

**MODULE 1**

Unit 1	Elements of Group 4
Unit 2	Elements of Group 5
Unit 3	Elements of Group 7

**UNIT 1 ELEMENTS OF GROUP 4****CONTENTS**

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**1.0 INTRODUCTION**

In CHM 101 you have studied the general characteristics of the elements of the *s*-block, as well as the periodicity in their properties. You have also studied these aspects of the chemistry of elements of Group 13, which belongs to *p*-block. You would have noticed that while *s*-block elements show a regular gradation in properties down the group, the elements of Group 13 show some irregularities. It was also pointed out that the first element in each group shows some anomalous behaviour.

Now we extend our study to another group of *p*-block elements, namely, Group 4, which consists of carbon, silicon, germanium, tin and lead. This is the first group in which the transition from non-metals, C and Si through typical metalloid, Ge, to weakly electropositive

metals, Sn and Pb, can be clearly seen. However, this does not imply that the properties of carbon are completely non-metallic; its crystalline forms are lustrous, one allotrope (graphite) conducts electricity. Tin and lead, on the other hand, form amphoteric oxides and volatile chlorides. We will discuss these properties in this unit. In the next unit you will study the chemistry of Group 5 elements.

## 2.0 OBJECTIVES

After studying this unit you should be able to:

- explain the occurrence, extraction and uses of the elements of carbon family;
- explain allotropy and describe different forms in which these elements exist;
- compare the general characteristics of the elements of carbon family;
- explain catenation with special reference to carbon;
- describe internal  $\pi$ -bonding and the concept of complex formation by elements of this group;
- explain the nature of bonding in carbides;
- describe the chemistry of halides, hydrides and oxides of these elements;
- describe the structure and uses of silicates and silicones; and
- describe the chemistry of divalent compounds of these element.

### How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

## 3.0 MAIN CONTENT

### 3.1 Occurrence, Extraction and Uses

All the elements of this group are important in some manner or another. While carbon is an essential constituent of all living beings, silicon is present in rocks as well as many minerals. Both silicon and germanium are important components of semiconductors and transistors. Tin and lead also find various uses in everyday life. In the following paragraphs you will study the occurrence, extraction and uses of elements of this group.

#### 3.1.1 Occurrence

Amongst all elements of this group, carbon is the only one to occur in the elemental state as diamond and graphite. These are the two naturally occurring allotropic forms of carbon. As stated above, carbon, in the combined form, is an essential constituent of all living systems; you will study about such carbon compounds in courses on Organic Chemistry and Biochemistry. The inorganic carbonates of sodium, calcium and magnesium are widely distributed in the rocks, soil and water. Air contains about 0.03% of carbon dioxide. Coal and petroleum, which are called fossil fuels, because of their origin from the prehistoric plant and

animal life, are mixtures of complex compounds of carbon with hydrogen containing small amounts of oxygen or sulphur.

Silicon is the second most abundant element in the earth's crust forming about 27.7%. Oxygen with its relative abundance of 46.6% ranks first. Silicates are present in the rocks. Clays are essentially alumino-silicates of Na or Ca. Common sand is an impure form of silica. Glass which is a mixture of silicates has been known since antiquity. Germanium is a rare element. It occurs in traces in coal, in rare mineral argyrodite,  $4\text{Ag}_2\text{S} \cdot \text{GeS}_2$ , in germanite,  $\text{Cu}_3(\text{Ge,Fe})\text{S}_4$ , and as admixture in zinc and tin ores. Tin occurs mainly as cassiterite or tin stone,  $\text{SnO}_2$  and lead as galena,  $\text{PbS}$ .

## Allotropy

Many elements exist in more than one form. These forms are called allotropes, and the phenomenon is called allotropy. The two common allotropic forms of carbon, viz., diamond and graphite are well-known. These are, in fact, giant macromolecules consisting of C atoms linked by a network of covalent bonds (Figs, 1.1 and 1.2). Each carbon in diamond is tetrahedrally bonded to four other carbons with a bond distance of 154 pm. Here you may note that SiC also has the same structure but the alternate atom in it is Si in place of carbon. In diamond, the strong covalent bonds formed within the giant macromolecule result in a structure which is without any mobile electrons and thus it behaves as an insulator. The rigid, three dimensional linkages make diamond one of the hardest substances known. In contrast to diamond, graphite is very soft because it has a two dimensional sheet structure with regular planar hexagons (Fig. 1.2). The bond length is 142 pm showing some multiple bond character, intermediate between a double and a single bond. Different layers are at a distance of 335 pm from each other and are thus held by weak van der Waals forces only. These layers can slide over one another easily, imparting softness to graphite. In graphite, each carbon forms three bonds with other carbon atoms leaving one electron which is delocalised over the whole planar structure. These delocalised electrons make graphite a good conductor of electricity. Metallic lustre can also be attributed to these delocalised electrons. Carbon exists in amorphous form also; for example, as lampblack.

Silicon and germanium exist only in one form, i.e., the diamond form. Tin shows polymorphism and exists in two crystalline forms: grey or  $\alpha$ -tin, which is a semimetallic form, stable below 286 K, and white or  $\beta$ -tin, the stable metallic form, which is a good conductor of electricity. Grey tin has a diamond structure whereas the white tin has a tetragonal structure. Due to a close-packed lattice, density of S-tin,  $7.31 \times 10^3 \text{ kg m}^{-3}$ , is considerably higher than that of  $\alpha$ -tin,  $5.75 \times 10^3 \text{ kg m}^{-3}$ . The two forms are interconvertible as shown in following equilibrium:

Grey ( $\alpha$ -tin)                  White ( $\beta$ -tin)                  tin (liq)

Lead, again, exists only in one crystalline form which has a distorted cubic close packed structure.

### 3.1.2 Extraction

As said above, diamond and graphite occur in nature. However, diamond can also be formed when carbon is subjected to high temperature and pressure. Moissan (1896) got artificial diamonds by quick quenching of a solution of carbon in iron. The sudden expansion of iron led to tremendous pressure which resulted in the separation of carbon in crystalline form. Though small in size, these artificial diamonds find many uses in industry. Artificial graphite can be manufactured on a large scale by heating coke with silica at  $\sim 2775/\text{K}$  for 25-35 hours.

You may be aware that a new form of element carbon called fullerenes in which the atoms are arranged in closed shells was discovered in 1985 by Dr Robert F. Curl, Dr. Harold W. Croto and Dr. Richard E. Smalley who have incidentally won the 1996 Nobel Prize in Chemistry jointly. A detailed information of the discovery, properties and uses of fullerenes has been given in App.-I.

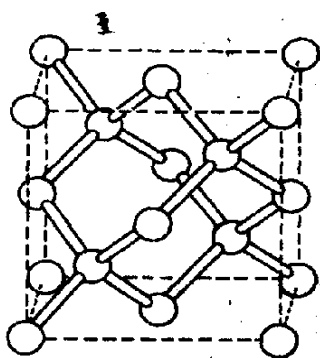


Fig. 1.1: Structure of Diamond

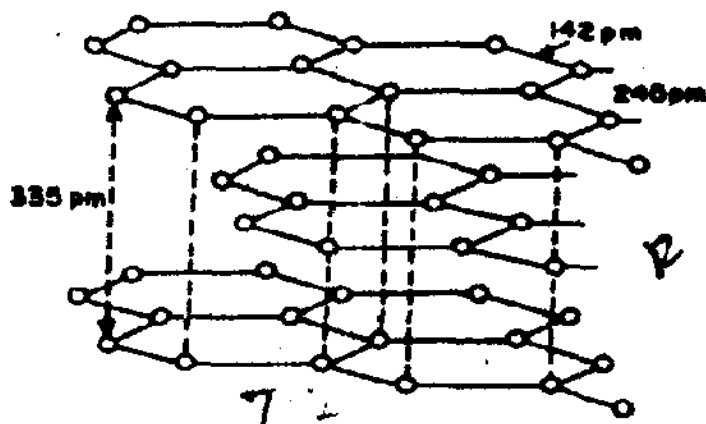
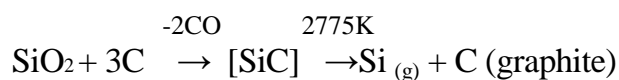


Fig. 1.2: Structure of Graphite

Tin has many peculiar properties. It is known to be able to cry. It produces a special characteristic sound when bent. Tin is sensitive to cold. In severe winter it turns grey, begins to crumble and breaks up into a powder. This serious disease is called Tin Plague. In fact, Napoleon's retreat from Russia has been attributed to this 'Tin Plague'.

In India, diamond mines are found in Parma district of Madhya Pradesh. Panna Mines have produced some famous diamonds like the kohlnoor. This historic diamond weighs 186 carats. Weight of diamonds is usually quoted in carats; 1 carat = 0.200 g.



Three other forms of carbon are manufactured on a large scale because of their vast industrial uses. These are coke, charcoal and carbon black or lampblack.

Destructive distillation is heating a substance to high temperatures in the absence of air and distilling off the volatile substances so formed.

The first two are formed by the destructive distillation or pyrolysis of coal and hardwood or bones in the absence of air. Carbon black is formed when petroleum gases or natural gas is burnt in a limited supply of air.

Commercial form of silicon is obtained by reduction of  $\text{SiO}_2$  with C or  $\text{CaC}_2$  in an electric furnace. High purity silicon is obtained either from  $\text{SiCl}_4$  or from  $\text{SiHCl}_3$ . These volatile compounds are purified by exhaustive fractional distillation and then reduced with very pure Zn or Mg. The resulting spongy Si is incited, grown into cylindrical single crystals, and then purified by zone refining. Ge is also obtained by the reduction of  $\text{GeO}_2$  with C or  $\text{H}_2$ . Tin is obtained by the reduction of its oxide with carbon. Lead is normally obtained from  $\text{PbS}$ . The ore is roasted in air to give the oxide which is then mixed with coke and limestone and reduced in a blast furnace.

Zone refining, applied mainly to metals, is based on the principle that the solubility of an impurity B in a main component A in the solid state may differ from the solubility of B in A in the liquid state; when a narrow molten zone is made to pass (e.g., by movement of a heater outside a tube containing a long bar of the material) along a bar of impure A, the distribution of B between the solid and liquid material alters so that the impurity B tends to segregate towards one end of the bar, with pure material at the other end.

Moderator is the material used in a nuclear reactor to moderate or slow down neutrons from the high velocities at which they are created in the fission process.

### 3.1.3 Uses

Diamonds are used in jewellery on account of their high refractive and dispersive power. Due to their exceptionally hard nature, inferior quality diamonds are used for industrial purposes mainly in the form of grit and powder in cutting, drilling, grinding and polishing tools. Graphite electrodes are used in the extraction of aluminium. Graphite is also used for making crucibles, as a lubricant in heavy machines and as pencil lead, etc. Very pure graphite is used as a neutron moderator in nuclear reactors. Coke is mainly used in metallurgy. Carbon black is used to strengthen rubber, as a pigment in inks, paints, paper and plastics. Activated carbon has enormous surface area and is used extensively in sugar industry as a decolorising agent. Amongst the compounds of carbon,  $\text{CO}_2$  finds an important use as a fire extinguisher and in refrigeration as dry ice.

Silicon finds uses in both elemental and combined forms. Very pure silicon is used in making semiconductors and in solar cells which are becoming increasingly important. Hyperfine Si is one of the purest materials used in the production of transistors. Silicates

are used in glass and cement manufacture. Silicones (cf. sub-section 1.5.3) are also widely used as lubricants. Their inert nature makes them ideal for use in gas chromatography, e.g., methylphenyl silicones. Germanium is used largely in transistor technology. However, its use in optics is growing; germanium is transparent in infrared region and is, therefore, used in infrared windows, prisms and lenses.

Due to its resistance to corrosion, tin is used to coat mild steel plate. Tinning of copper and brass utensils has been an age old practice in India. Tin is also used for making various alloys like bronze, pewter, gun metal, etc. Tin-lead alloys are fusible and low melting. Solders, which are low melting alloys, are used to join pieces of metal together. Soldering is a very common practice for joining components of an integrated circuit. Sn-Pb alloys are also used as bearing metal or type metal. Lead is used as an inert material, e.g., for building roofs, and for cable sheathing. Lead gets covered with a layer of  $\text{PbSO}_4$ , which is insoluble and does not get attacked by common reagents. Lead pipes were used in municipal water supply at one time. Soft water, however, tends to dissolve lead and may cause lead poisoning. Therefore, galvanised iron (GI) pipes are now used for water supply. Due to their low chemical reactivity, lead coated chambers are used in many industrial preparations like that of sulphuric acid. In view of its high density, lead is also used in making shielding blocks for radioactivity experiments. Organolead compounds, e.g., tetraethyllead,  $\text{Et}_4\text{Pb}$  and tetramethyllead,  $\text{Me}_4\text{Pb}$ , are used as antiknock additives to petrol for internal combustion engines. However, in recent times, because of their polluting nature, many countries have reduced or altogether stopped their use. One of the major uses of lead still is in the storage batteries. Storage batteries also called lead-acid batteries have a supporting grid of lead-tin alloy (91:9) with  $\text{PbO}_2$  as the oxidising agent and spongy Pb as the reducing agent. The electrolyte is dilute  $\text{H}_2\text{SO}_4$ .

### SELF ASSESSMENT EXERCISE 1

Tick on the correct answer:

Diamond is not a conductor of electricity because,

- i) it is very hard in nature.
- ii) it has a tetrahedral arrangement of atoms.
- iii) it does not have a layer structure.
- iv) it does not have delocalised electrons.

### 3.2 General Characteristics

The outer shell electronic configuration of all the elements is given in Table 1.1. It shows that the elements of this group can attain a closed shell configuration by gain, loss or sharing of four electrons. Therefore, they may be expected to show a valency of four. Let us discuss their physical properties, chemical properties and some of their important compounds.

Table 1.1: Physical Properties of Group 4 Elements

Property	Carbon (C)	Silicon (Si)	Elements Germanium (Ge)	Tin (Sn)	Lead (Pb)
Electronic configuration	[He]2s <sup>2</sup> 2p <sup>2</sup>	[Ne] 3s <sup>2</sup> 3p <sup>2</sup>	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>2</sup>	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>2</sup>	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>
Atomic number	6	14	32	50	82
Atomic weight	12.01	28.08	72.59	118.69	207.19
*Ionic radius (pm)	15 (+4)	41 (+4)	93 (+2)	112 (+2)	120 (+2)
	260 (-4)	271 (-4)	53 (+4)	71 (+4)	84 (+4)
Covalent radius (pm)	77	117	122	140	154
Boiling point (K)	5100	2628	3103	2543	2017
Melting point (K)	3823	1683	1210	505	600
Density (10 <sup>3</sup> × kg m <sup>-3</sup> )	2.22 (gr**)	2.33	5.32	7.3	11.3
	3.51 (d**)				
Electronegativity (A/R)	2.5	1.74	2.0	1.7	1.55
Ionisation energy I (kJ mol <sup>-1</sup> )	I	1086	787	760	707
	II	2352	1577	1534	1409
	III	4619	3230	3308	2943
	IV	6220	4355	4409	3821

\* Oxidation states are given in brackets \*\* gr = graphite, d = diamond

### 3.2.1 Physical Properties

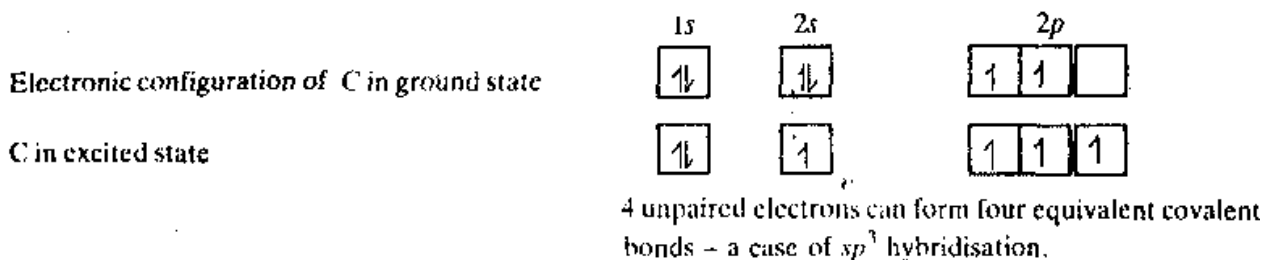
You must have noticed in case of Group 13, that *p*-block elements show more than one stable oxidation state. The elements of Group 4 show oxidation states of +2 and +4, which are also the valencies shown by these elements, except carbon where oxidation state varies from -4 to +4. However, the valency and the stable oxidation state for a given element may not be the same. Valency, as you know, can be defined in terms of the number of electrons lost, gained or shared in bond formation. Oxidation state or oxidation number, on the other hand, is equal to the charge the atom would have if all the electrons in a covalent bond it forms were assigned to the more electronegative atom in the bond. Table 1.2 gives some simple rules to deduce the oxidation state.

Table 1.2: Rules to Deduce the Oxidation State

Species	Oxidation state
Uncombined element.	-0
Combined O except peroxides	2
Combined O in peroxides	-1
Combined H except hydrides	+1
Combined H in hydrides Alkali metals (Group 1) Alkaline earth metals (Group 2)	-1
	+1
	+2
Sum of all oxidation numbers in a neutral molecule	0

The ionisation energies (Table 1.1) indicate that a very large amount of energy is required to form a M<sup>4+</sup> ion, therefore, not many ionic compounds are formed by Group 4 elements in the +4 oxidation state. On the other hand, the promotion of one of the *ns* electrons to the *np* vacant orbital, as shown below, can allow a tetravalency. In fact, most of the tetravalent

compounds formed by elements of this group are covalent in nature. Electronic configuration of carbon in the ground and excited state is given as an example.

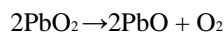


As we go down the group, the stability of +4 oxidation state decreases, the heavier elements of the group have a tendency to change from +4 to +2 states. This is reflected in the oxidising power of their tetravalent compounds. For example,  $\text{CO}_2$ ,  $\text{SiO}_2$  and  $\text{GeO}_2$  do not act as oxidants;  $\text{SnO}_2$  is a mild oxidising agent while  $\text{PbO}_2$  is a strong one. In fact, stannous salts are reducing agents. The tendency to form ionic compounds in the +2 oxidation state increases as we go down the group;  $\text{PbF}_2$  and  $\text{PbCl}_2$  are well defined ionic compounds.

Lead (IV) oxide converts hot HCl to  $\text{Cl}_2$ :



It loses oxygen on heating to give lead (II) oxide:



The increasing stability of the divalent state down the group, especially in the case of lead compounds is attributed to the "inert pair effect". This effect has been ascribed to an increase in the stability of  $ns^2$  electrons in the ionic compounds. However, the higher stability of covalent compounds such as tetraalkyllead,  $\text{R}_4\text{Pb}$ , compared to the dialkyllead species,  $\text{R}_2\text{Pb}$ , points to the ready participation of the  $s$  pair electrons in covalently bonded tetravalent compounds of these elements. Since the sum of the first two ionisation energies also decreases down the group, it becomes increasingly favourable thermodynamically, for Sn and Pb to form compounds in oxidation state +2 which are more ionic in character.

The covalent radii of the elements, as expected, increase with increase in atomic number. This increase, however, is not uniform. You may have noticed in Table 1.1 that when we move from carbon to silicon the covalent radius increases sharply, and then the increase is gradual. This can be explained as follows. A large increase in the size of silicon is due to the introduction of the 3rd shell. When we go down to germanium, the 4th shell is introduced, no doubt, but the effective nuclear charge resulting from addition of eighteen protons to the nucleus outbalances the effect of the additional shell leading to only a marginal increase in size. Similarly, in case of Pb, the increase in covalent radius is very small in comparison to that in Sn. This is further reflected in the ionisation energies and electron affinities of these elements.



Going through the data given in Table 1.1, you will notice that carbon has higher electronegativity as compared to other elements of the group. As a result, it can accept (gain) electrons and can form negative ions<sup>2</sup> of the kind C<sup>-2</sup>, in acetylides and C<sup>4-</sup> in methanides, while the other elements in the group are unable to do so. When we see the electro-negativity trends in the group, we find that the value decreases down the group as expected, with Ge as an exception whose electronegativity is slightly higher than that of Si. As explained above, this could be due to the higher effective nuclear charge in case of Ge.....

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If we go through the data for ionisation energies given in Table 1.1, we find that the first and second ionisation energies decrease down the group from C to Sn as expected, but they increase slightly when we move to Pb. On the other hand, both the 3rd and the 4th ionisation energies vary irregularly, their sequence is C > Ge > Si > Pb > Sn.

