

## SEMESTER III: CHMMAJ201-4

### Inorganic Chemistry-1

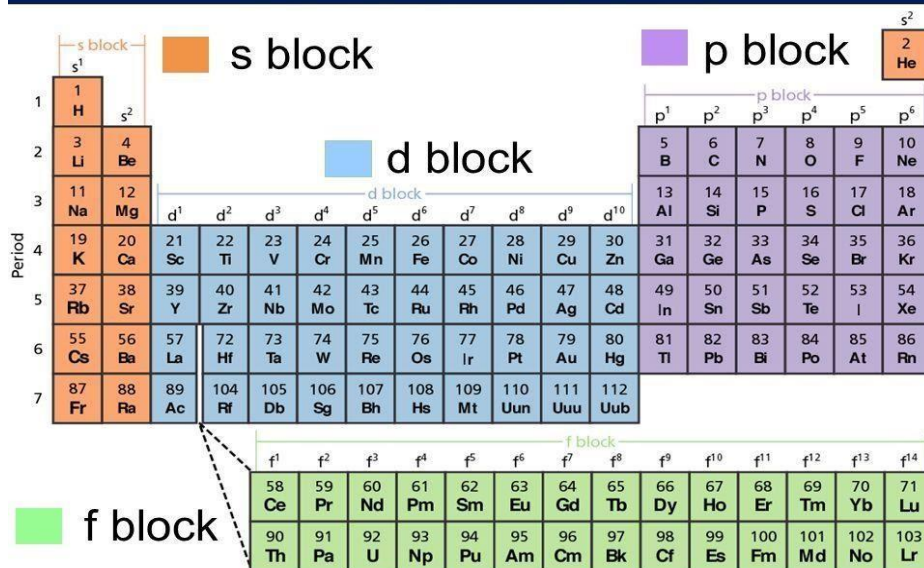
#### UNIT 1: Chemistry of s and p block elements

**1. Introduction:** In s-block elements the last electron enters the outermost s orbital. The general electronic configuration is  $ns^{1-2}$ . Hydrogen, Helium, group-1 metals and group-2 metal are belongs to the s-block elements. Some of the general properties of s-block elements are given below--

- (i) They are good conductors of heat and electricity.
- (ii) They are malleable and ductile.
- (iii) Exhibit group valency of 1 and 2 for IA and IIA groups respectively.
- (iv) Elements are very reactive as their last shell contains 1 or 2 electrons which can be given off easily.
- (v) They form colourless compounds except chromates, dichromates, permanganates etc.
- (vi) Their cations are diamagnetic.
- (vii) They form ionic compounds (except Li and Be).
- (viii) Their solutions in liquid ammonia are good conductor of electricity and are good reductant.
- (ix) Oxides are basic in nature.

In p-block elements the last electron enters the outermost p orbital. The elements from group-13 to group-18 are referred as p-block elements. As Their valence shell electronic configuration is  $ns^2np^{1-6}$ . The difference in inner core of the elements greatly influences many physical as well as chemical properties of p-block elements.

# s, p, d, and f blocks



Metal, non-metal and metalloid are present in p-block elements. They show variable valences and oxidation states. They form coloured complexes.

- **Inert Pair Effect:**

The p-block elements display two oxidation states. This is in sharp contrast to the s-block elements that display only one oxidation state, the group number. The higher oxidation state is equal to the group number minus 10 (i.e. number of s and p electrons in the valence shell) and the lower one is two units less than the group number (i.e. number of p electron in the valence shell). The lower oxidation state becomes more stable on descending the group. This is referred to as the inert pair effect. The higher oxidation state is displayed only when both the ns and np electrons are involved in bond-formation. On the other hand, the lower oxidation state is observed when only the np electron(s) participate in bond formation. On moving down the group the ns electrons tend to remain inert and do not participate in bond formation. This reluctance of the outermost s orbital electron pair to participate in bond formation is called inert pair effect. The reason for this effect is explained in terms of bond energy. On one hand energy is needed to uncouple the s-electrons and on the other hand energy is released during bond formation. If the energy released is sufficient to unpair the s-electrons, then they participate in bond formation, otherwise they do not. The bond energy decreases down the group and hence inert pair effect is prominent for the lower members.

- **Relative stability of different oxidation states**

1. **For group-1** elements the common and stable oxidation state is +1. The first IE is lower than any other group elements and the 2<sup>nd</sup> IE is very high which is greater than IE of noble gas elements. This fact suggests the stable +1 oxidation state of Gr.-1 elements.

2. **For group-2** elements the common oxidation state is +2. The third IE is very high so that M<sup>3+</sup> ion is never formed. The 3<sup>rd</sup> IE is often greater than the sum of 1<sup>st</sup> and 2<sup>nd</sup> IE. Although the 2<sup>nd</sup> IE is higher than 1<sup>st</sup> IE, Gr. 2 metals form M<sup>2+</sup> as lattice energy is higher in M<sup>2+</sup> ion than M<sup>+</sup> form.

Elements	Electronic configuration	Elements	Electronic configuration
Li	[He]2s <sup>1</sup>	Be	[He]2s <sup>2</sup>
Na	[Ne]3s <sup>1</sup>	Mg	[Ne]3s <sup>2</sup>
K	[Ar]4s <sup>1</sup>	Ca	[Ar]4s <sup>2</sup>
Rb	[Kr]5s <sup>1</sup>	Sr	[Kr]5s <sup>2</sup>
Cs	[Xe]6s <sup>1</sup>	Ba	[Xe]6s <sup>2</sup>

3. **For group-13** elements the common oxidation state is +3. But on descending the group stability of +3 oxidation state decreases and stability of +1 oxidation state increases. For heavier congeners Tl the stable oxidation state is +1. This occurs due to the inert pair effect which is a consequence of lanthanide contraction and relativistic effect. Sometime Ga(Gallium) shows +2 oxidation state which is very unstable.

