrides are not so.

## Trends in Solubility of the Hydroxides, Sulphates and Carbonates

### (i) Solubility of the Hydroxides

Solubility of alkaline earth metals hydroxides increases down the group. This is a trend which holds for the whole group.

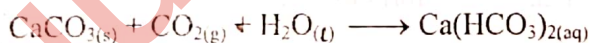
- Magnesium hydroxide**  $\text{Mg}(\text{OH})_2$  appears to be insoluble in water. However, if we shake it with water, filter it and test the pH of the solution, we find that it is slightly alkaline. This shows that there are more hydroxide ions in the solution than there were in the original water. Some magnesium hydroxide must have dissolved.
- Calcium hydroxide**  $\text{Ca}(\text{OH})_2$  solution is used as "lime water". 1 litre of pure water will dissolve about 1 gram of calcium hydroxide at room temperature.
- Barium hydroxide**  $\text{Ba}(\text{OH})_2$  is soluble enough to be able to produce a solution with a concentration of around  $0.1 \text{ mol dm}^{-3}$  at room temperature.

### (ii) Solubility of the Sulphates

The solubilities of sulphates of alkaline earth metals, gradually decrease down the group.  $\text{BeSO}_4$  and  $\text{MgSO}_4$  are fairly soluble in water.  $\text{CaSO}_4$  is slightly soluble and  $\text{SrSO}_4$  and  $\text{BaSO}_4$  are almost insoluble.

### (iii) Solubility of the Carbonates

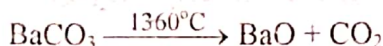
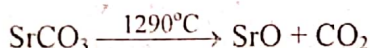
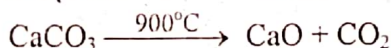
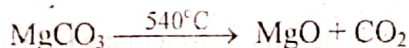
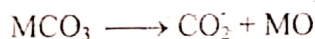
The carbonates tend to become less soluble as we go down the group. Carbonates are insoluble in water and therefore occur as solid rock minerals in nature. However they dissolve in  $\text{H}_2\text{O}$  containing  $\text{CO}_2$  due to the formation of bicarbonates.



## Trends in Thermal Stability of the Carbonates and Nitrates

### The effect of heat on the Group 2 Carbonates

All carbonates decompose on heating at appropriate temperature evolving  $\text{CO}_2$ .



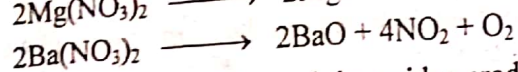
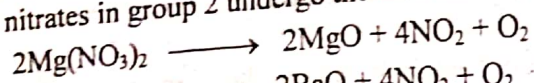
The stability of the carbonates of these metals increases on moving down the group.

**Reason:**

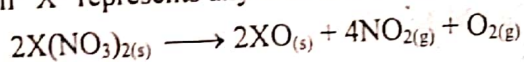
The ease of decomposition of the carbonates can be related to the size of metal ion. Smaller the positive ion, greater the lattice energy of resulting oxide. Hence higher the stability of the product and easier the decomposition of original carbonates.

**The effect of heat on the Group 2 Nitrates**

All the nitrates in group 2 undergo thermal decomposition to give the metal oxide, nitrogen dioxide and oxygen.



- The nitrates are white solids, and the oxides produced are also white solids. Brown nitrogen dioxide gas is given off together with oxygen.
- Magnesium and calcium nitrates normally have water of crystallization, and the solid may dissolve in its own water of crystallization to make a colourless solution before it starts to decompose.
- Again, if "X" represents any one of the elements:



- As we go down the group, the nitrates also have to be heated more strongly before they will decompose. The nitrates also become more stable to heat as we go down the group.

**Summary**

Both carbonates and nitrates become more thermally stable as you go down the Group. The ones lower down have to be heated more strongly than those at the top before they will decompose.

**Exercise: Q.3iv(b) How Beryllium differs from other members of its group?**

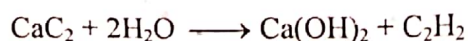
**Ans.** Beryllium, the first element of the group differs from rest of alkaline earth metals due to its small atomic size and comparatively high electronegativity. The main points of difference are:

1. **Hardness:** Beryllium is the hardest of all the elements of its group.
2. **Melting and Boiling Points:** The melting and boiling points of beryllium are the highest.
3. **Formation of Covalent Compounds:** Beryllium has a tendency to form covalent compounds. Thus when it reacts with other elements the electronegativity difference is not so large and the bond is therefore covalent.
4. **Reaction with Water:** Beryllium does not react with water even at high temperature. Other alkaline earth metals decompose water, liberating  $\text{H}_2$  gas.
 
$$\text{Mg} + \text{H}_2\text{O} \longrightarrow \text{MgO} + \text{H}_2$$
5. **Reaction with hydrogen:** Beryllium does not react with hydrogen directly to form its hydride. Its hydride however has been prepared indirectly. The rest of the alkaline earth metals combine with hydrogen to form hydrides. The hydrides of Be and Mg are covalent, whereas the hydrides of other metals are ionic.
6. **Reaction with alkalis:** Beryllium reacts with alkalis to form hydrogen.
 
$$\text{Be} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{BeO}_2 + \text{H}_2$$
 Other alkaline earth metals do not react with alkalis.
7. **Behaviour of oxides and hydroxides:** The oxides and hydroxides of beryllium are amphoteric, i.e. dissolve in both acids and alkalis to form salts.
 
$$\text{BeO} + \text{H}_2\text{SO}_4 \longrightarrow \text{BeSO}_4 + \text{H}_2\text{O}$$
8. **Behaviour of Carbides:** Beryllium carbide is decomposed by water to form methane ( $\text{CH}_4$ ).
 
$$\text{Be}_2\text{C} + 2\text{H}_2\text{O} \longrightarrow 2\text{BeO} + \text{CH}_4$$

$$\text{Be}_2\text{C} + 4\text{H}_2\text{O} \longrightarrow 2\text{Be}(\text{OH})_2 + \text{CH}_4$$

The carbide of other alkaline earth metals are decomposed by water to form acetylene ( $\text{C}_2\text{H}_2$ ).

**For example:**

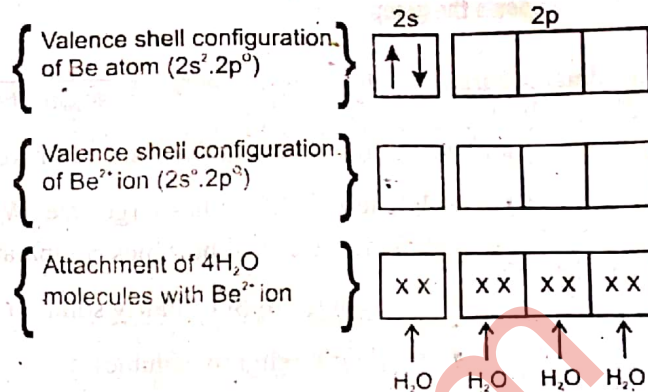


9. **Behaviour of Nitrides:**  $\text{Be}_3\text{N}_2$  is volatile while the nitrides of other alkaline earth metals are non-volatile.

10. **Number of Molecules of Water of Crystallization:**

The salts of  $\text{Be}^{2+}$  ion cannot have more than four molecules of water of crystallization while other alkaline earth metals have more than four molecules of water of crystallization. The reason is that in case of  $\text{Be}^{2+}$  ion there are only four orbitals, one 2s and three 2p. Orbital which can accept lone pairs of electrons denoted by O-atoms on each of the water molecules.

On the other hand, other alkaline earth metals like Mg can extend their coordination number to six by using one 3s, three 3p and two 3d orbitals belonging to their outermost shell.



11. **Formation of complex compounds:**  $\text{Be}^{2+}$  ion, on account of its small size, forms stable complex compounds like  $[\text{BeF}_3]^-$ ,  $[\text{BeF}]^{2-}$  while  $\text{M}^{2+}$  ions derived from other alkaline earth metals form very few complex compounds.



1. Among the alkaline earth metal atoms which has the highest ionization potential?

Ans. Ionization potential decreases from top to bottom in a group due to increase in atomic radius and shielding effect. Beryllium (Be) is the first member of alkaline earth metals so it has highest ionization potential.

2. Explain why Ca, Sr, Ba, and Ra are placed in one group of the periodic table?

Ans. The placement of elements in a group is based on their valence shell electronic configuration and similarities in properties. Since Ca, Sr, Ba and Ra have same valence shell electronic configuration i.e.  $ns^2$  and show similarity in chemical properties, so they are placed in same group which is Group 2 or IIA.

3. Explain the following

a. Alkaline earth metals form  $\text{M}^{2+}$  ions but no  $\text{M}^{+1}$  ions.

Ans. Alkaline earth metals have two electrons in their valence shell. On losing these electrons, they form  $\text{M}^{2+}$  ions

$$\text{M} \longrightarrow \text{M}^{2+} + 2e^-$$

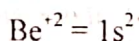
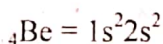
$\text{M}^{2+}$  ion has complete octet and is stable.

b. Although the value of 2<sup>nd</sup> ionization potential of alkaline earth metals is higher than that of 1<sup>st</sup> ionization potential yet these metals form  $\text{M}^{2+}$  ions instead of  $\text{M}^+$  ion.

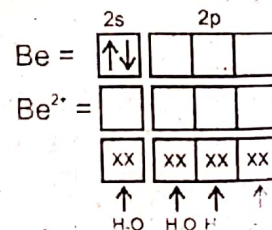
Ans. Alkaline earth metals have two electrons in their valence shell. By losing these electrons, they form  $\text{M}^{2+}$  ions which are highly stable due to complete octet. On the other hand,  $\text{M}^+$  ions of alkaline earth metals still have 1 valence electron and do not follow noble gas electronic configuration.

c. Beryllium salts have never more than four molecules of water of crystallization.

Ans. Beryllium atom has no vacant d-orbitals.



In  $\text{Be}^{2+}$ , there are only four empty orbitals which can accept lone pairs of electrons donated by O-atoms on each of the water molecule.





The solubility of the sulphates of alkaline earth metals decreases whereas the solubility of their hydroxides increases down the group.

Ans. Charge density  $\propto$  lattice energy  $\propto \frac{1}{\text{solubility}}$

Similarly if the cationic and anionic radii are comparable, the compound is almost insoluble.

(i) Sulphate ion ( $\text{SO}_4^{2-}$ ) has large size. When we move down the group from Be to Ba, the size of cation ( $\text{M}^{2+}$ ) increases and becomes comparable with  $\text{M}^{2+}$  ion, so solubility decreases.

- $\text{BeSO}_4, \text{MgSO}_4$  (Fairly soluble)
- $\text{CaSO}_4$  (slightly soluble)
- $\text{SrSO}_4, \text{BaSO}_4$  (almost insoluble)

(ii) Hydroxide ion ( $\text{OH}^-$ ) is small in size. When cationic radius of  $\text{II}_A$  metals increases, the lattice energy decreases while solubility increases.

- $\text{Be}(\text{OH})_2$  (Quite insoluble)
- $\text{Mg}(\text{OH})_2$  (Sparingly soluble)
- $\text{Ba}(\text{OH})_2$  (More soluble)

e. **The thermal stability of carbonates of alkaline earth metals increases in atomic numbers.**

Ans. An alkaline earth metal carbonate decomposes thermally because the electrostatic attraction in converting from carbonates to oxides is considerable. Smaller the size of metal cation, more is the lattice energy of the resulting oxide and hence higher the stability of product.

f. **Alkaline earth metals salts impart colour to the Bunsen flame.**

Ans. The alkaline earth metals have comparatively low ionization energy. During excitation, the valence electrons ( $ns^2$ ) absorb some energy and upon de-excitation, they give out absorbed energy in the form of light in the visible region of electromagnetic spectrum. In this way colour is imparted by atoms to the flame. Flame colour of Ca is orange red, Sr is red while for Ba, it is pale green.

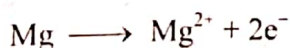
g.  **$\text{MgSO}_4$  is more soluble in water than  $\text{BaSO}_4$ .**

Ans. In a compound, when the size of cation and anion is comparable, the value of lattice energy is high and is almost insoluble.

- $\text{Mg}^{2+}$  is smaller in size than  $\text{SO}_4^{2-}$  while  $\text{Ba}^{2+}$  has almost the size of  $\text{SO}_4^{2-}$  ion. Thus lattice energy of  $\text{BaSO}_4$  is very high than  $\text{MgSO}_4$ , therefore  $\text{BaSO}_4$  is less soluble in water than  $\text{MgSO}_4$ .

h. **Alkaline earth metals form  $\text{M}^{2+}$  ions but not  $\text{M}^{3+}$  ions.**

Ans. When alkaline earth metals lose their valence electrons,  $\text{Mg}^{2+}$  ions are formed.



