## IITM COLLEGE OF ART, SCIENCES and COMMERCE B.Sc. 2<sup>nd</sup> semester Lecture Notes Section-C

## (P-Block elements, Boron family, Carbon family)

Group 13 to 18 constitute p-block elements. The general configuration for all the atoms belonging to p-block is **ns<sup>2</sup>np<sup>1-6</sup>**. The s and p block elements together forms **representative elements**.

The s-block and p-block elements are so called because their valence electrons are in an s orbital or p orbital respectively. They are also called Typical Elements to distinguish them from the **transition** and inner transition series

# Characteristic Properties of Elements in p-Block of Modern Periodic Table:

Atomic and Ionic Radii - As we move down the group in the p-block one additional shell than the previous element gets included into the following element. This at last increases the nuclear and the ionic radius of each next element down the group, which at last demonstrates that the nuclear and the ionic radii increment down the group. The pattern is not same over the period. As we move towards right in a period the Atomic radii and the Ionic radii of pblock elements diminishes. The atomic radius increases enormously from Boron to Aluminium. This expansion is because of more prominent screening impact created by the eight electrons exhibited in the penultimate shell.

**Ionization Energies -** There are high ionization possibilities in p-block elements. The ionization energies of p-block elements increase towards right in a period because of effectively expanding atomic charge. As indicated by the general patterns the ionization energy values diminishes down the group yet don't diminish smoothly. Ionization Energies in Non-metals is higher than metals. It is most extreme for a noble gas since noble gasses have totally filled configuration. A few elements at the base of a group like Lead, Tin, Thallium, Bismuth, and so forth acts nearly as a metal with low ionization energies.

**Melting and Boiling Points** – The melting and boiling points decrease from top to bottom in a group. The decrease in melting points do not show a regular pattern. However, the decrease in boiling point follow a regular trend down the group.

**Oxidation States** – The oxidation state is related to the number of electrons in the valence shell. The valence shell configuration of group 13 is  $ns^2np^1$ . Since there are three electrons in the valence shell, +3 is the most common oxidation state in their compounds. However, on moving down the group +1 oxidation state becomes more stable than +3 oxidation state. In fact, TI prefers to form compounds in +1 oxidation state rather than in +3 oxidation state. This can be explained as:

Except B and AI, all the elements have either d-electrons (Ga ,In) or both d and f electrons(TI) in there inner electrons. We know that d and f electrons have poor screening effect. Due to this, the nuclear force of attraction increases ad holds the outer *ns*<sup>2</sup> electrons tightly. The two electrons in the s-subshell are inert as they do not get paired. This is called **inert pair effect.** Only 1 electron in p subshell take part in bond formation .Thus the oxidation state decrease by two units in the group top to bottom.

**Electropositive Character –** Electropositive character decreases in a period as the nuclear charge increases and size decreases from left to right in the period. Thus, group 13 is less electropositive and less metallic than the elements of group 1 and 2.B is non metal . Electropositive character increases from top to bottom as the size increases and ionization energy decreases from B to TI.

**Covalent Character –** From the electronic configuration of these elements, all of them would be expected to form M 3+ type ions and the compounds would be ionic. However, the second and third ionisation energies of boron are so high that it has little tendency to form B3+ ion and other elements have higher tendency to form such ions under suitable conditions due to lower ionisation energies. Thus these elements form ionic compounds. Further if trivalent ions are formed, the smaller ions will have more polarising power and will tend to give covalent compounds. This tendency goes on decreasing down the group. That is why B gives covalent compounds, Al forms both covalent and ionic compounds and the higher members result mainly in ionic compound formation.

#### **Anomalous Properties of Boron :**

- Though aluminium is a metal, Boron is a non-metal.
- Aluminium is a good conductor of electricity but Boron is not.

- Boron exists in two structures amorphous and crystalline. Aluminium is a delicate metal and does not exist in various structures.
- The boiling point and melting point of boron are much higher as compared to those of aluminium.
- Boron frames just covalent compounds while aluminium shapes even some ionic compounds.
- The oxides and hydroxides of boron are acidic in nature though those of aluminium are amphoteric.
- The trihalides of boron (BX<sub>3</sub>) are monomers whereas, aluminium halides subsists as dimers (Al<sub>2</sub>X<sub>6</sub>).
- The hydrides of boron are quite inert while those of aluminium are flimsy o.

## **Diagonal Resemblance of Boron With Silicon :**

- Boron and Silicon show the distinctive properties of non-metals. These don't shape cations. Both exist in crystalline and amorphous structures.
- Boron Oxide (B2O3) and silica (SiO2) are both acidic and break up in solutions that are alkaline in nature to frame borates and silicates separately.
- $B_2 O_3 + 6NaOH \rightarrow 2Na BO3 + 3H2O$
- SiO2 + 2NaOH  $\rightarrow$  Na2SiO3 + H2O
- Silicates and borates have tetrahedral SiO4 and BO4 auxiliary units individually.
- The chlorides of both Si and B get hydrolyzed by water to form respective silicic acid and boric acid.

 $\begin{array}{l} \mathsf{BCI}_3 + 3\mathsf{H}_2\mathsf{O} \rightarrow \mathsf{H}_3\mathsf{BO}_3 + 3\mathsf{HCI}\\ \mathsf{SiCI}_4 + 3\mathsf{H}_2\mathsf{O} \ \rightarrow \mathsf{H}_2\mathsf{SiO}_3 + 4\mathsf{HCI} \end{array}$ 

- The hydrides of Boron and Silicon are very stable. Various unstable hydrides are additionally known which burst into flames on introduction to air and are effortlessly hydrolyzed.
- Both these elements are semiconductor by nature.

## HYDRIDES OF BORON: DIBORANE

Boron forms a large number of polymeric hydrides called boranes, e.g. B<sub>2</sub>H<sub>6</sub>, B<sub>4</sub>H<sub>10</sub>,

 $B_5H_9$ ,  $B_5H_{11}$  etc. Diborane ( $B_2H_6$ ) is an important member of this series.

## Preparation of diborane (B<sub>2</sub>H<sub>6</sub>):

Diborane can be prepared by the following methods:

- $\begin{array}{ll} (i) & \text{By the action of ionic hydrides like NaH or CaH_2 on BCl_3} \\ & & 6\text{NaH} + 3BCl_3 \rightarrow B_2H_6 + 6\text{NaCl} \\ & & 3\text{CaH}_2 + 2BCl_3 \ \rightarrow B_2H_6 + 3CaCl_2 \end{array}$
- (ii) By the reduction of BF3 with Li H, Li (BH4) or Na (BH4)  $8BF_3 + 6LiH \rightarrow B_2H_6 + 6LiBF_4$  $BF_3 + 3Na(BH4) \rightarrow 2B_2H_6 + 3Na F$
- (iii) By the reduction of BCl3 with Li [AlH4]  $4BCl_3 + 3Li(AlH_4) \rightarrow 2B_2H_6 + 3LiCl + 3AlCl_3$
- (iv) By the reduction BCl<sub>3</sub> vapours with molecular hydrogen  $2BCl_3$  (vapours) +  $6H_2 \rightarrow B_2H_6$  + 6HCl

**Properties:** It is an inflammable colourless gas, extremely toxic and reactive and stable only at low temperatures in absence of moisture.

## (A) Decomposition:

## (i) By heat:

When heated between 100°C and 250°C, it changes into a number of boranes:  $2B_2H_6 \rightarrow B_4H_{10} + H_2$  $5B_2H_6 \rightarrow B_{10}H_{14} + 8H_2$ 

#### (ii) By water:

B2H6 is readily decomposed (hydrolysed) by water into boric acid and H<sub>2</sub>.

 $\mathsf{B2H6} + \mathsf{6H2O} \rightarrow \mathsf{2H3BO3} + \mathsf{6H2O}$ 

## (iii) By aqueous alkalies:

On passing B2H6 into an aq. solution of alkalies, e.g. KOH, at 0 °C, potassium

hypoborate, K<sub>2</sub> [B2H6O2], is obtained solution. B2 H6 + 2KOH  $\rightarrow$  K2[B2

H6O2] (pot. hypoborate) On diluting this solution, potassium metaborate is formed.

 $\text{K2[B2H6O2]} + 2\text{H2O} \rightarrow 2\text{KBO2} + 5\text{H2}$ 

Evolution of H2 in alkaline medium makes it a useful reducing agent.

## (B) <u>Combustion:</u>

B2H6 is an extremely reactive gas hence under controlled conditions, if reacted

with O2, gives large amount of energy at room temperature

B2H6 + 3O2  $\rightarrow$  B2O3 + 3H2O + Energy (Rocket fuel)

## (C) Action of halogens and halogen acids:

Under different conditions it reacts with halogens (except iodine) and halogen acids.

250C

 $\begin{array}{rrrr} \text{B2H6} + 6\text{Cl2} &\rightarrow & 2\text{BCl3} + 6\text{HCI} \text{ (vigorous reaction)} \\ \text{B2H6} + \text{Br2} &\rightarrow & \text{B2H5Br} + \text{HBr} \text{ (slow reaction)} \\ \text{. B2 H6} + \text{HX} &\rightarrow & \text{B2H5 X} \text{ (X = Cl, Br, I)} + \text{H2.} \end{array}$ 

#### (D) Reaction with alkali metal hydrides:

Alkali hydrides suspended in ether react with diborane and give alkali metal

borohydrides which are used as reducing agents.

 $B2H6 + 2LiH \rightarrow 2Li[BH4]$  $B2H6 + 2NaH \rightarrow 2Na[BH4]$ 

## (E) Reaction with ammonia:

Under different experimental conditions, diborane reacts with ammonia giving various products:

(i) At low temperature of about 1200C, excess of ammonia gives an addition compound, diammoniate of diborane.

 $B_2 + H_6 + 2NH_3 \rightarrow B_2H_6.2NH_3$  (white non-volatile solid)

(ii) At high temperature, B<sub>2</sub>H<sub>6</sub> and NH<sub>3</sub> in 1:2 ratio, react together to form borazine (or borazole) B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>

 $3B_2H_6 + 6NH_3 \rightarrow 2B_3N_3H_6 + 12H_2$ 



The electron diffraction and infra-red spectroscopic studies of B2H6 molecule have shown that this molecule has hydrogen bridge structure (Fig1 a) in which two irregular BH4 tetrahedra have one edge in common and thus two B atoms (B1 and B2) and four terminal Hatoms (Ht) are coplanar (lie in the same plane) while remaining two bridging H-atoms (Hb) are located at the centre above and below the plane, the two planes are perpendicular to each other.