Elements	Electronic Configuraton	Oxidation state	Example
B	[He]2s <sup>2</sup> 2p <sup>1</sup>	+3	B <sub>2</sub> O <sub>3</sub> , BF <sub>3</sub> , B(OH) <sub>3</sub>
Al	[Ne]3s <sup>2</sup> 2p <sup>1</sup>	+3	Al <sub>2</sub> O <sub>3</sub> , AlCl <sub>3</sub> , AlF <sub>3</sub>
Ga	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>1</sup>	+3, (+2)	GaCl <sub>3</sub> (+3), Ga <sub>2</sub> Cl <sub>4</sub> (+2)
In	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>1</sup>	+3, (+2)	InCl <sub>3</sub> (+3), InCl <sub>2</sub> (+2)
Tl	[Xe]4f <sup>14</sup> 6s <sup>2</sup> 6p <sup>1</sup>	+1	TlI <sub>3</sub> (+1), Tl <sub>2</sub> SO <sub>4</sub>

4. **For group-14** elements the common oxidation state is +4. On des the group stability of +4 oxidation state decreases and stability of +2 oxidation state increases. Therefore the heavier congener Pb processes stable +2 oxidation state rather +4.

Ox. state	Example	Ox. state	Example	Electronic configuration
C(+4)	CH <sub>4</sub> , CF <sub>4</sub> , CCl <sub>4</sub>	C(+2)	CO	C = [He]2s <sup>2</sup> 2p <sup>2</sup>
Si(+4)	SiH <sub>4</sub> , SiCl <sub>4</sub>	Si(+2)	SiF <sub>2</sub>	Si = [Ne]3s <sup>2</sup> 3p <sup>2</sup>
Ge(+4)	GeF <sub>4</sub> , GeCl <sub>4</sub>	Ge(+2)	GeF <sub>2</sub> , GeCl <sub>2</sub> , GeBr <sub>2</sub>	Ge = [Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>2</sup>
Sn(+4)	SnCl <sub>4</sub>	Sn(+2)	SnF <sub>2</sub> , SnCl <sub>2</sub> , SnBr <sub>2</sub>	Sn = [Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup>
Pb(+4)	PbCl <sub>4</sub>	Pb(+2)	PbCl <sub>2</sub> , PbBr <sub>2</sub>	Pb = [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>

5. For group-15 elements the common oxidation state is +3 and +5. The elements lack of 'd' orbital processes +3 oxidation state but elements having 'd' orbital may have both +3 and +5 oxidation states. On descending group stability of +5 oxidation states decreases and stability of +3 oxidation state increases. Nitrogen exhibits a wide range of oxidation states from -III to +V.

Elements	Electronic configuration	Oxidation state with example
N	[He]2s <sup>2</sup> 2p <sup>3</sup>	NH <sub>3</sub> (-3), NH <sub>2</sub> -NH <sub>2</sub> (-2), NH <sub>2</sub> OH(-1), N <sub>2</sub> (0), N <sub>2</sub> O(+1), NO(+2), HNO <sub>2</sub> (+4), HNO <sub>3</sub> (+5)
P	[Ne]3s <sup>2</sup> 3p <sup>3</sup>	P <sub>4</sub> O <sub>6</sub> (+3), P <sub>4</sub> O <sub>10</sub> (+5)
As	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup>	As <sub>4</sub> O <sub>6</sub> (+3), As <sub>4</sub> O <sub>10</sub> (+5)
Sb	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup>	Sb <sub>4</sub> O <sub>6</sub> (+3), Sb <sub>4</sub> O <sub>10</sub> (+5)
Bi	[Xe]4f <sup>14</sup> 6s <sup>2</sup> 6p <sup>3</sup>	Bi <sub>2</sub> O <sub>3</sub> (+3)

6. The common oxidation state of group-16 elements are -2, +4 and +6 but for oxygen common oxidation state is -2. Lower oxidation states of oxygen are -1 in peroxide, -1/2 in superoxide and -1/3 in ozonides. Sulphur shows variety of oxidation state like +2 in S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, +2.5 in S<sub>4</sub>O<sub>6</sub><sup>2-</sup>, +5 in S<sub>2</sub>O<sub>6</sub><sup>2-</sup>. Po exhibits a stable +2 oxidation state. All the elements exhibit +4 and +6 oxidation state except O. The stability of higher oxidation state decreases down the group i.e oxidising ability increases down the group in the order Se(+6) < Te(+6) < Po(+6).

Elements	Electronic confign.	Oxidation state with example
O	[He] 2s <sup>2</sup> 2p <sup>4</sup>	OH <sub>2</sub> (-2), OF <sub>2</sub> (+2), H <sub>2</sub> O <sub>2</sub> (-1), O <sub>2</sub> F <sub>2</sub> (+1), KO <sub>2</sub> (-1/2), NaO <sub>3</sub> (-1/3)
S	[Ne] 3s <sup>2</sup> 3p <sup>4</sup>	H <sub>2</sub> S(-2), Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (+2), Na <sub>2</sub> S <sub>4</sub> O <sub>6</sub> (2.5), Na <sub>2</sub> S <sub>2</sub> O <sub>6</sub> (+5), H <sub>2</sub> SO <sub>4</sub> (+6)
Se	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup>	H <sub>2</sub> Se(-2), SeO <sub>2</sub> (+4), SeO <sub>3</sub> (+6)
Te	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup>	H <sub>2</sub> Te(-2), TeO <sub>2</sub> (+4), TeO <sub>3</sub> (+6)
Po	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>4</sup>	H <sub>2</sub> Po(-2), PoO <sub>2</sub> (+4), PoO <sub>3</sub> (+6)

7. In group-17, the common oxidation state is -1. Except fluorine, halogens exhibit several oxidation states in their oxide, oxoacids and interhalogens.