$\text{Mg}^{2+}$  has complete octet and is stable. For the formation of  $\text{Mg}^{3+}$  ion, we have to remove another electron from  $\text{Mg}^{2+}$ . A huge amount of energy ( $3^{\text{rd}}$  I.E) is required for this process and resulting  $\text{Mg}^{3+}$  is high unstable.

Properties		Alkaline Earth Metals	Alkali Metals
(i)	Electronic configuration	Two electron are present in the valence shell. The configuration is $ns^2$ .	One electron is present in the valence shell. The configuration is $ns^1$ .
(ii)	Valency	Bivalent.	Monovalent.
(iii)	Electropositive nature	Less electropositive	More electropositive
(iv)	Hydroxides	Weak basis, less soluble and decompose on heating	Strong basis, highly soluble and stable towards heat.
(v)	Bicarbonates	These are not known in free state. Exist only in solution.	These are not known in solid state.
(vi)	Carbonates	Insoluble in water. Decompose on heating.	Soluble in water. Do not decompose on heating ( $Li_2CO_3$ is an exception).
(vii)	Action of nitrogen	Directly combine with nitrogen and form nitrides.	Do not directly combine with nitrogen except Li.
(viii)	Action of carbon	Directly combine with carbon and form carbides.	Do not directly combine with carbon except Li.
(ix)	Nitrates	Decompose on heating evolving a mixture of $NO_2$ and oxygen.	Decompose on heating evolving only oxygen.
(x)	Solubility of salts	Sulphates, phosphates, fluorides, chromates, oxalates, etc., are insoluble in water.	Sulphates, phosphates, fluorides, chromates, oxalates, etc., are soluble in water.
(xi)	Physical properties	Are less reactive and comparatively harder metals. High melting points, Diamagnetic.	Soft, low melting points. Paramagnetic.
(xii)	Hydration of compounds	The compound are extensively hydrated. $MgCl_2 \cdot 6H_2O$ , $CaCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$ are hydrated chlorides.	The compound are less hydrated. $NaCl$ , $KCl$ and $RbCl$ form non-hydrated chlorides.
(xiii)	Reducing power	Weaker, as ionisation potential values are high and oxidation potential values are low.	Stronger, as ionisation potential values are low and oxidation potential values are high.

Explain the following:

a. The hydroxides of group IIA metals are weaker than those of group IA metals.

Ans. Basic character of hydroxides depends upon

- Size of cation
- Polarity of  $M-OH$  bond.

In case of alkali metal hydroxides, the size of cation is greater than alkaline earth metal cation. Moreover the polarity of  $M-OH$  bond is greater in alkali metal hydroxide. Therefore the alkali metal hydroxides have a more basic character than alkaline earth metal hydroxides.

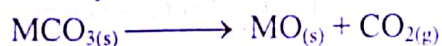
b. The carbonates of group IIA metals are less stable to heat than those of group IA metals.

Ans. • The carbonates of alkali metals are stable towards heat except  $Li_2CO_3$  which decomposes on heating to lithium oxide.



In case of large cation like  $K^+$  in  $K_2CO_3$  (pearl ash), the gain in electrostatic attraction is relatively much less and the decomposition is difficult.

- Alkaline earth metals decompose on heating and the ease of decomposition decreases down the group.



The ease of decomposition can be related to the size of the metal ion, the smaller the ion, the more is the lattice energy of the resulting oxide and hence higher the stability of the product.

c. KOH is stronger base than Ba(OH)<sub>2</sub>.

Ans. The basic character of hydroxide depends upon:

- Polarity of M – OH bond.
- Inter nuclear distance between oxygen of – OH.

The potassium cation (K<sup>+</sup>) has large size than barium cation (Ba<sup>2+</sup>). As a result there is greater polarity of K – OH bond and the Inter nuclear distance between oxygen of – OH. Therefore the ionization of KOH is more than Ba(OH)<sub>2</sub>. So KOH is stronger base than Ba(OH)<sub>2</sub>.

## GROUP 4 ELEMENTS

### Physical Properties of the Elements

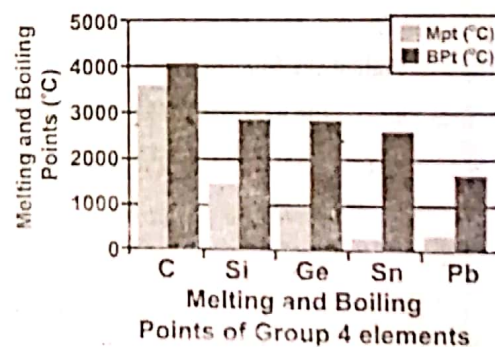
#### Electronic Configuration and Physical Properties of Group IVA Elements

Property	C	Si	Ge	Sn	Pb
Atomic Number	6	14	32	50	82
Electronic configuration	[He]2s <sup>2</sup> 2p <sup>2</sup>	[Ne]3s <sup>2</sup> 3p <sup>2</sup>	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>2</sup>	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup>	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>
Ionization energy (kJ/mol)	1086	736	760	707	715
Electron affinity (kJ/mol)	-122.5	-120	-116	-121	-101
Electronegativity	2.5	1.8	1.8	1.8	1.8
Atomic radius(pm)	77	117	122	140	154
Ionic radius of 2+ ion (pm)	60	71	73	93	121
Melting points (°C)	3570	1410	937	232	328
Boiling points (°C)	Sublimes	2355	2830	2270	1750
Density (g/cm <sup>3</sup> )	2.33	2.7	5.93	7.3	11.85

### Melting Points and Boiling Points

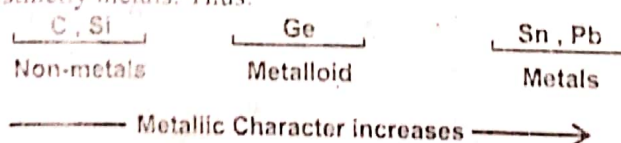
As we move down the group from C to Pb, the melting points as well as boiling points generally decrease, although the decrease is not in a regular order. This decrease in melting points as well as in boiling points indicates that inter-atomic forces also decrease in the same direction. The melting and boiling points of C and Si are notably high because of the tendencies of these elements to form giant molecules.

The low value for tin's melting point compared with lead is presumably due to forming a distorted 12-co-ordinated structure rather than a pure one. The tin values in the chart refer to metallic white tin.



### The Trend from Non-Metal to Metal in the Group 4 Elements

The change from non-metallic character with the increase in atomic number is the best illustrated by the elements of this group. The first two elements i.e. C and Si are distinctly non-metals, although electrical properties of Si are like those of a semi-metal (i.e. a metalloid); the third element i.e. Ge is partly a metal and partly a non-metal, while the last two elements i.e., Sn and Pb are distinctly metals. Thus:

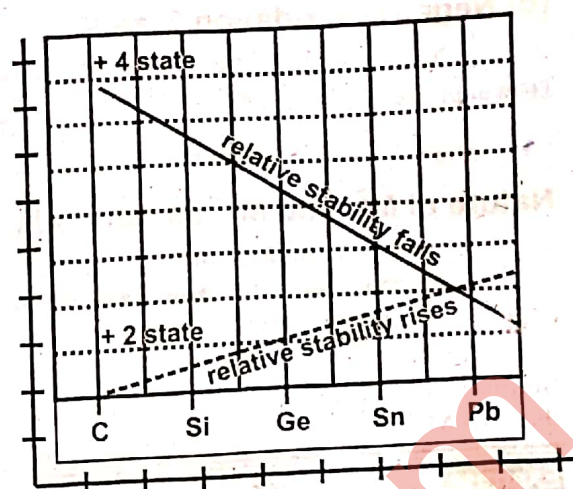


The change from non-metallic to metallic character with the increase in atomic number is due to the reduction in effective nuclear charge and increase in the number of available orbitals with the increase in the size of the atoms.

### Oxidation State

The most striking feature of the elements of group IVA is the existence of two oxidation states +2 and +4. The existence of compounds in which the elements show different oxidation numbers is typical of the p-block elements. It is interesting to consider the relative stabilities of the +2 and +4 oxidation states for the different elements. In carbon and silicon compounds the +4 state is very stable relative to +2. The +2 state is rare and easily oxidized to +4.

The steady increase in the stability of the lower oxidation state relative to the higher oxidation state on moving down the group from carbon to lead can easily be understood from figure.



Relative stabilities of the +4 and +2 oxidation state for the elements in group IVA

### Possible Oxidation State

#### (a) Inert pair effect and positive oxidation states:

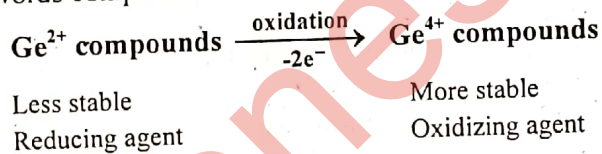
- **Carbon and silicon** show +4 oxidation states.

- **Ge, Sn and Pb** show +2 and +4 oxidation states which can be explained as follows:

- (1) When only two  $np^2$  electrons from the  $ns^2 np^2$  configuration are lost, we get the elements in +2 oxidation states. In this case  $ns^2$  electrons are inert and hence are not lost in the formation of  $M^{2+}$  cations. This pair of  $ns^2$  electrons is called inert pair of electrons. Since in the group the stability of +2 oxidation state also increases from  $Ge^{2+}$  to  $Pb^{2+}$  i.e.  $Ge^{2+} < Sn^{2+} < Pb^{2+}$ .
- (2) When all the four  $ns^2 p^2$  electrons are lost, we get the elements in +4 oxidation state, i.e.  $M^{4+}$  cations are formed. On descending the group stability of +4 oxidation state decreases i.e. the stability of  $M^{4+}$  cations decreases from  $Ge^{4+}$  to  $Pb^{4+}$  i.e.  $Ge^{4+} > Sn^{4+} > Pb^{4+}$ .

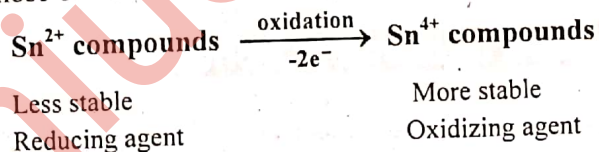
#### (i) For Ge

Compounds of  $Ge^{2+}$  are less stable than those of  $Ge^{4+}$  and hence the compounds of  $Ge^{2+}$  are readily oxidized into those of  $Ge^{4+}$ . In other words compounds of  $Ge^{2+}$  act as strong reducing agents while those of  $Ge^{4+}$  act as oxidizing agents.



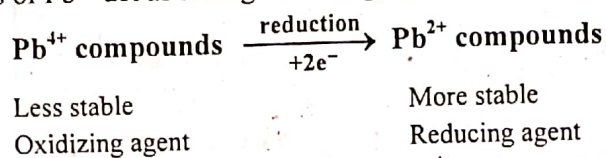
#### (ii) For Sn

The compounds of  $Sn^{2+}$  are less stable than those of  $Sn^{4+}$ . In other words, compounds of  $Sn^{2+}$  act as strong reducing agents while those of  $Sn^{4+}$  act as oxidizing agents.



#### (iii) For Pb

When we compare the stability of the compounds of  $Pb^{2+}$  and  $Pb^{4+}$  ions, we find that  $Pb^{2+}$  compounds are more stable than those of  $Pb^{4+}$  ( $PbCl_4$ ) and hence the compounds of  $Pb^{4+}$  are readily changed (reduced) into those of  $Pb^{2+}$ . In other words compounds of  $Pb^{4+}$  act as strong oxidizing agents while those of  $Pb^{2+}$  act as reducing agents.



Thus when we compare the stability of  $M^{2+}$  and  $M^{4+}$  cations of Ge, Sn and Pb, we find that their stability is in the order  $Ge^{2+} < Ge^{4+}$ ,  $Sn^{2+} < Sn^{4+}$ ,  $Pb^{2+} > Pb^{4+}$ .

## (b) Negative Oxidation States:

Since the electronegativities of these elements are low, they do not have much tendency to form the negative ions. However, carbon forms  $C^{4-}$  and  $C_2^{2-}$  ions in certain compounds, e.g.  $Be_4^{2+} C_2^{4-}$  or  $Be_2C$  ( $Be^{2+}$  and  $C^{4-}$  ions),  $Al_4^{3+} C_3^{4-}$  ( $Al^{3+}$  and  $C^{4-}$  ions),  $Na^+ CH_3^{-1}$  ( $Na^+$ ,  $C^{-4}$  and  $H^+$  ions),  $Na_2^{2+} C_2^{2-}$  ( $Na^+$  and  $C_2^{2-}$  ions),  $Ca^{2+} C_2^{2-}$  ( $Ca^{2+}$  and  $C_2^{2-}$  ions).