The decrease in the 1st and 2nd ionisation energies from C to Sn is because of the increase in atomic size down the group. The 3rd and 4th ionisation energies increase from Si to Ge because of poor shielding of 4s electrons offered by the 3d electrons against the increased nuclear charge in Ge. All the ionisation energies are slightly higher in case of Pb. This increase can again be attributed to the poor shielding effect of the 4f and 5d orbital electrons. Further, the s-electrons being more penetrating, experience higher nuclear charge which makes it difficult to remove them.

## SELF ASSESSMENT EXERCISE 2

Making use of the rules given in Table 1.2, find out the oxidation states and valency of C in the following compounds:

CH<sub>4</sub>, CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>Cl.

### 3.2.2 Multiple Bonding

In Group 14, carbon is the only element capable of forming comparatively stable multiple bonds with another C atom and also with N, O, etc. Examples are alkenes ( $\text{>C=C<}$ ), alkynes ( $\text{-C}\equiv\text{C-}$ ), imines ( $\text{>C=N-}$ ), nitriles ( $\text{-C}\equiv\text{N}$ ), ketones ( $\text{>C=O}$ ), etc. None of the other elements of the group forms stable compounds containing multiple bonds. Recently, some success has been achieved in synthesising compounds with  $\text{>Si}=\text{Si<}$  and  $\text{>Si}=\text{C<}$  double bonds, but their details are beyond the scope of this course. Stoichiometric analogues like SiO<sub>2</sub>, SnO<sub>2</sub> and (Me<sub>2</sub>SiO)<sub>n</sub> are known which are giant macromolecules containing M-O-M linkages.

The tendency of formation of multiple bonds easily, in case of carbon, is because of the high bond energy (Table 1.3) and a small atomic radius of carbon as compared to other elements of the group. So its p-orbitals can approach the p-orbitals of the other C, O or N atom for an effective overlap essential for π-bond formation.

A  $\pi$  bond is formed by the lateral overlap of two dumb-bell shaped orbitals, e.g.  $p$ - $\pi$  bond can be represented as:



C	Si	Ge	Sn	Bond	Pb
347	226	118	150	*E-E	-
611	318	-	-	E=E	-
837	-	-	-	E E	-
414	318	285	251	E-H	-
360	464	360	-	E-O	-
736	640	-	-	E=O	-

Table 1.3: Bond Energies of Group 4 Elements ( $\text{kJ mol}^{-1}$ )

\*E=Element, C, Si, Ge, Sn or Pb.

### ***pr-dr* Bonding**

You are familiar with a  $r$  bond formed by the lateral overlap of  $p$  orbitals. It is called a  $pr$ - $pr$  bond. A lateral overlap of  $p$  and  $d$  orbitals under favourable conditions can also lead to the formation of a  $\pi$  bond. Such a  $\pi$  bond formation is called  $pr$ - $dr$  bond. Let us understand this in case of C and Si compounds with nitrogen as the central atom, e.g., in trimethyl amine,  $(\text{CH}_3)_3\text{N}$ , and trisilyl amine,  $(\text{SiH}_3)_3\text{N}$ , (Fig.1.3). From your previous knowledge of hybridisation and the corresponding structures formed, you understand that trimethylamine has a pyramidal structure. Nitrogen being  $sp^3$  hybridised, the three methyl groups occupy three vertices of the pyramid and the 4th position is occupied by the lone pair on nitrogen. The structure of trisilyl amine,  $(\text{SiH}_3)_3\text{N}$ , is unexpectedly different. It has a trigonal planar structure with nitrogen in  $sp^2$  hybridised state. The three silyl groups are at the three corners of the triangle and the  $p$ , orbital of N which is perpendicular to the plane of the molecule is left with an electron pair. The arrangement of electrons of nitrogen in both the compounds can be shown as given below:

Electronic structure of N atom in  $(\text{CH}_3)_3\text{N}$



$sp^3$  hybridisation – tetrahedral structure, three unpaired electrons form bonds with three  $\text{CH}_3$  groups; 3 bond pairs and 1 lone pair.

Electronic structure of N atom in  $(\text{SiH}_3)_3\text{N}$



$sp^2$  hybridisation – trigonal planar structure, three unpaired electrons form bonds with three  $\text{SiH}_3$  groups, lone pair in  $p_z$  orbital.

In case of  $(\text{SiH}_3)_3\text{N}$ , the  $p_z$  orbital of N with a lone pair overlaps with the empty d-orbital of silicon and forms a  $\pi$ -bond. It may be noted that  $p_z$  orbital of N has energy comparable to d-orbital of Si. This kind of a  $\pi$  bond is called  $p\pi-d\pi$  bond. Since donation of lone pair is within the molecule, this is called internal  $\pi$ -bonding. This type of bonding is possible to some extent in Ge but not in case of Sn and Pb. Since C does not have any  $d$  orbitals, therefore, it does not show this type of bonding. The  $p\pi-d\pi$  overlap is indicated in the Fig. 1.3.

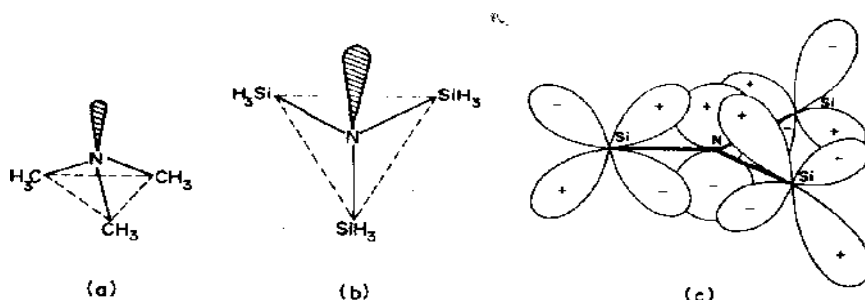


Fig. 1.3: (a) Structure of Trimethylamine (b) Structure of Trisilylamine  
(c)  $p\pi-d\pi$  Bond between N and Si in Trisilylamine

### 3.2.3 Catenation

Catenation is a property by virtue of which elements form long chain compounds by single or multiple bond formation between atoms of the same element. Carbon shows this tendency to a remarkable extent because of its small size and high bond energy (Tables 1.1 and 1.3), Si and Ge to a lesser extent and Sn and Pb to a very small extent. A few examples of their hydrides and halides can be cited here. In case of carbon we have alkanes, e.g., ethane, propane, butane, pentane, etc. These are chains of carbon hydrides having the general formula  $\text{C}_n\text{H}_{2n+2}$ , where  $n$  can be a large number, alkanes with  $n=100$  are known. Carbon also forms a number of catenated halides, e.g., polyvinylchloride (PVC). Silicon forms silanes having the general formula  $\text{Si}_n\text{H}_{2n+2}$ , but  $n$  does not exceed 8. Its halides also show catenation and have a general formula  $\text{Si}_n\text{X}_{2n+2}$ , where if  $\text{X}=\text{F}$ ,  $n=1-14$ ; if  $\text{X}=\text{Cl}$ , Br or I,  $n=1-10$ . Germanium forms germanes, with general formula  $\text{Ge}_n\text{H}_{2n+2}$ , where  $n=1-9$ . Germanium halides form dimers, e.g.,  $\text{Ge}_2\text{Cl}_6$ . Hydrides of Sn and Pb are much less stable, while  $\text{SnH}_4$  and  $\text{Sn}_2\text{H}_6$  have been prepared, analogous methods fail for the preparation of  $\text{PbH}_4$ . No catenated halides are known for Sn and Pb.

### SELF ASSESSMENT EXERCISE 3

Define catenation

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### 3.2.4 Chemical Properties

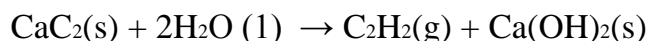
In general, the chemical reactivity of Group 4 elements increases down the group. Their chemical reactions are listed in Table 1.4, followed by a brief description of carbides, halides, fluorocarbons, hydrides and oxides.

#### Carbides

When carbon is linked to elements of lower or approximately the same electronegativity, the binary compounds so formed are termed as carbides, e.g.,  $\text{CaC}_2$ ,  $\text{Al}_4\text{C}_3$ ,  $\text{Be}_2\text{C}$ , etc. However, compounds of carbon with hydrogen, oxygen, sulphur, phosphorus, nitrogen and halogens are excluded from this definition. Depending upon the bonding between the element and carbon, carbides are classified into three groups, viz., saltlike or ionic carbides, interstitial carbides and covalent carbides.

##### a) Salt-like or Ionic Carbides

Ionic carbides are formed by elements of Groups 1, 2, 3, 11, 12 and 13 except boron. Most of these are colourless and non-conducting in the solid state. These carbides are decomposed by water and dilute acids liberating either acetylene or methane. They are named as acetylides and methanides, respectively.



(Calcium acetylide)



Most of the acetylides have cubic structure similar to the sodium chloride structure. One cell axis is, however, elongated to accommodate the  $(\text{C}=\text{C})^{2-}$  ion making the symmetry of the crystal tetragonal and not cubic. In Fig. 1.4, you will observe that the coordination number of each ion is six.

Fig. 1.4: Structure of Ionic Carbides

Reagent	Reaction	Remarks
Hot concentrated HCl	$M + 2HCl \longrightarrow MCl_2 + H_2$	M = Sn, and Pb, but not C, Si, Ge. Reaction with Pb is also slow because of insoluble $PbCl_2$ formed.
Hot concentrated $H_2SO_4$	$M + 2H_2SO_4 \longrightarrow MO_2 + 2SO_2 + 2H_2O$ $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$	M = Pb, Sn, Ge (slow); not Si. In case of lead, insoluble $PbSO_4$ slows down the reaction.
Concentrated $HNO_3$	$3M + 4HNO_3 \longrightarrow 3MO_2 + 4NO + 2H_2O$ $3Pb + 2HNO_3 \longrightarrow 3PbO + 2NO + 4H_2O$	M ≠ Si, Pb, Ge and Sn give hydrated oxides. Fuming nitric acid renders lead passive.
HF	$Si + 6HF \longrightarrow 2H_2 + H_2SiF_6$	Only HF attacks Si, stability of $SiF_6^{2-}$ .
Aqueous alkali	$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$	Not C, Ge, Pb; $SiO_3^{2-}$ is formed fast. $Sn(OH)_6^{2-}$ is formed very slow.
Molten alkali		Not C, $SiO_4^{4-}$ , $GeO_4^{4-}$ , $Sn(OH)_6^{2-}$ , $Pb(OH)_4^{2-}$ are formed.
$O_2$ or air, heat	$M + O_2 \longrightarrow MO_2$ $Pb \xrightarrow{O_2} PbO \xrightarrow{H_2O} Pb(OH)_2 \xrightarrow{CO_2} \text{basic carbonate.}$ $\text{molten Pb} + O_2 \longrightarrow PbO \xrightarrow[O_2]{743 K} Pb_3O_4$	M = C, Si, Ge, Sn. Lead reacts slowly with cold, moist air.
$H_2O$ , 293K	$\text{lead} + \text{soft water} \xrightarrow{O_2} Pb(OH)_2$ $\text{lead} + \text{hard water} \xrightarrow{O_2} \text{protective layer of insoluble } PbSO_4 \text{ or } PbCO_3$	Poisonous.
Steam, heat (strongly)	$M + 2H_2O \longrightarrow MO_2 + 2H_2$ $C + H_2O \longrightarrow CO + H_2$	M = Sn, Si. Not Ge.
S, heat	$M + 2S \longrightarrow MS_2$	All except lead, which gives $PbS$ .
$Cl_2$ , heat	$M + 2Cl_2 \longrightarrow MCl_4$	All except lead which gives $PbCl_2$ .
Metals, heat		Carbides and silicides, lead and tin alloys.

## b) Interstitial Carbides

These are formed by combination of carbon with some transition metals like Ti, W, V, etc. These carbides resemble interstitial hydrides which you have studied in CHM 121. They are non-stoichiometric compounds. Carbon atoms are adjusted in the interstitial spaces of the metal lattices without causing any appreciable distortion. At the same time carbon atoms further stabilise the lattice, resulting in very high melting points, high conductivity and increased hardness of these carbides. The ability of carbon atoms to enter the interstices without appreciably distorting the metal lattice requires that the interstices and hence the metal atoms should be relatively large. Lattices of metals with atomic radius less than 130 pm get distorted, e.g., iron, cobalt and nickel do not form typical interstitial carbides. Their carbides are intermediate in properties between ionic and interstitial. The transition metals mentioned above have atomic radii 126, 125 and 125 pm, respectively.

## c) Covalent Carbides

These are formed by combination of carbon with elements of almost equal electronegativity like boron and silicon. Silicon carbide, SiC, known as carborundum and boron carbide,  $B_{12}C_3$  are giant macromolecules having covalent bonding all through. Both carbides are very hard, infusible and chemically stable substances. You have already studied the characteristics of  $B_{12}C_3$ . Boron carbide is harder than silicon carbide

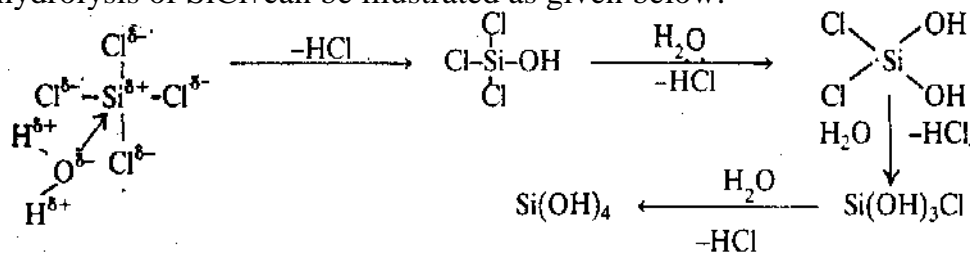
and is used as an abrasive.)The structure of SiC, which is similar to that of diamond, is shown in Fig. 1.1.

## Halides

All the elements of the group form dihalides (except carbon) and tetrahalides. All the four tetrahalides, namely, fluorides, chlorides, bromides and iodides are known for all the elements of the group, except  $\text{PbBr}_4$  and  $\text{PbI}_4$ . The tetrahalides are volatile covalent compounds with tetrahedral structure. The mixed halides of carbon, i.e., chlorofluorocarbons form an important class of compounds, these are discussed after halides. The tetrahalides of carbon are relatively inert to hydrolysis while  $\text{SiCl}_4$  gets readily hydrolysed to give silicic acid:



The tetrahalides of Ge are hydrolysed less readily, while in case of Sn and Pb halides, the reaction is often incomplete and can be suppressed on addition of appropriate halogen acid. The suggested mechanism for hydrolysis is the formation of a complex between the halide and water molecule. This complex dissociates to give the hydroxy compound. The process continues till the completely hydrolysed product is obtained. To form such a complex, the central atom in the tetrahalide has to extend its octet to accommodate the incoming water molecule. This requires the presence of *d*-orbitals. Since *d*-orbitals are not available in case of carbon, carbon halides are inert towards hydrolysis. A plausible mechanism for hydrolysis of  $\text{SiCl}_4$  can be illustrated as given below:



Hydrolysis in the presence of alkali will be faster because of the stronger nucleophile, i.e.,  $\text{OH}^-$ , now available. It may be mentioned that in acidic solutions, water gets protonated and thus does not remain an effective nucleophile.

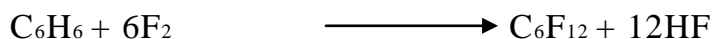
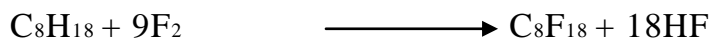
The formation, stability and properties of the dihalides are discussed later in Section 1.6.

## Fluorocarbons

Fluorocarbons are the synthetic equivalents of hydrocarbons in which some or all of the hydrogens have been replaced by fluorine atoms, e.g.  $\text{CF}_4$ ,  $\text{C}_2\text{F}_4$ ,  $\text{C}_2\text{F}_6$ , etc. Replacement of H by F greatly increases both the thermal stability and the chemical inertness because of the greater strength of the C-F bond and the larger size of the

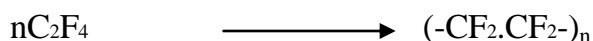
fluorine compared to hydrogen atoms. The bond energy of C-F bond is  $489 \text{ kJ mol}^{-1}$  compared with C-H bond energy of  $414 \text{ kJ mol}^{-1}$ . Fluorocarbons are resistant to attack by acids, alkalis, oxidizing and reducing agents.

It is possible to synthesise a number of fluorocarbons and their derivatives by reacting hydrocarbons with fluorine either directly or in the presence of catalyst, or by using other fluorinating agents, like  $\text{CoF}_3$ ,  $\text{AgF}_2$  and  $\text{MnF}_3$ :



Like hydrocarbons, fluorocarbons are capable of forming carbon chains of indefinite lengths. They are not oxidised by oxygen because carbon bonded to fluorine can be considered to be effectively oxidised. However, they are attacked by hot metals like molten sodium. On burning, they split at C-C bond rather than at C-F bond.

$\text{CF}_4$  is the simplest fluorocarbon. It is a colourless gas obtained by the reaction of carbon tetrachloride with silver fluoride at 575 K. Perfluoroethane,  $\text{C}_2\text{F}_6$ , is analogous to ethane,  $\text{C}_2\text{H}_6$ . Tetrafluoroethene,  $\text{C}_2\text{F}_4$  can be polymerised thermally or in aqueous emulsions to a chemically inert plastic, polytetrafluoroethene (PTFE), commercially known as Teflon.



Teflon has an extremely low coefficient of friction. It is used as a protective coating in non-stick kitchen utensils, razor blades, bearings, etc. Mixed chlorofluorocarbons such as  $\text{CCl}_2\text{F}_2$ ,  $\text{CFCl}_3$  and  $\text{CF}_3\text{Cl}$  are known as 'Freons'. They are volatile, thermally stable and chemically inert compounds with low viscosity. Therefore, they are used in refrigeration, in aerosol propellants and in heat transfer processes.  $\text{CF}_3\text{CHBrCl}$  is a safe anaesthetic.

## Hydrides

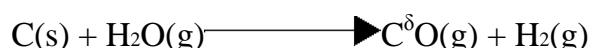
All the elements in the group form covalent hydrides. The stability of the hydrides decreases down the group, because of decreasing M-H bond energies (Table 1.3). Thus while  $\text{CH}_4$  and other alkanes are stable compounds,  $\text{PbH}_4$  has not even been properly characterised, so far. We have already discussed the catenation in hydrides of these elements.

The availability of d-orbitals coupled with lower bond energy of the M-H bond makes hydrolysis of the hydrides of heavier elements easier as compared to that of alkanes. For example, methane does not undergo hydrolysis at all due to non-availability of d-orbitals in C, but silanes do so in presence of dilute alkali. Hydrolysis of the hydrides of heavier elements follows a complicated pattern depending upon factors such as stability of the parent hydride to side-reactions, like oxidisability, etc.

## Oxides

All the elements in the group form mainly mono and dioxides. The dioxides are all thermally stable except for  $\text{PbO}_2$ , the reason being an increase in stability of +2 oxidation state down the group (see subsection 1.3.1). Acidic character of the dioxides decreases down the group;  $\text{CO}_2$  and  $\text{SiO}_2$  are acidic oxides, while  $\text{GeO}_2$ ,  $\text{SnO}_2$  and  $\text{PbO}_2$  are amphoteric. Carbon is exceptional in forming gaseous mono and dioxides,  $\text{CO}$  and  $\text{CO}_2$ .

Carbon monoxide is obtained on passing steam over red hot coke. The product, a mixture of  $\text{CO}$  and  $\text{H}_2$ , is called water gas and is used as a fuel.



The electronic structure of  $\text{CO}$  has been debated. The molecule is expected to show a large dipole moment because of the electronegativity difference between carbon and oxygen. But the molecule has only a small dipole moment of 0.112 D. The sign of the dipole moment has been found to be  $\text{C}^\delta\text{-O}^\delta\text{+}$  which is opposite to that expected in view of the higher electronegativity of oxygen as compared to carbon. To explain this, in addition to the normal double bond, oxygen is supposed to form a coordinate bond with C by donating and sharing its lone pair of electrons. As a result oxygen gets a partial positive charge on it decreasing the electronegativity difference. The valence bond structure is represented below. It may be mentioned that  $\text{CO}$  is the most stable diatomic molecule, with the highest bond energy of  $1071 \text{ kJmol}^{-1}$ .



Carbon monoxide is a colourless and odourless gas. Because of its lack of smell, it is very dangerous. If inhaled it forms a very stable compound, carboxyhaemoglobin, with haemoglobin. Haemoglobin is the oxygen carrying protein in blood. Formation of carboxyhaemoglobin prevents it from acting as an oxygen carrier and death eventually occurs from asphyxia. Carbon monoxide has reducing properties. It is an important reducing agent, reducing metallic oxides to the metals at high temperatures forming carbon dioxide.