## **Bridged structure of diborane**



The structure of Diborane molecule consists of four <u>hydrogen</u> atoms and that of two boron atoms coming on the same plane. In between these planes, there are said to be two dividing atoms of hydrogen.

The boron atom is known to be sp3 hybridized and has four hybrid orbitals. From these four hybrid orbitals, three of the orbitals have one electron each, and of which one is an empty orbital. The two electrons of the hybrid orbitals in each of the boron atoms form 2 bonds with the 1s hydrogen atoms. The two atoms of boron left with that of each unpaired electron orbital and empty orbital forms the two bridgings (B–H–B) bonds with that of the two 1s hydrogen atoms, is also called as the banana bond.

## **BORAZINE :**

Inorganic benzene is also known as borazine which is an inorganic and a cyclic compound. There are three BH units and three NH units alternate. The chemical formula of inorganic benzene is:

 $B_3N_3H_6$ 



## Why is borazine called "inorganic benzene"?

Borazine is called "inorganic benzene" because the compound is isoelectronic and isostructural with benzene. The other similarities are it is a colourless liquid with aromatic smell. Borazine is said to be aromatic because the number of pi electrons obeys 4n+2 rule and the B-N bond lengths are all equal.

#### Preparation of Borazine :

There are three different ways to prepare inorganic benzene and they are:

- Stock and Pohlands method:

  - $3B_2H_6+6NH_3 \rightarrow 3[B_2H_6.NH_3] \rightarrow 2B_3N_3H_6+12H_{.}$
- The yield obtained by this method is low because there is a simultaneous formation of solid polymeric by-products

#### .Heating BCI<sub>3</sub> with NH<sub>4</sub>CI:

- $3NH_4CI + 3BCI_3 \rightarrow B3N3H3CI3$
- $\bullet \quad B_3N_3H_3Cl3 \text{+} \ NaBH_4 \rightarrow B3N3H6 \text{+} \ B2H6$

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STRUCTURE OF BORAZINE:
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Borazine is isoelectronic with benzene and has similar connectivity, so it is sometimes referred to as "inorganic benzene". This comparison is not rigorously valid due to the <u>electronegativity</u> difference between boron and nitrogen. <u>X-ray crystallographic</u> structural determinations show that the bond lengths within the borazine ring are all equivalent at 1.429 Å, a property shared by benzene. However, the borazine ring does not form a perfect hexagon. The bond angle is 117.1° at the boron atoms and 122.9° at the nitrogens, giving the molecule distinct symmetry.

The <u>electronegativity</u> of boron (2.04 on the <u>Pauling scale</u>) compared to that of nitrogen (3.04) and also the electron deficiency on the boron <u>atom</u> and the lone pair on nitrogen favor alternative <u>mesomer</u> structures for borazine.



## CHEMICAL PROPERTIES :

It reacts with water and alcohol to give addition product, which above 100°C releases H<sub>2</sub> gas.

 $\begin{array}{l} \mathsf{B3N3H6} + \mathsf{3H2O} \rightarrow [\mathsf{BH}(\mathsf{OH})\mathsf{NH2}] \mathsf{3} \rightarrow [\mathsf{B}(\mathsf{OH})\mathsf{NH}] \mathsf{3} + \mathsf{3H2} \\ \mathsf{B3N3H6} + \mathsf{3ROH} \rightarrow [\mathsf{BH}(\mathsf{OR})\mathsf{NH2}] \mathsf{3} \rightarrow [\mathsf{B}(\mathsf{OR})\mathsf{NH}] \mathsf{3} + \mathsf{3H2} \end{array}$ 

On heating , borazine gives a product similar to naphthalene, biphenyl etc.
TRIHALIDES OF BORON –

Lewis Acid Character

The halides react with water to form boric acid..All three lighter boron trihalides (BF<sub>3</sub>, BCl<sub>3</sub>, and BBr<sub>3</sub>) form stable adducts with common Lewis bases.The sequence for the Lewis acidity is  $BF_3 < BCl_3 < BBr_3$ , where  $BBr_3$  is the strongest Lewis acid. This trend is commonly attributed to the degree of -bonding in the planar boron trihalid that would be lost upon pyramidization(The conversion of a molecule's trigonal planar geometry to a tetrahedral one) of the the BX<sub>3</sub>molecule. Boron tribromide (BBr<sub>3</sub>) is a colorless, fuming liquid that is an excellent demethylating or dealkylating agent. Boron tri chloride (BCl<sub>3</sub>) is a colourless, dangerously reactive gas that is a valuable reagent in organic synthesis. Boron trifluoride (BF<sub>3</sub>) is a pungent, colorless, corrosive, toxic gas that forms white fumes in moist air.

## **Boron Halides**

Boron undergoes halogenation to form trihalides with the molecular structure  $BX_3$ , as in the following:

 $2B + 3Br2 \rightarrow 2BBr3$ 

In its most familiar compounds, boron has the formal oxidation state III, or +3. These include oxides, sulfides, nitrides, and halides. The trihalides form planar trigonal structures and are Lewis acids because they readily form adducts with electron-pair donors, which are called Lewis bases. For example, fluoride (F<sup>-</sup>) and boron trifluoride

(BF<sub>3</sub>) combine to give the tetrafluoroborate anion, BF<sub>4</sub><sup>-</sup>. Boron trifluoride is used in the petrochemical industry as a catalyst. The halides react with water to form boric acid: BX3+ 3H2O  $\rightarrow$  B(OH)3+ 3HX

where X can be Cl, Br, or I.

#### Lewis Acidity of Boron Halides

All three lighter boron trihalides,  $BX_3$  (X = F, Cl, Br), form stable adducts with common Lewis bases. Their relative Lewis acidities can be evaluated in terms of the relative exothermicities of the adduct-forming reaction. Such measurements have revealed the following sequence for the Lewis acidity:  $BF_3 < BCl_3 < BBr_3$  (in other words,  $BBr_3$  is the strongest Lewis acid).

This trend is commonly attributed to the degree of  $\pi$ -bonding in the planar boron trihalide that would be lost upon pyramidalization (the conversion of the trigonal planar geometry to a tetrahedral one) of the BX<sub>3</sub> molecule, which follows this trend **BF<sub>3</sub> > BCI<sub>3</sub> > BBr**<sub>3</sub> (that is, BBr<sub>3</sub> is the most easily pyramidalized). The criteria for evaluating the relative strength of  $\pi$ -bonding are not clear, however. One suggestion is that the F atom is small compared to the larger CI and Br atoms, and the lone pair electron in the 2p<sub>z</sub>orbital of F is readily and easily donated, and overlaps with the empty 2p<sub>z</sub> orbital of boron. As a result, the pi donation of F is greater than that of CI or Br. In an alternative explanation, the low Lewis acidity for BF<sub>3</sub> is attributed to the relative weakness of the bond in the adducts F<sub>3</sub>B-L.

#### Boron Tribromide

Boron tribromide (BBr<sub>3</sub>) is a colorless, fuming liquid compound that contains boron and bromine. The reaction of boron carbide with bromine at temperatures above 300 °C leads to the formation of boron tribromide. The product can be purified by vacuum distillation.

BBr<sub>3</sub> is decomposed by water and alcohols. It is an excellent demethylating or dealkylating agent for the cleavage of ethers, also with subsequent cyclization (formation of cyclic molecules), often in the production of pharmaceuticals. The mechanism of ether dealkylation proceeds via the formation of a complex between the boron center and the ether oxygen followed by the elimination of an alkyl bromide to yield a dibromo(organo)borane. The dibromo(organo)borane can then undergo hydrolysis to give a hydroxyl group, boric acid, and hydrogen bromide as products. The electronics industry uses boron tribromide as a boron source in pre-deposition processes for doping in the manufacture of semiconductors.

#### **Boron Trichloride**

Boron trichloride (BCl<sub>3</sub>) is a colorless gas that is a valuable reagent in organic synthesis, but is also dangerously reactive. Boron trichloride is produced industrially by direct chlorination of boron oxide and carbon at 500 °C. The synthesis is analogous to the Kroll process for the conversion of titanium dioxide to titanium tetrachloride. In the laboratory, BF<sub>3</sub> reacts with AlCl<sub>3</sub> to create BCl<sub>3</sub> via halogen exchange. Boron trichloride does not form dimers, although there is some evidence that may indicate dimerization at very low temperatures (20 K). NMR studies of mixtures of boron trihalides shows the presence of mixed halides, which may indicate a four center intermediate (that is, a dimer). The absence of dimerization contrasts with the other trihalides of group 13, which contain four or six coordinate metal centers.

Boron trichloride is a starting material for the production of elemental boron. It is also used in the refining of aluminium, magnesium, zinc, and copper alloys to remove nitrides, carbides, and oxides from molten metal. It has been used as a soldering flux for alloys of aluminium, iron, zinc, tungsten, and monel. Aluminum castings can be improved by treating the melt with boron trichloride vapors.

#### **Boron Trifluoride**

Boron trifluoride (BF<sub>3</sub>) is a pungent, colorless, toxic gas that forms white fumes in moist air. The molecule is isoelectronic with the carbonate anion, CO<sub>3</sub><sup>2-</sup>. BF<sub>3</sub> is commonly referred to as "electron deficient" because of its exothermic reactivity toward Lewis bases. BF<sub>3</sub> is manufactured by the reaction of boron oxides with hydrogen fluoride. Since boron trifluoride is corrosive, the metals suitable for handling boron trifluoride include stainless steel, monel, and hastelloy. In the presence of moisture, boron trifluoride corrodes stainless steel. Polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinylidene fluoride, and

## HALIDE OF ALUMINIUM

polypropylene show satisfactory resistance.

Aluminium chloride (AICl<sub>3</sub>) is a compound of <u>aluminium</u> and <u>chlorine</u>. The solid has a low melting and boiling point, and is covalently bonded. It sublimes at 178 ° C. Molten AICl<sub>3</sub> conducts <u>electricity</u> poorly, unlike more ionic halides such as sodium chloride. It exists in the solid state as a six-coordinate layer lattice.

Aluminium chloride is highly deliquescent, and it can explode in contact with water because of the high heat of hydration. It partially hydrolyses with H<sub>2</sub>O, forming some hydrogen chloride and/or hydrochloric acid.