## Nature of $M^{2+}$ and $M^{4+}$ compounds:

The nature of the compounds of  $M^{2+}$  and  $M^{4+}$  cations can be predicted by Fajan's rule which states that:

**"The smaller the cation, the greater is the amount of covalent character in its compounds"**

Since  $Sn^{4+}$  ion is smaller than  $Sn^{2+}$ , the compounds of  $Sn^{4+}$  are covalent in nature while those of  $Sn^{2+}$  are ionic. Similarly  $Pb^{4+}$  compounds are covalent and those of  $Pb^{2+}$  are ionic. In general the compounds of  $M^{4+}$  are covalent and those of  $M^{2+}$ . As we move down the group, the tendency of given cations to form ionic compounds increases.

**Exercise: Q.3(viii) Discuss the inert pair effect in the:**

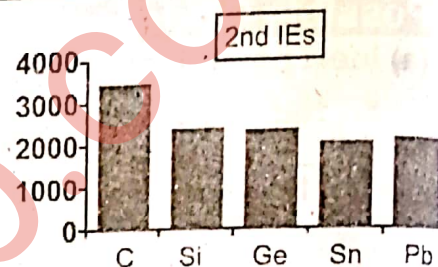
(i) formation of ionic bonds (ii) formation of covalent bonds

## The inert pair effect in the formation of ionic bonds

If the elements in Group 4 form  $2+$  ions, they will lose the p electrons, leaving the  $s^2$  electron pair unused. For example, to form a lead (II) ion, lead will lose the two 6p electrons, but the 6s electrons will be left unchanged - an "inert pair".

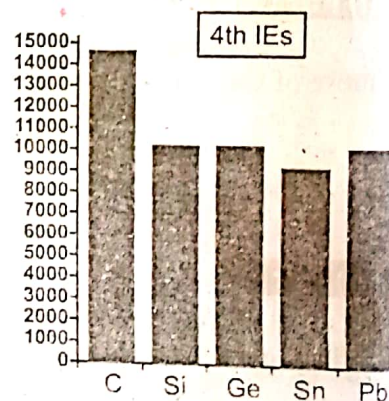
We would normally expect ionization energies to fall as we go down a Group as the electrons get further from the nucleus. That doesn't quite happen in Group 4.

- This first chart shows how the total ionization energy needed to form the  $2+$  ions varies as we go down the Group. Notice the slight increase between tin and lead. This means that it is slightly more difficult to remove the p electrons from lead than from tin.
- However, if we look at the pattern for the loss of all four electrons, the discrepancy between tin and lead is much more marked. The relatively large increase between tin and lead must be because the  $6s^2$  pair is significantly more difficult to remove in lead than the corresponding  $5s^2$  pair in tin.



**Reason:** The reasons for all this lie in the Theory of Relativity. With the heavier elements like lead, there is what is known as a relativistic contraction of the orbitals, which tends to draw the electrons closer to the nucleus than we would expect. Because they are closer to the nucleus, they are more difficult to remove. Heavier the element, greater is the effect.

This affects 's' electrons much more than p electrons. In the case of lead, the relativistic contraction makes it energetically more difficult to remove the 6s electrons than we might expect. The energy releasing terms when ions are formed (like lattice enthalpy or hydration enthalpy) obviously are not enough to compensate for this extra energy. That means that it doesn't make energetic sense for lead to form  $4+$  ions.

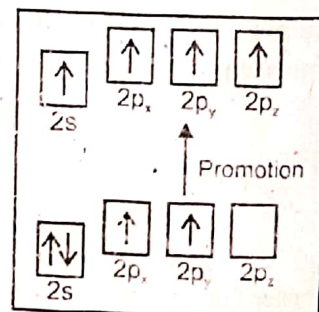
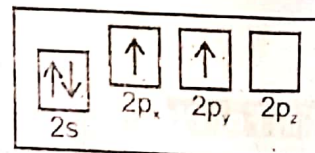


## The inert pair effect in the formation of covalent bonds

### Tetravalency of Carbon

We need to think about why carbon normally forms four covalent bonds rather than two?

- Using the electrons-in-boxes notation, the outer electronic structure of carbon looks like this:
- There are only two unpaired electrons. Before carbon forms bonds, though, it normally promotes one of the s electrons to the empty p orbital.
- That leaves 4 unpaired electrons which (after hybridization) can go on to form 4 covalent bonds.
- It is worth supplying the energy to promote the s electron, because the carbon can then form twice as many covalent bonds. Each covalent bond that forms releases energy, and this is more than enough to supply the energy needed for the promotion.



## Inert pair effect in Lead (Pb)

- One possible explanation for the reluctance of lead to do the same thing lies in falling bond energies as we go down the Group. Bond energies tend to fall as atoms get bigger and the bonding pair is further from the two nuclei and better screened from them.
- For example, the energy released when two extra Pb - X bonds (where X is H or Cl or whatever) are formed may no longer be enough to compensate for the extra energy needed to promote a 6s electron into the empty 6p orbital.
- This would be made worse, of course, if the energy gap between the 6s and 6p orbitals was increased by the relativistic contraction of the 6s orbital.

## The Chlorides of Carbon, Silicon and Lead

The chlorides of carbon, silicon and lead all have the formula  $XCl_4$  like  $CCl_4$ ,  $SiCl_4$  &  $PbCl_4$ .

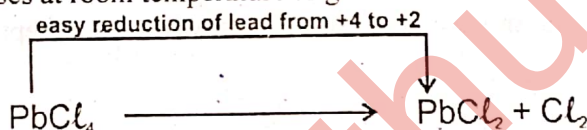
- They are all simple covalent molecules with a typical tetrahedral shape.
- All of them are liquids at room temperature. (Although at room temperature, lead (IV) chloride will tend to decompose to give lead (II) chloride and chlorine gas)

## Stability

- At the top of Group 4, the most stable oxidation state shown by the elements is +4. This is the oxidation state shown by carbon and silicon in  $CCl_4$  and  $SiCl_4$ . These therefore have no tendency to split up to give dichlorides.
- However, the relative stability of the +4 oxidation state falls as we go down the Group, and the +2 oxidation state becomes the most stable by the time we get to lead.
- Lead (IV) chloride decomposes at room temperature to give the more stable lead (II) chloride and chlorine gas.

## Lead (II) Chloride, $PbCl_2$

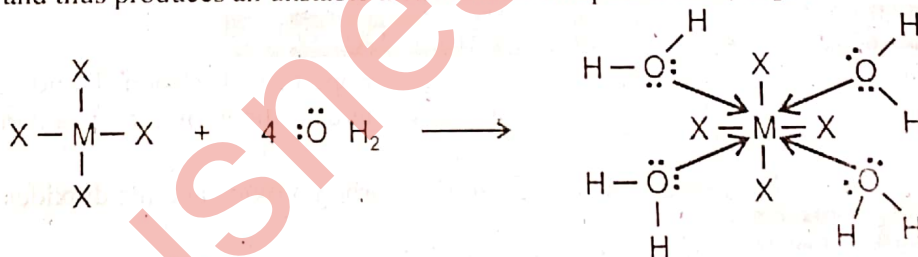
- Lead (II) chloride is a white solid, melting at  $501^\circ C$ .
- It is very slightly soluble in cold water, but more soluble in hot water.
- Lead (II) chloride is mainly ionic in character.



## Reaction with Water (hydrolysis)

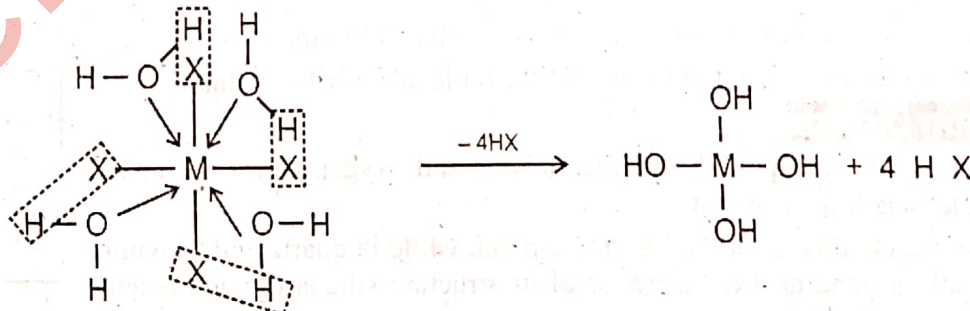
Actually the hydrolysis of tetra halides takes place through the following two steps:

**1<sup>st</sup> step:** In this step, oxygen atom of  $H_2O$  which acts as a donor attacks the central atoms of the halide to form a coordinate bond with it and thus produces an unstable intermediate compound  $MX_4 \cdot 4H_2O$ .

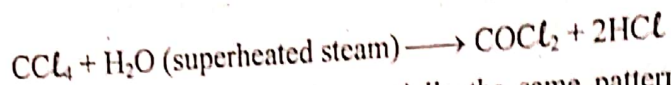


Unstable intermediate compound ( $MX_4 \cdot 4H_2O$ )

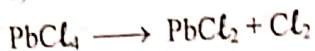
**2<sup>nd</sup> step:** In this step four  $HX$  molecules are eliminated from this unstable intermediate compound and hydroxide of the central element is formed. Thus X atoms of  $MX_4$  molecule are replaced by  $OH^-$  ions.



- The ease with which the tetrahalides are hydrolyzed by  $H_2O$  decreases from Si to Sn as the metallic character of the central atom increases in this order. Thus  $GeX_4$  and  $SnX_4$  tetrahalides are less readily hydrolyzed than  $SiX_4$  tetrahalides.
- It may be mentioned here that empty orbitals are always available with any atom and they can be utilized if sufficient energy is provided for the reaction to occur, e.g.,  $CCl_4$  undergoes hydrolysis when superheated steam is used.



- Hydrolysis of tetrahalides of Pb follows essentially the same pattern but due to the instability of tetravalent compounds of Pb, some decomposition of  $PbCl_4$  to  $PbCl_2$  also takes place.

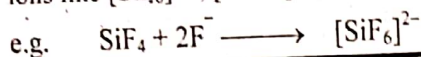


$PbCl_4$  is hydrolysed by  $H_2O$  as follows:



### Reaction with halide ion:

- Excepting the tetrahalides of C, those of Si, Ge, Sn and Pb react with halide ions and form the hexahalo complex ions like  $[SiF_6]^{2-}$ ,  $[GeX_6]^{2-}$ .



### Q. Why the tetrahalides of C are not hydrolyzed while those of Si, Ge and Sn get readily hydrolyzed.

- Ans. • C atom being a member of 2<sup>nd</sup> period of the periodic table, has no d-orbitals in its valence shell and hence is unable to accommodate the lone pair donated by the donor oxygen atom of  $H_2O$  molecule to form an unstable intermediate compounds. Thus the tetrahalides of carbon are not hydrolyzed.
- On the other hand Si, Ge and Sn have vacant d-orbitals which can accept the lone pair and thus these tetrahalides get readily hydrolyzed.

### Oxides

The elements of group IVA form three types of oxides i.e., Monoxides (MO type oxides); Dioxides ( $MO_2$  type); other oxides like  $C_3O_2$ ,  $Pb_3O_4$ ,  $Pb_2O_3$  etc. But we will discuss only the structural differences between carbon dioxide and silicon dioxide and the trends in acid-base behaviour of the oxides as we go down Group 4.

### Oxides of Group 4 elements

#### The structures of carbon dioxide and silicon dioxide

There is an enormous difference between the physical properties of carbon dioxide and silicon dioxide (also known as silicon (IV) oxide or silica). Carbon dioxide is a gas whereas silicon dioxide is a hard high-melting solid. The other dioxides in Group 4 are also solids.

This obviously reflects a difference in structure between carbon dioxide and the dioxides of the rest of the Group.

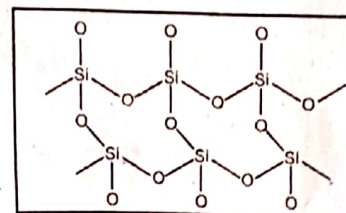
#### Structure of Carbon Dioxide

- It is a triatomic molecule.
- It has two double bonds between carbon and oxygen atoms.
- Carbon is  $sp$ -hybridized and oxygen is  $sp^2$  - hybridized.
- The molecule of  $CO_2$  is linear and net dipole moment is zero.
- The solid  $CO_2$  has a face - centered cubic structure.
- The bond lengths between carbon and oxygen have values 115 pm.
- All three atoms have completed their octet. So the molecule of  $CO_2$  is stable.

#### Structure of Silicon Dioxide

It is a macromolecular compound, in which silicon and oxygen atoms are linked together covalently in tetrahedral basic unit.

In cristobalite, these units are joined as in diamond, while in quartz and tridymite they are arranged spirally around an axis. Because of its structure silicon dioxide is non-volatile and hard unlike carbon dioxide.



Silicon dioxide

**Similarities between CO<sub>2</sub> and SiO<sub>2</sub>**

- (i) 4 valence electrons.
- (ii) 4 covalent bonds formation.