Elements	Elec. Confign.	Ox. state	Example
F	[He]2s <sup>2</sup> 2p <sup>5</sup>	-1	HF(-1)
Cl	[Ne]3s <sup>2</sup> 3p <sup>5</sup>	-1, 1,3,5,7	HCl(-1), HOCl(+1), HClO <sub>2</sub> (+3), HClO <sub>3</sub> (+5), HClO <sub>4</sub> (+7)
Br	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>5</sup>	-1, 1,3,5,7	HBr(-1), HOBr(+1), HBrO <sub>3</sub> (+5), HBrO <sub>4</sub> (+7)
I	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>5</sup>	-1, 1,3,5,7	HI(-1), HOI(+1), HIO <sub>3</sub> (+5), HIO <sub>4</sub> (+7)

8. For group-18 elements the oxidation states are +2, +4, +6 and +8.

Elements	Oxidation state with example
He	
Ne	
Ar	
Kr	KrF <sub>2</sub> ,
Xe	XeF <sub>2</sub> (+2), XeF <sub>4</sub> (+4), XeF <sub>6</sub> (+6), XeO <sub>4</sub> (+8)
Rn	RnF <sub>2</sub> (+2), RnF <sub>4</sub> (+4), RnF <sub>6</sub> (+6)

**2. Diagonal relationship:** The element having similar chemical properties with their own group elements also have the same chemical properties with the element lying diagonally in the next higher group is called the diagonal elements and this phenomenon is known as diagonal relationship.

Group ↓ Period →	1	2	13	14
2	Li	Be	B	C
	Na	Mg	Al	Si

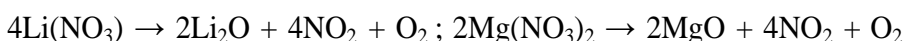
**Causes of Diagonal relationship:** Chemical and physical properties depend on different parameter like atomic size, electronegativity and polarising power. Diagonal elements have similar chemical properties because they have more or less same atomic size, electronegativity and polarising power. Let us consider the pair Li-Mg, to reach Li to Mg there are two roots:

i.  $\text{Li} \rightarrow \text{Be} \rightarrow \text{Mg}$  and ii.  $\text{Li} \rightarrow \text{Na} \rightarrow \text{Mg}$ ; if we consider the first path then from Li to Be  $Z^*$ , electronegativity increases but atomic size decreases and from Be to Mg  $Z^*$ , electronegativity decreases but atomic size increases. As a whole Li and Mg have similar  $Z^*$ , electronegativity and atomic size remains same, therefore chemical properties remains almost same. Similar facts are happen in path (ii) but in the reverse order.

### Chemical similarities between Li and Mg

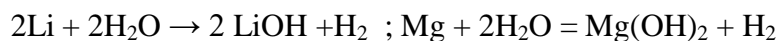
i. Both Li and Mg form hydrated salt e.g  $\text{LiCl} \cdot 2\text{H}_2\text{O} - \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

ii. Oxyacid salt of both Li and Mg are thermally unstable.

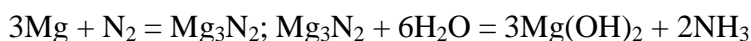


iii. Hydration energy of both Li and Mg are almost comparable.

iv. Both react with water to form hydroxide.



v. Both form nitride when burnt in nitrogen.



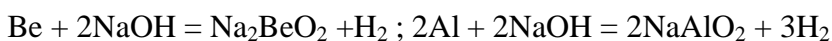
### Chemical similarities between Be and Al

i. Both form covalent compound having lower melting point and higher solubility in organic solvent as they have high polarising power.

ii. They form hydrated species e.g.  $\text{Be}(\text{H}_2\text{O})_4^{2+}$  and  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ .

iii. Both Be and Al are rendered passive by  $\text{HNO}_3$  due to formation of their inert oxide coating.  $\text{Be} + 2\text{HNO}_3 \rightarrow \text{BeO} + \text{H}_2\text{O} + 2\text{NO}_2$ ;  $2\text{Al} + 2\text{HNO}_3 \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{NO}_2$ ;

iv. Be forms beryllates while Al forms aluminates on action with alkalis.



v. Both the metal form amphoteric oxide.



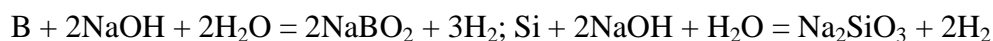
vi. Both  $\text{BeCl}_2$  and  $\text{AlCl}_3$  forms dimeric structure through the bridging by Cl.

### Chemical similarities between B and Si

i) B exist as borates while Si exist as silicates in nature.

ii) Both forms covalent compounds as sum of the ionisation energy is very high.

iii. B forms metaborates and Si forms metasilicates on reaction with alkalis.

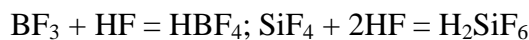
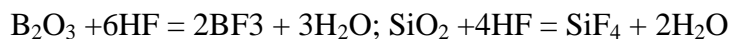


iv. Properties of their oxide are similar.

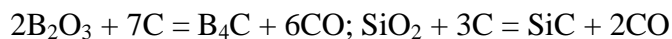
a) Reacts with strong alkali.



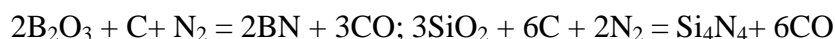
b) Reaction with HF.



v. On heating with C in electric furnace they form carbides.



vi. On heating with mixture of N<sub>2</sub> and C, they form nitrides.