<u>Aluminium</u> also forms a lower chloride, aluminium(I) chloride (AlCI), but this is very unstable and only known in the vapour phase.

reaction of the elements, <u>aluminium</u> and <u>chlorine</u>. It is commercially available in large quantities.

#### Structure

:



Al atoms in AlCl<sub>3</sub> complete their octets by forming dimers, i.e.it has dimeric structure in which the configuration of chlorine atoms about Al atoms is roughly tetrahedral. In the crystalline state it has layered lattice structure with six coordination no. around. It has polymeric structure at room temperature. At melting point (192.4) C it changes to dimer Al  $_2$ Cl<sub>6</sub> where c.no. of Al is 4 Al<sub>2</sub>Cl<sub>6</sub> has bridged structure. Each Al is tetrahedrally surrounded by 4 Cl atoms. At

still higher temp. Al<sub>2</sub>Cl<sub>6</sub> dissociates to form monomer AlCl<sub>3</sub>. It is a planar triangular with c.no. of Al 3

#### AICl<sub>3</sub> exists as dimer but BF<sub>3</sub> doesn't???

BCI3 and AICI3 both are the example of *electron deficient compounds*, as there are only six electrons in the valency shell of central atom after the formation of the molecule, thus, both the compounds have strong tendency to gain (*two*) electrons, so that their *octet* is completed. In both the cases central atom undergoes *sp2 hybridisation* and both acquire *trigonal planar geometry*. The *sp2 hybridisation* involves **one** s and **two** p orbitals, and **one** p orbital remains **unhybridised**, this unhybridised p orbital lies **perpendicular to the (trigonal) plane of the molecule** which being empty, may *recieve two electrons* from a suitable donor so as to complete it's octet. Now, remember, Chlorine atoms attached to the central atom possess *lone pairs* (three).

The electron deficiency (octet) of Boron in BCI3 is compensated (completed) by formation of *co-ordinate bond between* the *lone pair* of peripheral Chlorine atom and the *empty unhybridised p orbital* of Boron atom, forming  $p\pi$ –  $p\pi$  bonding. Thus, the electron deficiency of BCI3 is compensated by formation of  $p\pi$ – $p\pi$  bonds *within the molecule* so **no dimer forms.** 

However, the electron deficiency of Aluminium atom in AICI3 is compensated (completed) by formation of *co-ordinate bond between lone pair* of Chlorine atom of *another* AICI3 molecule and the *empty unhybridised p orbital* of Aluminium atom, thus forming *dimer*.

So, it is interesting to know that both BCI<sub>3</sub> & AICI<sub>3</sub> are

- 1. halides of group 13 elements
- 2. Electron deficient
- 3. sp2 hybridised
- 4. Have empty one p orbital perpendicular to the plane of the molecule. But, former doesn't forms dimer and later forms a dimer, because both the molecules compensate their electron deficiency by *different ways*. Now, then the question arises is; why both these species are completing it's octet by different ways? This is because, Boron atom is so *small* that it cannot accommodate *four bigger sized* Chlorine atoms, however, Aluminium being bigger atom can do that efficiently and thus

compensates it's electron deficiency by forming dimer.

## **CARBON FAMILY**

Group 14 include Carbon (C) , Silicon (Si), Germanium(Ge) ,tin(Sn) ,lead(Pb) and ununquadium (uuq) which is radioactive. **Occurrence** 

- > Carbon is the 17th most abundant element by weight in the earth crust.
- > It occurs in the native state in form of coal ,graphite and diamond.
- In combined state it occurs widely as metal carbonates, hydrocarbons ,carbohydrates and carbon dioxide in air.
- Silicon is the second most abundant element by weight in the earth crust. It widely occurs in form of silica, and in a wide variety of silicates and clays.
- Germanium occurs in traces and is mainly recovered from flue dust arising from roasting of zinc ore.
- > Germanium and silicon are used to make transistors and Semiconductor devices.
- The natural abundance of tin and lead are 2ppm and 13 ppm. Tin occurs mainly as tinestone or cassitertite.
- > The principal ore of lead is galena. Other words of lead are anglestite and cerussite.

## Electronic configuration :

The general valence shell electronic configuration of elements of group 14 is ns<sup>2</sup> np<sup>2</sup> where n is the number of the outermost principal shell.

Element	Atomic Number	Electronic Configuration	
Carbon	6	[He] 2s <sup>2</sup> 2p <sup>2</sup>	
Silicon	14	[Ne] 3s <sup>2</sup> 3p <sup>2</sup>	
Germanium	32	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>2</sup>	
Tin	50	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup>	
Lead	82	[Xe] 4f <sup>4</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>	

## Covalent radii :

The covalent radii of group 14 elements are smaller than those of the elements of group 13. When we move from group 13 to group 14 within the same period ,the effective nuclear charge increases and hence the covalent radius decreases due to stronger attractive influence of the nucleus on the outer electrons.

Covalent radii of group 14 elements regularly increases as we move down the group. It is due to addition of a new energy shells in each succeeding element. The increase in covalent radius from Silicon onwards is however small due to ineffective shielding of the valence electrons by the intervening d and f orbitals.

## lonisation enthalpy

The first ionisation enthalpies of group 14 elements are higher than those of elements of group 13. Because of greater nuclear charge and smaller size of the atoms of group 14 elements.

The first ionisation enthalpy decreases steadily on moving down the group from carbon to tin. The decrease is very sharp from carbon to silicon while there is a slight

increase in the first ionization enthalpy of lead as compared to that of tin. The decrease in ionization enthalpy down the group from C to Sn is due to increase in atomic size and screening effect of the inner electrons which outweigh the effect of increased nuclear charge. The small increase in ionization enthalpy from Sn to Pb is due to a considerable increase in nuclear charge which outweights the shielding effect of all the electrons in the inner shells including those of 4f and 5d electrons.

## Electronegativity :

The elements of group 14 are more electronegative than group 13 elements because of smaller size.

Electronegativity decreases down from Carbon to Silicon and remains constant from Si to Sn and then slightly increases for Pb.

## Metallic Character :

They are less electropositive and hence less metallic then group 13 elements because of smaller atomic size and higher ionization enthalpy.

On moving down the group metallic character increases. Carbon is strictly nonmetallic, silicon is non-metal, germanium is a metalloid where tin and lead are soft metal with low melting point.

## Melting and boiling point :

The melting and boiling point of group 14 elements are much higher than those of corresponding elements of group 13. The atoms of group 14 form four covalent bonds with each other and hence there exist strong binding forces between their atoms both in the solid as well as in the liquid state. The melting point and boiling point decreases as we move down the group due to corresponding decrease in the interatomic forces of attraction.

## **ALLOTROPES**

Carbon has multiple <u>allotropes</u>. The most common is <u>graphite</u>, which is carbon in the form of stacked sheets. Another form of carbon is <u>diamond</u>, but this is relatively rare. <u>Amorphous carbon</u> is a third allotrope of carbon; it is a component of <u>soot</u>. Another allotrope of carbon is a <u>fullerene</u>, which has the form of sheets of carbon atoms folded into a sphere. A fifth allotrope of carbon, discovered in 2003, is

called <u>graphene</u>, and is in the form of a layer of carbon atoms arranged in a honeycomb-shaped formation.

Silicon has two known allotropes that exist at room temperature. These allotropes are known as the amorphous and the crystalline allotropes. The amorphous allotrope is a brown powder. The crystalline allotrope is gray and has a metallic <u>luster</u>

Tin has two allotropes:  $\alpha$ -tin, also known as gray tin, and  $\beta$ -tin. Tin is typically found in the  $\beta$ -tin form, a silvery metal. However, at standard pressure,  $\beta$ -tin converts to  $\alpha$ -tin, a gray powder, at temperatures below 13.2° Celsius/56° Fahrenheit. This can cause tin objects in cold temperatures to crumble to gray powder in a process known as <u>tin pest</u> or tin rot.

## Anomalous Behaviour Of Carbon :

Carbon, the first member of group 14 ,shows an anomalous behaviour i.e. differ from rest of the members of its family.

The main reason for this difference are :

1) exceptionally small atomic size

b) higher electronegativity

c)higher ionisation enthalpy

d) absence of d orbital in the valence shell

The main point of differences are:

Carbon in form of diamond is very hard as compared to other members of group
14.

2) It has higher melting point and boiling point than other members of the group14.

3) Carbon has only 4 valence orbitals ,therefore ,at the maximum, it can

accommodate 4 pairs of electrons around it. The maximum covalency of carbon is 4.

The other elements of this group due to the presence of d- orbital can expand their covalency to 6.

4) Due to small size and high electronegativity , carbon has a strong tendency to form  $p\pi$ -  $p\pi$  multiple bonds either with itself or with the other items such as oxygen, nitrogen and sulphur.

The remaining elements do not form  $p\pi$ -  $p\pi$  bonds because their atomic orbitals are too large and diffused to have effective overlapping. Instead due to the presence of dorbitals, they have a tendency to form  $d\pi$ - $p\pi$  bonds. Even this tendency to form  $d\pi$  $p\pi$  bonds decreases down the group from Si to Pb as the size of the d- orbitals increases.

<u>Catenation</u> : Carbon has the property of **catenation** which may be defined as the ability of like atoms to link with one another through covalent bonds. This is due to

smaller size and higher electronegativity of carbon atoms and unique strength of carbon carbon bonds. The property of catenation mainly depends upon the strength of element – element bond. Since the bond energy of C-C bond is very large, carbon forms long straight or branched chains or rings of different sizes and shapes. However ,as we move down the group, the element- element bond energies decrease rapidly ,and therefore, the tendency for catenation decreases in the order  $C >> Si > Ge \cong Sn >> PX$ 

## CARBIDES :

- Carbides are generally formed at high temperatures (> 1500 °C).
- Carbides are generally quite stable and exhibit high melting points.
- Carbides can be classified as salt-like, interstitial, and covalent.

## Types of Carbides :

Carbides are compounds composed of carbon and less electronegative elements and they are distinguished by their chemical bonding (ionic, covalent). They are generally prepared from metals or metal oxides at high temperatures (1500 °C or higher) by combining the metal with carbon. Carbides are used in key industrial applications.