**Dissimilarities between CO<sub>2</sub> and SiO<sub>2</sub>**

- (i) Silicon atoms are much larger in size than carbon atoms and thus tend to be surrounded by more oxygen atoms.
- (ii) Silicon form only single bond with oxygen atoms while carbon forms double bonds.
- (iii) Carbon forms a linear molecule of CO<sub>2</sub> with two oxygen atoms while silicon atom is bound to four oxygen atoms in a tetrahedral structure which results in the formation of silicon dioxide crystal. The simplest formula for silica is SiO<sub>2</sub>. However the whole crystal of silicon can be considered as one molecule.

**Exercise: Q.3(ix) Discuss in detail acid-base trend in group 4 oxides.**

**The Acid-Base behaviour of the Group 4 oxides**

The oxides of the elements at the top of group 4 are acidic, but acidity of the oxides falls as we go down the group. Towards the bottom of the group, the oxides become more basic - although without ever losing their acidic character completely. The trend is therefore from acidic oxides at the top of the group towards amphoteric ones at the bottom.

**Carbon Monoxide (CO)**

- The electronic structure of carbon monoxide can be represented as:  $\begin{array}{c} \times \\ \times \end{array} \text{C} \begin{array}{c} \times \\ \times \end{array} \text{:O:}$
- It is usually written as:  $\times \text{C} \equiv \text{O:}$
- Carbon monoxide is usually treated as if it was a neutral oxide, but in fact it is very, very slightly acidic. It doesn't react with water but it will react with hot concentrated sodium hydroxide solution to give a solution of sodium methanoate.



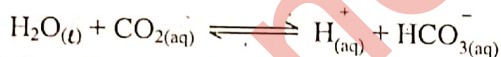
The fact that the carbon monoxide reacts with the basic hydroxide ion shows that it must be acidic.

**CO<sub>2</sub> & SiO<sub>2</sub>**

These are both weakly acidic.

**With Water**

- Carbon dioxide does react with water to a slight extent to produce hydrogen ions (strictly, hydroxonium ions) and hydrogen carbonate ions. Overall reaction is:

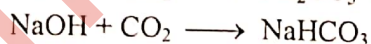


The solution of carbon dioxide in water is sometimes known as carbonic acid, but in fact only about 0.1% of the carbon dioxide has actually reacted. The position of equilibrium is well to the left-hand side.

- Silicon dioxide doesn't react with water because of the difficulty of breaking up the giant covalent structure.

**With Bases**

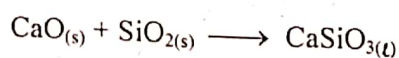
- Carbon dioxide reacts with sodium hydroxide solution in the cold to give either sodium carbonate or sodium hydrogen carbonate solution - depending on the reacting proportions.



- Silicon dioxide also reacts with sodium hydroxide solution, but only if it is hot and concentrated. Sodium silicate solution is formed.



- Similarly in the blast furnace during extraction of iron, calcium oxide (from the limestone which is one of the raw materials) reacts with silicon dioxide to produce a liquid slag, calcium silicate. This is also an example of the acidic silicon dioxide reacting with a base.





## Germanium, Tin and Lead Oxides

### The Monoxides

All of these oxides are amphoteric (they show both basic and acidic properties).

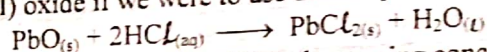
#### The Basic Nature of the Oxides

These oxides all react with acids to form salts. For example, they all react with concentrated hydrochloric acid. This can be summarized as:



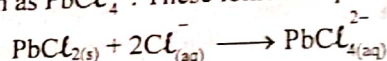
Where X can be Ge and Sn, but unfortunately needs modifying a bit for lead.

- Lead (II) chloride is fairly insoluble in water and, instead of getting a solution, it would form an insoluble layer over the lead (II) oxide if we were to use dilute hydrochloric acid - stopping the reaction from going on.



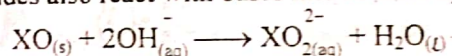
However, in this example we are talking about using concentrated hydrochloric acid.

- The large excess of chloride ions in the concentrated acid react with the lead (II) chloride to produce soluble complexes such as  $PbCl_4^{2-}$ . These ionic complexes are soluble in water and so the problem disappears.



#### The Acidic Nature of the Oxides

All of these oxides also react with bases like sodium hydroxide solution.



Lead (II) oxide, for example, would react to give plumbate (II) ions ( $PbO_2^{2-}$ ).

### The Dioxides

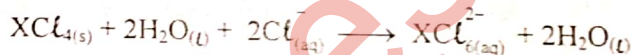
These dioxides are again amphoteric - showing both basic and acidic properties.

#### The Basic Nature of the Dioxides

The dioxides react with concentrated hydrochloric acid first to give compounds of the type  $XCl_4$ :



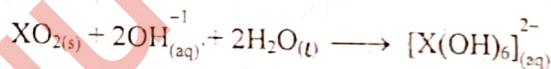
These will react with excess chloride ions in the hydrochloric acid to give complexes such as  $XCl_6^{2-}$ .



- In case of lead (IV) oxide, the reaction has to be done with ice-cold hydrochloric acid.
- If the reaction is done any warmer, the lead (IV) chloride decomposes to give lead (II) chloride and chlorine gas. This is an effect of the preferred oxidation state of lead being +2 rather than +4.

#### The Acidic Nature of the Dioxides

The dioxides will react with hot concentrated sodium hydroxide solution to give soluble complexes of the form  $[X(OH)_6]^{2-}$ .



Some sources suggest that the lead (IV) oxide needs molten sodium hydroxide. In that case, the equation is different.



1. Why tin melting point is low as compared to lead?

Ans. The low melting point of tin (232°C) compared with lead (328°C) is presumably due to tin forming a distorted 12-co-ordinated structure rather than a pure one.

2. Give trend of conductivity in 4th group element.

Ans. There is a clear trend from the typically non-metallic conductivity behaviour of carbon as diamond, and the

typically metallic behaviour of white tin and lead. Unlike diamond (which doesn't conduct electricity), silicon, germanium and grey tin are semiconductors. White tin and lead are normal metallic conductors of electricity.

3. Which of the following metals are semiconductors Pb, C, Si, Ge?

Ans. Silicon (Si) and Germanium (Ge) are semiconductors. Lead (Pb) is normal metallic conductors while carbon as diamond is non-conductor of electricity.

4. Arrange following cations in increasing order of their stability.  $\text{Sn}^{4+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Pb}^{2+}$

Ans.  $\text{Ge}^{4+} > \text{Sn}^{4+} > \text{Sn}^{2+} < \text{Pb}^{2+}$

## GROUP 7-ELEMENTS (HALOGENS)

### Atomic and Physical Properties

The Electronic Configurations and the Important Physical Properties of the Halogens

Properties	Fluorine	Chlorine	Bromine	Iodine
Atomic number	9	17	35	53
Electronic configuration	$[\text{He}]2s^2 2p^5$	$[\text{Ne}]3s^2 3p^5$	$[\text{Ar}]3d^{10}, 4s^2, 4p^5$	$[\text{Kr}]4d^{10}, 5s^2, 5p^5$
Physical appearance	Pale yellow gas	Greenish yellow gas	Red-brown liquid	Shiny grayish black solid
Ionization energy ( $\text{kJmol}^{-1}$ )	1681	1251	1140	1008
Electron affinity, ( $\text{kJmol}^{-1}$ )	-322	-349	-325	-295
Electronegativity	4.00	3.00	2.8	2.5
Ionic radius (pm)	136	181	196	216
Covalent radius (pm)	72	99	114	133
Melting point ( $^{\circ}\text{C}$ )	-220	-101	-7.2	-114
Boiling point ( $^{\circ}\text{C}$ )	-188	-34.6	58.8	184.4
Density ( $\text{g/cm}^3$ )	0.00181	0.00321	3.12	4.93
Oxidation states	-1	-1,+1,+3,+5,+7	-1,+1,+3,+5,+7	-1,+1,+3,+5,+7
Bond energy ( $\text{kJmol}^{-1}$ ) (X-X)	154.80	242.67	192.46	150.6

**Exercise:** Q.3(x) Explain in detail the trends in group 7 of following physical properties. (i) Electronegativity (ii) Electron affinity

#### Trends in Atomic radius

Atomic radius increases as we go down the group due to:

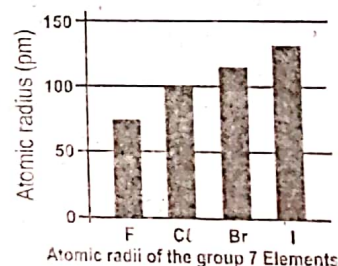
(i) increase in number of shells (ii) greater shielding effect (iii) less nuclear charge

#### Trends in Electronegativity

Halogens have large values of electronegativity. These values decrease as we proceed from F to I in the group. Large electronegativity values of halogen atoms indicate that X atoms have a strong tendency to form  $\text{X}^-$  (Halide) ions.

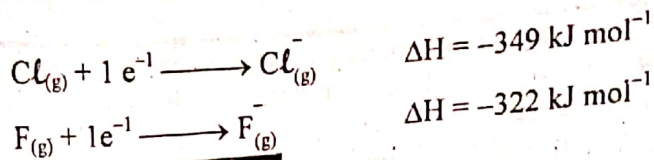
#### Trends in first electron affinity

Electron affinity values decrease from Cl to I while F has less electron affinity than Cl.



Q. Electron affinity of fluorine is less than chlorine although electron affinity values decrease down the group. Justify it.

Ans. Actually fluorine has very small size (72 pm) and seven electrons in 2s and 2p subshells have thick electronic cloud. This thick electronic cloud repels the incoming electron. Thus fluorine has electron affinity less than that of chlorine.



### Trends in melting and boiling points

The melting and boiling points of the halogens regularly increase from F to I. Halogens are diatomic non-polar molecules. London dispersion forces are present between molecules. These forces become progressively more prominent as the size of molecules increase in halogens.

- $\text{F}_2$  and  $\text{Cl}_2$  are gases at ordinary temperature.
- $\text{Br}_2$  is a heavy liquid.
- $\text{I}_2$  is a solid.

### Bond enthalpies (bond energies or bond strengths)

"Bond enthalpy is the heat needed to break one mole of covalent bonds (gaseous state) to produce individual gaseous atoms"

Examples:

(i) For chlorine,  $\text{Cl}_{2(g)}$ , it is the heat energy needed to carry out this change per mole of bond:  $\text{Cl} - \text{Cl}_{(g)} \longrightarrow 2\text{Cl}_{(g)} \quad \Delta H = 242.67 \text{ kJ mol}^{-1}$

(ii) For bromine, the reaction is still from gaseous bromine molecules to separate gaseous atoms.  $\text{Br} - \text{Br}_{(g)} \longrightarrow 2\text{Br}_{(g)} \quad \Delta H = 192.46 \text{ kJ mol}^{-1}$

It has following two reasons:

- $\text{F} - \text{F}$  bond length is very small as compared to other  $\text{X} - \text{X}$  bond lengths. This makes the F atoms in  $\text{F}_2$  molecule repel each other and helps the dissociation of  $\text{F}_2$  molecule into F atoms.
- $\text{X} - \text{X}$  bond in  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  molecules is stronger than  $\text{F} - \text{F}$  bond in  $\text{F}_2$  molecule. This is due to the possibility of the existence of multiple bonds in  $\text{X} - \text{X}$  bond involving d-orbitals.

### Bond Enthalpies in the Hydrogen Halides, $\text{HX}_{(g)}$

In hydrogen halides, the halogen atom is attached to a hydrogen atom. As the halogen atom gets bigger, the bonding pair gets more and more distant from the nucleus. The attraction is less, and the bond gets weaker. There is nothing complicated happening in this case.



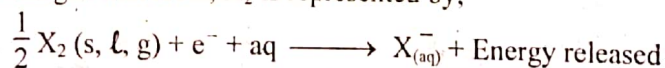
This is important in the thermal stability of the hydrogen halides - how easily they are broken up into hydrogen and the halogen on heating.

- Hydrogen fluoride and hydrogen chloride are very stable to heat. They don't split up into hydrogen and fluorine or chlorine again if heated to any normal lab temperature.
- Hydrogen bromide splits slightly into hydrogen and bromine on heating.
- Hydrogen iodide splits to an even greater extent.

As the bonds get weaker, they are more easily broken.