• **Anomalous behaviour of first member of each group:**

1. **In group-1**, Li and its compounds differ from those of the other group elements. This is because of the smaller size and its consequence of the Li metal. Due to smaller size, it has high polarising power, high lattice energy and high hydration energy which effect on the chemical properties of Li. The anomalous behaviour of Li is as follows.

a) The solubility of many Li compounds in water is very low compared to other group elements. That is Li compounds are covalent while other Gr.-1 metal compounds are ionic.

b) Li<sub>2</sub>CO<sub>3</sub> and LiNO<sub>3</sub> are thermally less stable than Na<sub>2</sub>CO<sub>3</sub> and NaNO<sub>3</sub>.

c) Li can form nitride on reaction with N<sub>2</sub> but other group elements do not form (Size effect).

d) Li only form monoxide Li<sub>2</sub>O but group elements form peroxide and superoxide along with monoxide. (e.g. Na<sub>2</sub>O<sub>2</sub>, KO<sub>2</sub>)

e) Except Li other Gr.-1 metals form alum.

2. **In group-2**, Be differs from the rest of the group elements for three reasons

a) It is extremely small in size and according to Fajan's rule its ionic potential value is highest in the group. As a result it forms covalent compounds while other elements form ionic compound.

b) Be has high electronegativity compared to other group elements. Thus when Be reacts with other elements, the difference in electronegativity becomes small and hence compound becomes covalent.

c) Due to lack of d-orbital Be form only 4 bonds but other elements of the group may extent up to 6 bonds. E.g. Be form Be(H<sub>2</sub>O)<sub>4</sub> while Mg form Mg(H<sub>2</sub>O)<sub>6</sub>.

3. **In group- 13** elements, the first elements B differs from other elements.

a) Due to small size B form interstitial metal boride on reaction with metal.

b) Boron compounds are covalent both in solid and solution due to high IE of B<sup>3+</sup> formation.

c) B has high melting point due to unusual crystal structure in which unit cell contain B<sub>12</sub> unit known as icosahedrons.

d) Due to high affinity towards oxygen, it gives rise extensive chemistry involving boron-oxygen link, e.g-borates.

e) Boron only in the group form B-B-B, B-H, B-H-B and B-B bonds.

4. **In group-14** elements, chemical properties of C differs from other elements due to i) small size ii) high electronegativity, iii) restriction of valence shell to octate and iv) high tendency to form p-p  $\pi$  bonds. The following are the anomalous behaviour of C

a) The melting point of C is very high due to high C-C bond energy compared to other elements in the group.

b) C has highest catenation properties and form long chain hydrocarbon through C-C. C=C and C $\equiv$ C bond formation. That happens due to small size and high C-C bond energy.

c) Chemical reactivity of the C is least in the group.

d) Strong tendency to form oxide and fluoride complexes.

5. **In group-15**, Nitrogen shows anomalous behaviour from the rest of the group elements, these are as follows

a) Nitrogen has no scope for valence expansion due to lack of d-orbital but other can expand their valence. Example, N forms only NCl<sub>3</sub> but P forms both PCl<sub>3</sub> and PCl<sub>5</sub>.

b) Nitrogen forms very strong  $p\pi - p\pi$  bonds due to its small size.

c) Nitrogen does not form p-d and d-d  $\pi$  bonds therefore does not form the higher valent oxo compound which gives important chemistry for P and other elements.

d) First element of the group N have high electronegativity, this results in strong hydrogen bonding in their compounds.

6. **In group-16** i) oxygen differs from rest of the group in that it is more electronegative and form ionic compounds. ii) H bonding is very important for oxygen compounds, but recently weak H-bonding in S compounds has been proven. iii) Co ordination number cannot increase beyond 4, but other can show up to 6. iv) Oxygen form strong  $\pi$  bonds in their compounds but  $\pi$  bond becomes weaker in heavier congeners.

7. **In group-17**, fluorine shows somehow different properties from rest of the elements due to its small size and high electronegativity.

i) The small bond dissociation energy of F<sub>2</sub> and small size of F<sup>-</sup> ion, the fluoride compounds have high lattice energy. The lattice energy if somehow greater than their hydration energy, therefore some fluoride compounds are least soluble in water (e.g. LiF, CaF<sub>2</sub>).

ii) Due to small size F<sup>-</sup> ion become hard and almost non polarisable. Therefore in fluoride compounds only weak van der Wall force is operating as a consequence molecules are volatile and low melting (e.g. fluorocarbons).

iii) Bond dissociation energy of  $F_2$  is very low due to repulsion of non-bonding electron pairs in  $F_2$  molecule. Therefore bond energies of fluoride compounds are very high.

iv) It has the highest electronegativity in the periodic table. Therefore fluoride compounds are prone to strong H bonding.

v) In fluorine substituted compounds acid-base properties are greatly influenced compared to non-substituted compounds (e.g.  $CF_3COOH$  is more acidic than  $CH_3COOH$ ).