## Saline Carbides :

Salt-like (saline) carbides are composed of the highly electropositive atoms, such as the alkali, alkali earth, and group-III metals, mixed with carbon. Aluminum forms carbides, but other elements from group XIII do not. These materials have isolated carbon centers, often described as "C<sup>4-</sup>" in the metanides, "C<sub>2</sub><sup>2-</sup>" in the acetylides, and "C<sub>3</sub><sup>4-</sup>" in the sesquicarbides.

- Methanides are carbides that decompose in water and generate water; aluminum carbide (Al<sub>4</sub>C<sub>3</sub>) and beryllium carbide (Be<sub>2</sub>C) are examples of this class of carbides.
- Acetylides are formed from alkali, alkali earth, and lanthanoid metals with the acetylide anion C2<sup>2-</sup>. Lanthanoids also form carbides with the formula M2C3. Metals from group XI also form acetylides, such as copper(I) acetylide and silver acetylide. Carbides of the actinide elements, which have the structure MC2 and M2C3, are also described as salt-like derivatives of C2<sup>2-</sup>.
- The polyatomic ion C<sub>3</sub><sup>4-</sup> is referred to as an allylenide or sesquicarbide and is found in Li<sub>4</sub>C<sub>3</sub> and Mg<sub>2</sub>C<sub>3</sub>. The allylenide is linear and isoelectronic with CO<sub>2</sub>.

## Covalent Carbides :

Covalent carbides are found in carbides of silicon and boron. The reason these two elements form "covalent" carbides is due to their similar electronegativity and size to carbon. Because of this, their association is completely covalent in character. Silicon carbide has two similar crystalline forms, which are both related to the diamond structure. Boron carbide (B<sub>4</sub>C), on the other hand, has an unusual structure that includes icosahedral boron units linked by carbon atoms. In this respect, boron carbide is similar to the boron-rich borides. Both silicon carbide (also known as carborundum) and boron carbide are very hard and refractory materials. Both materials have important industrial applications.

## Interstitial Carbides :

Interstitial carbides describe the carbides of the group-IV, -V, and VI transition metals. These carbides are metallic and refractory. They are formed so that the carbon atoms fit into octahedral interstices in a close-packed metal lattice when the metal atom's radius is greater than ~135 pm. When the metal atoms are cubic-close-packed (ccp), then filling all of the octahedral interstices with carbon achieves 1:1 stoichiometry with <sup>3</sup>since the octahedral interstices lie directly opposite each other on either side of the layer of metal atoms, filling only one of these with carbon achieves 2:1 stoichiometry. As a result of the packing, they are quite stable and have very high melting points and low electrical resistance.

#### FLUOROCARBONS :

These are most amazing compounds of fluorine and have recently gained much importance because of their interesting uses. Fluorocarbons are derivatives of hydrocarbons in which hydrogen atoms are replaced by fluorine atoms. Fluorocarbons containing 1-20 carbon atoms have been prepared recently.