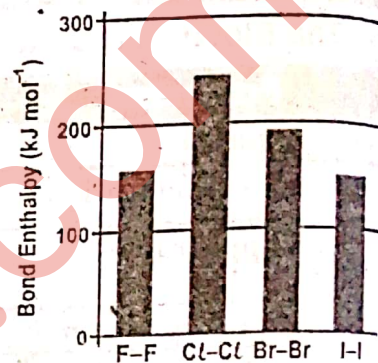
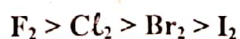
### Strength of halogens as oxidizing agents

A substance that has a tendency to accept one or more electrons is said to show oxidizing property. The halogens due to high electron affinity values have a great tendency to accept electron and hence act as strong oxidizing agent. The oxidizing property of a halogen molecule,  $\text{X}_2$  is represented by;

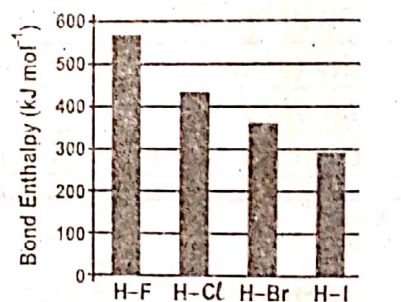


### Relative Reactivities of the Halogens as Oxidizing Agents

It has been seen that the values of E are decreasing from  $\text{F}_2$  to  $\text{I}_2$  the oxidizing power of halogens is also decreasing in the same direction i.e. the oxidizing power of halogens is in the order:



Bond Enthalpies of Halogens (X<sub>2</sub>)



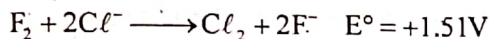
Bond Enthalpies of Hydrogen Halides (HX)

**Relative reactivities**

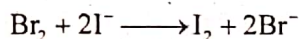
Due to the relative strength as oxidizing agents, it is possible for each free halogen to oxidize the ions of other halogens next to it, in the family. Standard electrode potential measures oxidizing power.

Standard reduction potential, $E^\circ$ (V)	$F_2$	$Cl_2$	$Br_2$	$I_2$
$X_2 + 2e^- \longrightarrow 2X^-$	+2.87	+1.36	+1.07	+0.54

- Fluorine can oxidize all the halide ions to molecular halogens. (A reaction will occur if the value of  $E^\circ$  is positive).



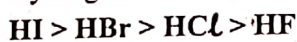
- In the similar way, chlorine will oxidize both bromide and iodide ions, while bromine can oxidize only iodide ion.



- Iodine being a weak oxidizing agent cannot oxidize chloride or bromide ion.

**Acidity of the hydrogen halides (HX)**

Hydrogen halides (HX) act as acids as well as reducing agent. The order for both properties is same i.e.,



- All the halogen acids in the gaseous states are essentially covalent but in the aqueous solution they ionize to give solvated proton ( $H_3O^+$ ) and hence act as acids.



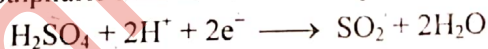
- HF ionizes only slightly while HCl, HBr, and HI ionize completely. Hence HF is the weakest acid and strength of these acids increases from HF to HI.
- HF (weakest acid) < HCl < HBr < HI (strongest acid).
- The weakest acidic nature of HF is due to the fact that the dissociation energy of H – F bond in H – F molecule is the highest and hence this molecule has least tendency to split up into  $H^+$  and  $F^-$  ions in aqueous solution.
- The order of the acidic strength of HX acids can be explained by finding out the relative order of the acidity of the conjugate bases viz  $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$  of these acids.
- The hydrides show no acidic character when perfectly dry.

**Halide ions as reducing agents and trends in reducing strength ability of halide ions (The Redox Reactions between halide ions and concentrated sulphuric acid)****With Bromide ions**

The bromide ions are strong enough reducing agents to reduce the concentrated sulphuric acid. In the process, the bromide ions are oxidized to bromine.



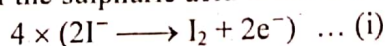
The bromide ions reduce the sulphuric acid to sulphur dioxide gas. This is a decrease of oxidation state of the sulphur from +6 in the sulphuric acid to +4 in the sulphur dioxide.



The overall ionic equation for the reaction:

**With Iodide ions**

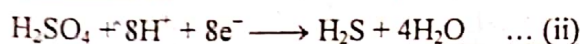
Iodide ions are stronger reducing agents than bromide ions. They are oxidized to iodine by the concentrated sulphuric acid. The reduction of the sulphuric acid is more complicated than before. The iodide ions are powerful enough reducing agents to reduce it.



- first to sulphur dioxide (sulphur oxidation state = +4)
- then to sulphur itself (oxidation state = 0)
- and all the way to hydrogen sulphide (sulphur oxidation state = -2).

The most important of this mixture of reduction products is probably the hydrogen sulphide.

The half-equation for its formation is:



Combining (i) & (ii):



- **Fluorides and Chlorides ions** do not reduce concentrated sulphuric acid.

### Summary of the trend in reducing ability

- Fluoride and chloride ions won't reduce concentrated sulphuric acid.
- Bromide ions reduce the sulphuric acid to sulphur dioxide. In the process, the bromide ions are oxidized to bromine ( $\text{Br}_2$ ).
- Iodide ions reduce the sulphuric acid to a mixture of products including hydrogen sulphide. The iodide ions are oxidized to iodine ( $\text{I}_2$ ).
- Reducing ability of the halide ions increases as we go down the group. i.e.  $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

### Explaining the trend

When a halide ion acts as a reducing agent, it gives electrons to something else. That means that the halide ion itself has to lose electrons. The bigger the halide ion, the farther the outer electrons are from the nucleus, and the more they are screened from it by inner electrons. It therefore gets easier for the halide ions to lose electrons as we go down the group because there is less attraction between the outer electrons and the nucleus.



#### 1. Give reasons of the following

(a) **HI is stronger acid than HF.**

**Ans.** The strength of an acid is directly proportional to its proton ( $\text{H}^+$ ) releasing power. In HF strong hydrogen bonding is present and partially positive hydrogen is entrapped between two strong electronegative fluorine atoms. Consequently it becomes difficult for proton to be ionized in water which makes it weak acid.

On the other hand in HI dipole-dipole interaction is present which is weaker than hydrogen bonding. Therefore proton ( $\text{H}^+$ ) releasing power of HI is more which makes it strong acid.

(b) **Although H-bonding in HF is stronger than that in  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}$  has much higher boiling point.**

**Ans.** The boiling point of a substance depends upon strength of intermolecular forces. In water there are two hydrogen bonds per molecule and has three dimensional structure. That is why it has higher boiling point ( $100^\circ\text{C}$ ) than HF, which has linear structure and one hydrogen bond per molecule.

(c) **The acidic character of hydrides of VIIA elements increases on descending the group.**

**Ans.** All the hydrides of halogens (HX) act as acids in their aqueous solutions. The acidic strength varies in the order  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

It can be explained in terms of strength of  $\text{H}-\text{X}$  bonds, which is in the order  $\text{H}-\text{I} < \text{H}-\text{Br} < \text{H}-\text{Cl} < \text{H}-\text{F}$ . Since  $\text{H}-\text{I}$  bond is weakest, therefore, HI is the strongest acid. On the other hand  $\text{H}-\text{F}$  bond is strongest, hence it is the weakest acid among all the halogen acids.

#### 2. Illustrate the oxidizing properties of halogens by giving example of two typical reactions.

**Ans.** In each case, a halogen higher in the Group can oxidize the ions of one lower down.

(i) Chlorine can oxidize the bromide ions (in potassium bromide solution say) to bromine:



The bromine appears as an orange solution.

(ii) Chlorine can also oxidize iodide ions (in potassium iodide solution say) to iodine:

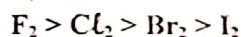


The iodine appears either as a red solution or as a dark grey precipitate if the chlorine is in excess.

**Note:** Fluorine and chlorine can oxidize various coloured dyes to colourless substances. Colour of litmus or universal indicator can be decolourized when exposed to fluorine or chlorine.

3. Arrange the halogens in the decreasing order of their oxidizing power.

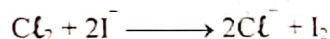
**Ans.** The order of decreasing power as an oxidizing agent is:



4. Give reasons for the following:

(a) Chlorine is a stronger oxidizing agent than iodine.

**Ans.** Chlorine has the ability to take electrons from iodide ions. Iodine can't get these electrons back from the chloride ions formed. That means that chlorine is a more powerful oxidizing agent than either iodine. Chlorine can also oxidize iodide ions (in potassium iodide solution say) to iodine:



(b) Halogens are the best oxidizing agents.

**Ans.** The halogens are best oxidizing agents due to following factors:

- (i) Low bond dissociation energy
- (ii) High electron affinities of atoms
- (iii) High hydration energies of ions

Fluorine and chlorine can oxidize various coloured dyes to colourless substances. Colour of litmus or universal indicator can be decolourized when exposed to fluorine or chlorine

(c) Fluorine is a better oxidizing agent than chlorine.

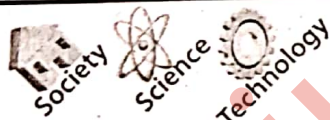
**Ans.** Following two reasons make fluorine a better oxidizing agent than chlorine:

- (i) The atomization energy of fluorine is abnormally low than that of chlorine. This reflects the low bond enthalpy of fluorine.
- (ii) The hydration enthalpy of the fluoride ion is very high.



(d) Electronegativity of halogens decreases in the order  $F > Cl > Br > I$

**Ans.** Halogens are most electronegative elements in the periodic table. Down the group the halogen atoms get bigger and bonding pair gets further and further away from the halogen nucleus, so is less strongly attracted towards it. In other words, as we go down the Group, the elements become less electronegative.



### Food and Beverage Canning

As early as 1940, can manufacturers began to explore adapting cans to package carbonated soft drinks. The can had to be strengthened to accommodate higher internal can pressures created by carbonation (especially during warm summer months), which meant increasing the thickness of the metal used in the can ends. Otherwise, distortion of the end would strain the seal, creating potential leaks or making cans unstackable for storage and transport.

Another concern for the new beverage can was its shelf life. Even small amounts of dissolved tin or iron from the can could impair the drinking quality of both beer and soft drinks. Fortunately, beer, which is only mildly acidic, is relatively noncorrosive. In addition, beer ages naturally, so it has a limited shelf life of about three months in any package. In contrast, the food acids, including carbonic, citric and phosphoric, in soft drinks present a risk for rapid corrosion of exposed tin and iron in the can. The consequences of off-flavors, color changes and leakage through the metal needed to be addressed. At this point, the can was upgraded by improving the organic coatings used to line the inside, making cans heavier and more encasing.

## Elements/Metals – Their Mining and Extraction

Different elements/metals are not obtained such rather these are obtained after passing through different steps.

These steps are as follows:

1. Mining and enrichment
2. Reduction
3. Refining and Casting

In fact some special methods are used to obtain each metal from its ores and to develop it into useful articles, yet few steps are common in the metallurgy of every metal. These are follows.

### 1. Mining

#### i. Crushing

Obtaining ores by digging the rocks and hills is called mining. This work is done by engineers and laborers with the help of machines. But prior to this work it is confirmed by survey and analysis that obtaining metals from this is economical or not.

#### ii. Grinding

Breaking of rocks and larger stones into smaller size stones is called crushing. This is done by jaw crushers.

#### iii. Hand picking, jugging and shaking

In Pakistan and other under developed countries where labour is cheap, metallic stones are picked and separated by hands. Heavy metals are separated from useless material i.e. gangue, by shaking with "chaage". In some countries this process is done by pressurized water.

#### iv. Magnetic separation

The ground ore is passed over a magnetic belt which separates the magnetic metal from gangue. This process is used for metals, which have magnetic properties like iron.

### 2. Reduction

For the complete separation of a metal from gangue, ores are heated at high temperature. At its melting point, molten metal is separated from solid gangue. It must be remembered that different metals are mixed with different compounds according to the type of impurities present in the metal ore and then they are passed through the process of reduction. The process of reduction is carried out in the blast furnace.

#### Blast Furnace

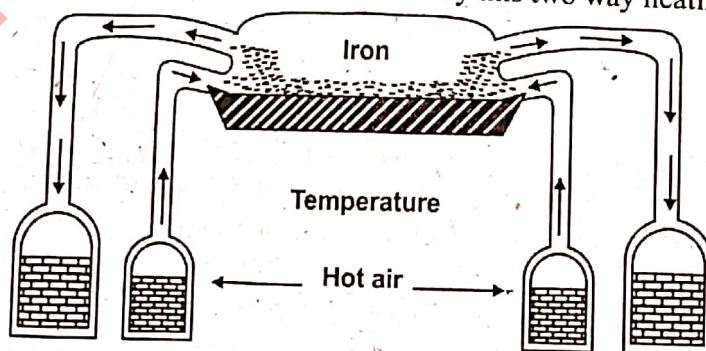
It is lined inside with fire bricks. Its height and capacity are kept according to the requirement. Hot gases enter from lower side and ores are charged from the top of the furnace. Temperature is maintained at  $1500^{\circ} - 3000^{\circ}\text{C}$ . This furnace is usually used for iron and copper metallurgy.

### 3. Refining of Metals

Metals extracted in the above process are further refined by the following process.