Carbon dioxide is the other important oxide of carbon. It is formed whenever carbon or any of its compounds is completely burnt in air. In the laboratory, the gas is made by the action of an acid on a carbonate.  $\text{CaCO}_3$ , in the form of marble chips is usually taken:

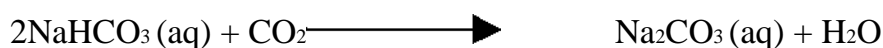


Increase in the concentration of  $\text{CO}_2$  in the atmosphere has recently been causing concern, wrapping of earth's thermal radiation by  $\text{CO}_2$ , can lead to a general warming up of the planet and expose it to the dangers of green house effect. Lowering of the pH of the surface ocean water can also have disastrous consequences for marine life.



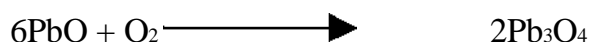
CO<sub>2</sub> is a colourless gas with a faint smell. Its structure can be represented by O=C=O. It can be easily liquified by application of pressure even at the ordinary ambient temperatures. If liquid CO<sub>2</sub> is allowed to expand rapidly, solid CO<sub>2</sub> is obtained. Solid CO<sub>2</sub> is known as dry ice. When it is used as a refrigerant, it does not pass through the liquid phase (*cf.*, water). Solid carbon dioxide is also used as a freezing mixture in organic solvents like acetone or methanol.

Carbon dioxide is an acidic oxide which forms carbonates and bicarbonates with bases:



In presence of sunlight and chlorophyll, plants are able to synthesise carbohydrates from water and carbon dioxide. You have read about this process called photosynthesis in Unit 5. Being a non-supporter of combustion, CO<sub>2</sub> is used in fire extinguishers.

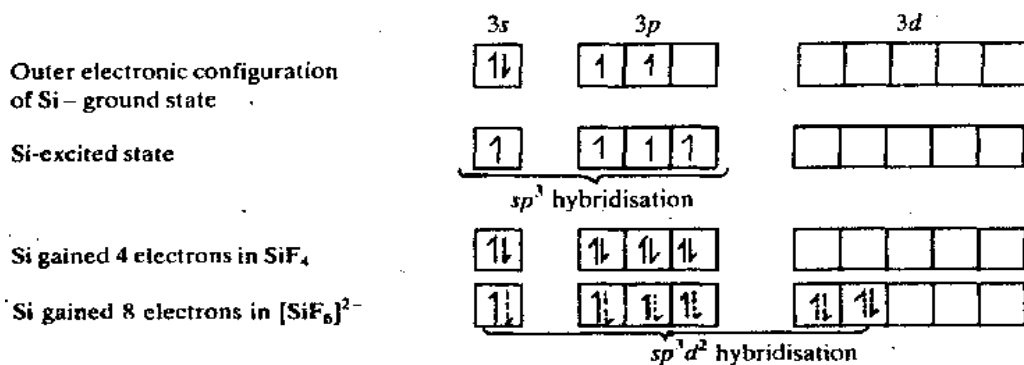
Silicon forms an important acidic oxide, silicon dioxide discussed in detail in Section 1.5 and an unstable monoxide, SiO. Germanium and tin form amphoteric oxides. GeO<sub>2</sub> is mainly acidic, while SnO and SnO<sub>2</sub> are amphoteric in nature, dissolving both in alkalis and acids. As explained in sub-section 1.3.1, PbO<sub>2</sub> being unstable behaves as an oxidant; the lower oxide, PbO, is quite stable. If PbO is carefully heated in air to a temperature between 675 and 750 K, it is converted into trilead tetraoxide, Pb<sub>3</sub>O<sub>4</sub> or 2PbO·PbO<sub>2</sub>, also called 'red lead':



Red lead is used as a pigment in paints and in the manufacture of crystal glass.

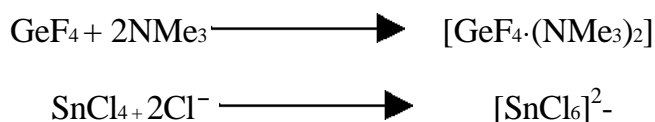
### 3.2.5 Complex Formation

Carbon, can have a maximum coordination number of four, since, after gaining four electrons, it attains a stable noble gas configuration with 8 electrons in the outer shell. Therefore, carbon compounds do not form complexes. Other elements of the group also acquire a noble gas configuration in a similar manner but even then they have empty *d*-orbitals available for bonding. Therefore, they can form complexes by expanding the coordination number to six or even eight in the case of heavier elements. This can be shown taking Si as an example:



It can be assumed that the four singly filled hybrid orbitals are used in forming covalent bonds with four F atoms. The two vacant hybrid orbitals are utilised in forming coordinate bonds by accepting a pair of electrons each from the two F<sup>-</sup> ions. However, once the complex is formed all the bonds become equivalent.

The tetravalent compounds of the heavier elements function as Lewis acids and are able to accept electron pairs from bases. This is possible because of the availability of *d* orbitals, e.g,



#### SELF ASSESSMENT EXERCISE 4

- i. Why is C-H bond essentially non-polar? Explain in the space given below.
- ii. Using the concept of hybridisation, predict the shape of [SiF<sub>6</sub>]<sup>2-</sup> ion.

### 3.3 Anomalous Behaviour of Carbon

We have discussed in the earlier sections how and in what ways carbon behaves differently from the rest of the elements in the group; the reasons have also been discussed. Let us list all of them here:

- Carbon has a maximum covalency of 4 and can not form complex compounds.
- Carbon is the only element in the group that can form stable derivatives with double and triple bonds, which show special characteristics.
- Carbon forms gaseous oxides, i.e., CO and CO<sub>2</sub> whereas others form solid oxides.
- Carbon has a much higher electronegativity and higher ionisation energy than other elements in the group.
- Carbon has a unique capacity of catenation and forms a very large number of stable compounds, with long chains or rings of carbon atoms, which can occur in many isomeric forms.
- Carbon forms stronger bonds not only with itself but also with elements like halogens, oxygen, nitrogen and sulphur than any other element in the group.

### 3.4 Silica and Silicates

The earth's crust is largely composed of silica and silicates, which are the principal constituents of all rocks and the sands, clays and soils that are the breakdown products of rocks. Most inorganic building materials are based on silicate minerals. These include natural silicates such as sandstone, granite and slate, and manufactured materials such as cement, concrete and ordinary glass. Some of the properties and important uses of silica and silicates are described below.

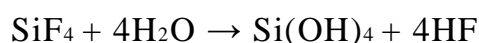
#### 3.4.1 Silica

Silicon dioxide,  $\text{SiO}_2$ , is commonly known as silica. Its amorphous as well as crystalline forms are known. Flint is the amorphous form of silica. The crystalline forms are quartz, tridymite and cristobalite which have different structures. Quartz is the purest and the most stable form of silica. It is a colourless solid having a specific gravity of 2.65 and is also called rock crystal. Each crystalline form can exist in two modifications, one stable at lower temperatures while the other at high temperatures. These forms can be interconverted with change in temperature.

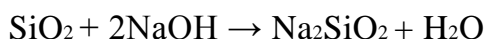
In hydrolysis of silicon tetrachloride, silicic acid is obtained which on drying and ignition gives silica as a fine white powder.



Silica is insoluble in water and acids except hydrofluoric acid with which it forms volatile silicon tetrafluoride,  $\text{SiF}_4$ . When passed in water,  $\text{SiF}_4$  is hydrolysed to give soluble  $\text{H}_2\text{SiF}_6$  and silicic acid as an insoluble white solid:



These reactions are used in analytical chemistry. Silica is acidic in nature and gives silicates when fused with alkalies.



Quartz gets coloured due to the presence of some impurities and is prized as a gemstone, e.g., amethyst which is purple.

$\text{SiO}_2$  differs from  $\text{CO}_2$  in an important respect that it is a solid at room temperature whereas  $\text{CO}_2$  is a gas. You know that  $\text{CO}_2$  is a simple linear molecule in which carbon is attached to two oxygen atoms by means of two double bonds. On the other hand,  $\text{SiO}_2$  forms a giant or macromolecular structure in which each silicon atom is

surrounded tetrahedrally by four covalently bonded oxygen atoms and each oxygen, in turn, is bonded to two silicon atoms (Fig. 1.5). However, the overall stoichiometry or the silicon-oxygen ratio remains the same, i.e.  $\text{SiO}_2$ .

Silica is the chief constituent of glass. Silica gel is an amorphous form of  $\text{SiO}_2$  with a porous structure. It is used as a dehydrating agent as well as a catalyst. Silica gel is being increasingly used as an adsorbent in chromatography.

Silica when fused with sodium carbonate gives sodium silicate (water glass):

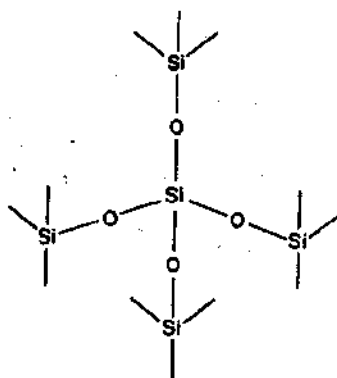
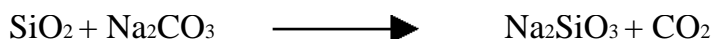
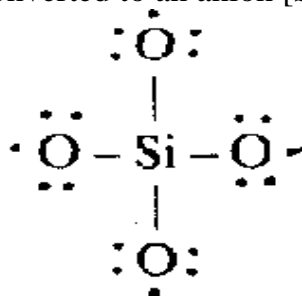


Fig. 1.5: Structure of Silicon dioxide

### 3.4.2 Silicates

Silicates are regarded as the salts of silicic acid,  $\text{H}_4\text{SiO}_4$ . All the silicates are comprised of  $\text{SiO}_4$  units. These units have a tetrahedral structure formed as a result of  $sp^3$  hybridisation (cf.  $\text{SiF}_4$ , Sub-sec. 1.3.5). Since 4 valence electrons from silicon and 6 valence electrons from each oxygen are insufficient to complete the octet of all the atoms, therefore, oxygens acquire electrons from other atoms and become negatively charged to produce discrete anion  $(\text{SiO}_4)^{4-}$ . This can be made clear by writing the electronic formula as given below:

Silicon atom has its octet completed but each oxygen atom is still short of one electron to complete its octet. As said above, they can complete their octet by taking up 4 electrons from a metal, getting converted to an anion  $[\text{SiO}_4]^{4-}$



The  $[\text{SiO}_4]^{4-}$  tetrahedra can be represented in three ways as shown in Fig. 1.6. One silicate differs from the other only in the manner in which the units are linked together. The simple silicates are salts of orthosilicic acid,  $\text{H}_4\text{SiO}_4$ , and contain the orthosilicate ion,  $[\text{SiO}_4]^{4-}$ , e.g.  $\text{Zr}^{4+}\text{SiO}_4$ .

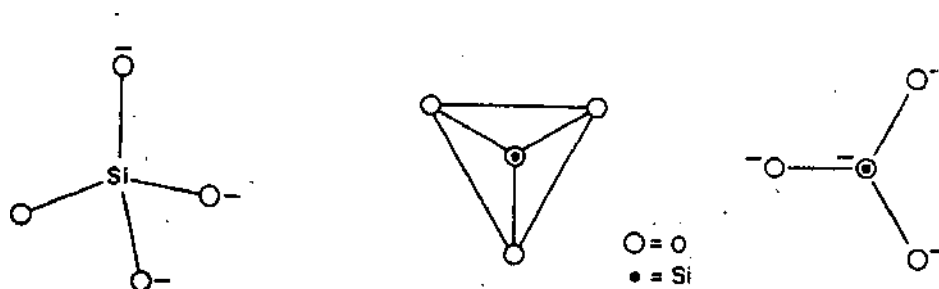
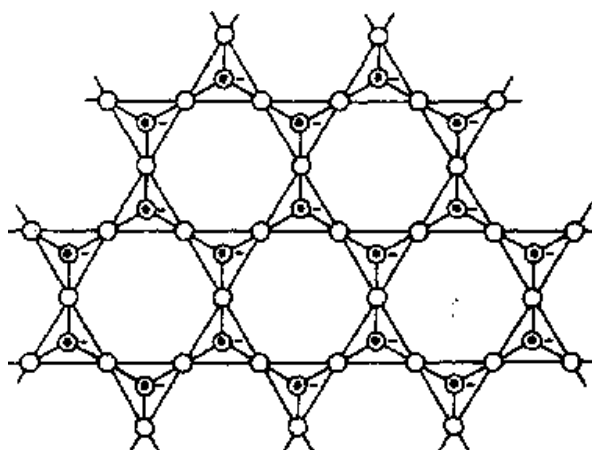


Fig. 1.6: Representations of  $[\text{SiO}_4]^{4-}$  Tetrahedra.

In some silicates, the oxygen atoms of  $\text{SiO}_4$  units tend to complete their octet by sharing electrons with other silicon atoms, the oxygen atoms, thus, form bridges of the type Si-O-Si to other silicon atoms. The number of such bridges can vary from one to four. This leads to the formation of complex silicates. Any oxygen which fails to pick up electrons from the other silicon atom is not able to complete its octet. The resulting silicate chains are, therefore, negatively charged anions. The metal cations generally present in silicate minerals are  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  etc. Depending upon the way these  $\text{SiO}_4$  units are linked, silicates of different structure and complexity are obtained. Some representative types are given in Fig. 1.7.

In addition to the types where linkages between  $\text{SiO}_4$  units are two-dimensional, complex silicates result from three dimensional linkages between  $\text{SiO}_4$  tetrahedra.

Silicate industry is a very important industry and it plays an important role in national economy. From these mineral silicates, glass, ceramics, cement, etc. are 38 manufactured. Let us study, in brief the uses of some mineral silicates.



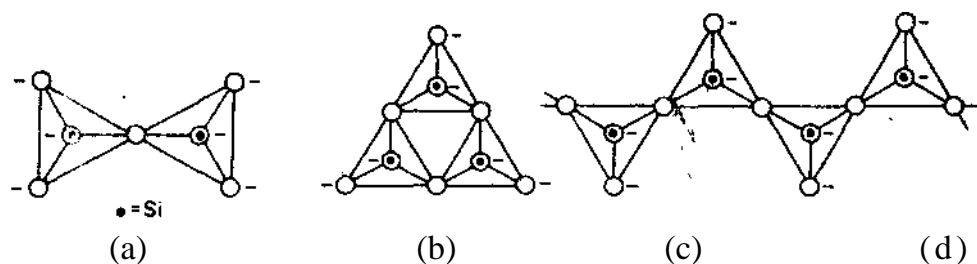


Fig. 1.7: Structure of (a) Pyrosilicates, e.g., Thortveitite,  $\text{Sc}_2\text{Si}_2\text{O}_7$   
 (b) Cyclic silicates, e.g., Wollastonite,  $\text{Ca}_2(\text{Si}_3\text{O}_9)$   
 (c) Chain silicates, e.g., Spodumene,  $\text{LiAl}(\text{SiO}_3)_2$   
 (d) Sheet Silicates, e.g., Talc,  $\text{Mg}_3(\text{OH})_2(\text{Si}_2\text{O}_5)_5$

## Mica

Micas are layer structured silicates. They have toughness, elasticity, transparency, high dielectric strength, chemical inertness and thermal stability up to 775 K. Therefore, mica sheets are used for furnace windows, for electrical insulation and in vacuum tubes.

In some silicates,  $\text{Si}^{4+}$  ion in the lattice is replaced by  $\text{Al}^{3+}$  ion. Aluminosilicates resulting from this isomorphous replacement have negatively charged macro anions. Micas and Zeolites are some of the common aluminosilicates.

## Asbestos

Asbestos are fibrous silicates. They have high tensile strength, great flexibility, resistance both to heat and flame and also to corrosion by acids or alkalies and are low cost materials. Asbestos is used as a thermal insulator for lagging steam pipes, for making fire proof textiles and as an insulator. Prolonged exposure to airborne suspensions of asbestos fibre dust can be very dangerous and there has been increasing concern at the incidence of asbestosis.

## Clay

Clays are essential components of soils, formed by weathering and decomposition of igneous rocks. When mixed with water, clays become soft, plastic and mouldable. Clays have been used since times immemorial for pottery and for making bricks, tiles, etc. Some clays like fuller's earth have high adsorptive capacity and marked cation exchange properties. They are extensively used as oil and grease absorbents in petroleum industry. Talc is valued for its softness, smoothness, dry lubricating properties and chemical inertness. Its whiteness makes it suitable for use in cosmetic and toilet preparations as well as in ceramics and paper industry.

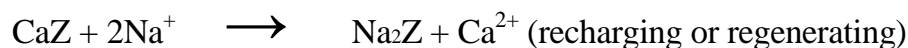
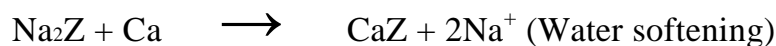
## Cement

The basic raw materials for cement manufacture are lime, silica and alumina. Portland cement is obtained by calcining a suitable mixture of limestone and clayey material and adding small amounts of gypsum and powdering the mixture. This powdered mixture hardens into a solid mass on reacting with water and gives a water resistant product. Cement slurry alone or mixed with sand or concrete can be made to set in any desired shape. This property makes it an excellent building material.

## Zeolites

Zeolites, also called Permutits, are sodium aluminosilicates used in softening of water. These are used as cation exchangers and remove the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions from hard water.

Zeolites are also aluminosilicates with open pore structure and contain equal number of anions and cations.



The calcium and magnesium salts of permutit can be converted back into the sodium salt by treatment with a concentrated solution of sodium chloride.

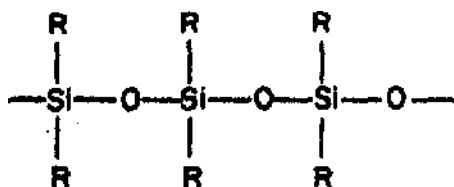
The method of melting glass was discovered about 5,000 B.C. in Egypt or Mesopotamia probably by some potters when they were firing their pots. The first articles of glass were probably the glass beads.

When a mixture of silicates mainly of sodium and calcium is melted and then supercooled, i.e. cooled immediately to a low temperature, a transparent solid is obtained which is called glass. There are different varieties of glass but most of them are a mixture of either only different silicates or mixture of borates and silicates. Borates make glass heat resistant. Borate glasses like Borosil are used for making laboratory and kitchen ware. Lead glasses have a very high refractive power and are used for making optical components like lenses, prisms, etc. Sodium glasses are soft, replacement of sodium by potassium makes glass hard. Introduction of a suitable amount of different coloured metallic oxides makes the glass coloured. Metallic oxides used are  $\text{Cu}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{U}_3\text{O}_8$ ,  $\text{MnO}_2$ ,  $\text{NiO}$ ,  $\text{Co}_2\text{O}_3$ , etc. giving red, green, yellow, violet, black and blue colours to the glass, respectively.

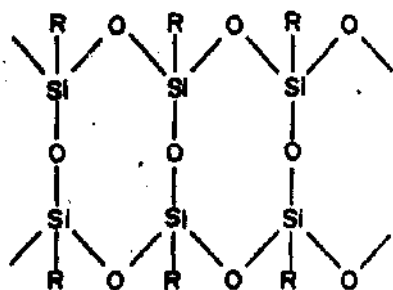
### 3.4.3 Silicones

Silicones are a group of organosilicon polymers. Unlike  $\text{SiCl}_4$  which on complete hydrolysis gives  $\text{SiO}_2$ , alkylsubstituted chlorosilanes on hydrolysis do not give the expected silicon compound analogous to ketone but get hydrolysed to long chain

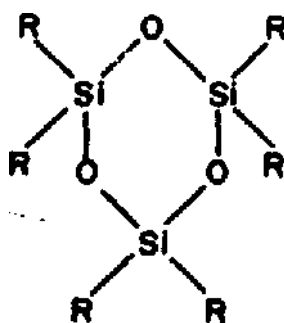
polymers or silicones. While the hydrolysis of trialkylmonochlorosilane yields Linear silicic acid polymer hexalkyldisiloxane, the alkyldichlorosilane gives straight chain polymers with active hydroxyl groups at each end of the chain and trichlorosilane gives complex cross-linked polymers. The chain size is limited by the size of alkyl group and the amount of cross-linking is regulated by the relative amounts of di- and tri-methyl-chlorosilanes. Thus silicones with desired properties can be obtained as oils, greases or rubbers. They are chemically inert, heat resistant upto ~500K, water repellent, good-electrical insulators and show little viscosity change with temperature. They are used as lubricants, insulators, protective coating and heating oils.