## PREPARATION :

> By direct reaction between carbon and gaseous fluorine

```
C \, + \, 2F_2 \ \rightarrow CF_4
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By action of SbF3 on chloro derivatives

 $3CCl_4 + 2SbF_3 \rightarrow 3CCl_2F_2 + 2SbCl_3$ 

By fluorination of CH<sub>4</sub> in presence of nitrogen

 $CH_4 + F_2 \ {}_{\rightarrow} \ CH_3F + HF$ 

## **SILICATES :**

**Silicates** are the minerals containing silicon and oxygen in tetrahedral SiO<sub>4</sub><sup>4-</sup> units which are linked together in several patterns. Depending on the way the tetrahedral units are linked, the silicates are classified into the following types.

1. Ortho silicates (or Nesosilicates)

- 2. Pyro silicate (or Sorosilicates)
- 3. Cyclic silicates (or Ring silicates)
- 4. Chain silicates (or pyroxenes)
- 5. Sheet or phyllosilicates
- 6. Three dimensional (or tecto) silicates

**Ortho silicates (or Neso or Island silicates)** are the simplest silicates which contain discrete SiO<sub>4</sub><sup>4-</sup> tetrahedral units. Structural unit of ortho silicate unit is shown below.



top view

7. side view

8. The ortho silicate ion is the strong conjugate base of weak orthosilicic acid as well as it will not persist in aqueous solutions. Hence in nature, ortho silicate minerals are rare and only found with cations which form highly insoluble salts.

- 9. Examples of Ortho silicates:
- 10. 1) Phenacite (also known as phenakite) Be<sub>2</sub>SiO<sub>4</sub>
- 11.2) Willemite Zn<sub>2</sub>SiO<sub>4</sub> A minor silicate ore of zinc. Highly fluorescent (green) under shortwate UV.
- 12. Note: The Be<sup>2+</sup> and Zn<sup>2+</sup> ions are tetrahedrally surrounded by the oxygen atoms of silicate.

**Pyro silicate (or Soro silicate or disilicate)** contain  $Si_2O_7^{6-}$  ions which are formed by joining two tetrahedral  $SiO_4^{4-}$  which share one oxygen atom at one corner (one oxygen is removed while joining). Structure of pyrosilicate is shown below.



- 13. The pyrosilicate ion is less basic than orthosilicate ion. There only one mineral in nature containing pyrosilicate ion.
- 14.E.g. 1) Thortveitite Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>

**Cyclic silicates** contain  $(SiO_3)_n^{2n}$  ions which are formed by linking three or more tetrahedral SiO<sub>4</sub><sup>4-</sup> units cyclically. Each unit shares two oxygen atoms with other units.



1) Benitoite - BaTi(SiO<sub>3</sub>)<sub>3</sub> : containing three tetrahedra arranged cyclically  $[Si_3O_9)^{6-}$ ].

2) Beryl - Be<sub>3</sub>Al<sub>2</sub>(SiO<sub>3</sub>)<sub>6</sub> : containing six-silicate rings [Si<sub>6</sub>O<sub>18</sub>)<sup>12-</sup>]. It is an aluminosilicate. Each aluminium is surrounded by 6 oxygen atoms octahedrally. Well-known varieties of beryl include emerald and aquamarine.

**Chain silicates** or pyroxenes contain  $(SiO_3)_n^{2n}$  ions which are formed by linking 'n' number of tetrahedral  $SiO_4^{4}$  units linearly. Each unit shares two oxygen atoms with other units.

## **Chain Silicates**



Examples of chain silicates:

1) Spodumene - LiAl(SiO\_3)\_2 - a pyroxene mineral consisting of lithium aluminium inosilicate

2) Diopsite - CaMg(SiO<sub>3</sub>)<sub>2</sub>

3) Wollastonite - Ca<sub>3</sub>(SiO<sub>3</sub>)<sub>3</sub>

Note: The formula of cyclic silicates as well as chain silicates is  $(SiO_3)_n^{2n}$ . Hence these are considered as an oligomers of the unknown  $SiO_3^{2^-}$  ion.

The general formula of **Sheet or Phyllo or two dimensional (2-D) silicates** is  $(Si_2O_5)n^{2n}$ . Each SiO<sub>4</sub> tetrahedron shares three oxygen atoms with others and thus by forming two-dimensional sheets. These silicates can be cleaved easily just like graphite. The layers are held together by weak van der Waal's forces.

## Sheet (phyllo) Silicates



E.g.

1) Talc -  $Mg_3Si_4O_{10}(OH)_2$ : It is the main ingredient of soap stone. It is the softest material with a smooth and greasy touch.

2) Micas : General formula is X<sub>2</sub>Y<sub>4-6</sub>Z<sub>8</sub>O<sub>20</sub>(OH,F)<sub>4</sub>

Where X = K, Na, or Ca

Y = AI, Mg, or Fe

$$Z = Si \text{ or } AI$$

E.g. Muscovite mica -  $KAI_2(AISi_3O_{10})(F,OH)_2$  - split into thin layers extremely easily

and Lepidolite - KLi<sub>2</sub>Al(Al,Si)<sub>3</sub>O<sub>10</sub>(F,OH)<sub>2</sub>

3) Clay : It is an aluminosilicate with sheet structure.

4) Kaolinite - AISiO<sub>5</sub>(OH)<sub>5</sub>

## THREE DIMENSIONAL SILICATES (TECTO SILICATES)

The general formula of **three dimensional (3-D) or tecto or Framework silicates** is (SiO<sub>2</sub>)<sub>n</sub>. All the oxygen atoms of SiO<sub>4</sub> are shared with other tetrahedra

and thus by forming three-dimensional network.

E.g.  $SiO_2$  - Quartz, Tridymite and Crystobalite - These are the crystalline forms of silica.

When SiO4<sup>4-</sup> units are replaced by AIO4<sup>5-</sup> units, three

dimensional **aluminosilicates** are formed.

E.g. Feldspar, Zeolites, Ult etc.,

## SOME POINTS :

\* Silicate minerals are very common in the Earth crust since Oxygen and Silicon are the most abundant elements.

\* The degree of polymerization is denoted by Oxygen to Silicon ratio (O/Si). Greater the degree of polymerization, lower will be the O/Si ratio. The values of O/Si for ortho silicates (lease polymerized) = 4:1 while for tecto silicates (most polymerized silicate) = 2:1.

\* With increase in the degree of polymerization, there is decrease in the charge per silicon atom as well as the basicity of silicate mineral. Indeed, silica (SiO<sub>2</sub>) is an acidic oxide.

\* The basic silicate minerals readily react with weak acids and undergo weathering.

#### Silicones - structure and uses :

A **silicone** or **polysiloxane** is any of a number of <u>polymers</u> that include any synthetic compound made up of repeating units of <u>siloxane</u>, which is a chain of alternating <u>silicon</u> atoms and <u>oxygen</u> atoms, combined with <u>carbon</u>, <u>hydrogen</u>, and sometimes other <u>elements</u>.

They are typically heat-resistant and either liquid or <u>rubber</u>-like, and are used in sealants, adhesives, lubricants, medicine, cooking utensils, and thermal and electrical insulation.

Some common forms include <u>silicone oil</u>, <u>silicone grease</u>, <u>silicone rubber</u>, <u>silicone resin</u>, and silicone <u>caulk</u>

The silicones are a group of organosilicon polymers. They have a wide variety of commercial uses.

#### **Preparations :**

The complete hydrolysis of SiCl4 yields silica SiO2, which has a very stable threedimensional structure. The fundamental research of F.S. Kipping on the hydrolysis of alkylsubstituted chlorosilanes led, not to the expected silicon compound analogous to a ketone, but to long-chain polymers called silicones.



The starting materials for the manufacture of silicones are alkyl-substituted chlorosilanes. Thus the hydrolysis of trialkylmonochlorosilane R3SiCl yields hexa- alkylsiloxane.



The dialkyldichlorosilane R2SiCl2 on hydrolysis gives rise to straight chain polymers and, since an active OH group is left at each end of the chain, polymerisation continues and the chain increases in length.

The hydrolysis of alkyl tricholorosilane RSiCl3 gives a very complex cross-linked polymer.



#### Uses :

- 1. Silicones act as excellent insulators for electric motors and other appliances as they can withstand high temperatures.
- 2. Straight chain polymers of 20 to 500 units are used as silicone fluids. They are water repellent because of the organic side group. These polymers are used in waterproofing textiles, as lubricants and as polish.
- 3. Silicone rubber retain their elasticity even at low temperatures and resist chemical attack. They are mixed with paints to make them damp-resistant.
- 4. Silicone resins, a cross-linked polymer used as non-stick coating for pans and are used in paints and varnish.
- 5. Silicone oils are highly stable and non-volatile even on heating. Hence used for high temperature oil bath, high vacuum pump etc.

## IITM COLLEGE OF ART, SCIENCES and COMMERCE B.Sc. 2<sup>nd</sup> semester Lecture Notes Section-C

## P-block elements (Nitrogen family, Oxygen family and Halogen family)

The general valence shell electronic setup of group fifteen elements is ns<sup>2</sup>, np<sup>1-6</sup>. Group 15 elements include nitrogen, phosphorus, arsenic, antimony and bismuth. Nitrogen is the real constituent of the air and records for 78% of it by volume. It is the primary member of this group and happens in a free state as a diatomic gas, N<sub>2</sub>. Phosphorus is a fundamental constituent of animal and plant matter. Phosphate groups are constituents of nucleic acids, that is, DNA and RNA. Around 60% of bones and teeth are made out of phosphates. Phosphoproteins are available in egg yolk, milk, and bone marrow. The rest of the elements of the group, that is, arsenic, antimony, and bismuth, mostly happen as sulfides. For example, Stibnite, Arsenopyrite, and bismuth glance.

#### **Oxides of Nitrogen**

Nitrogen reacts with oxygen and results in a number of nitrogen oxides. The oxidation states of all these oxides are pretty different. They are in the range of +1 to +5. We will look at some of the important oxides below.



This is a colourless and non-flammable gaseous compound that has neutral properties. We know it by the common name, laughing gas. We can prepare it by the decomposing ammonium nitrate under high temperature. This compound is insoluble in water and works as a powerful <u>oxidizer</u> at higher temperatures. It has a slightly sweet odour and appears as a colourless gas. When inhaled in a small amount it causes mirth and euphoria. It is the world's number one inhaled anaesthetic as it works as a quick pain reliever. It can cause a narcotic effect at higher concentrations and lead to death by asphyxia. Laughing gas formula is written as N<sub>2</sub>O NH<sub>4</sub>NO<sub>3</sub>  $\rightarrow$  N<sub>2</sub>O + 2H<sub>2</sub>O

2) Nitrogen Monoxide, NO

This is a colourless and gaseous compound. We can usually prepare it by reducing dilute nitric acid with copper.

 $2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 22H_2O + 2NO$ 

## 3) Dinitrogen Trioxide, N<sub>2</sub>O<sub>3</sub>



Dinitrogen trioxide is a deep blue solid. It has acidic properties. It is prepared by mixing equal parts of nitric oxide and nitrogen dioxide and by further cooling the <u>mixture</u> below  $-21 \degree C$  ( $-6 \degree F$ ).

 $NO \ + \ NO_2 \ \rightarrow \ N_2O_3$ 

#### 4) Nitrogen Dioxide, NO<sub>2</sub>

 $\dot{O} - \dot{N} = \dot{O}$ Nitrogen dioxide is a common oxide of nitrogen. It is a reddish-brown toxic <u>gas</u>. We can know its presence with a sharp odour.



It has angular structure with O-N-O bond angle 134  $^\circ$  . As it has unpaired electron , it has tendency to dimerise.

#### 5) Dinitrogen Tetroxide, N<sub>2</sub>O<sub>4</sub>

It has planar structure and nitrogen – nitrogen bond is long and weak.



Dinitrogen tetroxide is a colourless solid that we can find in equilibrium with nitrogen dioxide. It is a powerful oxidizer and is a common reagent in the production of many chemical compounds.

 $N_2O_4 \rightleftharpoons 2NO_2$ 

#### 6) Dinitrogen Pentoxide, N<sub>2</sub>O<sub>5</sub>



Dinitrogen pentoxide is a colourless solid. Its characteristic property is that it sublimes slightly above room temperature. It is unstable. It is a potentially dangerous oxidizer. We can prepare it by dehydrating nitric acid (HNO3) with phosphorus (V) oxide:  $P_4O_{10} + 12HNO_3 \rightarrow 4H_3PO_4 + 6N_2O$ X- ray studies of this molecule has confirmed that in solid state  $N_2O_5$  exists as  $NO_2^+$  $NO^{3-}$  called Nitronium nitrate. In vapour state, it consists of  $N_2O_5$  molecule.

#### **PHOSPHOROUS:**

This element exists in a few allotropic forms. The main allotropes of phosphorus include the white phosphorus, red phosphorus and black phosphorus. In addition to these, there also exists a violet phosphorus. However, that is not a significant allotrope. So, let us start with the various allotropes of phosphorus now. White Phosphorus