#### Open-Hearth Process:

A fire furnace is used to remove the impurities of metal. It is lined inside with fire bricks and is just like a room. Burning gases are entered from one side and exhaust gases are removed from the opposite end. The process is operated from opposite ends after an interval. Metals melt in a shorter time by this two way heating.



## Applications of Bleaching Powder

Bleaching powder is actually a mixture of calcium hypochlorite ( $\text{Ca(OCl)}_2$ ) and the basic chloride  $\text{CaCl}_2 \cdot \text{H}_2\text{O}$  with some slaked lime,  $\text{Ca(OH)}_2$ .

Bleaching powders take time to dissolve in water and longer to work but have a longer shelf life in comparison to liquid bleaches and can be used on items like upholstery, carpet and some delicate fabrics. However, bleaching powder should never be combined with ammonia or used on colored fabrics as it will cause fading.

- Bleaching powder is highly effective for cleaning inside the home and outdoors. It can be used for removing mildew from fabric, cleaning countertops and for removing mold from grout between tiles, bathmats and shower curtains. Outside, the agent can be used on plastic furniture, unpainted cement, paving and painted surfaces to eliminate mildew and other stubborn stains.
- Bleaching powder can be used to safely disinfect and sterilize many things around the home including second hand goods, trash cans, pet accessories and baby toys and furniture. Bleaching powder is a highly effective means of returning the luster to white porcelain and glassware. Glassware can regain its sparkle by adding a small amount of powdered bleach to dishwasher when washing glasses.
- To kill any annoying weeds growing from cracks and crevices in the garden a strong mixture of bleaching powder and water is applied. Moss and algae on garden walkways can be easily eliminated by scrubbing with bleaching powder diluted in water. Powdered bleach is also useful for sanitizing garden tools to avoid diseases spreading between plants. Adding powdered bleach to the water of cut flowers will help to preserve their freshness by preventing the growth of bacteria in the vase.
- Bleaching powder is used for the disinfection of drinking water or swimming pool water.
- It is used as a sanitizer in outdoor swimming pools in combination with a cyanuric acid ( $\text{CNOH}$ )<sub>3</sub> stabilizer, which reduces the loss of chlorine due to ultraviolet radiation. The calcium content hardens the water and tends to clog up some filters; hence, some products containing calcium hypochlorite also contain anti-scaling agents.
- Bleaching powder is used for bleaching cotton and linen. It is also used in bathroom cleaners, household disinfectant sprays, moss and algae removers, and weed killers.
- In addition, bleaching powder may be used to manufacture chloroform.
- Bleaching powder is used also in sugar industry for bleaching sugar cane juice before its crystallization.

## Commercial Uses of Halogens

1. Chlorine is used as a cheap industrial oxidant in the manufacture of bromine
2. Iodine is dissolved in alcohol, commonly known as tincture of iodine is used as a mild antiseptic for cuts and scratches. Iodine is also mixed with the detergents used in cleaning dairy equipment.
3. Small quantities of fluorine are used in rocket propulsion. Much larger quantities are used to make uranium (VI) fluoride for the separation of  $^{238}\text{U}$  and  $^{235}\text{U}$ :



4. Fluorine is also used to make a wide range of fluorocarbon compounds for use as refrigerants, aerosol propellants, anaesthetics and fire-extinguisher fluid. One of the most important fluorocarbons is poly (tetrafluoroethene), PTFE, frequently sold under the trade name **Fluon** or Teflon.
5. Halogens and their compounds are used for bleaching, refrigeration and as aerosols, etc.

## Iodine deficiency and Goiter

### Iodine Deficiency

Iodine is an element that is needed for the production of thyroid hormone. The human body cannot synthesize iodine, so it is an essential element. The deficiency of iodine leads to enlargement of thyroid a condition called goiter. Hypothyroidism and mental retardation in children and infants is observed if their mothers suffer from iodine deficiency during pregnancy.

Before 1920, iodine deficiency was common in Appalachian, north-western US regions, and in most of Canada. Approximately, 40% of the world's population remains at the risk of iodine deficiency.



## Goiter:

The term goiter refers to the abnormal enlargement of thyroid gland due to deficiency of iodine in diet. It results in swelling in neck. It is important to know that the presence of goiter does not necessarily mean that the thyroid gland is malfunctioning (hypothyroidism). A goiter can also occur in a gland that is producing too much thyroid hormone (hyperthyroidism) or even the correct amount of hormone (euthyroidism). A goiter indicates there is a condition present which is causing the thyroid to grow abnormally.

## Fluoride Deficiency and Toxicity

### Fluoride Toxicity

Fluoride toxicity or fluoride poisoning is a condition in which more fluoride is taken than the amount required for normal growth, development and metabolism. Fluoride toxicity is characterised by a variety of signs and symptoms. Poisoning most commonly occurs following ingestion of conspicuous amount of fluoride containing products. Symptoms appear within minutes of exposure. Fluoride is found in many common household products e.g. toothpaste, dietary supplements, insecticides, rodenticides etc. Fluoride toxicity results,

1. Arthritis
2. Stiff painful joints with or without swelling
3. Asthma, especially after showering
4. Painful bony lumps where tendons and ligaments attach to bones

### Fluoride Deficiency

- Fluoride deficiency results when the amount of its uptake is less than required.
- Fluoride deficiency results in brittle bones or demineralization of bones

### Cavities

#### Weakened tooth enamel

Fluoride deficiency can lead to a higher likelihood of developing bone fractures and possibly even osteoporosis.



### 1. How different metals are extracted?

Ans. Different metals are obtained after passing through different steps. These steps are as follows:

1. Mining and enrichment (crushing, grinding, hand picking, jugging, shaking, magnetic separation)
2. Reduction (by using blast furnace)
3. Refining and Casting (by using open hearth process)

### 2. What problems are caused by fluorides deficiency?

Ans. Fluoride deficiency results in brittle bones or demineralization of bones

### 3. What is goiter?

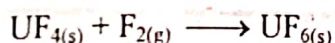
Ans. The term goiter refers to the abnormal enlargement of thyroid gland due to deficiency of iodine in diet. It results in swelling in neck. It is important to know that the presence of goiter does not necessarily mean that the thyroid gland is malfunctioning (hypothyroidism). A goiter can also occur in a gland that is producing too much thyroid hormone (hyperthyroidism) or even the correct amount of hormone (euthyroidism). A goiter indicates there is a condition present which is causing the thyroid to grow abnormally.

### 4. What problem is caused by examining?

Ans. Examining occurs when too little parathyroid hormone is released by the parathyroid glands, or the parathyroid hormone that is released does not work properly. Examining leads to low levels of calcium in the blood, which can cause a number of different symptoms. The most common are muscle cramps, pain and twitching. Examining can be successfully treated with calcium and vitamin D supplements but regular blood test monitoring is needed.

### 5. How fluoride is useful for uranium separation?

Ans. Small quantities of fluorine are used in rocket propulsion. Much larger quantities are used to make uranium (VI) fluoride for the separation of  $^{238}\text{U}$  and  $^{235}\text{U}$ :



## KEY POINTS

- Alkali metals have only one electron in s-orbital of their valence shell. They lose one electron of the valence shell forming monovalent positive ions ( $M^{+1}$ ).
- Alkaline earth metals have two electrons in s-orbital of their valence shell. They lose two electrons forming dipositive ions  $M^{2+}$ .
- Lithium behaves different from the other alkali metals.
- Beryllium is the only member of group 2 which reacts with alkalies to give hydrogen. The other members do not react with alkalies.
- Nitrates of lithium, magnesium and barium on heating give oxygen, nitrogen peroxide and the corresponding metallic oxides.
- The pair of outermost electrons that does not readily take part in chemical combination is termed as inert pair.
- The electronic configuration of group 4 elements show that they have four electrons in their valence shells, two electrons of which are in s-orbital and the remaining two are in p-orbitals.
- The halogens are very reactive. Intermolecular forces in halogens increase down the group. fluorine is a gas but iodine is solid.
- Halogens form ionic compounds with s-block metals, covalent compound with p-block elements and complex ions with d-block metals. Fluorides are usually ionic.
- Halogens show oxidation states -1, +1, +3, +5, +7 but fluorine shows the oxidation state of +1 only.
- Oxidizing power of halogens decreases down the group in the following order:  
 $F_2 > Cl_2 > Br_2 > I_2$ .
- Reducing power of halide ions decrease from  $I^-$  to  $Br^-$ . Chloride and fluoride ions are not reductants.

## EXERCISE

Q1. Multiple Choice Questions. Encircle the correct answer.

- ⊛ Read the question carefully.
  - ⊛ Try to answer the question yourself before reading the answer choices.
  - ⊛ Guess only if you can eliminate one or more answer choices.
  - ⊛ Drawing a picture can help.
  - ⊛ Don't spend too much time on any one question.
  - ⊛ In-depth calculations are not necessary; approximate the answer by rounding.
- (i) Oxides and hydroxides of Group I elements are:  
 (a) acidic                      (b) alkaline                      (c) neutral                      (d) amphoteric
- (ii) The flame colour of sodium metal or its compounds is  
 (a) bright crimson                      (b) violet                      (c) golden yellow                      (d) bright blue
- (iii) When sodium burns in air, it forms sodium:  
 (a) monoxide                      (b) peroxide                      (c) oxide                      (d) superoxide
- (iv) The carbonates of alkali metals are not affected by heat except:  
 (a)  $Li_2CO_3$                       (b)  $Na_2CO_3$                       (c)  $K_2CO_3$                       (d)  $Rb_2CO_3$
- (v) Green is characteristic flame color of  
 (a) calcium                      (b) barium                      (c) strontium                      (d) sodium
- (vi) All the carbonates, sulphates and phosphates of alkaline earth metals are ..... In water.  
 (a) sparingly soluble                      (b) soluble                      (c) insoluble                      (d) less soluble
- (vii) The first ionization energy is higher for the  
 (a) alkaline earth metals                      (b) alkali metals                      (c) halogens                      (d) noble gases
- (viii) Which one of the element has the maximum electron affinity?

- (a) F (b) Cl (c) Br (d) I
- (ix) Which pair has both members from same period of periodic table?  
(a) Na-Ca (b) Na-Cl (c) Ca-Cl (d) Cl-Br
- (x) Melting points and boiling points of alkali metals  
(a) decreases from top to bottom (b) increase from top to bottom  
(c) first increases then decreases (d) remains unchanged
- (xi) Which one of the following oxides is amphoteric in nature  
(a) rubidium oxide (b) barium oxide (c) antimony oxide (d) sulphur oxide
- (xii) Oxidizing power of halogen depends upon  
(a) energy of dissociation (b) electron affinity (c) heat of vaporization (d) all of above
- (xiii) Which of following oxide is Amphoteric in nature?  
(a) MgO (b) BeO (c) CO<sub>2</sub> (d) SnO<sub>2</sub>
- (xiv) Select the correct increasing order of atomic radius?  
(a) Ne > O > S > Al (b) Ne < O > S > Al (c) Ne < O < S < Al (d) Ne > O < S > Al
- (xv) Due to inert pair effect ..... the stable oxidation states ..... for Sn and Pb.  
(a) 2+, 4+ (b) 1+, 4+ (c) 4+, 2+ (d) 2+, 3+
- (xvi) Highest electron affinity is shown by?  
(a) F (b) I (c) Br (d) Cl
- (xvii) Which is the strongest reducing agent?  
(a) HF (b) HCl (c) HI (d) HBr
- (xviii) Substance boiling at higher temperature among following is?  
(a) HI (b) HF (c) HCl (d) HBr
- (xix) Group VII-A elements are generally called:  
(a) halogens (b) noble gases (c) inert gases (d) metalloids
- (xx) The radioactive element in halogen group is:  
(a) radon (b) radium (c) astatine (d) bromine

### SOLVED EXERCISE MCQs

Q. No	Answer	Reason																
(i)	(b) alkaline	Elements of group I (alkali metals) are highly electropositive. Their oxides and hydroxides are alkaline in nature. e.g. Na <sub>2</sub> O, KO <sub>2</sub> , KOH etc.																
(ii)	(c) golden yellow	Sodium and its compounds give golden yellow flame colour.																
(iii)	(b) peroxide	Sodium will undergo a similar reaction, but only if the supply of oxygen is limited. $4\text{Na} + \text{O}_2 \xrightarrow{\text{Limited supply of oxygen}} 2\text{Na}_2\text{O}$ In the presence of excess of oxygen, sodium forms the pale yellow peroxide. $2\text{Na} + \text{O}_2 \xrightarrow{\text{Abundant supply of oxygen}} \text{Na}_2\text{O}_2$ Sodium peroxide (Pale Yellow)																
(iv)	(a) Li <sub>2</sub> CO <sub>3</sub>	The carbonates of alkali metals are stable towards heat except Li <sub>2</sub> CO <sub>3</sub> which decomposes on heating to lithium oxide. $\text{Li}_2\text{CO}_3 \longrightarrow \text{Li}_2\text{O} + \text{CO}_2$																
(v)	(b) barium	<table border="1"> <thead> <tr> <th>Elements</th> <th>Flame colour</th> <th>Elements</th> <th>Flame colour</th> </tr> </thead> <tbody> <tr> <td>Li</td> <td>red</td> <td>Ca</td> <td>orange-red</td> </tr> <tr> <td>Na</td> <td>golden yellow</td> <td>Sr</td> <td>Red</td> </tr> <tr> <td>K</td> <td>lilac (pink)</td> <td>Ba</td> <td>pale green</td> </tr> </tbody> </table>	Elements	Flame colour	Elements	Flame colour	Li	red	Ca	orange-red	Na	golden yellow	Sr	Red	K	lilac (pink)	Ba	pale green
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(xvii)	(c) HI	HF, HCl, HBr and HI act as reducing agents in the following order: HF < HCl < HBr < HI
(xviii)	(b) HF	The boiling points of hydrogen halides are as follow: HF = 19.5°C, HCl = -85.0°C, HBr = -66.7°C, HI = -35.3°C
(xix)	(a) halogens	Group VIIA elements are called the halogens from Greek <b>hals</b> , "salt" and <b>gennan</b> , "to form or generate", because they are literally the salt formers.
(xx)	(c) astatine	<b>Astatine</b> is a rare halogen. It is radioactive and its most stable isotope has a half life of 8.3 hrs.