Linear Silicone Polymer



Cross linked Silicone Polymer



Cyclic Silicone

### SELF ASSESSMENT EXERCISE 5

Which silicon compound is used as a:

- i) dehydrating agent
- ii) cation exchanger
- iii) lubricant
- iv) thermal insulator



### 3.5 Chemistry of Divalent Silicon, Germanium, Tin and Lead Compounds

The trend in Group 4 is in keeping with the general trend in *p* block elements that the lower oxidation state becomes more stable as we go down the group. In other words, the stability of oxidation state IV decreases and that of oxidation state II increases on going from silicon to lead. This is reflected in a decrease in the reducing property of the +2 state and an increase in the oxidising property of +4 states. Ge (II) is a strong reducing agent, Sn(II) is a mild reducing agent and Pb(II) is not a reducing agent. On the other hand Ge (IV) has no oxidising property, Sn(IV) is a mild oxidant and Pb(IV) is a strong oxidant. Reasons for this we have already discussed in Sec. 1.3. However, you remember that divalent lead compounds are predominantly ionic while tetravalent lead compounds are covalent. Vapours of tin and lead halides have been shown to contain monomers,  $\text{MX}_2$ . This is expected since both metals are weakly electropositive, tin less than lead.  $\text{SnCl}_2$  is, in fact, soluble in organic solvents and does not conduct electricity in the molten state, whereas  $\text{PbCl}_2$  is only sparingly soluble in alcohol and molten  $\text{PbCl}_2$  is a good conductor. Thus  $\text{SnCl}_2$  is best regarded as covalent and  $\text{PbCl}_2$  mainly as ionic. The following brief discussion about divalent compounds of these elements highlights the trends indicated above.

Divalent silicon compounds are thermodynamically unstable under normal conditions. But, some  $\text{SiX}_2$  compounds have been formed in high temperature reactions and have been trapped by rapid chilling to liquid nitrogen temperature.

Divalent germanium halides are stable.

When anhydrous HF is passed over germanium metal at 475 K,  $\text{GeF}_2$  is formed. It is polymeric having fluorine bridges. Other dihalides are less stable than the fluoride and can be prepared by reacting the corresponding tetrahalide with germanium.

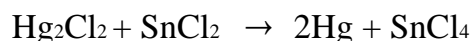
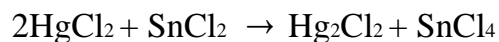
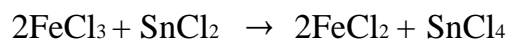


$\text{GeF}_2$  and  $\text{GeCl}_2$  react exothermically with solutions of alkali metal halides to give the hydrolytically stable  $\text{GeX}_3^-$  ion.

Divalent tin halides,  $\text{SnF}_2$  and  $\text{SnCl}_2$ , are important compounds.

When Sn is heated with gaseous HF or HCl,  $\text{SnF}_2$  or  $\text{SnCl}_2$  is obtained.  $\text{SnF}_2$  is less soluble in water.  $\text{SnO}_2$  hydrolyses in water to the basic chloride. However, if a slightly acidic solution of  $\text{SnCl}_2$  is taken,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  crystallises out. It is soluble in organic solvents, which shows its covalent nature. Despite their covalent nature, in aqueous halide solutions,  $\text{SnF}_2$  and  $\text{SnCl}_2$ , like the corresponding germanium halides, give complex ions,  $[\text{SnX}_3]^-$ . Divalent tin halides act as Lewis acids and form adducts with donor solvents, such as acetone, pyridine, etc.

In the presence of air or oxygen, Sn(II) compounds are oxidised to Sn(IV). Stannous chloride is used as a mild reducing agent. It reduces ferric salts to ferrous, cupric to cuprous, chromates to chromic salts, and mercury, gold and silver salts to the metals, e.g.



Stannous fluoride is used in tooth pastes as a source of fluoride ions to harden dental enamel. Stannous chloride is widely used as a mild reducing agent and as a mordant in calico printing.

### Divalent Lead

Of the four elements, only lead forms stable, well defined ionic compounds in the divalent state. The oxide, PbO has two forms. The red one is called litharge and the yellow one massicot. The halides unlike those of tin are always anhydrous. Except acetate and nitrate, lead(II) salts are generally insoluble in water giving characteristic properties and are thus used for characterisation of many anions like halides, sulphates, chromates, etc. All lead(II) salts are poisonous.

### SELF ASSESSMENT EXERCISE 6

Categorise the following compounds into oxidising and reducing agents: CO, GeO, PbO<sub>2</sub>, SnCl<sub>2</sub> and PbCl<sub>4</sub>

## 4.0 CONCLUSION

Group 4 comprises of the elements, Carbon, Silicon, Germanium, Tin and Lead. In this group, we observed for the first time the transition from non-metallic behaviour for carbon and silicon, through metalloid for Germanium to electropositive metallic behaviour for Sn and Pb.

## 5.0 SUMMARY

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 .....  
 .....

Let us recollect what we have studied in Unit 1 about different aspects of the elements of carbon family. The members of this family, carbon, silicon, germanium, tin and lead have been studied from the points of view of the trends in physical and chemical properties.

An increase in tendency of ionic bond formation and covalent radii of the elements has been observed down the group.

Electronegativity and ionisation energies show a decrease on moving from carbon to lead. Heavier elements in the group show metallic character also. Going down the group, the lower oxidation state, +2, becomes more stable. Silicon compounds are supposed to have internal  $\pi$ -bonding.

Allotropic forms of carbon and tin have been described.

Carbon is unique in having the important property of catenation. It also possesses the ability to form multiple bonds. This ability is responsible for the formation of a large number of carbon compounds. Carbon forms a number of binary compounds called carbides. It forms fluorocarbons which find a number of uses in industry.

Tin and lead are closely related elements. They can be tetravalent forming covalent compounds such as hydrides and tetrahalides. They can also be divalent forming compounds containing the ions  $\text{Sn}^{2+}$  and  $\text{Pb}^{2+}$ . Sn and Pb show inert pair effect. Both of them find their uses as alloys and in metal coating.

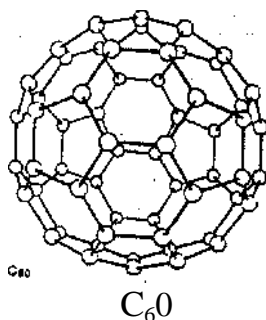
Different types of silicates and their structures have also been discussed. Silicates, in Permutit and glass have special importance industrially. Structures and some important uses of organosilicon compounds or silicones have been described.

## 6.0 TUTOR MARKED ASSIGNMENT

1. Diamond and graphite both are allotropic forms of carbon; still only graphite is used as a lubricant. Why?
2. What are the properties responsible for the anomalous behaviour of carbon?
3. Why are tin and lead incapable of showing the property of catenation?
4. Why is trisilylamine a very weak and trimethylamine a good Lewis base?
5. Give reactions to show that  $\text{CO}_2$  is an acidic oxide and  $\text{SnO}_2$  is an amphoteric oxide.
6. Explain the following briefly:
  - i)  $\text{SiC}$  is as hard as diamond.
  - ii)  $\text{CCl}_4$  is not hydrolysed while  $\text{SiCl}_4$  or  $\text{SnCl}_4$  get hydrolysed easily.
  - iii)  $\text{PbBr}_4$  and  $\text{PbI}_4$  do not exist.
  - iv)  $\text{SiO}_2$  is a solid whereas  $\text{CO}_2$  is a gas.

**APPENDIX -1****FULLERENES - Great Balls of Carbon**

As was mentioned in a previous unit, fullerenes are the new form of element carbon in which carbon atoms are 'symmetrically arranged in closed shells. They are formed when vapourised carbon condenses in an atmosphere of inert gas and produces clusters with 60 carbon atoms and clusters with 70. The  $C_{60}$  cluster has a great symmetry and it was thought to be a truncated icosahedron cage' structure i.e., a polyhedron with 20 hexagonal (6-angled) surfaces and 12 pentagonal (5 - angled) surfaces (see Fig. in the margin). The pattern of a football has exactly this structure therefore, the  $C_{60}$  molecule is sometimes called as football molecule also. The diameter of a  $C_{60}$  molecule is only 0.7 mm. The structure also resembles the geodesic dome designed by the American architect R.Buckminster Fuller for the 1967 Montreal world exhibition. The researchers therefore named this allotrope of carbon as *Buckminsterfullerene* after him.



The physicists who first discovered fullerenes had a very simple method for making them, they vapourised a graphite rod by passing a very high current through it. The vapour was prevented from reacting with the air by enclosing the rod in an inert helium atmosphere. The product obtained by this method was a fluffy, black soot. This carbon condensate was extracted with an organic solvent to get a mixture of  $C_{60}$  and  $C_{70}$ . The structure was confirmed using X-ray crystallography and other spectroscopic techniques. The chemists proposed its structure corresponding to an aromatic three dimensional system in which single and double bonds alternated.

**Properties**

As you might guess fullerenes have very different properties from diamond and graphite. For instance,  $C_{60}$  dissolves in benzene to form a wine-red solution and has mustard colour crystals. It is stable in the dark. If kept in air and exposed to ultraviolet light, the cage breaks into fragments.

Birch reduction was done to confirm the presence of double bonds in fullerenes. It uses lithium metal dissolved in liquid ammonia to reduce (or hydrogenate) the fullerene double bonds leading to  $C_{60}H_{36}$ . Osmium tetroxide ( $OsO_4$ ) reacts with one of the double bonds in the cage and if an excess of 4-tert-butylpyridine is present in the reaction mixture, a stable compound can be isolated.

The C<sub>60</sub> structure is hollow, with room for one or more other atoms, attempts were made to enclose a metal atom. Potassium, lanthanum and various other metals have been used for this purpose.

### Uses

Fullerenes are now finding use in organic chemistry, electrochemistry and semiconductor technology. They act as superconductors when doped with alkali metals. Fullerenes may find use as optical limiters since C<sub>60</sub> is transparent to low intensity but opaque to high intensity light. This property can be used to protect optical sensors from intense light. Some researchers think that fullerenes will make excellent lubricants by acting like tiny ball bearings. Many more applications will now be found owing to the aromatic and highly stable form of these molecules.

## 7.0 REFERENCES/FURTHER READINGS

*A New Concise Inorganic Chemistry*, J. D. Lee, ELBS, London, 3rd ed., 1977.

*Chemistry: Facts, Patterns and Principles*, W. R. Kneen, M. J. W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

*Advanced Inorganic Chemistry*, F. A. Cotton & G. Wilkinson, Wiley Eastern Ltd.; New Delhi, 3rd ed., 1986.

*Principles of Inorganic Chemistry*, B. R. Puri and L. R. Sharma, Shoban Lal Nagin Chand & Co., New Delhi, 11th ed., 1986.

## UNIT 2 ELEMENTS OF GROUP 5

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- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
  - 3.1 Occurrence, Extraction and Uses
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### 1.0 INTRODUCTION

We now extend our study to another group of the periodic table, namely, Group 5 consisting of nitrogen, phosphorus, arsenic, antimony and bismuth. Like the preceding groups, elements of this group also exhibit regular gradation in the physical and chemical properties. Nitrogen and phosphorus are distinctly non-metallic, arsenic and antimony are metalloids, while in bismuth metallic characteristics, predominate. The first element in the

group, nitrogen shows some exceptional behaviour. We will briefly discuss the chemistry of these elements and some of their important compounds in this unit.

## 2.0 OBJECTIVES

After studying this unit you should be able to:

- describe the occurrence, extraction and uses of the Group 5 elements;
- discuss the general characteristics of the Group 5 elements;
- discuss the properties of hydrides, halides, oxides and oxoacids of group 5 elements;
- explain how nitrogen-nitrate balance is maintained through nitrogen cycle;
- explain how atmospheric nitrogen is fixed;
- describe the use of phosphorus in fertilisers; and
- discuss the reasons for the uniqueness of Nitrogen in the group.

### How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

## 3.0 MAIN CONTENT

### 3.1 Occurrence, Extraction and Uses

Group 5 of the periodic table contains some very important elements. Nitrogen is a major component of the earth's atmosphere. Both nitrogen and phosphorus are essential constituents of all plant and animal tissues. They are also put to a variety of uses as elements and in the form of their compounds. Let us see, how these elements occur in nature and how they are extracted from their natural sources.

#### 3.1.1 Occurrence

Nitrogen is the most abundant uncombined element accessible to man. It comprises 78.1% of the atmosphere by volume. Despite its ready availability in the atmosphere, nitrogen is relatively less abundant ( $1.9 \times 10^{-3}$  %) in the crustal rocks and soils of earth. A few major minerals are saltpetre,  $\text{KNO}_3$  and Chile saltpetre,  $\text{NaNO}_3$ . Phosphorus is the eleventh element in order of abundance in the crustal rocks of the earth, its occurrence being to the extent of 0.112%. All its known terrestrial minerals are orthophosphates. The major minerals of the phosphate family are the apatites,  $\text{Ca}_5(\text{PO}_4)_3\text{X}$  and the common members are fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , chlorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$  and hydroxyapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ . In addition, there are vast deposits of amorphous phosphate rock, phosphorite,  $\text{Ca}_3(\text{PO}_4)_2$ .

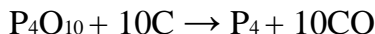
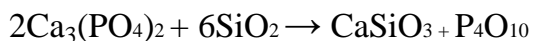
As we have said above, both nitrogen and phosphorus occur in all living beings. They are present in the proteins and in the genetic material deoxyribonucleic acid or DNA.

Phosphorus as  $\text{Ca}_3(\text{PO}_4)_2$  is also present in bones and teeth. Arsenic, antimony and bismuth are comparatively less abundant in the earth's crust, their abundances being  $1.8 \times 10^{-4}\%$ ,  $2.0 \times 10^{-5}\%$  and  $8.0 \times 10^{-8}\%$ , respectively. They mostly occur as sulphides.

### 3.1.2 Extraction

Nitrogen is obtained commercially from air. Initially air is cooled to remove water vapour and carbon dioxide and then it is repeatedly compressed to about  $2 \times 10^4$  kPa. and allowed to expand rapidly. This causes the temperature to fall and eventually, the air liquefies. Fractional distillation of liquid air enables separation of nitrogen, oxygen and the noble gases.

Phosphorus is extracted from the phosphate rock by heating it with sand and coke in an electric furnace (Fig. 2.1) at a temperature of about 1800 K. The nonvolatile silicon dioxide displaces the more volatile phosphorus pentoxide which is then reduced by coke.



Arsenic, antimony and bismuth can be obtained from their sulphide ores. The ore is roasted in air to convert the sulphide to the oxide which is then reduced by heating with coke.

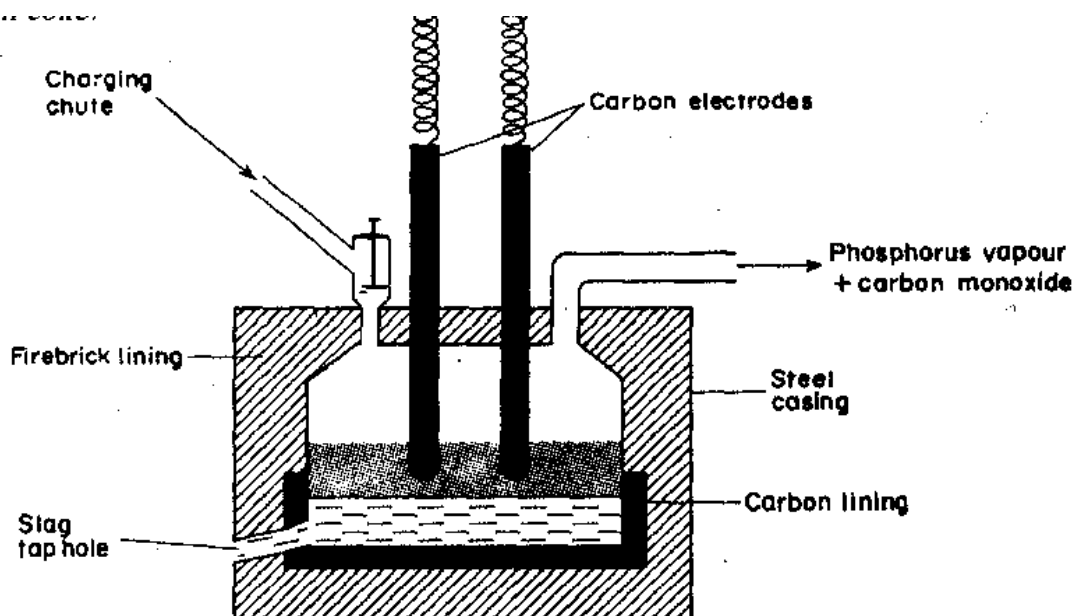


Fig. 2.1: Electric Furnace for Extracting Phosphorus



### 3.2 Uses

The main use of elemental nitrogen is to create an inert atmosphere in the iron and steel industry and in many other metallurgical and chemical processes where the presence of air would involve fire, explosion hazards or undesirable oxidation products. It is also used in the packaging of processed foods and pharmaceuticals and to pressurise electric cables, telephone wires and rubber tyres, etc. Liquid nitrogen is also frequently used for freezing of foodstuffs, freeze grinding of normally soft and rubbery materials like meat, preservation of biological specimens and for in-transit refrigeration.

Red phosphorus is used in matches, fire works and as a component of phosphor-bronze alloys used for making bearings. The main use of elemental arsenic; antimony and bismuth is in the production of various alloys.

Besides the use of elemental nitrogen, compounds of nitrogen have extensive applications in various fields. Ammonia is used in various forms as a fertiliser, e.g., as  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{HPO}_4$ , etc. Its applications also include refrigeration, as a pH controller in food and beverage industry, pharmaceuticals and in water purification. Nitric acid is another important compound of nitrogen. Its major uses include manufacture of  $\text{NH}_4\text{NO}_3$ , explosives like nitroglycerine, nitrocellulose and TNT. Hydrazine,  $\text{N}_2\text{H}_4$  and its methyl derivatives,  $\text{McNHNH}_2$  and  $\text{Me}_2\text{NNH}_2$ , are used as rocket fuels. Nitrous oxide,  $\text{N}_2\text{O}$ , is used as an anaesthetic.

Sulphides of phosphorus,  $\text{P}_4\text{S}_3$  and  $\text{P}_4\text{S}_{10}$  are used in match industry. Phosphoric acid is used in fertilisers, cleaning of metals, rust proofing, pharmaceuticals, etc. Disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4$ , is widely used as an emulsifier in the manufacture of pasteurised cheese. Sodium dihydrogen phosphate,  $\text{NaH}_2\text{PO}_4$ , is used as a constituent in the undercoat for metal paints. Calcium phosphates are used in baking powders and tooth-pastes. Synthetic  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  (1 - 2%) is added to table salt to impart free flowing properties. Sodium tripolyphosphate,  $\text{Na}_5\text{P}_3\text{O}_{10}$  is used in detergents and in softening water. Phosphorus compounds like malathion, parathion, etc., are used as pesticides.

Arsenic compounds find extensive use in agriculture as herbicides for weed and pest control, e.g., monosodium methyl arsenate, MSMA and disodium methyl arsenate, DSMA. Arsenic acid is used as a wood preservative. Sodium arsenite is used for aquatic weed control. Arsenic oxide,  $\text{As}_2\text{O}_5$ , is used to decolourise bottle glass. Antimony compound, antimonial lead, is used in storage batteries. Compounds of antimony with aluminium, gallium and indium,  $\text{AlSb}$ ,  $\text{GaSb}$  and  $\text{InSb}$ , find applications in infrared devices and in diodes.

### 3.2 General Characteristics

Elements of this group have  $ns^2np^3$  electronic configuration in their outermost shell. However, the electronic configuration of the core differs. In the case of nitrogen and phosphorus, it is that of the preceding noble gas, whereas for arsenic and antimony it is noble gas plus  $d^{10}$  and for bismuth it is noble gas plus  $d_{1f}^{14}$ . This is reflected in the properties of these elements which we will discuss below.

### 3.2.1 Physical Properties

As we have said earlier, the elements of this group show a systematic gradation of properties (Table 2.1). Nitrogen is gaseous in nature and exists as a diatomic molecule  $N_2$ . This is due to the very high bond energy of the  $N=N$  bond,  $946 \text{ kJ mol}^{-1}$ , which is nearly six times the  $N-N$  bond energy,  $160 \text{ kJ mol}^{-1}$ . On the contrary  $P-P$  bond is quite weak, its energy of  $490 \text{ kJ mol}^{-1}$  is only  $\sim 2.5$  times the  $P-P$  bond energy,  $209 \text{ kJ mol}^{-1}$ . Therefore, phosphorus exists as tetra-atomic  $P_4$  molecules in the gaseous state. In the solid state, it exists in different allotropic forms about which you will study in the following subsection.