It is a common allotrope of phosphorus. White phosphorus is a waxy and translucent solid. It is very delicate and needs proper handling. It is insoluble in water. However, it dissolves in carbon disulphide or carbon tetrachloride. It breaks down in boiling caustic soda in a latent air and produces sodium hypophosphite and phosphine.

P4 +	3 NaOH + 3H <sub>2</sub> O	$\rightarrow$ PH3	+	3NaH <sub>2</sub> PO <sub>2</sub>
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White	Caustic	Phosphine	Sodium
phosphorus	soda		hydrophosphite

Structure of White Phosphorus



In the above diagram, we see the structure of white phosphorus. As we can see, it has a tetrahedral shape. Every phosphorus particle has a covalent bond with three different atoms of phosphorus. There exist weak Van Der Waals forces of attraction between these particles. We must remember that this element is very reactive and too harmful.

- The melting point is quite low at 44°C.
- As we see, the bond angle in a P<sub>4</sub> particle is 60°. This is comparatively very less as compared to a normal bond angle or a hypothetical bond angle. Therefore, it has a strain in itself. This is why white phosphorus is highly unstable and reactive.
- White phosphorus catches fire suddenly in the air at around 35°C. As you can notice, this temperature is marginally higher than the normal room temperature. This is the reason why it is kept in water. After combustion, it produces phosphorus pentoxide.  $P_4 + 5O_2 \rightarrow 2P_2O_5$  or  $P_4O_{10}$
- When it comes in contact with moist air, white phosphorus undergoes an oxidation reaction. This reaction leads to a sparkling discharge of light. As an outcome, it sparkles oblivious.
- White phosphorus displays chemiluminescence.

Red Phosphorus

• We can obtain red phosphorus by heating white phosphorus to around 250°Celsius within the sight of daylight.

White phosphorous  $\xrightarrow{540 \text{ K}}$  Red phosphorus (Inert atmosphere)

- Red phosphorus is iron-grey in colour. It is a radiant and bright crystalline solid.
- It is non-poisonous and does not have any odour. Red Phosphorus does not dissolve I water and also in carbon tetrachloride.
- It doesn't break up in boiling caustic soda-like white phosphorus. In fact, it disintegrates in alcoholic potash.
- We can find it in the state of a polymeric solid.



- It is steady under ordinary conditions and doesn't catch fire in the air.
- However, it experiences burning when we warm it to around 400°C.
- Red phosphorus doesn't show chemiluminescence.
- •

## Black Phosphorus

.

• We can prepare black phosphorus from white phosphorus by heating it to 470K at inert temperature.

White phosphorus  $\xrightarrow{470 \text{ K}}$  Black phosphorus

(Inert atmosphere)

- Black phosphorus is the most stable allotrope of phosphorus. It has a layered structure. It is a very highly polymerised form of the element.
- We can find black phosphorus in two main forms. They are alpha black phosphorus and beta black phosphorus.



- While beta black phosphorus forms when white phosphorus is heated at 473K, alpha black phosphorus forms when we heat red phosphorus at 803K.
- Beta black phosphorus conducts electricity while alpha black phosphorus doesn't conduct electricity.

## Uses of Phosphorus

Phosphorus compounds assume a vital part of life forms. Phosphorus forms a basic constituent in the animal and plant matter.We find it present in blood, bones and the brain of all the animals and also, in living cells. A few of its compounds find applications in industries. The most essential of these chemicals are orthophosphoric acid and phosphatic composts.

## **Oxides of Phosphorus**

<u>Phosphorus</u> forms two common oxides, phosphorus(III) oxide (or tetraphosphorus hexoxide),  $P_4Q_6$ , and phosphorus(V) oxide (or <u>tetraphosphorus decaoxide</u>),  $P_4O_{10}$ . Both oxides have a structure based on the tetrahedral structure of elemental white phosphorus. Phosphorus(III) oxide is a white <u>crystalline solid</u> that smells like garlic and has a poisonous vapour. It oxidizes slowly in air and inflames when heated to 70 <u>°C</u> (158 °F), forming P<sub>4</sub>O<sub>10</sub>. It is the acid <u>anhydride</u> of <u>phosphorous acid</u>, H<sub>3</sub>PO<sub>3</sub>, that is produced as

## 1)Phosphorus Oxide

P<sub>4</sub>O<sub>6</sub> dissolves slowly in cold water. Phosphorus(V) oxide is a white flocculent powder that can be prepared by heating elemental phosphorus in excess oxygen. It is very stable and is a poor oxidizing agent. The P<sub>4</sub>O<sub>10</sub> molecule is the acid anhydride of <u>orthophosphoric acid</u>, H<sub>3</sub>PO<sub>4</sub>. When P<sub>4</sub>O<sub>10</sub> is dropped into water, it makes a hissing sound, heat is liberated, and the acid is formed. Because of its great <u>affinity</u> for water, P<sub>4</sub>O<sub>10</sub> is used extensively as a drying agent for gases and for removing water from many compounds

 $.\mathsf{P4O_{10}+6H_2O} \rightarrow 4H_3PO_4$ 

## Preparation

It is obtained by the combustion of phosphorus in a limited supply of air at low temperature.  $P_4 + 3 O_2 \rightarrow P_4 O_6$ By-products include red phosphorus sub oxide

## **Chemical Properties**

Phosphorus trioxide reacts with water to form <u>phosphorous acid</u>, reflecting the fact that it is the anhydride of that acid.<sup>[2]</sup>

 $P_4O_6 + 6 H_2O \rightarrow 4 H_3PO_3$ 

It reacts with <u>hydrogen chloride</u> to form  $H_3PO_3$  and <u>phosphorus trichloride</u>.

 $P_4O_6 + 6 \text{ HCl} \rightarrow 2 \text{ H}_3PO_3 + 2 \text{ PCl}_3$ 

With chlorine or bromine it forms the corresponding <u>phosphoryl halide</u>, and it reacts with iodine in a sealed tube to form <u>diphosphorus tetra iodide</u>.<sup>[1]</sup>

P4O6 reacts with ozone at 195 K to give the unstable compound P4O18.[3]



## 2) Phosphorus Tetraoxide

#### Diphosphorus tetraoxide, or phosphorus tetroxide is an inorganic

<u>compound</u> of <u>phosphorus</u> and <u>oxygen</u>. It has the empirical <u>chemical formula</u> P 20

Solid phosphorus tetroxide (also referred to as phosphorus(III,V)-oxide) consists of variable mixtures of the mixed-valence oxides  $P_4O_7$ ,  $P_4O_8$  and  $P_4O_9$ 

## Preparation

Phosphorus tetroxide is obtainable by <u>thermal decomposition</u> of <u>phosphorus trioxide</u>, which <u>disproportionate</u> above 210 °C to form phosphorus tetroxide, with elemental phosphorus as a by-product:

## 3) Phosphorus Pentoxide:

**Phosphorus pentoxide** is a <u>chemical compound</u> with molecular formula  $\underline{P}_4\underline{O}_{10}$  (with its common name derived from its <u>empirical formula</u>,  $P_2O_5$ ). This white crystalline solid is the <u>anhydride</u> of <u>phosphoric acid</u>. It is a powerful <u>desiccant</u> and <u>dehydrating agent</u>.

## Preparation

 $P_4O_{10}$  is prepared by burning tetra phosphorus with sufficient supply of oxygen:  $P_4$  + 5  $O_2 \rightarrow P_4O_{10}$ 

For most of the 20th century, phosphorus pentoxide was used to provide a supply of concentrated pure <u>phosphoric acid</u>. In the thermal process, the phosphorus pentoxide obtained by burning white phosphorus was dissolved in dilute <u>phosphoric acid</u> to produce concentrated acid.<sup>[6]</sup> Improvements in filter technology is leading to the "wet phosphoric acid process" taking over from the thermal process, obviating the need to produce <u>white phosphorus</u> as a starting material.<sup>[7]</sup> The dehydration of phosphoric acid to give phosphorus pentoxide is not possible as on heating metaphosphoric acid will boil without losing all its water.



## **Oxoacids of Phosphorus :**

In simple terms, oxoacids are the acids containing oxygen. Phosphorus is one such element that forms a number of oxoacids. A few common oxyacid include  $H_3PO_4$ ,  $H_3PO_3$ , etc.

In oxoacids of phosphorus, we see that the phosphorus is tetrahedrally surrounded by other atoms. Generally, it is clear that there are at least one P=O bond and one P–OH bond in these acids. P–P or P–H bonds are also present besides the P=O bonds and P–OH bonds in oxoacids of phosphorus. In these cases, the oxidation state of phosphorus is less than +5.

These acids are generally seen to jump to higher and lower oxidation states. For example, upon heating, phosphorous acid disproportionates to result in phosphoric acid and phosphine.

The P-H bonds in oxoacids are not ionisable to give H<sup>+</sup> ions. On the other hand, the H atoms attached to oxygen in P-OH form are ionisable. Hence, we can say that basicity is the property exhibited by the H atoms that are attached to oxygen.

As a result, phosphorous acid, H<sub>3</sub>PO<sub>3</sub> is dibasic as it has two P-OH bonds. Similarly, phosphoric acid, H<sub>3</sub>PO<sub>4</sub> is tribasic as it has three P-OH bonds. The oxoacids of phosphorus that have P-H bonds exhibit strong reducing properties. For example, hypophosphorous acid containing two P-H bonds is a very good reducing agent. 4AgNO<sub>3</sub> + 2H<sub>2</sub>O + H<sub>3</sub>PO<sub>2</sub>  $\rightarrow$  4Ag + 4HNO<sub>3</sub> + H<sub>3</sub>PO<sub>4</sub>

Few	Popula	ar Oxoa	cids of	Phos	phorus
	· opan				p1101 a0

Name	Formula	
Hypophosphoric acid	$H_4P_2O_6$	
Metaphosphoric acid	HPO <sub>2</sub>	
Pyrophosphoric acid	H4P2O7	
Hypophosphorous acid	H <sub>3</sub> PO <sub>2</sub>	
Phosphorous acid	H <sub>3</sub> PO <sub>3</sub>	
Peroxophosphoric acid	H <sub>3</sub> PO <sub>5</sub>	
Orthophosphoric acid	H <sub>3</sub> PO <sub>4</sub>	

1) Phosphorus acid, H<sub>3</sub>PO<sub>3</sub>



Phosphorous acid is a diprotic acid. This means that it ionizes two protons. We can describe it in a better manner by the structural formula HPO(OH)<sub>2</sub>. We can prepare phosphorous acid by the hydrolysis of phosphorus trichloride with acid or steam. PCl3 +  $3H_2O \rightarrow HPO(OH)_2 + 3HCI$ 

#### 2) Orthophosphoric acid, H<sub>3</sub>PO<sub>4</sub>

Phosphoric acid is a triprotic acid. This means that it can ionise three protons. It is a non-toxic acid, when pure. It is solid at the room temperature and pressure. We can prepare phosphoric acid by adding sulfuric acid to tricalcium phosphate rock:  $Ca_5(PO_4)_3X + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4.2H_2O + HX$  (X can be F, Cl, Br, and OH).



#### 3) Metaphosphoric Acid (HPO<sub>3</sub>)n

We can obtain it by warming orthophosphoric acid to around 850 K. It does not exist as a monomer. It exists as a cyclic trimer, cyclic tetramer or <u>polymer</u>.



## 4) Hypo phosphorous acid (HPA

Hypophosphorous acid (HPA), or **phosphinic acid**, is a phosphorus oxyacid and a powerful reducing agent with molecular formula  $H_3PO_2$ . It is a colorless low-melting compound, which is soluble in water, dioxane, and alcohols.



#### 5) Pyro phosphoric acid,

Pyrophosphoric acid, also known as **diphosphoric acid**, is the inorganic compound with the formula  $H_4P_2O_7$  or, more descriptively,  $[(HO)_2P(O)]_2O$ . Colorless and odorless, it is soluble in <u>water</u>, diethyl ether, and ethyl alcohol. The anhydrous acid crystallizes in two polymorphs, which melt at 54.3 °C and 71.5 °C. The compound is not particular useful, except that it is a component of polyphosphoric acid and the conjugate acid of the pyrophosphate anion. Anions, salts, and esters of pyro phosphoric acid are called pyrophosphates.



#### 6)Hypophosphoric Acid

Hypophosphoric acid is a mineral acid with the formula  $H_4P_2O_6$ , with **phosphorus** in a formal oxidation state of +4. In the solid state it is present as the dihydrate,  $H_4P_2O_6\cdot 2H_2O$ . In hypophosphoric acid the **phosphorus** atoms are identical and joined directly with a P-P bond.

**Chemical formula:** H<sub>4</sub>P<sub>2</sub>O<sub>6</sub> **Molar mass:** 161.98 g/mol



# Oxygen family( Group-16)

Group 16 consists of elements oxygen, sulphur, selenium, tellurium, and polonium, The four members are called chalcogens, because these are ore forming elements. Polonium is radioactive element with short half life period. The general configuration of oxygen family is  $ns^2np^{6}$ . The