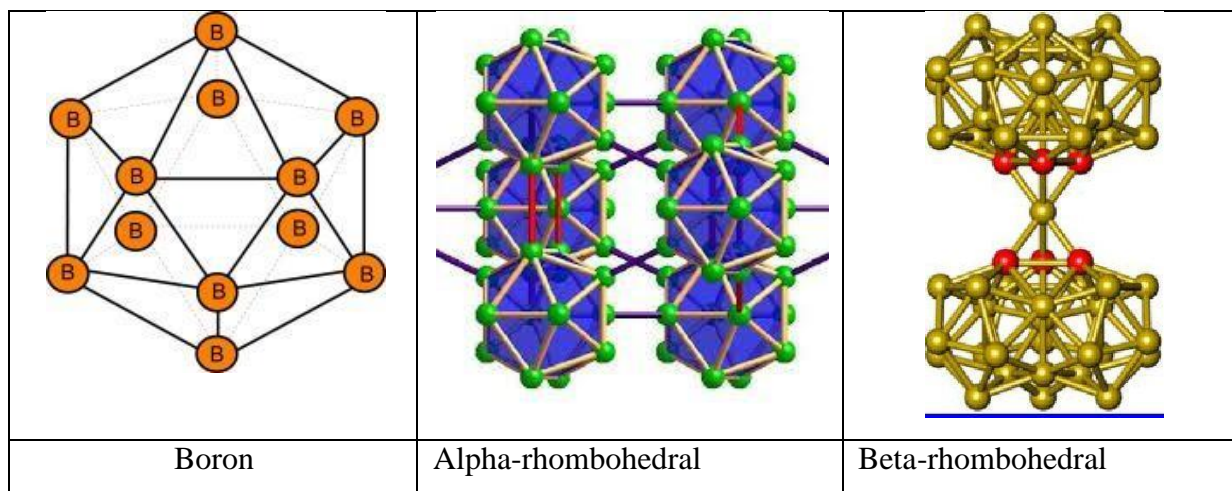
- **Allotropy:**

Many elements occur in more than one form, known as allotropes, which have very different physical and chemical properties.

### Summary of allotropes of Gr-13 to Gr-16

#### Group-13

Elemental boron has several allotropic structures. The alpha-rhombohedral B has a closed packed arrangement of  $B_{12}$  icosahedra and tetragonal B has layers of  $B_{12}$  icosahedra joined by B-B bonds and beta-rhombohedral B has a complicated structure where  $B_{12}$  icosahedra are present at the centre.



#### Group-14

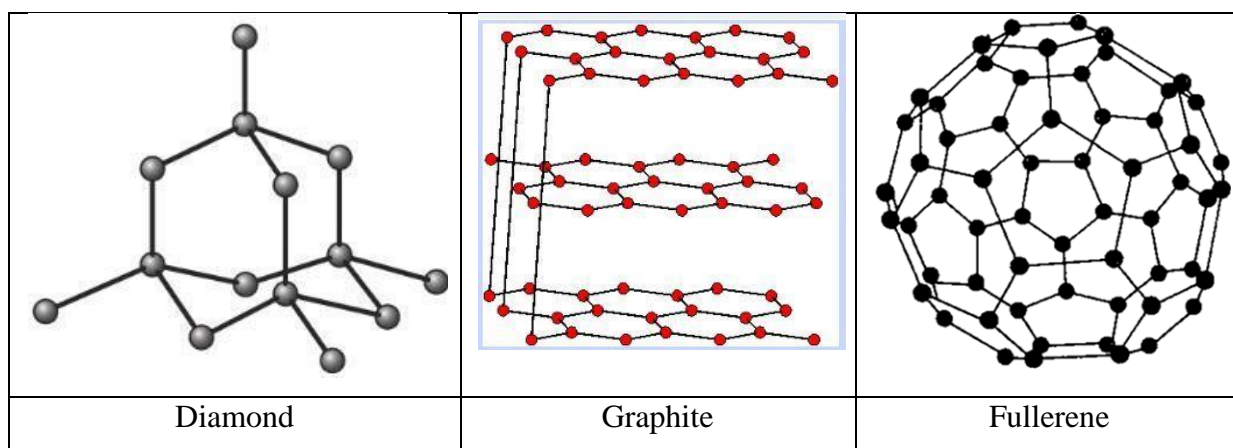
Carbon has two types of allotropic form, crystalline and amorphous. Crystalline allotropes are diamond, graphite and fullerene ( $C_{60}$ ).

Diamond has an infinite solid state structure based on tetrahedrally linked C atoms. Since each C atom is linked with another four C atoms, there is no free electron in the crystal to conduct electricity. Therefore diamond is an insulator.

The thermodynamically more stable form of C is graphite, which has a layer structure. Each layer has shared hexagons based on  $sp^2$  carbon atoms and the layers are separated by 335 pm.

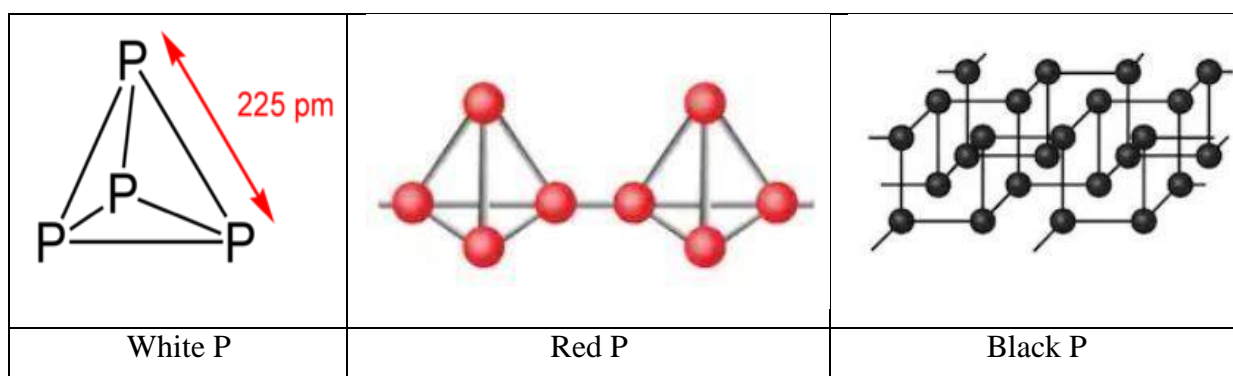
Three valence electrons of C are engaged to form sigma bonds whereas fourth electron present in p orbital perpendicular to the hexagonal plane. These p orbitals generate a delocalized band of  $\pi$  molecular orbitals which extend over the whole layer. Therefore graphite conduct electricity.

Fullerene is most stable allotrope and has formula  $C_{60}$  but other  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$  are also known. They are composed of sigma bonded hexagonal and pentagonal ring of the cage are based on  $Sp^2$  hybridised and additionally there is a delocalized  $\pi$  system perpendicular to the surface of the spherical shell.