The change from non-metallic to metallic character with increase in the atomic number is well illustrated in this group. The first two elements, nitrogen and phosphorus, are nonmetals, arsenic and antimony are metalloids whereas bismuth is predominantly metallic in nature. In keeping with this trend, the electronegativity of these elements decreases gradually on moving down the group. The density, melting and boiling points of the elements increase with increase in atomic number.

Atomic radii, as expected, increase with increase in atomic number. As a consequence, ionisation energies decrease on descending the group. Nitrogen shows an exceptionally high ionisation energy which is due to its small atomic size. As discussed above, all the elements of this group have five electrons in their valence shell, they exhibit a highest oxidation state of +5 by using all five electrons in forming bonds. As one goes down the group, the tendency of the pair of  $s$  electrons to remain inert increases and only  $p$  electrons are used in bonding, resulting in an oxidation state of +3. The stability of +3 state relative to the +5 state thus increases on moving down the group. In the case of nitrogen, a very wide range of oxidation states exists: -3 in  $NH_3$ , -2 in  $N_2H_4$ , -1 in  $NH_2OH$ , 0 in  $N_2$ , +1 in  $N_2O$ , +2 in  $NO$ , +3 in  $HNO_2$ , +4 in  $NO_2$  and +5 in  $HNO_3$ . The negative oxidation states of nitrogen arise because of its higher electronegativity (3.05) than that of hydrogen (2.1). As you can see from the Table 2.1, the energy required to produce  $M^{5+}$  is so immense that it is never formed. The compounds formed by these elements in +5 oxidation state are thus predominantly covalent. However, in case of Sb and Bi, the sum of the first three ionisation energies is just low enough to form  $M^{3+}$  ions. But fluorine is the only element which gives an electronegativity difference enough to permit the formation of ionic bonds. Thus  $SbF_3$  and  $BiF_3$  exist as ionic solids.

Table 2.1: Some physical properties of Group 5 elements

Property	Nitrogen N	Phosphorus P	Arsenic As	Antimony Sb	Bismuth Bi
Atomic number	7	15	33	51	83
Electronic configuration	[He]2s <sup>2</sup> 2p <sup>3</sup>	[Ne]3s <sup>2</sup> 3p <sup>3</sup>	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>3</sup>	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>3</sup>	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>3</sup>
Ionic radius (pm)	171 (-3)	212 (-3)	222 (-3)	62 (+5)	120 (+3)
Covalent radius (pm)	70	110	121	141	148
van der Waals radius (pm)	150	180	200	220	
Bond energy (E-E, kJ mol <sup>-1</sup> )	160	209	180	142	-
Melting point (K)	63	317 <sup>w</sup>	1090	903	544
Boiling point (K)	77	553 <sup>w</sup>	883	1653	1833
Density (10 <sup>3</sup> × kg m <sup>-3</sup> )	0.81 <sup>a</sup>	1.82 <sup>a</sup>	5.73	6.7	9.8
Electronegativity (A/R)	3.05	2.05	2.2	1.8	1.63
Electron affinity (kJ mol <sup>-1</sup> )	+9	-72	-77	-101	-110
Ionisation energy (kJ mol <sup>-1</sup> )					
(I + II + III)	8,839	5,864	5,478	4,866	4,766
(I + II + III + IV + V)	25,755	17,090	16,357	14,469	14,490
Common oxidation states <sup>a</sup>	-3, -2, -1, 0, 1, 2, 3, 4, 5	-3, (1), 3, 5	-3, 3, 5	(-3), 3, 5	3, (5)

a = density of liquid at boiling point; w = white; \* the oxidation states in bracket correspond to less stable oxidation state of the element.

Since, it is not easy from energy considerations to gain three electrons to achieve stable noble gas configuration, the formation of the tri-negative ion (M<sup>3-</sup>) is rare. But, nitrogen being the smallest and the most electronegative of all the members of the group, forms trivalent anion with reactive metals which have low ionisation energies. Thus, nitrogen forms ionic nitrides such as Li<sub>3</sub>N, Be<sub>3</sub>N<sub>2</sub>, Mg<sub>3</sub>N<sub>2</sub>, Ca<sub>3</sub>N<sub>2</sub>. As the electronegativity of the other elements of the group, i.e., P, As, Sb and Bi, is low, most of their compounds are covalent in nature.

Nitrogen is not able to extend its coordination number beyond four, the other elements have coordination numbers of five as well as six. The extension of coordination number is due to the availability of *rf*-orbitals in P, As, Sb and Bi, using which these elements can attain *sp*<sup>3</sup>*d* and *sp*<sup>3</sup>*d*<sup>2</sup> hybridisation, e.g., in PCl<sub>5</sub> and PCl<sub>6</sub><sup>-</sup>, respectively. Thus, nitrogen does not function as a Lewis acid whereas phosphorus, arsenic, antimony and bismuth do so. The hydrides of this group and their alkyl derivatives act as Lewis bases, forming a number of addition complexes, e.g., NH<sub>3</sub>.BF<sub>3</sub>, CaCl<sub>2</sub>.4NH<sub>3</sub>, etc.

Nitrogen forms strong *pit-pit* multiple bonds but other elements of the group do not show this behaviour. This property also differentiates nitrogen from other elements of the group. Apart from the nitrogen molecule, N=N, compounds having *pit-pit* multiple bonding include nitrates, NO<sub>3</sub><sup>-</sup>, nitrites, NO<sub>2</sub><sup>-</sup>, azides, N<sup>3-</sup>, cyanides, O=N<sup>-</sup>, oxides of nitrogen, etc. Thus, the oxides N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> are monomeric due to the presence of multiple bonds but analogous P<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> exist as dimers, P<sub>4</sub>O<sub>6</sub> and P<sub>4</sub>O<sub>10</sub>. However, phosphorus and the heavier elements of the group show *dπ-pπ* bonding.

### 3.2.2 Allotropic Forms of Phosphorus

Phosphorus exists as discrete tetrahedral P<sub>4</sub> molecules in the gaseous and liquid states and also in the solid state as white phosphorus. Because of angular strain in the P<sub>4</sub> molecule in which the angles are only 60°, it is reactive. It spontaneously catches fire in air. White phosphorus is soft, appreciably volatile and poisonous, soluble in organic solvents but not

in water. In fact, it is stored under water to protect it from oxygen. Phosphorus glows in the dark with faint green glow, due to phosphorescence.

Phosphorescence is a form of luminescence in which a substance emits light of one wavelength after having absorbed electromagnetic radiation of shorter wavelength. It may continue for a considerable time after excitation.

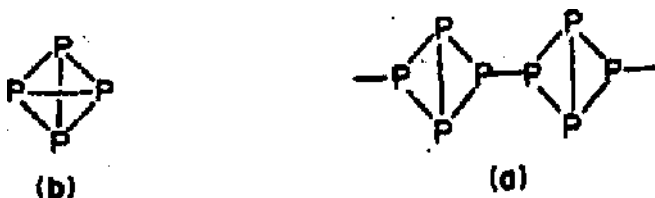
Above 1600 K,  $P_4$  molecules begin to dissociate into  $P_2$  molecules. Rapid cooling of this vapour gives brown phosphorus which probably contains  $P_2$  molecules. If white phosphorus is heated above 1000 K for sometime, one of the P-P bonds in  $P_4$  is broken and a polymeric form of phosphorus known as red phosphorus is formed. Because of its polymeric structure in which angles are less strained, it is less reactive. Heating white phosphorus under high pressure results in black phosphorus which is inert and has layer structure (Fig. 2.2), resembling graphite. Like graphite it has metallic lustre and is a conductor of heat and electricity. Black phosphorus is the most metallic of the allotropes of phosphorus and is often called metallic phosphorus.

Reactivity of the various allotropic forms of phosphorus towards other substances decreases in the order, brown > white > red > black, the last one being almost inert. Similarly, arsenic, antimony and bismuth also have a number of allotropic forms. Generally, the metallic allotropes become more stable with increasing atomic number.

### 3.2.3 Chemical Properties

Nitrogen is quite inert at room temperature because of the great strength of the N=N bond,  $946 \text{ kJ mol}^{-1}$ . It is a blessing, in the sense that our atmospheric oxygen might otherwise disappear with some of the nitrogen to form oceans of nitric acid. White phosphorus is very reactive while red and black allotropes are not. Arsenic, antimony and bismuth are fairly reactive.

With oxygen, nitrogen combines only at very high temperatures to yield nitric oxide; white phosphorus combines so readily giving trioxide and pentoxide that it is stored under water.



Arsenic, antimony and bismuth on heating in air form the trioxides  $As_2O_3$ ,  $Sb_2O_3$  and  $Bi_2O_3$ , respectively. All except nitrogen react with halogens to form halides  $EX_3$  and  $EX_5$ ; bismuth yields only  $BiX_3$  (inert pair effect).

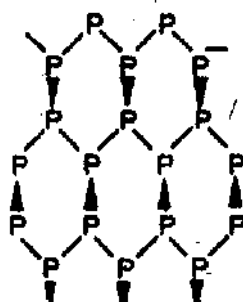
All react with sulphur, except nitrogen, to form the sulphides.

Only nitrogen reacts with hydrogen under suitable conditions to form ammonia.

All the elements of Group 5 react with metals; nitrogen forming nitrides, phosphorus and arsenic giving phosphides and arsenides whereas antimony and bismuth form alloys.

Hot concentrated sulphuric acid converts phosphorus, arsenic, antimony and bismuth to  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{AsO}_3$  (arsenious acid),  $\text{Sb}_2(\text{SO}_4)_3$  and  $\text{Bi}_2(\text{SO}_4)_3$ , respectively. With nitric acid, phosphorus forms phosphoric acid arsenic forms arsenous and arsenic acids, antimony and bismuth form  $\text{Sb}_2\text{O}_5$  and  $\text{Bi}(\text{NO}_3)_3$ , respectively.

The action of alkalis is different on different elements — phosphorus forms alkali hypophosphites and phosphine, arsenic forms alkali arsenites  $\text{AsO}_3^{3-}$ , whereas antimony and bismuth remain unaffected.



Scan Fig. 2.2: Allotropes of Phosphorus: (a) Red Phosphorus (b) White Phosphorus and (c) Black Phosphorus.

These reactions are summarised in Table 2.2

Table 2.2: Some Reactions of Group 5 elements

$\text{E} + \text{O}_2 \xrightarrow{\text{Heat}} \text{E}_x\text{O}_y$	Nitrogen forms NO when a mixture of $\text{N}_2$ and air is passed through an electric arc; P gives $\text{P}_2\text{O}_3$ and $\text{P}_2\text{O}_5$ ; As, Sb and Bi yield $\text{As}_2\text{O}_3$ and $\text{Bi}_2\text{O}_3$ .
$\text{E} + \text{F}_2 \longrightarrow \text{E}_x\text{F}_y$	Not N and P; As, Sb and Bi form $\text{AsF}_3$ , $\text{SbF}_3$ and $\text{BiF}_3$ , respectively.
$\text{E} + \text{X}_2 \longrightarrow \text{E}_x\text{X}_y$ (X = Cl, Br, I)	Not N; P gives $\text{PX}_3$ and $\text{PX}_5$ ; As, Sb and Bi form $\text{EX}_3$ .
$\text{E} + \text{S} \longrightarrow \text{E}_x\text{S}_y$	Not N; P gives $\text{P}_4\text{S}_3$ ; As, Sb and Bi form $\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ and $\text{Bi}_2\text{S}_3$ , respectively.
$\text{P} + \text{KOH} + \text{H}_2\text{O} \longrightarrow \text{PH}_3 + \text{KH}_2\text{PO}_2$	Not N, Sb and Bi; As reacts with fused alkalis to form $\text{Na}_3\text{AsO}_3$ and $\text{H}_2$ .
$\text{As} + \text{H}_2\text{SO}_4 \xrightarrow{\text{hot \& conc.}} \text{H}_3\text{AsO}_3$	Not N; P forms $\text{H}_3\text{PO}_4$ whereas Sb and Bi yield $\text{Sb}_2(\text{SO}_4)_3$ and $\text{Bi}_2(\text{SO}_4)_3$ , respectively.
$\text{As} + \text{HNO}_3 \xrightarrow{\text{dil}} \text{H}_3\text{AsO}_3$	Conc. $\text{HNO}_3$ oxidises P, As, Sb and Bi to $\text{H}_3\text{PO}_4$ , $\text{H}_3\text{AsO}_4$ , $\text{Sb}_2\text{O}_5$ and $\text{Bi}(\text{NO}_3)_3$ , respectively.

Before we discuss the compounds of Group 5 elements, try the following

**SELF ASSESSMENT EXERCISE 1**

Explain briefly in the space given below, why

- Nitrogen exists as  $N_2$  whereas phosphorus exists as  $P_4$  molecules in the gaseous state.
- White phosphorus is more reactive than red phosphorus.

**3.3 Hydrides**

All elements of Group 5 form trihydrides of the type  $EH_3$ . In addition to these, nitrogen also forms  $N_2H_4$  and  $N_3H$ , and phosphorus gives  $PaH^$ . Bond energy of the M-H bond decreases from  $NH_3$  to  $BiH_3$  because of increase in the size of the element on descending the group. Consequently, the stability of the hydrides decreases from  $NH_3$  to  $BiH_3$ ; bismuth hydride decomposes quite rapidly at room temperature. As you have studied in Unit 3, the variation in boiling point of trihydrides is one of the strongest pieces of evidence for hydrogen bond formation by nitrogen. Properties of these trihydrides are summarised in Table 2.3.

Table 2.3: Properties of Group 5 hydrides,  $EH_3$

Property	Ammonia $NH_3$	Phosphine $PH_3$	Arsenic $AsH_3$	Stibine $SbH_3$	Bismuth $BiH_3$
Melting point (k)	195	139	157	185	-
Boiling point (k)	240	186	211	256	295
Solubility in water (V/N at 293 K)	739	0.26	0.20	0.20	-
Odour	Pungent	decaying	Garlic-like	-	-
Bond energy, E-H ( $kJ\ mol^{-1}$ )	389	322	297	255	-
Bond angle	$106^{\circ}47'$	$93^{\circ}30'$	$92^{\circ}$	$91^{\circ}30'$	-
Dipole moment (D)	1.44	0.55	0.15		
Decomposition to elements (K)	775	On gentle heating	295	295	very unstable

The central atom in the trihydrides is  $sp^3$  hybridised. As one of the positions in the tetrahedron is occupied by a lone pair, the structure of these hydrides is pyramidal, (Fig. 2.3). The tetrahedron is distorted due to repulsion between the lone pair of electrons and the bond pairs. With the decrease in the electronegativity of the central atom, the bond pairs of electrons go further away from the central atom. This results in a decrease in the repulsion of the bonding pairs in the vicinity of the central atom resulting in a decrease in

the bond angles which become close to  $90^\circ$  (Table 2.3). E-H bond then consists of almost pure  $p$ -orbitals and the lone pair is almost in a pure  $s$ -orbital. As we go down the group, lone pair resides mainly in the  $s$ -orbital from where it is more difficult to be removed. This is the reason why ammonia acts as a better donor than other hydrides of the group. Thus,  $\text{NH}_3$  readily forms ammonium salts with  $\text{H}^+$ . Phosphonium salts are formed with  $\text{H}^+$  only under anhydrous conditions but other hydrides,  $\text{AsH}_3$ ,  $\text{SbH}_3$  and  $\text{BiH}_3$  do not form such salts. Let us now discuss the hydrides of nitrogen in brief.

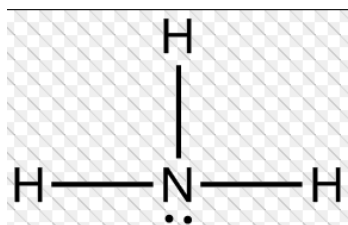
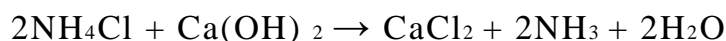


Fig. 2.3: Structure of Ammonia

### 3.3.1 Ammonia

As described earlier, ammonia is an important industrial chemical of all the nitrogen compounds; it is produced in the largest quantities. Ammonia can be obtained in the laboratory by heating ammonium salts with an alkali:



Ammonia is manufactured industrially by Haber process. Nitrogen from air and hydrogen from synthesis gas, are reacted together at a high pressure of about 250 atmosphere and at a temperature of 800 K in the presence of a finely divided catalyst.



As Le Chatelier's principle would tell you, high pressure will favour the forward reaction, which proceeds with reduction in volume. Since the forward reaction is exothermic, high temperatures would favour the back reaction resulting in dissociation of ammonia. However, to enable the reaction to proceed at a reasonable rate, the reaction is carried out at 800 K in the presence of a finely divided iron catalyst containing traces of oxides of Mo, K and Al. The above pressure and temperature is optimum to give about 15% yield of  $\text{NH}_3$ . The unreacted gases are recycled.

A mixture of carbon monoxide and hydrogen, obtained from methane,  $\text{CH}_4$ , naphtha,  $\text{C}_7\text{H}_{16}$  and water at 1175 K and 30 atm. pressure in presence of a catalyst is known as synthesis gas.

Le Chateller's Principle: If the conditions controlling the equilibrium of a system are changed, the system moves in such a way as to oppose the effects of the change.

Ammonia has a strong characteristic pungent smell. It is a colourless gas at room temperature and can be easily liquefied by either increasing the pressure or decreasing the temperature. It is highly soluble in water; it is more soluble than any other gas because of

hydrogen bonding with water. The ammonia solution in water is generally called ammonium hydroxide. The name ammonium hydroxide is, however, misleading and the solution should better be called 'aqueous ammonia'. The solution has  $\text{NH}_3(\text{aq})$ ,  $\text{NH}_4^+(\text{aq})$  and  $\text{OH}^-(\text{aq})$  ions:

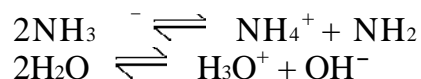


The equilibrium constant  $K$  for the above reaction is only  $1.81 \times 10^{-5}$ . This value is quite low, suggesting that the aqueous solution is a weak alkali. Ammonia solution, in the presence of  $\text{NH}_4\text{Cl}$ , is used as a buffer solution in the pH range of 10. This mixture is also used for precipitation of metal hydroxides selectively. You must have studied simple reactions of ammonia, e.g., with  $\text{HCl}$  in your school chemistry.

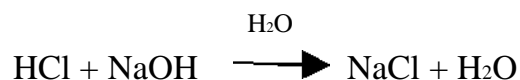
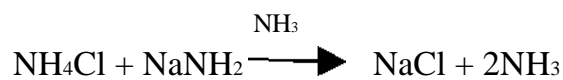
As we have discussed earlier,  $\text{NH}_3$  molecule has a pyramidal structure, having a lone pair of electrons at the apex. The ammonium ion formed on reaction with  $\text{H}^+$  has a tetrahedral structure. Ammonia functions as a donor molecule towards Lewis acids and many complex ions having ammonia as a ligand are known, e.g.,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Ag}(\text{NH}_3)_2]^+$ ,  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ , etc. Ammonia is linked to the metal ions through its lone pair.

#### Liquid Ammonia as a Non-aqueous Solvent

Liquid ammonia functions as a good solvent for many substances and many types of reactions. In this behaviour, it resembles water as a solvent. Both are self-ionising, the difference being in the lower degree of ionisation of ammonia:

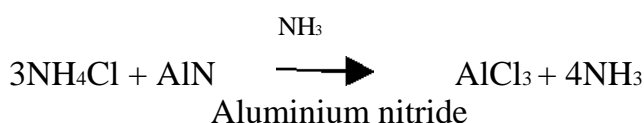
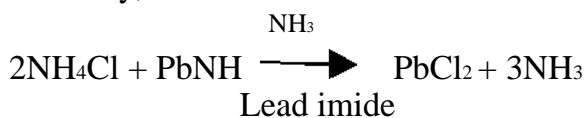


As you know, all those substances, which on dissolving in water produce hydronium ion, are acids and all those which produce hydroxide ion are bases, e.g.,  $\text{HCl}$ ,  $\text{HNO}_3$  are acids in water and  $\text{NaOH}$ ,  $\text{Ca}(\text{OH})_2$  are bases. Similarly, all those substances which dissolve in liquid ammonia to give  $\text{NH}_4^+$  ions are acids and those which give amide ions,  $\text{NH}_2^-$ , are bases. Thus,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$  are acids and  $\text{NaNH}_2$  is a base in liquid ammonia. Acid-base neutralisation reaction in liquid ammonia, thus, can be a reaction giving a salt and the solvent. Compare the corresponding reaction in water, e.g.