The group 16 elements of modern periodic table consist of 5 elements oxygen, sulphur, selenium, tellurium and polonium. The elements in this group are also known as the chalcogens or the ore-forming elements because a large number of elements can be extracted from the sulphide or oxide ores.



Occurrence of group 16 elements of the modern periodic table

Oxygen is abundantly found on the earth. Estimating the proportions of different types of atoms found in the universe, oxygen was claimed as the fourth abundant element after hydrogen, helium, and neon. It constitutes about 89% of water, 46% of the earth crust and 20 % of the air.

Period	Element	Symbol	Atomic Number	Electronic Configuration
2	Oxygen	0	8	[He] 2s <sup>2</sup> 2p <sup>4</sup>
3	Sulphur	S	16	[Ne] 3s <sup>2</sup> 3p <sup>4</sup>
4	Selenium	Se	34	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>4</sup>
5	Tellurium	Те	52	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>4</sup>
6	Polonium	Ро	84	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>4</sup>

### Oxygen:

The chemical symbol for oxygen is given as O. It is a colourless and odourless gas used in the respiration process by humans, which is converted into carbon dioxide. Oxygen exists as a diatomic molecule ( $O_2$ ). Oxygen is also found as a triatomic molecule ( $O_3$ ) in traces, it is known as ozone. Oxygen combines readily with many elements. During the combination with some elements, the evolution of heat energy takes place, this process is known as combustion.

#### Sulphur:

Sulphur is denoted by the symbol S. It is a non-metal which ranks ninth on the basis of cosmic abundance. About 1 atom in every 20,000-30,000 atoms is a sulphur atom. Sulphur is found in the combined state as well as in the free state. About 0.09 % of sulphur is found in seawater in the form of sulphates. The meteorite contains 12 % of sulphur, a large amount of sulphur is found from the underground deposits of pure sulphur present in dome-like structures. Here sulphur is formed by the action of anaerobic bacteria on the sulphate minerals such as gypsum.

#### Selenium:

Selenium is rarer than oxygen or sulphur. It is found in the free state as well as in the combined state with heavy metals (as lead, silver, or mercury) in a few minerals. Grey metallic form of the selenium is the most stable form of the element under normal conditions.

#### Tellurium:

Tellurium is a chemical element having atomic number 52 and has the properties between metals and non-metals. It is one of the rarest stable elements found in the earth's crust. It is often found in a free state and in compounds with elements such as copper, lead, silver or gold.

#### Polonium:

It is the rarest element among the group 16 elements. It is a radioactive element. Polonium is sometimes used in scientific applications for alpha radiation

# Atomic and Physical Properties and the Trends of Group 16 elements

- Atomic and Ionic Radii: The atomic and ionic radius increases as we move from Oxygen to Polonium.
- **Ionization Enthalpy:** Ionization enthalpy decreases with increase in the size of the central atom. Therefore, it decreases as we move from Oxygen to Polonium since the size of the atom increases as we move down.
- Electron Gain Enthalpy: The elect
- ron gain enthalpy decreases with increase in the size of the central atom moving down the group. Oxygen molecule has a less negative electron gain enthalpy than sulfur. This is on the grounds that Oxygen, because of its compressed nature encounter more repulsion between the electrons effectively present and the approaching electron.
- Electronegativity: The electronegativity decreases as we move down the group. Therefore, it decreases as we move from oxygen to polonium due to increase in nuclear size.Learn about Electronegativity here in detail.
- Nature of the Group 16 Elements: Oxygen and Sulfur are non-metals, Selenium and Tellurium are metalloids and Polonium is a metal under typical conditions. Polonium is a <u>radioactive</u> element.
- Allotropy: Each one of the element of group 16 displays allotropy. Oxygen has two allotropes: Oxygen and Ozone. Sulphur exists as many allotropic forms but only two of them are stable, which are: Rhombic Sulphur and Monoclinic Sulphur. Selenium and Tellurium are found in both <u>amorphous and crystalline</u> forms.
- The Melting and Boiling Points: As the atomic size increases from oxygen to tellurium, the melting and boiling points also increase. The huge distinction between the melting and boiling points of oxygen and sulfur might be clarified on the premise that oxygen exists as a diatomic atom while sulfur exists as a polyatomic particle.
- **Oxidation States:** The group 16 elements have a configuration of ns<sup>2</sup> np<sup>4</sup> in their outer shell, they may accomplish noble gas configuration either by the gain of two electrons, framing M<sup>-2</sup> or by sharing two electrons, in this manner shaping two covalent bonds.

Thus, these elements indicate both negative and positive oxidation states. The regular oxidation states showed by the elements of group 16 incorporate -2, +2, +4 and + 6. **Chemical Properties** 

The group sixteen elements react with hydrogen to form hydrides of the sort  $H_2E$ , where E could be any element- oxygen, sulfur, selenium, tellurium or polonium.

 $H_2 + E \rightarrow H_2E$ 

Hydrogen Group 16 Hydride

Element

### The Physical States of Hydrides of Group 16 Elements

Water is an odourless and colourless liquid but the hydrides of the various elements of this group are poisonous gases which are colourless with disagreeable smells. The boiling point of these hydrides extraordinarily diminishes from water to hydrogen sulfide, and after that increases. Water has an anomalously high boiling point since its particles are bonded with each other by the hydrogen bonds in both its liquid as well as solid states.

#### **Oxoacids of Sulfur**

- ÷.
- 1) Sulphuric Acid, H<sub>2</sub>SO<sub>4</sub>



Sulphuric acid is possibly the most common oxoacid. We have seen a lot of applications of this acid, haven't we? It is a diprotic acid. It signifies its property of ionising into two protons. In sulphuric acid, one atom of sulphur bonds to two hydroxyl groups. The other two oxygen atoms form pie bonds with the atom.

Thus, sulphuric acid exhibits tetrahedral geometry. As the bond length of the sulphuroxygen bond (S=O) is quite less as compared to the bond length of S-OH, the oxygen atoms repel the OH groups. Hence, the bond angle of O=S=O bond is greater than the HO-S-OH bond angle. We produce it industrially by the contact process.

## 2) Sulphurous Acid, H<sub>2</sub>SO<sub>3</sub>



Sulphurous acid is a diprotic acid and thus, gives rise to two protons. In sulphurous acid, one atom of sulphur bonds with two hydroxyl groups. Also, one oxygen atom forms a pie bond with the sulphur atom. We prepare this by dissolving sulfur dioxide in water. As of this date, we do not have any evidence of the existence of sulphurous acid in solution phase. However, the molecule is capable to be isolated in its gaseous phase.

#### 3) Peroxodisulphuric Acid, H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

## Peroxydisulfuric acid, H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>



Peroxodisulphuric acid contains sulphur in +6 oxidation state. Thus, it acts as a very strong oxidizing agent. It is, also, very explosive in nature. We know it by the common name, Marshall's acid.

It contains one peroxide group that acts as a bridge between the two sulphur atoms. Each atom connects to one hydroxyl group (S-OH bond) and two oxygen atoms (S=O bond) other than the peroxide group. We can prepare it by the reaction of the chlorosulfuric acid with hydrogen peroxide. The reaction is given as follows:  $2CISO_3H + H_2O_2 \rightarrow H_2S_2O_8 + 2HCI$ 

4)-Pyrosulphuric Acid, H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>



**Pyrosulphuric acid** is also known as oleum. Its molar mass is 178.13 g/mol. It is an anhydride of sulphuric acid, is a colourless, crystalline solid and has a melting point of 36°C. It can be prepared by reacting excess sulphur trioxide with sulphuric acid. The reaction goes like this:

 $H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$ 

It reacts with bases to form salts which are called pyrosulphates. We use it in the manufacturing of explosives and dyes. it is also used in petroleum refining. It is a strong dehydrating agent and is corrosive in nature. It can cause burns on the skin and irritation to the eyes. Long exposure can prove to be fatal.

# Group -17 (Halogen Family)

The group 17 elements include fluorine(F), <u>chlorine</u>(Cl), bromine(Br), iodine(I) and astatine(At) from the top to the bottom. They are called "halogens" because they give salts when they react with <u>metals</u>.

## **Electronic Configuration of Group 17 Elements**

The valence shell electronic configuration of these electrons is ns<sup>2</sup>np<sup>5</sup>. Thus, there are 7 electrons in the outermost shell of these elements. The element misses out on the octet configuration by one electron. Thus, these elements look out to either lose one electron and form a covalent bond or gain one electron and form an ionic bond. Therefore, these are very reactive non-metals.

## **Atomic Properties :**

## 1) Ionic and Atomic Radii

The nuclear and atomic radii of these elements keep on increasing as we move down the group. This happens because of the addition of an extra energy level. They have the minimal atomic radii compared to the other elements in the related periods. This can be attributed to the fact that their atomic charge is quite powerful.

#### 2) Ionisation Enthalpy

These elements have higher ionization enthalpy. This value keeps on diminishing as we move down the group. This happens because of the increase in the size of the nucleus. However, it is interesting to note that fluorine has the highest ionization enthalpy than any other halogen, thanks to its minute size!

## 3) Electron Gain Enthalpy

The electron gain enthalpy of these elements becomes less negative upon moving down the group. Fluorine has lesser enthalpy than chlorine. We can attribute it to the small size and the smaller 2p sub-shell of the atom of fluorine.

#### 4) Electro-Negativity

The halogens exhibit high electro-negativity values. However, it diminishes slowly on moving down the group from fluorine to iodine. this can be attributed to the increase in nuclear radii upon moving down the group.

## **Physical Properties :**

#### .Physical state:

The group 17 elements are found in diverse physical states. For example, Fluorine and Chlorine are gases. On the other hand, Bromine is a liquid and lodine is solid.

- Colour: These elements have a variety of colours. For example, while Fluorine is pale yellow in colour, lodine is dark violet in colour.
- **Solubility:** Florine and Chlorine are soluble in water. On the other hand, Bromine and lodine are very less soluble in water.
- Melting and boiling points: Melting and boiling points of these elements increase as we move down the group from Fluorine to Iodine. Thus, Fluorine has the lowest boiling and melting points.

•

## Chemical Properties.:

### 1) Oxidising Power

All the halogens are great oxidizing agents. Of the list, fluorine is the most powerful oxidizing agent. It is capable of oxidizing all the halide particles to halogen. The oxidizing power reduces as we move down the group. The halide particles also act as reducing agents. However, their reducing capacity decreases down the group as well.

### 2) Reaction with Hydrogen

All halogens react with hydrogen and produce acidic hydrogen halides. The acidity of these hydrogen halides reduces from HF to HI. Fluorine reacts violently and chlorine requires the sunlight. On the other hand, bromine reacts upon heating and iodine needs a catalyst