### Group-15

Phosphorus has several allotropes like white phosphorus, red phosphorus and black phosphorus. White phosphorus contains the symmetrical tetrahedral  $P_4$  unit with P-P distance 2.21 Å and inter bond angle  $60^\circ$ . Red phosphorus has polymeric structure with linked  $P_4$  tetrahedral. Black P has orthorhombic forms which consist of double layer lattice in which each P atom is bonded to three others at 2.23 Å and bond angle are  $100^\circ$ .



## Group-16

Oxygen has two allotropic forms, dioxygen ( $O_2$ ) and ozone ( $O_3$ ). Oxygen is more stable than ozone.

Sulphur has several allotropic forms. Solid S contains either i) cyclic species or ii) chains species.

**Cyclic species:** The most stable form of S is orthorhombic sulphur which contain  $S_8$  ring in crown conformation. Another form is monoclinic S which also contain  $S_8$  rings but in a different packing. Third one is  $\gamma$  monoclinic sulphur

**Chain species:** These are collectively called Catena sulphur. Examples are amorphous sulfur, Insoluble sulfur, Fibrous sulfur.

- **Catenation:**

The ability of an element to form compounds with element-element bonds is described as catenation. The catenating abilities follow the order –

In group 13,  $B > Al > Ga > In > Tl$

In group-14,  $C > Si = Ge > Sn = Pb$

In group-15,  $N < P > As > Sb > Bi$

In group -16,  $O < S > Se > Te > Po$

- **Complex formation tendency of s and p block elements:**

The small size and the more noteworthy charge of the elements of various groups of p-block empower them to have a more prominent propensity to form complexes as compared to the s-block elements. This tendency of forming complex diminishes down the group as the size of the atoms increments down the group.

- **Hydrides and their classification as ionic, covalent and interstitial**

**Types of Hydrides:** Hydrides are mainly divided into three major types or groups. The categories are decided based on what elements the hydrogen forms bonds with or simply on the basis of chemical bonding. The three types of hydrides are **ionic, covalent, and metallic or interstitial hydrides**. We will learn about them in detail below.

**Ionic Hydrides:** They are formed when hydrogen molecule reacts with highly electropositive s-block elements (Alkali Metals and Alkaline Earth Metals). In solid-state, the ionic hydrides are crystalline, non-conducting and non-volatile. Ionic hydrides include compounds such as sodium hydride (NaH), potassium hydride (KH), calcium hydride ( $CaH_2$ ), and others. This category encompasses all alkali metal hydrides in any form.

**Covalent Hydrides:** Covalent hydrides are formed when hydrogen reacts with other similar

electronegative elements like Si, C, etc. The most common examples are CH<sub>4</sub> and NH<sub>3</sub>. In general, compounds that are formed when hydrogen is reacted with non-metals are called covalent hydrides. The compounds share a covalent bond and are either volatile or non-volatile compounds. Covalent hydrides are also either liquids or gases. Covalent hydrides include compounds such as boron hydrides, nitrogen hydrides, silicone hydride (which is saline), and others

**Metallic Hydrides or Interstitial hydrides:** A hydrogen compound that forms a bond with another metal element is classified as a metal hydride. The bond is mostly covalent type but sometimes the hydrides are formed with ionic bonds. These are usually formed by transition metals and are mostly non-stoichiometric, hard, high melting and boiling points. Various types of metallic hydrides, including magnesium hydride, aluminum hydride, and cadmium hydride, were considered to be examples of this type of metallic hydride.

Li	Be	← Multicentre bonding →										B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac				Poorly Characterized						Covalent Hydride					
Ionic Hydride		Metallic hydride															

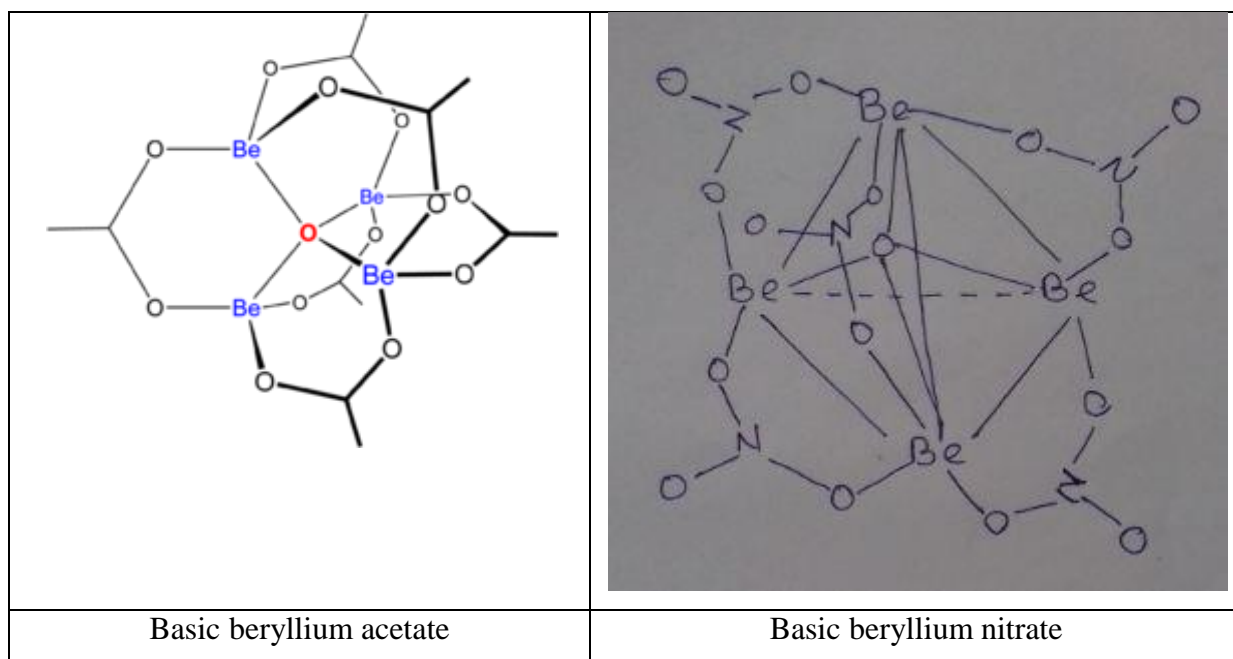
### Basic beryllium nitrate and acetate:

#### i) Basic beryllium nitrate:

Basic beryllium nitrate is covalent and has an unusual structure as shown in the figure below. In which four Be atoms located at the corner of the tetrahedron with six  $\text{NO}_3^-$  groups along the six edges of the tetrahedron and a oxygen (basic) at the centre. The chemical formula is  $[\text{Be}_4\text{O}(\text{NO}_3)_6]$ . Be form similar structure with formula  $[\text{Be}_4\text{O}(\text{R}_6)]$ , where  $\text{R} = \text{NO}_3^-, \text{HCOO}^-, \text{CH}_3\text{COO}^-, \text{C}_2\text{H}_5\text{COO}^-$  etc.

**Synthesis:** Nitrates of the metals can all be prepared in solution and can be crystallised as hydrated salts by the reaction of  $\text{HNO}_3$  with carbonates, oxides or hydroxides. Anhydrous nitrates can be prepared using liquid dinitrogen tetroxide and ethyl acetate.

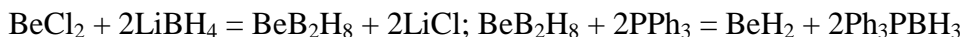
ii) **Basic beryllium acetate:** Basic beryllium acetate is formed when  $\text{Be}(\text{OH})_2$  is evaporated with acetic acid. The structure is similar to basic beryllium nitrate. It is a covalent molecule and soluble in organic solvents. It has low melting point (285) and boiling point(330).



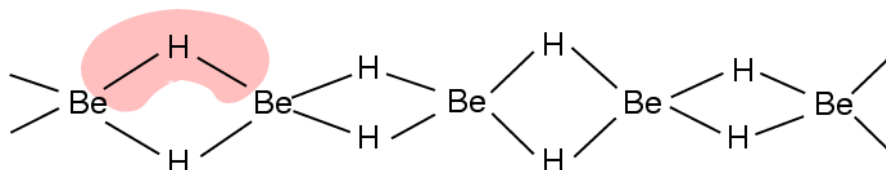
**Study of the following compounds with emphasis on structure, bonding, preparation, properties and uses**

**1. Beryllium hydride**

**Preparation:** i) Pure  $\text{BeH}_2$  can be prepared by reducing  $\text{BeCl}_2$  with lithiumborohydride ( $\text{LiBH}_4$ ) to give  $\text{BeB}_2\text{H}_8$ , then it heated in a sealed tube with triphenylphosphine( $\text{PPh}_3$ ).

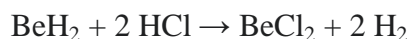
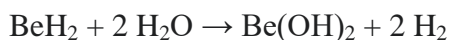


**Structure:** Beryllium hydride is covalent and polymeric and remains as  $(\text{BeH}_2)_n$ .



**Bonding:** Be is bonded to four H atoms. Be has two valence electrons and each H has one electron. Therefore Be has no sufficient electrons to make normal two centre two electrons covalent bond with four H atoms. That is why Be makes three centre two electrons (3c-2e) covalent bond to solve the problem. Therefore each Be atom bonded with four H atoms with 3c-2e bridge bond(which also called a 3c-2e banana bond).

**Reactions:**

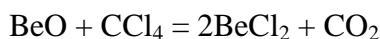
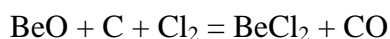


**Uses:** Beryllium hydride of high bulk density, suitable for use as a component of high-energy fuels, is prepared by the pyrolysis, in solution in an inert solvent, of a ditertiary-alkyl beryllium.

**2. Beryllium halides**

Be forms  $\text{BeX}_2$  type halides where  $\text{X} = \text{F}, \text{Cl}, \text{Br}$  and  $\text{I}$ . Beryllium halides are covalent, hygroscopic, do not conduct electricity and fume in air due to hydrolysis. Anhydrous halides cannot be obtained from materials made in aq. solution because hydrated ion  $[\text{Be}(\text{H}_2\text{O})_4]\text{X}_2$  converted to oxide of Be.

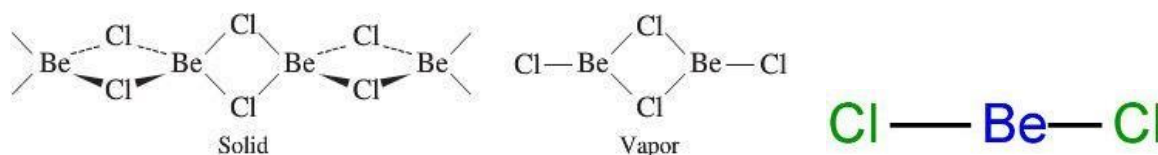
**Preparation:** Reaction of halogen on a mixture of the metal oxide and carbon at  $600\text{-}800^\circ\text{C}$  makes the corresponding halides.



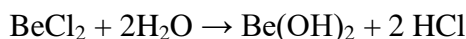
**Structure:**  $\text{BeF}_2$  is a glassy solid containing randomly oriented chain like  $\dots\text{F}_2\text{BeF}_2\text{Be}\dots$ . Each be is coordinated by four F atom making bridge bond similar to  $\text{BeH}_2$ .