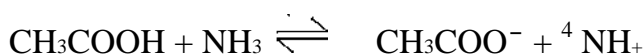
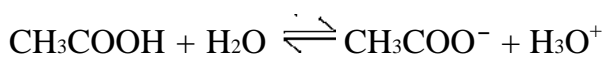




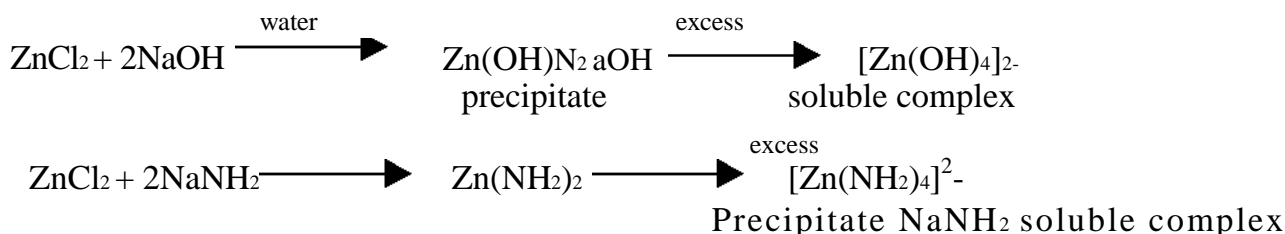
Similarly,



Thus, we see that imides like PbNH, and nitrides such as AlN, also function as bases in liquid ammonia. Liquid ammonia is a basic solvent because it can easily accept a proton. Therefore, those acids which are weak in water will be highly acidic in liquid ammonia. Thus, acetic acid is a weak acid in water ( $\text{pK}_a = 5$ ) but will function as a strong acid in liquid ammonia:



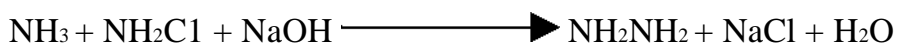
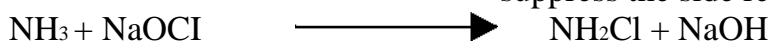
Reactions associated with complex formation are also comparable in water and liquid ammonia.



As you have learnt in Units 4 and 5, liquid ammonia dissolves alkali and alkaline earth metals giving blue solutions. This reaction is, however, less vigorous than the reaction of these metals with water.

### 3.3.2 Hydrazine, N<sub>2</sub>H<sub>4</sub>

Hydrazine is prepared by the action of sodium hypochlorite on ammonia in the presence of a small amount of gelatin, which helps to suppress the side reactions:



Anhydrous hydrazine may be obtained by distillation over NaOH or by precipitating  $\text{N}_2\text{H}_6\text{SO}_4$ , which is then treated with liquid  $\text{NH}_3$  to precipitate  $(\text{NH}_4)_2\text{SO}_4$ :



Hydrazine is a colourless, fuming liquid. It forms a dihydrate,  $\text{N}_2\text{H}_4 \cdot 2\text{H}_2\text{O}$  and two series of salts, e.g.,  $\text{N}_2\text{H}_5\text{Cl}$  and  $\text{N}_2\text{H}_6\text{Cl}_2$ . Hydrazine burns in air giving nitrogen and water. As this reaction is highly exothermic ( $\Delta H^\circ = -622 \text{ kJ}$ ), hydrazine is used as a rocket fuel along with liquid air or oxygen as an oxidant.

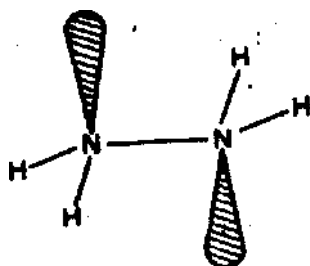
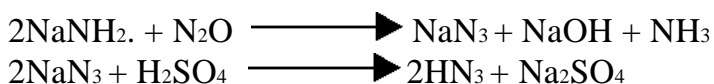


Fig. 2.4: Structure of Hydrazine

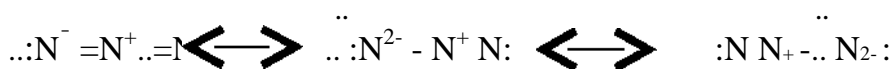
Hydrazine has a structure (Fig. 8.4) similar to that of hydrogen peroxide having two lone pairs of electrons and can act as a coordinating ligand forming complexes with metal ions like  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , etc. The bond energy of N-N bond in hydrazine is very small due to the repulsion of the nonbonding electrons which weaken the N-N bond. Thereby hydrazine is unstable, it decomposes to  $\text{N}_2$ ,  $\text{NH}_3$  and  $\text{H}_2$  at 500 K.

### 3.3.3 Hydrazoic Acid, $\text{HN}_3$ , and Azides

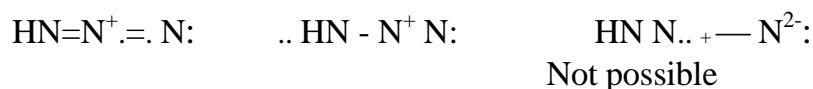
Hydrazoic acid is also known as hydrogen azide. It is a colourless, highly explosive liquid. When sodamide is reacted with  $\text{N}_2\text{O}$  at 450 K, sodium azide is formed which on treatment with sulphuric acid gives hydrazoic acid:



It is a weak acid and dissociates only slightly in water. With electropositive metals it forms azides.  $\text{Pb}(\text{N}_3)_2$  is covalent and explosive in nature and it is used as a detonator.  $\text{NaN}_3$  is ionic and non-explosive. For the azide ion,  $\text{N}_3^-$ , three resonance structures can be drawn:



For covalent azides and hydrazoic acid, which is largely covalent, three resonance structures may also be drawn. But, according to Pauling's adjacent charge rule, one structure is excluded, since in it, two adjacent atoms have the same charge.

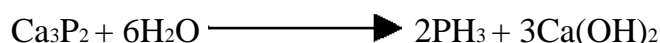


Thus the increased stability of the ionic azides may be due to a larger number of resonance forms.

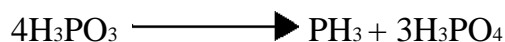
### 3.3.4 Phosphine, PH<sub>3</sub>

Phosphine, PH<sub>3</sub>, is the most stable hydride of phosphorus. It is intermediate in thermal stability between ammonia and arsine. Phosphine can be easily prepared by any of the following methods:

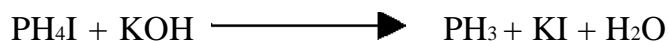
hydrolysis of metal phosphides such as AlP or Ca<sub>3</sub>P<sub>2</sub>:



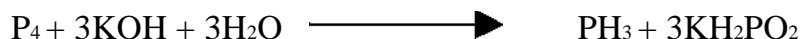
Pyrolysis of phosphorus acid at 480 - 485 K:



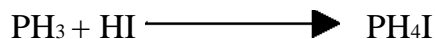
Alkaline hydrolysis of phosphonium iodide:



Alkaline hydrolysis of white phosphorus (industrial process):



Phosphine is a colourless, extremely poisonous gas having a faint garlic odour. As the P-H bond is not polar enough to form P-H---P or P-H---O bonds, unlike ammonia, phosphine is not associated in the liquid state and is much less soluble in water. In contrast to the basic nature of solutions of ammonia in water, aqueous solutions of phosphine are neutral, which is due to the much weaker tendency of PH<sub>3</sub> to protonate in water. However, it does react with HI to form phosphonium iodide:



Pure phosphine ignites in air at about 435 K, but when contaminated with traces of P<sub>2</sub>H<sub>4</sub> it is spontaneously inflammable:



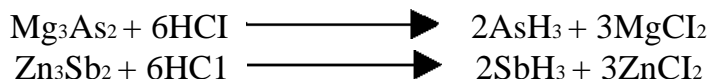
### 3.3.5 Arsine, Stibine and Bismuthine

AsH<sub>3</sub>, SbH<sub>3</sub> and BiH<sub>3</sub> are exceedingly poisonous, thermally unstable, colourless gases whose physical properties are compared with those of NH<sub>3</sub> and PH<sub>3</sub> in Table 7.3. As

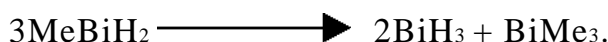
pointed out earlier, the thermal stability and basic character of these hydrides decrease from  $\text{NH}_3$  to  $\text{BiH}_3$ .

The thermal instability of  $\text{AsH}_3$  is realised in the detection of arsenic poisoning.

$\text{AsH}_3$  and  $\text{SbH}_3$  can be prepared by acid hydrolysis of arsenides and antimonides of electropositive elements like Na, Mg, Zn, etc.:



Bismuthine is extremely unstable and is best prepared by the disproportionation of methylbismuthine at 230 K:



### SELF ASSESSMENT EXERCISE 3

Explain briefly:

- i. Why ammonia acts as a Lewis base?
- ii. What type of substances act as acids or bases in liquid ammonia?
- iii. Why hydrazine is unstable?

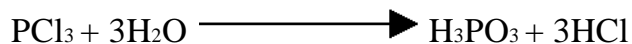
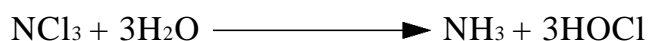
## 3.4 Halides

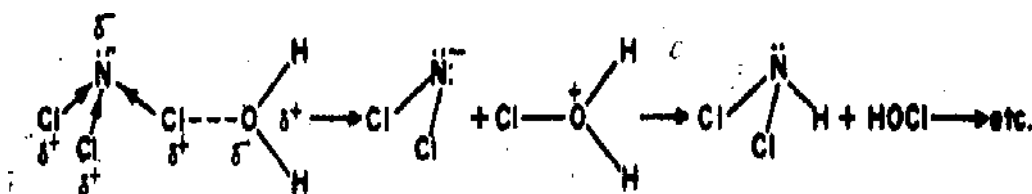
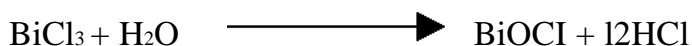
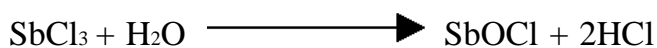
We have already discussed that Group 15 elements form compounds mainly in two oxidation states, +3 and +5. Both types of their halides, i.e. trihalides as well as pentahalides are known. We will discuss the trihalides first and then the pentahalides.

### 3.4.1 Trihalides

All the elements of Group 5 form trihalides,  $\text{MX}_3$ . Of all nitrogen halides, only  $\text{NF}_3$  is stable due to strong N-F bonds. All other trihalides of nitrogen,  $\text{NCl}_3$ ,  $\text{NBr}_3$  and  $\text{NI}_3$  are unstable. Of these,  $\text{NCl}_3$  is explosive and  $\text{NBr}_3$  and  $\text{NI}_3$  exist only as their ammoniates, i.e., as ammonia adducts and detonate on removing ammonia.

Except  $\text{NX}_3$ , all the trihalides hydrolyse rapidly to either hydrated oxides, e.g.,  $\text{As}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  or acids,  $\text{H}_3\text{PO}_3$  or oxochloride,  $\text{SbOCl}$  and  $\text{BiOCl}$ .  $\text{NCl}_3$  on hydrolysis gives  $\text{NH}_3$  and  $\text{HOCl}$  instead of  $\text{HNO}_2$  (nitrous acid) and  $\text{HCl}$ :

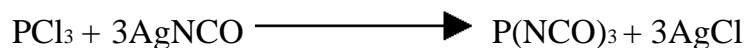
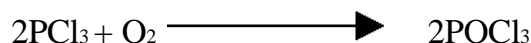
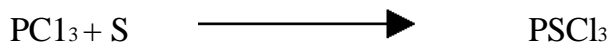
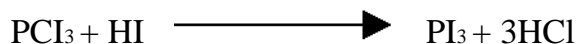
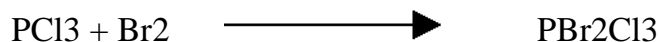
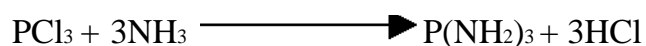




The mechanism of the hydrolysis of phosphorus trichloride is similar to that of silicon tetrachloride, explained in the preceding unit. It involves the formation of an intermediate four coordinate species  $\text{H}_2\text{O} \rightarrow \text{PCl}_3$ . The formation of this type of intermediate is impossible for nitrogen because of the non-availability of *d*-orbitals.  $\text{NCl}_3$ , therefore, hydrolyses by a different mechanism, which involves the attack of the Lewis base, water, on the partially positive chlorine to remove it in the form of a protonated hypochlorous acid molecule. Proton exchange with the  $\text{Cl}_2\text{N}^-$  anion then generates one molecule of  $\text{HOCl}$  and  $\text{NHCl}_2$  each.

Replacement of two more chlorine atoms with hydrogen produces the  $\text{NH}_3$  molecule:

The trihalides, except  $\text{NX}_3$ , act as Lewis acids, i.e. electron pair acceptors, forming haloanions,  $\text{SbCl}_4^-$ ,  $\text{BiCl}_4^-$ , etc. The trihalides can be oxidised to pentahalides. The ease of oxidation decreases from  $\text{PX}_3$  to  $\text{BiX}_3$ . However,  $\text{NX}_3$  is not oxidised at all. The trihalides function as halogenating agents.  $\text{PCl}_3$  reacts with  $\text{NH}_3$ , halogens,  $\text{HI}$ ,  $\text{S}$ ,  $\text{O}_2$  and  $\text{AgNCO}$  to give  $\text{P}(\text{NH}_2)_3$ ,  $\text{PX}_2\text{Cl}_3$ ,  $\text{PI}_3$ ,  $\text{PSCl}_3$ ,  $\text{POCl}_3$  and  $\text{P}(\text{NCO})_3$ , respectively. The following chemical equations represent these reactions:



Trihalides of the lighter elements of the group are predominantly covalent in nature; therefore, they can exist as discrete molecules which have a pyramidal structure, like  $\text{NH}_3$ . The trihalides of heavier elements, e.g.,  $\text{BiF}_3$ , are ionic in nature.

### 3.4.2 Pentahalides

Nitrogen does not form any pentahalides. The stability of other pentahalides of the group decreases in the order  $P > Sb > As > Bi$  and in the order  $F > Cl > Br$  for halogens.  $PF_5$ ,  $PCl_5$ ,  $PBr_5$ ,  $AsF_5$ ,  $SbF_5$ ,  $SbCl_5$ , and  $BiF_5$  are stable. However,  $PBr_5$  and  $SbCl_5$  readily lose halogen forming trihalides. The pentahalides get more oxidising as we go down in the group, except arsenic pentahalides,  $AsX_5$ , which are unexpectedly more oxidizing than those of the element following it in the group. All the pentahalides have trigonal bipyramidal structure in the gas phase (Fig.2.5). However, their structures differ in the solid state, e.g.,  $PCl_5$  splits into  $[PCl_4]^+ [PCl_6]^-$  which have tetrahedral and octahedral structures, respectively;  $PBr_5$  splits to give  $[PBr_4]^+ Br^-$ . Pentahalides are obtained by the action of excess of halogen on trihalides:

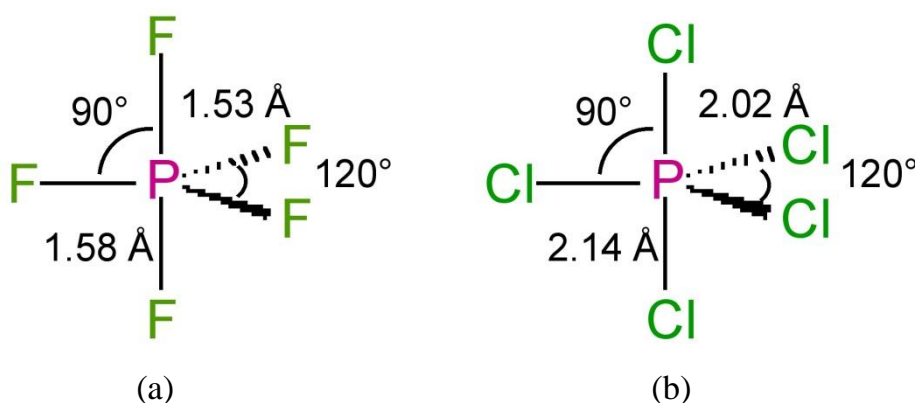
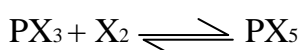


Fig. 2.5: Structure of  $PCl_5$  in (a) Gaseous state (b) Solid state

Pentahalides are good halogenating agents, e.g.,  $PCl_5$  is used for conversion of alcohols to alkyl halides and acids to acylchlorides as shown below:



They hydrolyse to give either oxoacids,  $H_3PO_4$ ,  $H_3AsO_4$ , or hydrated oxides like  $Sb_2O_3 \cdot nH_2O$  or oxohalides like  $BiOCl$ ; partial hydrolysis of  $PCl_5$  gives  $POCl_3$ . Almost all pentahalides can accept an electron pair and act as Lewis acids, as in  $PF_6^-$ ,  $PF_5$ ,  $L$ , etc.

**SELF ASSESSMENT EXERCISE 3**

Explain briefly why trihalides of nitrogen cannot be oxidised to pentahalides.

**3.5 Oxides**

As stated earlier, nitrogen forms a number of oxides,  $N_2O$ ,  $NO$ ,  $N_2O_3$ ,  $NO_2$  or  $N_2O_4$  and  $N_2O_5$ , and also very unstable  $NO_3$  and  $N_2O_6$ . All these oxides of nitrogen exhibit  $p\pi-p\pi$  multiple bonding between nitrogen and oxygen. This does not occur with the heavier elements in the group and consequently nitrogen forms a number of oxides which have no P, As, Sb or Bi analogues. The oxides of this group will be discussed briefly in this section.

$N_2O$	Nitrous oxides	Colourless	Rather unreactive
$NO$	Nitric oxide	Colourless	Moderately reactive
$N_2O_3$	Dinitrogen trioxide	Dark blue	Extensively dissociated as gas
$NO_2$	Nitrogen dioxide	Brown	Moderately reactive
$N_2O_4$	Dinitrogen tetroxide	Colourless	Extensively dissociated to $NO_2$ as gas and partly as liquid
$N_2O_5$	Dinitrogen pentoxide	Colourless	Unstable as gas; ionic solid
$NO, N_2O_6$			Not well characterised and quite unstable

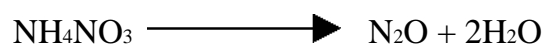
Important characteristics of oxides of nitrogen are listed in Table 2.4. Let us first describe the preparation, properties and structures of these oxides.

Table 2.4: Oxides of Nitrogen

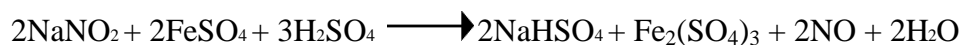
Formula	Name	Colour	Remarks
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Preparation

$N_2O$  is obtained generally by heating  $NH_4NO_3$ :

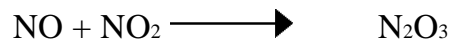


$NO$  is best prepared by the reduction of 8M  $HNO_3$  with reducing agents like  $Cu$  or by reduction of nitrous acid or nitrites by  $Fe^{2+}$  or  $I^-$  ions:



As you will study later, NO is formed as an intermediate in the manufacture of nitric acid by oxidation of NH<sub>3</sub>.

N<sub>2</sub>O<sub>3</sub> is obtained as an intense blue liquid or a pale blue solid on cooling an equimolar mixture of NO and NO<sub>2</sub>:

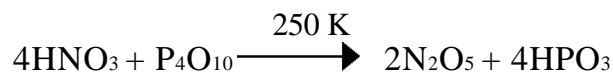


On warming, its colour fades due to its dissociation into these two oxides.

NO<sub>2</sub> can be prepared by reduction of cone. HNO<sub>3</sub> with Cu or by heating heavy metal nitrates:



N<sub>2</sub>O<sub>5</sub> is an anhydride of HNO<sub>3</sub>. It is best prepared by dehydrating HNO<sub>3</sub> with P<sub>4</sub>O<sub>10</sub> at low temperatures:



N<sub>2</sub>O is also known as laughing gas because it induces laughter. Mixed with N<sub>2</sub>, it is used as an anaesthetic by dentists.

### Properties and Structure

Oxides of nitrogen are all oxidising agents, N<sub>2</sub>O even supporting the combustion of S and P. NO which is thermally more stable, supports the combustion of Mg and P but not of S. Sulphur flame is not hot enough to decompose it. N<sub>2</sub>O and NO are neutral, while the other oxides are acidic.

N<sub>2</sub>O is isoelectronic with CO<sub>2</sub> and also has a linear structure. However, unlike CO<sub>2</sub>, N<sub>2</sub>O has a small dipole moment. The resonance structures of the molecule are given in Fig. 2.6.