## SHORT ANSWERS QUESTIONS

**Q.2. Give brief answers for the following questions.**

(i) Although Na and P are present in the same period yet their oxides are different in nature  $\text{Na}_2\text{O}$  is basic while  $\text{P}_2\text{O}_5$  is acidic why?

**Ans.** We know that Na is a metal and metals forms basic oxides.



While phosphorous is non-metal and non-metals form acidic oxides.



(ii) How acidic basic and amphoteric behaviour of oxides is explained?

**Ans:** Across the Period

In a given period, the oxides progress from strongly basic through weakly basic, amphoteric and weakly acidic to strongly acidic.

**Example:**



strongly basic    amphoteric    weakly acidic    acidic    strongly acidic

**Down the Group**

basic

The basicity of main group metal oxides increases on descending a group of the periodic table.

**Example:**  $\text{BeO} < \text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$

- The basicity of transition metal oxides (Sub group B) decreases from top to bottom.

(iii) Why the elements of group 1 are called alkali metals?

**Ans.** The name "alkali" came from Arabic, which means "The ashes". The Arabs used this term for these metals because they found that the ashes of plants were composed chiefly of sodium and potassium.

Alkali metals include the elements lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr). These are very reactive metals, produce strong alkaline solutions with water.

(iv) Why all group 1 metals have low ionization energies?

**Ans.** Group IA elements show low ionization energy due to loosely bonded valence electron of all metals with large radii in their periods.

(v) Why do the group 1 metals show strong electropositive character?

**Ans.** Group IA elements show strong electropositive character because they all have large atomic sizes among all periods hence they can easily loss electron as compared to other elements of their period.

(vi) Why do group 1 metals show strong reducing properties?

**Ans.** Group IA metals are strong reducing elements in nature because of their easy electron donating ability, they can easily give their electron to other elements hence they will reduce others.

**(vii) Why different colours are imparted by the atoms of the group 1 metals to the flame?**

**Ans.** We know that the outer electrons of alkali metals are loosely held with nucleus and hence it can be easily excited to higher energy levels even by small amount of energy by heating. When this excited electron come back to its original state it gives out the absorbed energy in form of visible light. Each metal atom will absorb different energy hence each will imparted different colours to the flame.

**(viii) Why the elements of group 2 are called alkaline earth metals?**

**Ans.** The word alkaline comes from that, these metals form alkaline solutions when they reacts with water while the word "earth" is used due to their abundance in earth crust which is also used to differentiate these metals from alkali metals.

**(ix) Why do the group 2 earth metals have high melting and boiling points than alkali metals?**

**Ans.** The melting and boiling points of alkaline earth metals are higher than alkali metals. The reason is that alkaline earth metals have 2 electrons in the outermost orbital. So the number of bonds which have been formed are greater. Therefore the melting points of alkali metals are low as compared to alkaline earth metals.

**(i)a How do group 1 metals resemble with group 2 metals.**

**Ans.** Group IA and IIA elements resembles as

- Both contains all metals.
- Both forms alkaline solution in water.
- Both forms salts with halogens.
- Both forms basic oxides.
- Both groups are reducing in nature.

**(ii)a How do group 1 metals differ form group 2 metals?**

**Ans.** Group IA are different from IIA because IA

- Contains only one valence electron
- Forms uni-positive cation.
- Larger atomic radii.
- Low ionization energies.
- More electropositive in nature

**(iii)a Discuss the metallic and non-metallic character of group 4 elements.**

**Ans.** Group IV elements include C, Si, Ge, Sn and Pb. Carbon is a non-metal, while silicon, Ge are metalloid which shows both metallic and non metallic properties. Sn and Pb are metals of group IV.

**(iv)a Discuss the general group trends of group 7 elements.**

**Ans.** Trends of group VIIA elements.

Atomic radii = Increases down the group.

Electronegativity = Decreases down the group.

Electron affinity = Decreases from Cl to I, but F has less than Cl.

Melting / B.Ps = MPs and BPs regularly increases down the group from F to I.

Bond enthalpies = Decreases from Cl to I while F shows low bond enthalpy.

**(v)a Why the term halogen is used for group 7 elements?**

**Ans.** The term halogen is derived from Latin word "Hals" means "salt" and "gen" means former. Because the halogens when combines with metals they form salts hence they are named as salt former (halogens).

**(vi)a Why does fluorine differ from other members of its group?**

**Ans.** Fluorine differ from other members due to its

- Small atomic radii

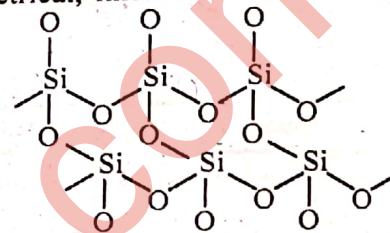
- High electronegativity
- Strong oxidizing power

(vii)a What is the structure of  $\text{CO}_2$  and  $\text{SiO}_2$  and why they differ?

Ans. The structure of  $\text{CO}_2$  and  $\text{SiO}_2$  are differ from each other because in case of  $\text{C} - \text{O}$  the bond length is small and it will energetically favourable for oxygen to form a double covalent bonds with carbon while in  $\text{Si} - \text{O}$  there is not as good of overlaps between the orbitals of the bonded atoms to lessened the bond length to that energetically favoured level for double bond.

(viii)a  $\text{CO}_2$  is a gas while  $\text{SiO}_2$  is a solid although  $\text{C}$  and  $\text{Si}$  belong to the same group?

Ans.  $\text{CO}_2$  molecule has a monomeric linear structure while  $\text{SiO}_2$  has an infinite three dimensional polymeric tetrahedral structure. The reason is that size of carbon atom is smaller than size of silicon atom. So, in  $\text{CO}_2$  each carbon atom forms two double bonds with two oxygen atoms. In this way a small, symmetrical, linear molecule of  $\text{CO}_2$  is formed, which is volatile and reasonably reactive.



Structure of silicon dioxide

In case of  $\text{SiO}_2$ , each silicon atom because of its large size is covalently bonded with four oxygen atoms and each oxygen atom is attached with two silicon atoms. In this way a three dimensional network is formed. So giant structure of  $\text{SiO}_2$  is very stable. Thus  $\text{SiO}_2$  exists as solid.

(ix)a  $\text{SnCl}_2$  is a solid while  $\text{SnCl}_4$  is a liquid. Why?

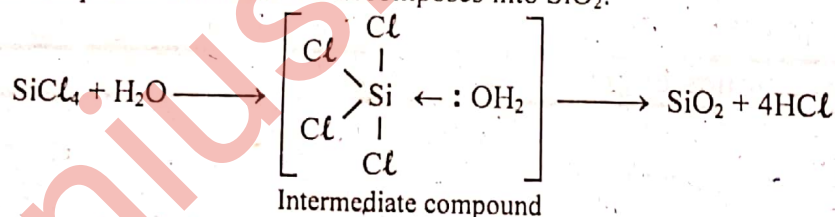
Ans. The physical state of a substance depends upon strength of binding forces between the atom. Ionic compounds are generally solids while covalent compounds may be solids, liquids or gases.  $\text{SnCl}_2$  is ionic while  $\text{SnCl}_4$  is covalent because  $\text{Sn}^{4+}$  has large polarizing power. It polarizes chloride ions and induces covalent character according to Fajan's Rule.

(x)a  $\text{C}$  and  $\text{Si}$  are always tetravalent but  $\text{Ge}$ ,  $\text{Sn}$  and  $\text{Pb}$  show divalency. Why?

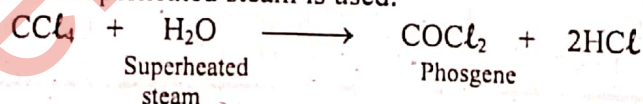
Ans.  $\text{C}$  &  $\text{Si}$  use all of their valence electrons (4 electrons) in bond formation. That is why they are tetravalent. On the other hand  $\text{Ge}$ ,  $\text{Sn}$  and  $\text{Pb}$  used only two valence electrons while other two electrons behave as inert pair, That is why these elements are divalent.

(xi)a  $\text{CCl}_4$  is resistant to hydrolysis but  $\text{SiCl}_4$  is readily hydrolyzed. Why?

Ans.  $\text{SiCl}_4$  gets hydrolyzed with the help of empty 3d orbitals which accommodate electron pairs of  $\text{H}_2\text{O}$  to form intermediate compound which further decomposes into  $\text{SiO}_2$ .

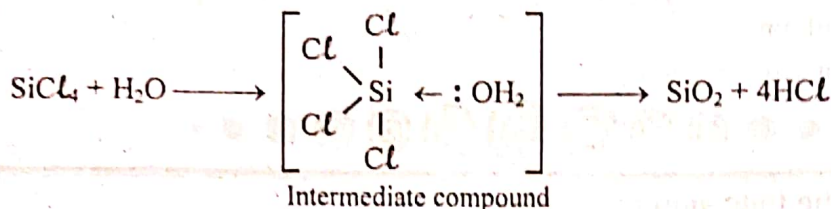


There is no empty d-orbital in carbon. Hence there is no possibility of such a reaction. However,  $\text{CCl}_4$  undergoes hydrolysis when superheated steam is used.



(xii)a  $\text{Si}-\text{Cl}$  bond is stronger than  $\text{C} - \text{Cl}$  bond, still  $\text{SiCl}_4$  hydrolyzed easily but  $\text{CCl}_4$  is not why?

Ans. The first step in the hydrolysis reaction is the attack by oxygen atom of water and formation of co-ordinate covalent bonds with the central atom. In the second step,  $\text{HCl}$  gas is evolved.



$\text{CCl}_4$  is a saturated molecule and carbon cannot increase its co-ordination number beyond four due to the absence of d-orbitals. Therefore  $\text{CCl}_4$  is not hydrolyzed by water.

In  $\text{SiCl}_4$ , Si can form an additional bond with water due to the availability of vacant d-orbital in it. Thus  $\text{SiCl}_4$  hydrolyzed easily.

**(xiii)a Explain why nitrates and carbonates of Li are not stable?**

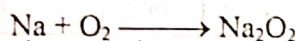
**Ans.** Carbonates and nitrates of Lithium are not stable because  $\text{Li}^+$  is a very small cation and very polarizing which favours to form oxides by decomposition. In generally small ions polarizes the anions more effectively than bigger ones as a result the bond between them becomes partly covalent in character, therefore they will be less stable.

**(xiv)a Differentiate the behaviour of Li and Na with atmospheric oxygen.**

**Ans.** Lithium when burnt in air forms Lithium monoxide which is a normal oxide ( $\text{O}^{2-}$ ).



While Na when burnt in air it forms sodium peroxide ( $\text{O}^-$ )



**(xv)a Alkali metal carbonates are more soluble than alkaline earth metal carbonates. Why?**

**Ans.** Alkali metal carbonates are more soluble than alkaline earth carbonates because.

- The lattice energy of alkali carbonates are low which favours easy ionization on water.
- Alkali metal carbonates are bonded by uni-positive cation which will be easily broken in water and becomes soluble.

**(xvi)a Explain why solubility of alkaline earth metal carbonates decrease down the group?**

**Ans.** Solubility of alkaline earth metal carbonate decreases down the group because of increase in the lattice energy, down the group the more electropositive metals will be strongly held with  $\text{CO}_3^{2-}$  ion.