BeCl<sub>2</sub> has a polymeric structure at solid state making Cl bridging. Be atoms are sp<sup>3</sup> hybridised with bridging Cl atoms. The ClBeCl bond angle is 109° and increase the bond length of Be-Be around 263 pm and hence minimises the repulsion between Be atoms.

In the gaseous state BeCl<sub>2</sub> form a mixture of dimer and monomer. In dimer Be is sp<sup>2</sup> hybridised whereas in monomer it is sp hybridised.



**Properties:** Beryllium chloride is stable in dry air. Beryllium chloride is a Lewis acid and has been used as a catalyst in some organic reactions. It hydrolyzes, evolving hydrogen chloride:



It forms a tetrahydrate, BeCl<sub>2</sub>•4H<sub>2</sub>O ([Be(H<sub>2</sub>O)<sub>4</sub>]Cl<sub>2</sub>). BeCl<sub>2</sub> is also soluble in oxygenated solvents such as ethers

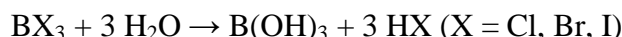
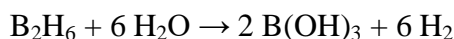
**Uses:** Beryllium chloride is used as a raw material for the electrolysis of beryllium, and as a catalyst for Friedel-Crafts reactions.

### 3. Boric acid and borates:

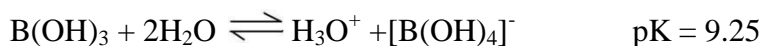
**Preparation:** i) Boric acid may be prepared by reacting borax (sodium tetraborate decahydrate) with a mineral acid, such as hydrochloric acid:



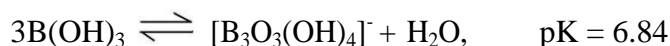
ii) It is also formed as a by product of hydrolysis of boron trihalides and diborane:



**Properties:** i) Orthoboric acid H<sub>3</sub>BO<sub>3</sub> is soluble in water and behaves as a weak acid. It does not donate protons like other acids but rather it accepts OH<sup>-</sup>. It is therefore a Lewis acid and may be written as B(OH)<sub>3</sub>.



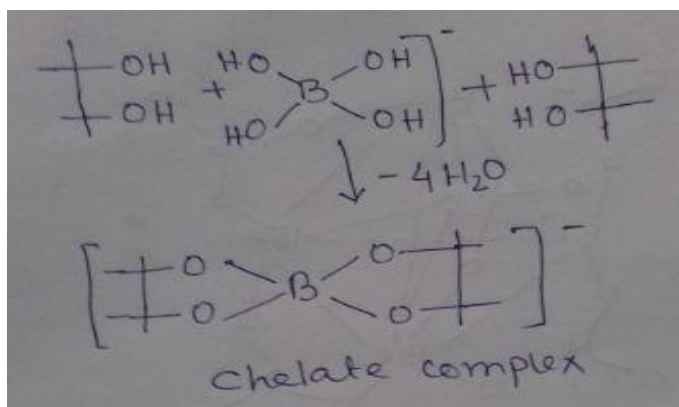
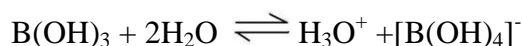
ii) Polymeric metaborate species are formed at higher concentration ‘



iii) Boric acid when heated above 170 °C, it dehydrates, forming metaboric acid (HBO<sub>2</sub>):



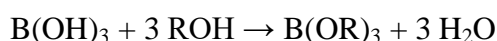
iv) Boric acid is a weak acid and hence cannot be titrated against strong base NaOH using phenolphthalein indicator. Because during titration no sharp end point is not obtained. But in presence of glycerol, mannitol or sugar (Cis diol) it behaves as strong acid. Because  $\text{H}_3\text{BO}_3$  first reacts with water to form  $\text{B}(\text{OH})_4^-$  and  $\text{H}^+$  is liberated and, this is a reversible reaction. Now glycerol is a complexing agent form a stable chelate complex with  $\text{B}(\text{OH})_4^-$  ion, as a result rate of formation of  $\text{H}^+$  will increase and  $\text{H}_3\text{BO}_3$  becomes a strong acid. Therefore  $\text{H}_3\text{BO}_3$  can be titrated with NaOH in presence of phenolphthalein indicator.



v) Boric acid dissolves in anhydrous sulfuric acid:

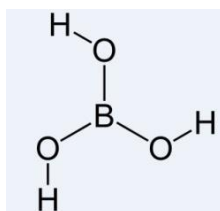


vi) Boric acid reacts with alcohols to form borate esters,  $\text{B}(\text{OR})_3$  where R is alkyl or aryl. A dehydrating agent, such as concentrated sulfuric acid is typically added:



A variety of salts are also known, involving the planar trigonal  $\text{BO}_3^{3-}$  borate anion

**Structure:**



**Uses:** i) Boric acid can be used as an antiseptic for minor burns or cuts.

ii) Boric acid also used as an insecticide to control of cockroaches, termites.

iii) The solution containing boric acid and borax used for fire retarding agent of wood by impregnation

**Borates:** Borates are boron-oxygen compounds which form boron oxyanions. These can be trigonal or tetrahedral in structure. In the simple borates, each B atom is bonded to three oxygen atoms arranged in an equilateral triangle.

i) Orthoborates : The orthoborates contain discrete  $\text{BO}_3^{3-}$  ions. Examples are  $\text{Mg}_3(\text{BO}_3)_2$  and  $\text{LnBO}_3$ .

ii) In metaborates simple units of  $\text{BO}_3$  or  $\text{BO}_4$  join together to form a variety of polymeric chain or ring structures. The example of a most common metaborate is borax  $[\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}]$  which is generally written as  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$