Fig. 2.6: Resonance Structures of Nitrous Oxide

NO has a total of 15 electrons. It is impossible for all of them to be paired and hence this is an odd electron molecule. In the gaseous state, it is paramagnetic. However, the liquid and the solid states are diamagnetic because loose dimers (Fig. 2.7) are formed cancelling out the magnetic effect of unpaired electrons.



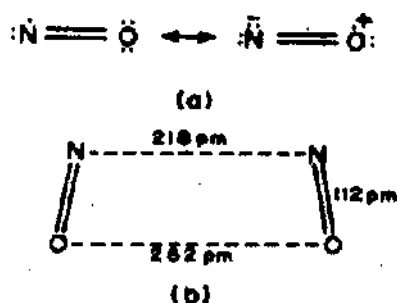


Fig. 2.7: (a) Resonance Structures of Nitric Oxide, and (b) Molecular Structure of Crystalline Nitric Oxide

The bonding in NO is best described by the molecular orbital theory.

Molecular orbital electronic configuration of NO molecule can be represented as  $\sigma s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p^2, \sigma 2p^2, \pi^y 2p^2, \pi^z 2p^2, \pi^* 2p^1$ . This gives a bond order of 2.5. If the unpaired electron occupying the antibonding  $\pi^* 2p_y$  orbital is removed, nitrosonium ion,  $\text{NO}^+$ , is formed and the bond order becomes 3. This is reflected in the shortening of the bond length from 115 pm in NO to 106 pm in  $\text{NO}^+$ . Nitrosonium ion is stable and forms salts like  $\text{NO}^+\text{Cl}^-$ . It is isoelectronic with CO and forms complexes with transition elements. The brown ring formed in the test for nitrates is due to the formation of a complex of iron,  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$ .

$\text{NO}_2$  with 23 electrons is again an odd electron molecule. In the gaseous state it is paramagnetic. On cooling, the gas condenses to a brown liquid and eventually to a colourless solid both of which are diamagnetic due to dimerisation.  $\text{NO}_2$  molecule is angular with  $\text{ONO}$  angle of  $134^\circ$ . The O-N bond length is 120 pm, intermediate between a single and a double bond. The odd electron is on nitrogen. The dimer has been shown to have a planar structure. The N-N bond length is very large, 175 pm, making this a very weak bond (Fig. 2.8).

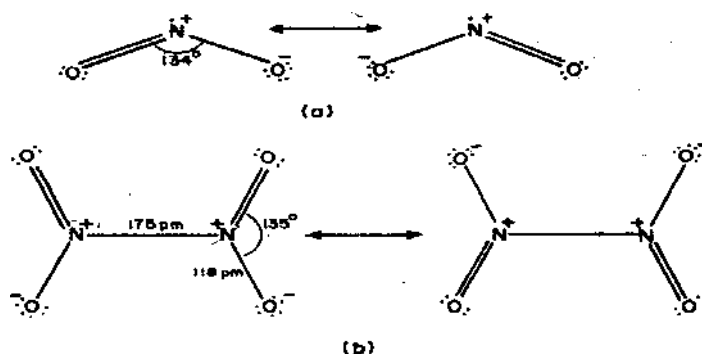


Fig. 2.8: Resonance Structure of (a)  $\text{NO}_2$ , and (b)  $\text{N}_2\text{O}_4$

Liquid  $\text{N}_2\text{O}_4$  undergoes self-ionisation to form  $\text{NO}^+$  and  $\text{NO}_2^-$  ions and therefore, it has been extensively studied as a non-aqueous solvent. Resonance structures of  $\text{N}_2\text{O}_3$  are shown in Fig. 2.9(a).

Solid  $\text{N}_2\text{O}_5$  exists in the ionic form,  $\text{NO}_2^+\text{NO}_3^-$ . In the gaseous form, the discrete  $\text{N}_2\text{O}_5$  molecules have an N-O-N bond angle close to  $180^\circ$ , Fig. 2.9(b).

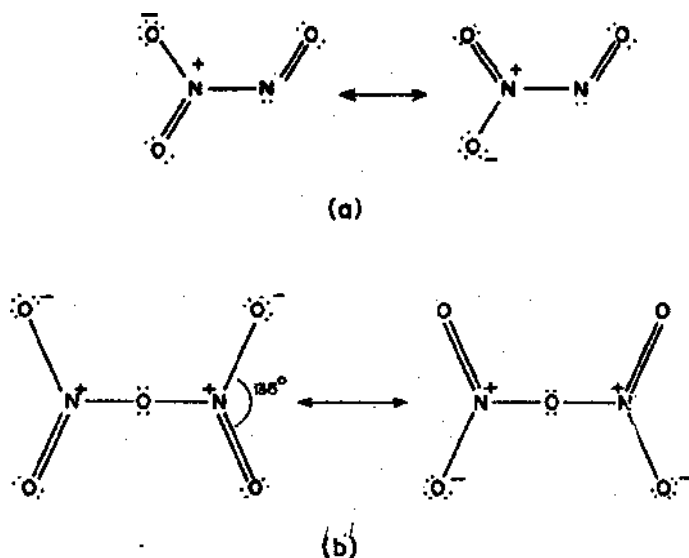
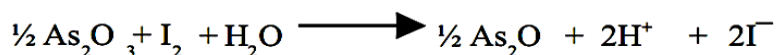


Fig. 2.9: Resonance Structures of (a)  $\text{N}_2\text{O}_3$ , and (b)  $\text{N}_2\text{O}_5$

### 3.5.2 Oxides of Phosphorus, Arsenic, Antimony and Bismuth

As discussed earlier, P, As and Sb form oxides in both +3 and +5 oxidation states whereas only one oxide of bismuth,  $\text{Bi}_2\text{O}_3$  is known. Remember the stability of higher oxidation states decreases on going down the group. Except  $\text{Bi}_2\text{O}_3$  others exist in dimeric form. Structures of oxides of phosphorus are shown in Fig 2.10. As expected. The basic character of oxides increases on descending the group. The oxides of P and As are acidic, those of Sb amphoteric and of Bi wholly basic. Also the higher oxidation states are more acidic.

$\text{As}^{\text{III}}$  is quantitatively oxidised to  $\text{As}^{\text{V}}$  by  $\text{I}_2$ . Therefore,  $\text{As}_2\text{O}_3$  is used as a primary standard in iodimetric titrations.



#### SELF ASSESSMENT EXERCISE 4

Explain briefly why NO is paramagnetic whereas  $\text{NO}^+$  is diamagnetic.

### 3.6 Oxoacids of Nitrogen, Phosphorus, Arsenic and Antimony

An oxoacid is the acid in which ionisable hydrogen atoms are attached to the central atom through oxygen atoms, e.g.,  $\text{Cl-OH}$ . N, P, As and Sb form a number of oxoacids as also do S, Se and Te in Group 16, and Cl, Br and I in Group 7. Let us, therefore, first familiarise ourselves with the nomenclature of oxoacids.

To distinguish between the oxidation states of the central atom in oxoacids, suffixes, ous and ic are used. The acids in which the central atom is in a lower oxidation state are termed ous acids, whereas those having central atom in a higher oxidation state are called ic acids. The oxoacids having halogens in their highest oxidation states are termed as peracids. In hypo-ous and hypo-ic acids the oxidation state of the central atom is lower than that in ous and ic acids, respectively.

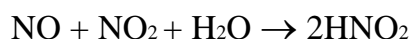
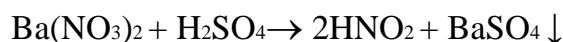
The prefixes ortho, meta and pyro are used to distinguish acids differing in the content of water. The most highly hydroxylated acid of an element in a particular oxidation state is called the ortho acid. The acid which has one water molecule less than the ortho acid is called meta acid. The pyro acid corresponds to the loss of one water molecule between two molecules of the ortho acid. You will find examples of all these types while you study the oxoacids in this unit and in the following two units.

### 3.6.1 Oxoacids of Nitrogen

Nitrogen forms a number of oxoacids. Most of them are known only in aqueous solutions or as their salts. We will discuss here the two better known oxoacids, i.e., nitrous acid and nitric acid.

#### Nitrous Acid, HNO<sub>2</sub>

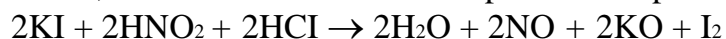
It is an unstable, weak acid which is known only in aqueous solution. It can be obtained by acidifying an aqueous solution of a nitrite or by passing an equimolar mixture of NO and NO<sub>2</sub> into water:



on trying to concentrate, the acid decomposes:



Nitrous acid and nitrites are good oxidising agents and convert iodides to iodine, ferrous salts to ferric, stannous to stannic and sulphites to sulphates, e.g.



With strong oxidising agents, like KMnO<sub>4</sub>, nitrous acid and nitrites function as reducing agents and get oxidised to NO<sub>3</sub> ions:



Structures of nitrous acid and nitrite ion are shown in Fig. 2.11.

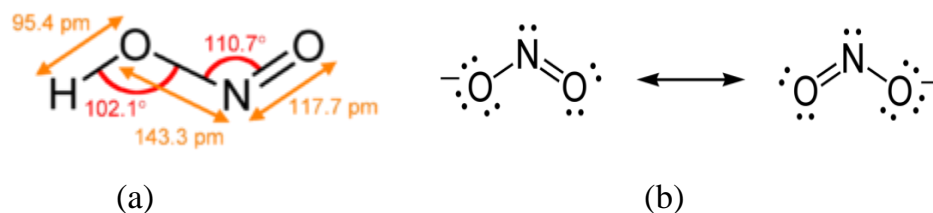


Fig. 2.11: (a) Molecular Structure of HNO<sub>2</sub>; (b) Resonance Structures of Nitrite Ion

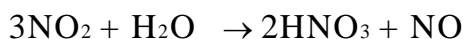
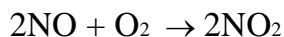
Nitrite ion is a good coordinating agent. Both nitrogen and oxygen have lone pairs capable of forming coordinate bond with metal ions. Nitrite ion can coordinate either through N or through O. Thus, isomerism occurs between M<sup>4</sup>—NO<sub>2</sub> and M<sup>4</sup>—ONO structures. Analogous organic derivatives are also known, the nitrites, R<sup>4</sup>—ONO and the nitro compounds, R—NO<sub>2</sub> where R is any alkyl or aryl group. Such ligands which can coordinate in two different ways are called ambidentate.

### Nitric Acid, HNO<sub>3</sub>

Nitric acid is one of the major acids of modern chemical industry. It has been known as a corrosive solvent for metals since the thirteenth century. HNO<sub>3</sub> is now almost exclusively manufactured by Ostwald process. In this process NH<sub>3</sub> is catalytically oxidised to give NO:



In the above reaction, about 96-98% of NH<sub>3</sub> is converted into NO. Since, the reaction is exothermic, reaction temperature can be maintained without external heating provided a heat exchanger is used. The mixture of gases is cooled and diluted with air. NO combines with O<sub>2</sub> to give NO<sub>2</sub> which is absorbed in water to give HNO<sub>3</sub> and NO, which is then recycled. The following equations represent various steps in this process:



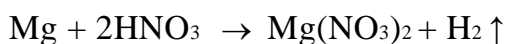
Nitric acid can be concentrated to 68% by distillation, when a constant boiling mixture is formed. More concentrated acid can be made by distilling the mixture with concentrated sulphuric acid.

Constant boiling mixture or azeotrope is a mixture of two or more liquids that distils at a certain temperature and has a constant composition at a given pressure. Its boiling point may be lower or higher than the boiling points of pure components.

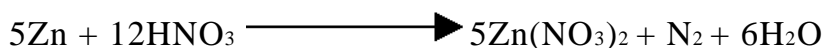
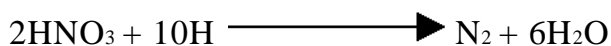
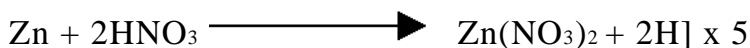
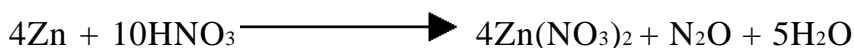
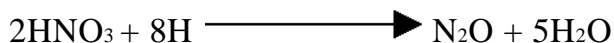
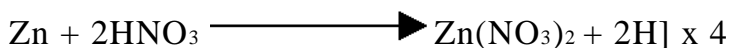
Pure nitric acid is a colourless liquid (b.p. 359 K); It decomposes readily in light giving a yellow colour due to the formation of nitrogen dioxide. It is a strong acid and is almost completely dissociated into ions in solution. It reacts with metals and with metal oxides, hydroxides and carbonates forming salts called nitrates.

The reaction of  $\text{HNO}_3$  with metals is of, particular interest because of the great variety of products obtained, e.g.,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$  and  $\text{NO}_2$  in addition to the nitrate or oxide of the metal. The nature of products formed depends upon the nature of the metal and reaction conditions, like concentration of the acid and temperature.

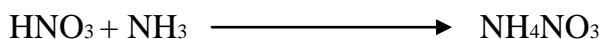
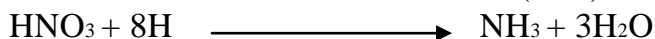
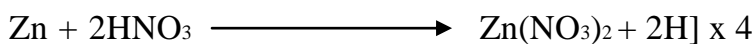
With very dilute acid, magnesium and manganese give hydrogen:



Other metals like Zn, Sn, Fe, etc., which also lie above hydrogen in the electrochemical series, liberate hydrogen from dilute nitric acid. But, since nitric acid is a strong oxidising agent and hydrogen a reducing agent, secondary reactions take place resulting in the reduction of nitric acid to  $\text{NH}_3$ ,  $\text{N}_2\text{O}$  or  $\text{N}_2$ . Thus, Zn reacts with dilute  $\text{HNO}_3$  in cold giving  $\text{N}_2\text{O}$  or  $\text{N}_2$  according to the following equations:



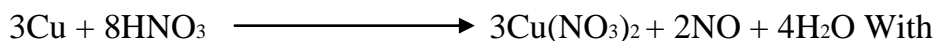
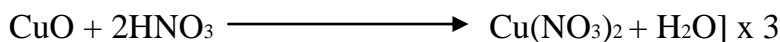
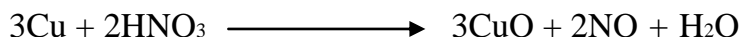
Very dilute  $\text{HNO}_3$  reacts with Zn to give  $\text{NH}_3$ , which is of course neutralised to form  $\text{NH}_4\text{NO}_3$ :



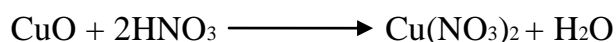
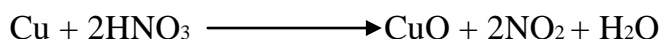
Similarly, iron and tin also give  $\text{NH}_4\text{NO}_3$  with dilute  $\text{HNO}_3$  in cold.

As you know, metals such as Cu, Bi, Hg, Ag, etc., lying below hydrogen in the electrochemical series do not liberate hydrogen from acids. With these metals, the action of

nitric acid involves the oxidation of metals into the metallic oxides which dissolve in the acid to form nitrates accompanied by evolution of NO or NO<sub>2</sub> depending upon whether the acid is dilute or concentrated. For instance, Cu, Ag, Hg and Bi react with dilute acid liberating NO:

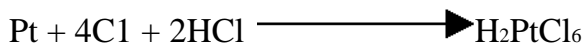
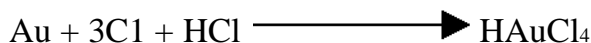
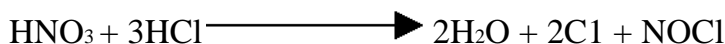


concentrated acid NO<sub>2</sub> is given off:

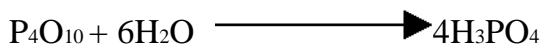
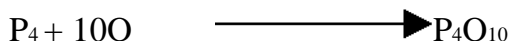
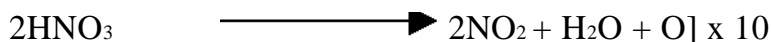


Concentrated nitric acid behaves essentially as an oxidising agent and metals like Al, Fe, Cr, etc., are rendered passive due to the formation of a layer of insoluble oxide on the metal surface.

Noble metals like Au, Pt, Rh and Ir are not attacked by nitric acid. However, a 1:3 mixture of conc. HNO<sub>3</sub> and conc. HCl known as aqua regia, dissolves Au and Pt as it contains free chlorine:

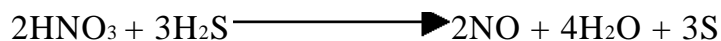
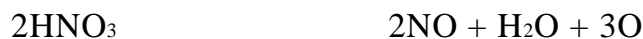


Conc. HNO<sub>3</sub> readily oxidises the solid nonmetals and metalloids to their respective oxoacids or hydrated oxides. Thus, P, As, Sb, S, I and Sn are oxidised to phosphoric acid, H<sub>3</sub>PO<sub>4</sub>, arsenic acid, H<sub>3</sub>AsO<sub>4</sub>, antimony pentoxide, Sb<sub>2</sub>O<sub>5</sub>, sulphuric acid, H<sub>2</sub>SO<sub>4</sub>, iodic acid, HIO<sub>3</sub> and metastannic acid, H<sub>2</sub>SnO<sub>3</sub>, respectively, e.g.,



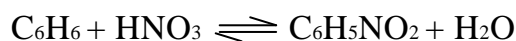


Dilute nitric acid also acts as an oxidising agent. Hence, reducing agents, such as,  $\text{H}_2\text{S}$ ,  $\text{HI}$  and  $\text{FeSO}_4$  are oxidised to  $\text{S}$ ,  $\text{I}_2$  and  $\text{Fe}_2(\text{SO}_4)_3$ ; respectively:



Nitric acid also oxidises many organic compounds. It converts a mixture of cyclohexanol and cyclohexanone to adipic acid which is the starting material for nylon polymers. Nitric acid also oxidised *p*-xylene to terephthalic acid which is used for the manufacture of terylene.

Concentrated nitric acid, in the presence of concentrated sulphuric acid, reacts with certain aromatic compounds forming nitro compounds, e.g., benzene is converted into nitrobenzene:



This process known as nitration is of great industrial importance because of usefulness of nitro compounds. Nitronium ion,  $\text{NO}_2^+$ , which is formed in the presence of the conc.  $\text{H}_2\text{SO}_4$ , is believed to be the active nitrating agent:



The molecular structure of nitric acid is shown in Fig. 2.2. In nitric acid the nitrogen and the three oxygen atoms are coplanar. Terminal N-O bonds are equivalent, the other N-O bond is much longer and corresponds to a single bond.

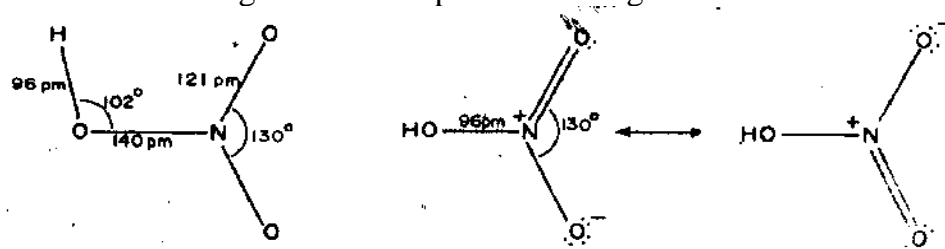


Fig. 2.12 (a) Molecular Structure of  $\text{HNO}_3$  2.12(b) Resonance Structures of  $\text{HNO}_3$

The nitrate ion is planar with equal N-O bonds. Its structure can be represented as a resonance hybrid as shown in Fig. 2.13.

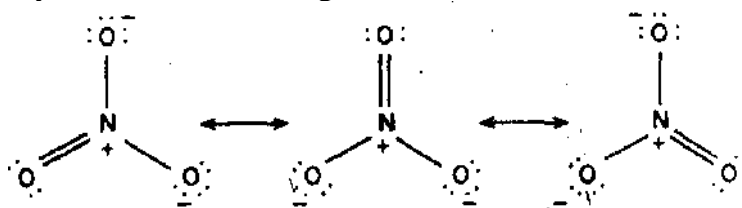


Fig. 2.13: Resonance Structures of Nitrate ion 3.6.2 Oxoacids of

Phosphorus, Arsenic and

## Antimony

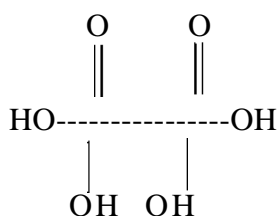
Phosphorus, arsenic and antimony also form a number of oxoacids. Oxoacids of arsenic and antimony are not well characterised. Their salts, however, are known. Phosphorus forms two series of oxoacids, the phosphoric and the phosphorous acids. The oxidation state of phosphorus is +5 in phosphoric acids whereas it is +3 in phosphorous acids. You may notice that hypophosphorous and phosphorous acids have direct P-H bond(s) also. However, this P-H bond is not ionisable, it does not give  $H^+$ , and hence, it does not confer acidity. These acids are, therefore, monobasic and dibasic, respectively. Table 2.5 summarises the properties of oxoacids of phosphorus.