## 3) Reaction with Oxygen

Halogens react with oxygen to form oxides. However, it has been found that the oxides are not steady. Beside oxides, halogens also form a number of halogen oxoacids and oxoanions.

#### 4) Reaction with Metals

As halogens are very reactive, they react with most of the metals instantly and form the resulting metal halides. For example, sodium reacts with chlorine gas and forms sodium chloride. This process is an exothermic one and gives out a bright yellow light and a lot of heat energy

 $2Na_{(s)} + CI_{2(g)} \rightarrow 2NaCI_{(s)}$ 

Metal halides are ionic in nature. This is because of the high electronegative nature of the halogens and high electropositivity of the metals. This ionic character of the halides reduces from fluorine to iodine.

## **Interhalogen Compounds**

We can refer to the Interhalogen Compounds as the subordinates of halogens. These are the compounds having two unique sorts of halogens. For example, the common interhalogen compounds include Chlorine monofluoride, bromine trifluoride, iodine pentafluoride, iodine heptafluoride, etc.

#### **Types of Interhalogen Compounds**

We can divide interhalogen compounds into four types, depending on the number of atoms in the particle. They are as follows:

- XY Compounds
- Compounds XY<sub>3</sub>
- Compounds XY<sub>5</sub>
- XY<sub>7</sub> Compounds

In these notations, we must understand that "X" is the bigger (or) less electronegative halogen. On the other hand, "Y" represents the smaller (or) more electronegative

halogen. We can calculate the number of particles in the atom by the concept of the radius ratio. The formula for the same is as follows:

Radius Ratio = Radius of Bigger Halogen Particle/Radius of Smaller Halogen Molecule With an increase in the radius proportion, we see that the number of atoms per molecule also increases. Therefore, we can make out that Iodine heptafluoride possesses the greatest number of particles per atom. This is because it has a magnificent radius proportion.

#### Preparation

We can manufacture these interhalogen compounds by two main methods. One of them includes the direct mixing of halogens and the other includes a reaction of halogens with the lower Interhalogen compounds.

- The halogen atoms react to form an interhalogen compound. One example includes the reaction when a volume of chlorine reacts with an equal volume of fluorine at 473K. The resultant product is chlorine monofluoride.
- In other cases, a halogen atom acts with another lower interhalogen to form an interhalogen compound. For example, fluorine reacts with iodine pentafluoride at 543K. This gives rise to the compound of Iodine Heptafluoride.

## **Properties**

- We can find Interhalogen compounds in vapour, solid or fluid state. A lot of these compounds are unstable solids or fluids at 298K. a few other compounds are gases as well. As an example, chlorine monofluoride is a gas. On the other hand, bromine trifluoride and iodine trifluoride are solid and liquid respectively.
- These compounds are covalent in nature. We can attribute it to the lesser electronegativity between the bonded molecules. Examples include Chlorine monofluoride, Bromine trifluoride and lodine heptafluoride. These compounds are covalent in nature.
- These interhalogen compounds are diamagnetic in nature. This is because they have bond pairs and lone pairs.
- Interhalogen compounds are very reactive. One exception to this is fluorine. This is because the A-X bond in interhalogens is much weaker than the X-X bond in halogens, except for the F-F bond.
- We can use the VSEPR theory to explain the unique structure of these interhalogens. In chlorine trifluoride, the central atom is that of chlorine. It has seven electrons in its outermost valence shell. Three of these electrons form three bond pairs with three fluorine molecules leaving four electrons.

## **Common Shapes of these Compounds**

Applying the VSEPR theory, we can see that it forms a trigonal bipyramid. The lone pairs take up the tropical positions. On the other hand, bond pairs take up the other three positions. The axial bond pairs bend towards the tropical position. This happens in order to minimize the repulsions that happen due to lone pair-lone pair bonds. Thus, it has the shape of a bowed T.



#### **Chlorine Pentafluoride**

Let us now take the case of lodine Pentafluoride. The central atom in lodine pentafluoride is the iodine atom. It has one lone pair and five bond pairs. This is the reason it has a square pyramidal shape. Similarly, let us consider the case of lodine heptafluoride. It has seven bond pairs and has the shape of pentagonal bipyramid.

#### **Uses of Interhalogen Compounds**

- We use interhalogen compounds as non-watery solvents.
- Also, we use these compounds as a catalyst in a number of reactions.
- We use UF<sub>6</sub> in the enrichment of  $^{235}$ U. We can produce this by using CIF<sub>3</sub> and BrF<sub>3</sub>.
- $U(s) + 3CIF_3(I) \rightarrow UF_6(g) + 3CIF(g)$

#### **Oxoacids of halogens**

Halogens produce several oxoacids. These are nothing but the acids containing oxygen in the acidic group.

An oxoacid is a compound having hydrogen, oxygen, and no less than one other element. These do not have any lesser than one hydrogen molecule bound to oxygen. This hydrogen is capable of separating into the H<sup>+</sup> cation and the anion of the acid. The fluorine atom is extremely small and thus, it is highly electronegative. Therefore, it can form a single oxoacid, HOF which is fluoric(I) acid or hypofluorous acid. The other elements of the halogen family produce several oxoacids.

We cannot isolate them in the pure state. They are stable in aqueous solution. They are also very stable in their salt forms. Halogens generally form four series of oxoacids namely hypohalous acids (+1 <u>oxidation</u> state), halous acids (+3 oxidation state), halic acids (+5 oxidation state) and perhalic acids (+7 oxidation state).

#### Structures of the Oxoacids of Halogens

We can see that the focal halogen molecule is  $sp^3$  hybridised in these oxoacids. We can find an X-OH bond in each oxoacid. In the majority of these oxoacids, "X = O" bonds are available. Hypohalous acids incorporate hypofluorous acid, hypochlorous acid, hypobromous acid and hypoiodous acid. The halogen has the oxidation condition of +1 in hypohalous acids.

#### **Some More Examples**

Chlorine is capable of forming four types of oxoacids. They are HOCI (hypochlorous acid), HOCIO (chlorous acid), HOCIO<sub>2</sub>(chloric acid) and lastly HOCIO<sub>3</sub> (perchloric acid). Bromine forms HOBr (hypobromous acid), HOBrO<sub>2</sub>(bromic acid) and HOBrO<sub>3</sub> (perbromic acid). Iodine forms HOI (hypoiodous acid), HOIO<sub>2</sub> (iodic acid) and HOIO<sub>3</sub> (periodic acid).

The central <u>atom</u> in the oxoacids is sp<sup>3</sup> hybridized. Every oxoacid has essentially one X-OH bond. Whereas most oxoacids have X=O bonds present in them.

# **IITM COLLEGE OF SCIENCES, ARTS AND COMMERCE**

## B.Sc. 2<sup>nd</sup> semester

## **QUESTION BANK**

# **INORGANIC CHEMISTRY**

## SHORT ANSWER TYPE QUESTIONS:

- 1. What are conditions of H- bonding?
- 2. Why does BeCl<sub>2</sub> give acidic solution in water?
- 3. Out of MgCO<sub>3</sub> and CaCO<sub>3</sub> which will give color flamation?
- 4. Why Li is best reducing agent in group 1?
- 5. What is Freon?
- 6. What is the formula of hydrazoic acid?
- 7. What kind of hydrogen bonding is present in o-nitrophenol?
- 8. Why do noble gases are monoatomic?
- 9. Why do boron and aluminium forms covalent compounds?
- 10. What happens when phosphorous trioxide is treated with cold H<sub>2</sub>O?
- 11. Give cause of anomalous behaviour of Li.
- 12.BF<sub>3</sub> exists while BH<sub>3</sub> does not exist , why?
- $13.H_3PO_4$  is a tribasic acid , why?
- 14. Why does acetic acid exists in dimeric form?
- 15. Write the reaction by which first noble gas was formed.
- 16.Define catenation.
- 17.Why is H<sub>3</sub>PO<sub>2</sub> monobasic?
- 18. Give two uses of H<sub>2</sub>

## SECTION – A

- 1. What are semiconductors? Explain what is meant by n-type and p-type
- 2. Semiconductors?
- 3. What are van der waals forces? Discuss with examples.
- 4. Discuss various types of van der waals forces with examples.

- 5. Explain the difference between intermolecular hydrogen bonding and intramolecular hydrogen bonding.
- 6. Water has maximum density at 4'C. Explain.
- 7. How does band theory explain electrical conductivity of metals?
- 8. Discuss intrinsic and extrinsic semiconductors.
- 9. o- nitrophenol is steam volatile while p-nitrophenol is not. Explain.
- 10. Give some applications of semiconductors.
- 11. Which one has high boiling point? Ethyl alcohol or dimethyl ether?
- 12.What is Hydrogen bond? Discuss the effect of hydrogen bonding on properties of substances.

## SECTION – B

- 1. Account for the increasing stability of peroxides and superoxides as the size of alkali metals increases.
- 2. Draw and discuss the structure of XeO<sub>3</sub>, XeF<sub>4</sub>, XeOF<sub>4</sub>, XeO<sub>2</sub>F<sub>2</sub>.
- 3. Alkali metals are more reactive than alkaline earth metals. Why?
- 4. What is diagonal relationship? Explain by taking the examples of Be and Al.
- 5. Why do noble gases form compounds only with  $F_2$  and  $O_2$ ?
- 6. Explain the following:
  - (a) Be and Mg do not impart any characteristics flame coloration.
  - (b) Li forms normal oxide , Na the peroxide and K the superoxide.
- 7. Give the reactions of partial and complete hydrolysis of XeF<sub>6</sub> with SiO<sub>2</sub>?
- 8. Write the functions of alkaline earth metals in biosystem. What are the factors responsible for late discovery of compounds of noble gases?
- 9. How the hydrides of s-block elements act as powerful reducing agents?
- 10. Explain the complexing ability of alkaline earth metals.
- 11.Explain the following:
  - (a) LiF is insoluble in water wheras other alkali metals fluorides are soluble.
  - (b) Alkali metals salts imparts color to the flame.
  - (c) He and Ne do not form compounds.

## SECTION – C

- 1. Why  $BF_3$  is weaker lewis acid than  $BCl_3$ ?
- 2. Draw structure of borazine. Why is it called inorganic benzene?
- 3. Why does AlCl<sub>3</sub> exist as dimer while BCl<sub>2</sub> exist as monomer?
- 4. What are silicones? Give their preparations, properties and uses.
- 5. What are carbides? Discuss interstitial carbides.
- 6. How does  $CaC_2$  and  $Al_4C_3$  differ?
- 7. Discuss the structure and bonding in diborane  $(B_2H_6)$ .
- 8. Write 4 diagonal similarities of boron with silicon.
- 9. Discuss the action of diborane with
  - (a) ammonia
  - (b) alkalies.

## SECTION – D

- 1. Explain why ICl<sub>7</sub> does not exist while IF<sub>7</sub> exist?
- 2. Draw the structure of  $P_4O_6$  and  $P_4O_8$ .
- 3. Give reasons:
  - (a) HNO<sub>2</sub> is weaker acid than HNO<sub>3.</sub>
  - (b) H<sub>3</sub>PO<sub>3</sub> is dibasic acid.
  - (c)  $H_3PO_4$  is stronger than  $H_3PO_3$
- 4. Write three chemicals equations where hydrogen peroxide acts as oxidizing agent.
- 5. Differentiate between the structure of white phosphorous and red phosphorous.
- 6. Explain why  $H_2SO_4$  is highly viscous?
- 7. Discuss the acidic, oxidising and reducing nature of  $H_2O_2$  with suitable example.
- 8. Draw the structure of sulphuric acid , Caro's acid and sulphurpus acid. , Marshall's acid.
- 9. Why are interhalogen compounds more reactive than halogens?

- $_{10.}\,$  Explain the structure of CIF  $_{3.}\,$
- 11. "Halogens are most reactive elements as a family." Comment.
- $_{12.}\,$  Describe the structure of  $H_3PO_{3.}\,$
- 13.Compare the acidic strength of following:
- $_{\rm 14.}\,$  HClO , HClO  $_{\rm 2}$  , HClO  $_{\rm 3}$  , HClO  $_{\rm 4}\,$
- 15. Write the names and structures of three oxides of nitrogen.
- $_{16.}\,$  Discuss the structure of  $N_2O_4$