**(xvii)a Oxidizing power of  $\text{F}_2$  is greater than  $\text{I}_2$ . Why?**

**Ans.** Fluorine ( $\text{F}_2$ ) has the ability to take electrons from iodide ions. Iodine can't get these electrons back from the fluoride ions formed. That means that fluorine is a more powerful oxidizing agent than either iodine. Fluorine can also oxidize iodide ions (in potassium iodide solution say) to iodine:



**(xviii)a HF is weak acid than HI. Why?**

**Ans.** The strength of an acid is directly proportional to its proton ( $\text{H}^+$ ) releasing power. In HF strong hydrogen bonding is present and partially positive hydrogen is entrapped between two strong electronegative fluorine atoms. Consequently it becomes difficult for proton to be ionized in water which makes it weak acid.

On the other hand in HI dipole-dipole interaction is present which is weaker than hydrogen bonding. Therefore proton ( $\text{H}^+$ ) releasing power of HI is more which makes it strong acid.

**(xix)a On what factors does the oxidizing power of halogens depend?**

**Ans.** The oxidizing power of halogens depends upon the following factors:

- Energy of dissociation
- Electron affinities of atoms



- (vii) Hydration energies of ions  
 (viii) Heats of vaporization (for Br<sub>2</sub> and I<sub>2</sub>)



3. Give detailed answers for the following questions.

(i) (a) The pattern of first ionization energy and melting and boiling point is not smooth. Justify it.

Ans. In general, as we move from left to right in a period, the ionization energy of the elements increases due to successive increase in the nuclear charge and decrease in atomic size. However there are certain elements which show irregular trends in period 3. For example ionization energy of Mg and P are higher than those of Al and S. Higher value of ionization energy of Mg as compared to Al can be explained as:

In case of Mg (1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>) it is more difficult to remove an electron from the completely filled 3s-orbital while in case of Al (1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>1</sup>) it is easier to remove the same from partially filled 3p-orbital. Since to remove an electron from a 3s-orbital of Mg atom requires more energy than to remove the same from a 3p-orbital of Al atom that is why ionization energy of Mg is higher than that of Al. Similarly higher value of P as compared to S has been explained on the same lines of argument as used in explaining the higher value of Mg compared to Al.

The values of First Ionization Energy of Period 3:

Period 3 Elements	Na	Mg	Al	Si	P	S	Cl	Ar
First Ionization Energies (kJ/mol)	496	738	578	786	1012	1000	1251	1520

(b) Why atomic radius increases in group and decreases along the period.

Ans. Periodic Trend in atomic radius

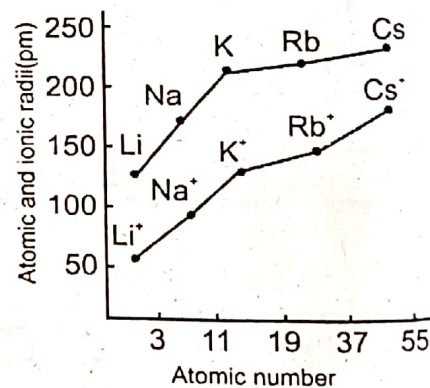
(a) Across the Period: Atomic radius decreases left to right in a period.

This is because of:

- Increase in atomic number.
- Increase in the positive charge in the nucleus. As positive nuclear charge increases, the negatively charged electrons in the shells are pulled closer to the nucleus.

(b) Down the Group: Atomic radius increases down the group. This is because of:

- Increase in number of shells.
- Increase in shielding effect down the group due to increase in intervening electrons. Thus atomic radius increases.



Atomic and ionic radii of alkali metals

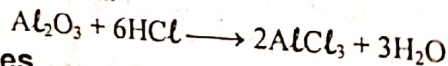
(iii) Discuss acid-base behaviour of (i) Aluminium oxide (ii) Sodium oxide

Ans. (i) Aluminium oxide (Al<sub>2</sub>O<sub>3</sub>)

As it is amphoteric oxide, it has reactions as both a base and an acid.

**Reaction with Acids**

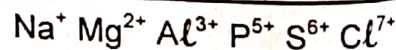
Aluminium oxide will react with hot dilute hydrochloric acid to give aluminium chloride solution.



**Reaction with Bases**

Aluminium oxide has also got an acidic side to its nature, and it shows this by reacting with bases such as sodium hydroxide solution. Various aluminates are formed (compounds where the aluminium is found in the negative ion).

possible because aluminium has the ability to form covalent bonds with oxygen. With hot, concentrated sodium hydroxide solution, aluminium oxide reacts to give a colourless solution of sodium tetrahydroxoaluminate.



- as the oxidation state increases
- Acidic character increases
  - Covalent nature increases

**(ii) Sodium oxide (Na<sub>2</sub>O)**

Sodium oxide is a simple strongly basic oxide. It is basic because it contains the oxide ion, O<sup>2-</sup>, which is a very strong base with a high tendency to combine with hydrogen ions.

**Reaction with Acids**

As a strong base, sodium oxide also reacts with acids. For example, it would react with dilute hydrochloric acid to produce sodium chloride solution.

**(iv)(a) Why are different types of oxides formed as you go down the group & period?**

Ans. **Periodic Trend in oxides**

**Across the Period**

In a given period, the oxides progress from strongly basic through weakly basic, amphoteric and weakly acidic to strongly acidic.

Example:



strongly basic      amphoteric      weakly acidic      acidic      strongly acidic

**Down the Group**

The basicity of main group metal oxides increases on descending a group of the periodic table.

Example: BeO < MgO < CaO < SrO < BaO

- The basicity of transition metal oxides (Sub group B) decreases from top to bottom.

**(c) Why is Beryllium chloride covalent and not ionic?**

Ans. If the electronegativity difference between two bonded atoms is less than 1.7, a covalent bond is formed between them.

In BeCl<sub>2</sub> (Beryllium chloride), the electronegativity difference between Be (E.N = 1.5) and Cl (E.N = 3.0) is 1.5. Therefore BeCl<sub>2</sub> is a covalent compound.

Furthermore,

**According to Fajan rule:**

Greater the charge density of a cation, greater will be its polarizing power and hence more covalent character it will induce.

$$\text{Charge density} \propto \frac{\text{charge}}{\text{size}} \propto \text{Polarizing Power} \propto \text{Covalent Character}$$

In BeCl<sub>2</sub>, due to small size and high charge Be<sup>2+</sup> has greater charge density. As a result, BeCl<sub>2</sub> is a covalent compound.

**(v) (a) Why do some metals form peroxides on heating in oxygen?**

Ans. The peroxide ion has a weak covalent bond between two oxygen atoms. Small size metal ions have high charge density. So, when they come closer to peroxide ion, they polarize it so much that peroxide ion is broken. e.g. Li<sup>+</sup>, Be<sup>2+</sup>, Mg<sup>2+</sup> have high charge density due to smaller size so they cannot form peroxides. The metals which have larger atomic size have low charge density, so they can form peroxides. e.g. Na<sup>+</sup>, Ba<sup>2+</sup>.

**(v) (b) Why do group 2 elements form nitrides on heating in air?**

Ans. To form a group 2 metal nitride, energy is given for two purposes. i.e (i) to form M<sup>2+</sup> ion and (ii) to break and convert nitrogen molecule into nitride ion (N<sup>3-</sup>). Since, M<sup>2+</sup> ions are small size so they have high charge density and hence develop strong attractions for N<sup>3-</sup> ion. Therefore a lot of energy is released as lattice energy. As a result, the energy given to form ions is compensated by the release of energy during lattice formation. Hence, the reaction becomes energetically favourable. Therefore, group 2 elements form nitrides. Similarly Li also form nitride.

(c) Discuss the trend in solubility of hydroxide of group 2 elements.

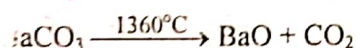
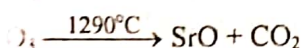
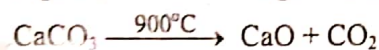
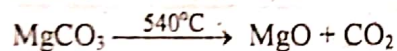
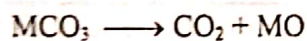
Ans. The solubility of alkaline earth metal hydroxides in water increases down the group.  $\text{Be}(\text{OH})_2$  is quite insoluble.  $\text{Mg}(\text{OH})_2$  is sparingly soluble while  $\text{Ba}(\text{OH})_2$  is more soluble.

This increase in solubility is due to increase in the size of cations. Due to greater ionic radii of group IIA cations, the lattice energy of hydroxide decreases.

(vi) Discuss the trends in thermal stability of the carbonates and nitrates.

Ans. Thermal stability of the carbonates

All carbonates decompose on heating at appropriate temperature evolving  $\text{CO}_2$ .



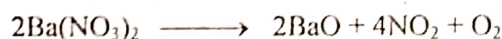
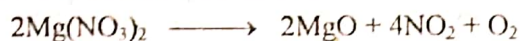
The stability of the carbonates of these metals increases on moving down the group.

Reason:

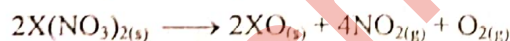
The ease of decomposition of the carbonates can be related to the size of metal ion. Smaller the positive ion, greater the lattice energy of resulting oxide. Hence higher the stability of the product and easier the decomposition of original carbonates.

### The effect of heat on the Group 2 Nitrates

All the nitrates in group 2 undergo thermal decomposition to give the metal oxide, nitrogen dioxide and oxygen.



- The nitrates are white solids, and the oxides produced are also white solids. Brown nitrogen dioxide gas is given off together with oxygen.
- Magnesium and calcium nitrates normally have water of crystallization, and the solid may dissolve in its own water of crystallization to make a colourless solution before it starts to decompose.
- Again, if "X" represents any one of the elements:



- As we go down the group, the nitrates also have to be heated more strongly before they will decompose. The nitrates also become more stable to heat as we go down the group.

(vii) Explain with examples that Beryllium oxide is Amphoteric?

Ans.  $\text{BeO}$  is amphoteric in nature. Since it reacts with both acids and bases.



Sodium beryllate

(xi) (a) Why is the bond enthalpy of F-F less as compared to Cl-Cl and Br-Br?

Ans. F - F bond length is very small as compared to other X - X bond lengths. This makes the F atoms in  $\text{F}_2$  molecule repel each other and helps the dissociation of  $\text{F}_2$  molecule into F atoms.

X - X bond in  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  molecules is stronger than F - F bond in  $\text{F}_2$  molecule. This is due to the possibility of the existence of multiple bonds in X - X bond involving d-orbitals.

(xi) (b) Explain the order  $F > Cl > Br > I$  with respect to oxidizing agent/power.

Ans: the values of  $E^\circ$  are decreasing from  $F_2$  to  $I_2$ , the oxidizing power of halogens is also decreasing in the same direction i.e. the oxidizing power of halogen is in the order:



### Relative reactivities

Due to the relative strength as oxidizing agents, it is possible for each free halogen to oxidize the ions of other halogens next to it, in the family. Standard electrode potential measures oxidizing power.

Standard reduction potential, $E^\circ$ (V)	$F_2$	$Cl_2$	$Br_2$	$I_2$
$X_2 + 2e^- \longrightarrow 2X^-$	+2.87	+1.36	+1.07	+0.54

- Fluorine can oxidize all the halide ions to molecular halogens. (A reaction will occur if the value of  $E^\circ$  is positive).



- In the similar way, chlorine will oxidize both bromide and iodide ions, while bromine can oxidize only iodide ion.



- Iodine being a weak oxidizing agent cannot oxidize chloride or bromide ion.

(xii) (a) Why is fluorine much stronger oxidizing agent than chlorine?

Ans. It is because:

- The bond dissociation energy of fluorine is quite low, so it will dissociate rapidly, to take up electron.
- The other factor is hydration energy. The  $F^-$  ion has high hydration energy due to small size, so it will form readily in solution. Thus fluorine will take up electrons readily to form  $F^-$  ions than chlorine. Hence, fluorine is a much stronger oxidizing agent than chlorine.

(xii) (b)  $HCl$  is strong acid as compared to  $HF$ . Why?

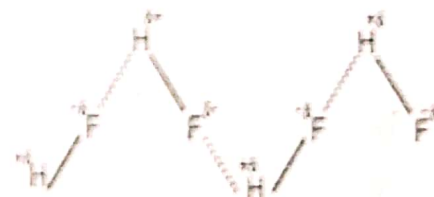
Ans.  $HCl$  is a stronger acid than  $HF$

A substance which has a tendency to give proton ( $H^+$ ) in an aqueous solution is called acid. The strength of an acid is directly proportional to its proton ( $H^+$ ) releasing power.

In  $HF$  strong hydrogen bonding is present and partially positive hydrogen is entrapped between two strong electronegative fluorine atoms.

Consequently it becomes difficult for proton to be ionized in water which makes it weak acid.

On the other hand in  $HCl$  dipole-dipole interaction is present which is weaker than hydrogen bonding. Therefore proton ( $H^+$ ) releasing power of  $HCl$  is more which makes it strong acid.



### Skill Activity

Try to draw a diagram of s-block elements which show that their atomic radii increases down the group and decreases from left to right in the period.