**Table 2.5: Oxoacids of phosphorus and their properties**

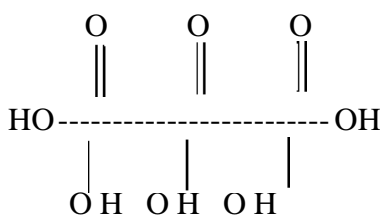
Acid	Nature	Preparation	Anion	Remarks
$H_3PO_2$ or $H_2PO(OH)O$ Hypophosphorous	Crystalline white solid	White P + 4 alkali	$H_2PO_2^-$ Hypophosphite	Strongly reducing monobasic $pK \sim 2$
$H_3P_2O_3$ or $HPO(OH)$ Orthophosphorous	Deliquescent colourless solid	$PO_4^{3-}$ or $PCl_6^-$ + $H_2O$	$H_2PO_3^-$ , $H_2PO_3^{2-}$ Phosphate	Reducing, but slow, dibasic $pK_1 - 2$ , $pK_2 - 2$
$H_4P_2O_6$ Pyrophosphoric	White solid	$PCl + H_3PO_3$	$H_2P_2O_5^{2-}$ Pyrophosphite	Reducing, dibasic
$H_4P_2O_4$ Hypophosphoric	White solid	Red P + alkali	$P_2O_6^{4-}$ , Hypophosphate	Not reducing or oxidizing, tetrabasic $pK_1 - 2$
$H_3PO_4$ Orthophosphoric	White solid	$P_4O_{10} + H_2O$	$H_2PO_4^-$ , $HPO_4^{2-}$ , $PO_4^{3-}$ phosphate	Not oxidising, tribasic
$H_4P_2O_7$ Orthophosphoric	Colourless solid	Heat phosphates or phosphoric acid	$P_2O_7^{4-}$ , Pyrophosphate	Tetrabasic $pK_1 - 2$
$HPO_3$ Metaphosphoric	Deliquescent solid	Heat $H_3PO_4$ to 600 K		

A large number of condensed phosphoric acids or their salts are known which have rings or chains of  $PO_4$  tetrahedra linked together through PO-P linkages, e.g. di or pyrophosphoric acid,  $H_4P_2O_7$  and triphosphoric acid,  $H_5P_3O_{10}$ :



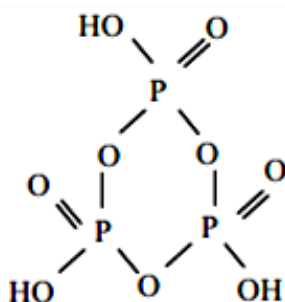


Diphosphate acid

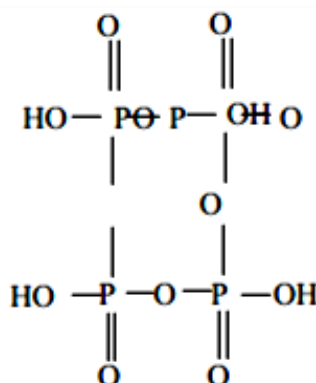


Triphosphoric acid

Sodium salt of triphosphoric acid,  $\text{Na}_5\text{P}_3\text{O}_{10}$ , forms stable chelate complexes with alkaline earth metal cations. It is, therefore, used in water softening. What is known as metaphosphoric acid and given the empirical formula  $\text{HPO}_3$  is in fact a mixture of cyclo-polyphosphoric acids containing  $-\text{P}-\text{O}-\text{P}-\text{O}-$  linkages. Two important cyclo-polyphosphoric acids are cyclotriphosphoric acid,  $\text{H}_3\text{P}_3\text{O}_9$  and cyclo-tetraphosphoric acid,  $\text{H}_4\text{P}_4\text{O}_{12}$ .



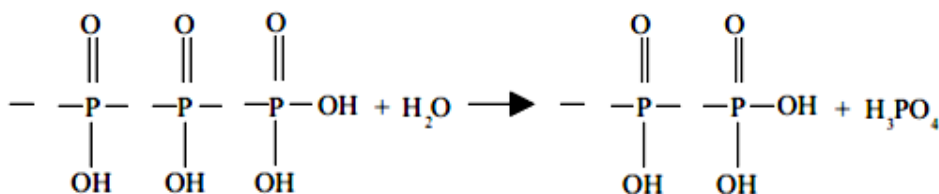
Cyclo-triphosphoric acid



Cyclo-tetraphosphoric acid

Salts of cyclo-polyphosphoric acids having 3-8 phosphorus atoms are known. Sodium cyclo-hexaphosphate,  $\text{Na}_6\text{P}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ , known as calgon is a useful compound. It forms soluble complexes with alkaline earth metal cations. Therefore, it is used in water softening.

The phosphate link,  $\text{P}-\text{O}-\text{P}$ , is very important in biological systems, as it is supposed to be the prime store of energy. The energy of the bond ( $29 \text{ kJ mol}^{-1}$ ) is released to the system when needed, by enzyme catalysed hydrolysis of the phosphate link in adenosine triphosphate (ATP), the high energy molecule:



Adenosine diphosphate (ADP)

Adenosine triphosphate (ATP)

### SELF ASSESSMENT EXERCISE 5

- Write one reaction each showing oxidising and reducing properties of  $\text{HNO}_2$ .
- Describe briefly the manufacture of nitric acid.

### 3.7 Nitrogen Cycle, Nitrogen Fixation. and Phosphate Fertilisers

We have, so far, studied the compounds of Group 5 elements. Now we will see some other aspects of their chemistry. You have already learnt about the nitrogen cycle in detail in the Foundation Course in Science and Technology. We will discuss it here briefly.

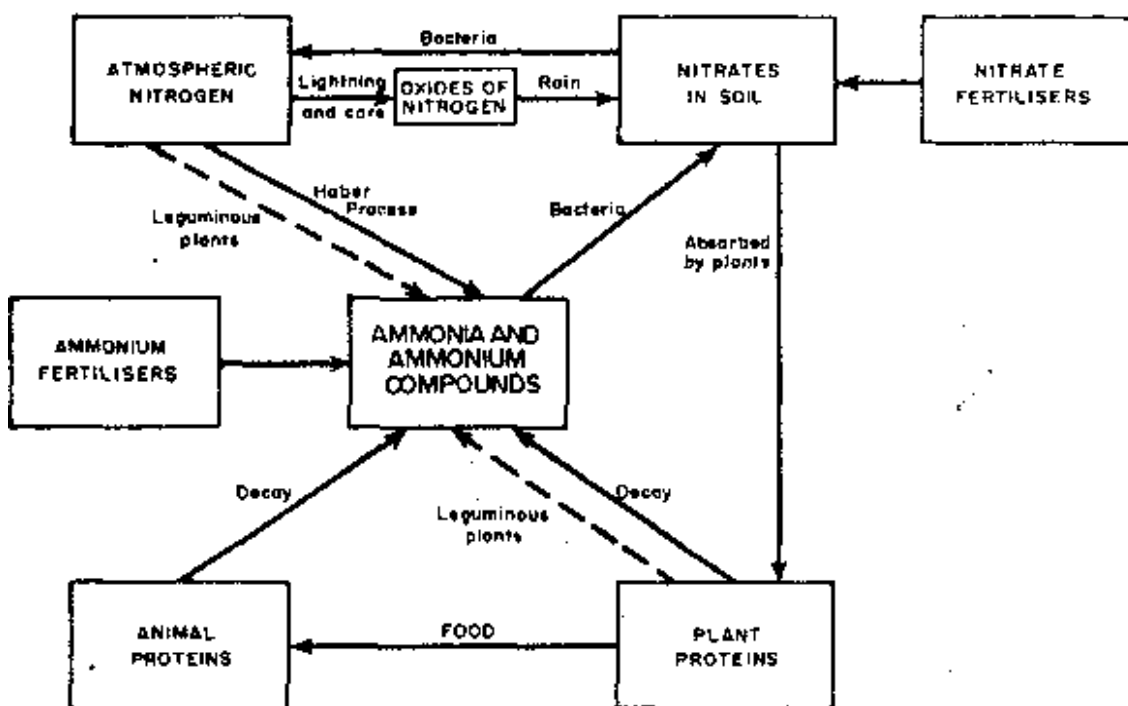
#### 3.7.1 Nitrogen Cycle

Nitrogen cycle as you know, is the continuous exchange of nitrogen between the atmosphere and the biosphere. Though, the atmosphere contains large reserves of nitrogen, most plants and animals cannot utilise it in the elemental form. Plants can utilise nitrogen in the form of ammonium salts or as nitrates, so atmospheric nitrogen has to be converted to this form or 'fixed' so that plants can utilise it.

One way of nitrogen fixation is by lightning discharges in the atmosphere, when nitrogen gets converted to nitric oxide and then to nitric acid. This nitric acid is washed down by rain into the soil, where it is neutralised by lime present in the soil to form calcium nitrate.

There is also a biological mode of nitrogen fixation. Certain bacteria, both free living or symbiotic, convert atmospheric nitrogen into ammonium salts. In the latter category is rhizobium which lives in the root nodules of leguminous plants like peas, beans, soya, etc. Such bacteria are called nitrogen fixing bacteria. It has been estimated that about  $90-175 \times 10^6$  tonnes of nitrogen is fixed biologically per year. The comparable figures for industrial fixation are about  $85 \times 10^6$  tonnes per annum.

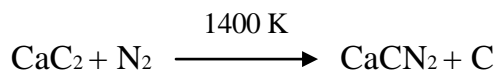
The ammonium salts and nitrates are taken up from the soil by plants which convert them into proteins and nucleic acids, essential components of all living beings. From plants these are passed on to the herbivores, the animals which live on plants and then on to the carnivores along the food chain.



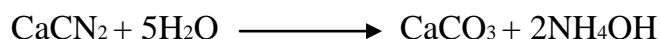
When the plants and animals die, their bodies decay, the nitrogenous compounds in their bodies get decomposed to ammonia and ammonium compounds by ammonifying bacteria present in the soil. The ammonium salts are converted to the nitrites by nitrosifying bacteria, and the nitrites oxidised to nitrates by nitrifying bacteria. An alternate path way is the conversion of nitrogenous compounds to elementary nitrogen by denitrifying bacteria. Release of nitrogen into the atmosphere, in a way, completes this cycle (Fig. 2.14).

### 3.7.2 Nitrogen Fixation

To meet the needs of the increasing world population, agricultural productivity needs to be increased. When the same soil is cropped intensively year after year, it gets depleted in nitrogen content which must be supplemented by artificial fertilisers to enhance production. In addition to the fertilisers there is also a great demand for other nitrogen compounds like polymers, explosives, etc. To meet these demands, we have to draw upon the atmospheric nitrogen. Atmospheric nitrogen can be fixed artificially by a variety of methods. One important method for the fixation of nitrogen is its conversion into  $\text{NH}_3$  by Haber process which you have already studied. Formation of calcium cyanamide is another such method. Calcium cyanamide is obtained by passing atmospheric  $\text{N}_2$  over calcium carbide at 1400 .K.



Calcium cyanamide is used in large amounts as a nitrogenous fertiliser because it is slowly hydrolysed in the soil to ammonia:



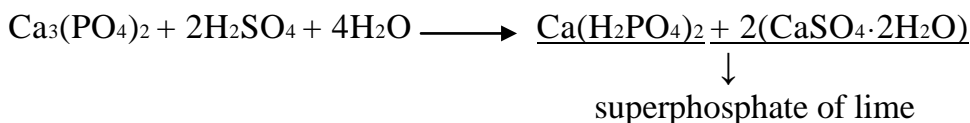
It is also used as a source of organic chemicals such as melamine.

You can see that the conversion of atmospheric nitrogen into ammonia by Haber process and by Cyanamide process is expensive because these processes need the use of high temperature and pressure. Therefore, considerable research is going on to discover catalytic reactions which will convert nitrogen into ammonia under normal conditions, as in the case of biological processes.

### 3.7.3 Phosphate Fertilisers

As mentioned earlier also, phosphorus like nitrogen is an essential constituent of living organism. Plants and animals take phosphorus for their growth through different sources. Plants assimilate phosphorus from the soil which contains small quantities of phosphorus as phosphates. Phosphates are very important fertilisers. Animals get their phosphorus from plants as well as from other non-vegetarian sources, e.g., eggs, meat, etc. Some of this phosphorus is returned to the soil on death and decay of plants and animals. To make up for the phosphorus deficiency in the Soil, especially in view of intensive agricultural activity, artificial fertilisers are needed. Phosphorite rock itself can be pulverised and used

as a phosphate fertiliser, but because  $\text{Ca}_3(\text{PO}_4)_2$  has a very low solubility it is able to deliver phosphate only slowly and in small amounts. However, treatment of  $\text{Ca}_3(\text{PO}_4)_2$  with dilute sulphuric acid gives a fertiliser known as superphosphate of lime, a mixture of  $\text{CaSO}_4$  and  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ :



Because  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  is water soluble, this mixture is a more effective fertiliser than phosphorite rock, hence, the name superphosphate. There are other phosphate fertilisers also, e.g., a mixture of  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{CaHPO}_4$ . In the manufacture of steel, a by-product phosphatic slag is obtained. This slag is also a very good fertiliser.

### SELF ASSESSMENT EXERCISE 6

Fill in the blanks in the following sentences:

- i. Continuous exchange of nitrogen between the atmosphere and the biosphere is called
- ii. Conversion of nitrogen into its compounds is known as
- iii. Bacteria which convert nitrogen into its compounds are called
- iv. Bacteria which convert nitrogen compounds into free nitrogen are known as
- v. The ammonium compounds are converted into the nitrites by.....
- vi. The nitrites are oxidised to the nitrates by .....
- vii. Superphosphate of lime is a mixture of.....and.....

### 3.8 Anomalous Behaviour of Nitrogen

As usual, nitrogen, the first element of Group 5 differs considerably from rest of the family members. These differences are due to the small size of nitrogen, its high electronegativity, tendency to form stable multiple bonds and non-availability of d-orbitals in the valence shell. These differences have been highlighted in various sections of this unit. Let us bring them together here and see how many of these you can recollect.

The elemental form of nitrogen is a stable gaseous molecule,  $\text{N}=\text{N}$ , whereas other elements exist as solids. In the gaseous state, P, As and Sb exist in the form of tetra-atomic molecules,  $\text{P}_4$ ,  $\text{As}_4$  and  $\text{Sb}_4$ . This is due to the fact that bond energy of triply bonded nitrogen is much greater than that of phosphorus, i.e.,  $E_{\text{N}=\text{N}} \gg E_{\text{P}=\text{P}}$ ; but the reverse is true for the single bonds  $E_{\text{P}-\text{P}} \gg E_{\text{N}-\text{N}}$ .

Nitrogen is very inert as a consequence of the high bond strength of  $\text{N}=\text{N}$ . The heavier elements are, however, comparatively more reactive. Nitrogen exhibits a large number of oxidation states such as -3, -2, -1, 0, +1, +2, +3, +4, +5. Other elements do not exhibit such a variety of oxidation states.

Except for  $\text{NF}_3$ , the halides of nitrogen,  $\text{NCl}_3$ ,  $\text{NBr}_3$ ,  $\text{NI}_3$  are unstable and highly explosive. The halides of other elements of this group are fairly stable. The oxides of nitrogen are gaseous, whereas the oxides of phosphorus, arsenic, etc. are solids.

Nitrogen cannot expand its octet, whereas phosphorus and other elements can; the latter elements can, therefore, have coordination numbers greater than four. Thus, compounds like  $\text{PF}_5$ ,  $\text{PF}_6$  have no nitrogen analogues. This has other effects also on the chemistry of nitrogen; for example, hydrolysis of  $\text{NCl}_3$  is slow and yields a different product from the hydrolysis of  $\text{PCl}_3$ , which is fast.

Since nitrogen is one of the most electronegative elements, it extensively enters into hydrogen bond formation. Other elements having comparatively low electronegativities do not form hydrogen bonds.

#### 4.0 CONCLUSION

The elements of group 5 exhibit regular gradation in both physical and chemical properties. While nitrogen and phosphorus are distinctly nonmetallic, arsenic and antimony are metalloids and bismuth shows metallic characteristics. As with other groups, the first element, nitrogen shows some anomalous behaviour.

#### 5.0 SUMMARY

Let us now summarise what you have learnt about Group 5 elements in this unit.

We have seen that these elements show a wide range of properties. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids and bismuth is a metal.

The principal method of industrial preparation of nitrogen is the fractionation of liquid air. Phosphorus is obtained commercially by treating a mixture of phosphorite rock, sand and coke in an electric furnace. Arsenic, antimony and bismuth are obtained by carbon reduction of their oxides at elevated temperatures. The uses of Group 5 elements have been reviewed.

These elements form hydrides. Of these hydrides, ammonia is most important and is prepared commercially by direct reaction of nitrogen and hydrogen (Haber process). Other important hydrides of nitrogen include hydrazine, and hydrazoic acid. All the Group 5 elements form trihalides, some pentahalides are also known. The elements, N, As, Sb and Bi, also form oxohalides of the type  $\text{MOX}$ , phosphorus forms oxohalides of the type  $\text{POX}_3$ .

Oxides of nitrogen are known for every positive oxidation state of nitrogen from +1 to +5. The important oxides of phosphorus contain phosphorus in oxidation states of +3 ( $\text{P}_4\text{O}_6$ ) and +5 ( $\text{P}_4\text{O}_{10}$ ). Arsenic, antimony and bismuth also form +3 oxides ( $\text{As}_4\text{O}_6$ ,  $\text{Sb}_4\text{O}_6$  and  $\text{Bi}_2\text{O}_3$ ) and +5 oxides ( $\text{As}_2\text{O}_5$  and  $\text{Sb}_2\text{O}_5$ ).

The most important oxoacid of nitrogen is nitric acid,  $\text{HNO}_3$ . It is an important industrial chemical. Another important oxoacid of nitrogen is nitrous acid which is unstable, except in solution. Phosphorus forms a large number of oxoacids, e.g., orthophosphoric acid, meta-phosphoric acid, pyrophosphoric acid, etc. These acids form phosphates which are important ingredients of fertilisers.

Oxoacids of arsenic and antimony are not well characterised. However, the corresponding salts are known.

In nature, nitrogen is constantly being taken up from the atmosphere and returned to it. This is called the nitrogen cycle. A brief account of nitrogen cycle and the fixation of nitrogen is also given.

As in the other groups, the first element of Group 5, i.e., nitrogen shows some anomalous behaviour. This has been highlighted.

## 6.0 TUTOR MARKED ASSIGNMENT

1. Write the electronic configuration of nitrogen and phosphorus in the ground state. Point out the major difference between the two, which is responsible for differences in various properties.
2. Explain why nitrogen is chemically less reactive.
3. Explain why  $\text{NF}_3$  is stable, while  $\text{NCl}_3$  and  $\text{NI}_3$  are explosives.
4. Why are  $\text{PBr}_5$  and  $\text{PI}_5$  less stable despite the fact that phosphorus (V) is not an oxidising state?
5. Why are the oxides of nitrogen so different from those of phosphorus?
6. For the three hydrides,  $\text{NH}_3$ ,  $\text{PH}_3$  and  $\text{AsH}_3$ .
  - a) give the shape of the molecule and state how the bond angle varies from  $\text{NH}_3$  -  $\text{PH}_3$  -  $\text{AsH}_3$ ?
  - b) state which is the strongest and which is the weakest base<sup>1</sup>? Why?
  - c) give an explanation, in terms of bonding, for the difference in the boiling points of ammonia and phosphine which are 240 K and 186 K, respectively.
7. Explain briefly why the hydrolysis of  $\text{NCl}_3$  and  $\text{PCl}_3$  yields different types of products.

## 7.0 REFERENCES/FURTHER READINGS

*A New Concise Inorganic Chemistry*, J. D. Lee, ELBS, London, 3rd ed., 1977.

*Chemistry: Facts, Patterns and Principles*, W. R. Kneen, M. J. W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

*Advanced Inorganic Chemistry*, F. A. Cotton and G. Wilkinson, Wiley Eastern Ltd.; New Delhi, 3rd ed., 1986.

*Principles of Inorganic Chemistry*, B. R. Puri and L. R. Sharma, Shoban Lal Nagin Chand & Co., New Delhi, 1<sup>st</sup> ed., 1986.

## UNIT 3 ELEMENTS OF GROUP 7

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- 2.0 Objectives
- 3.0 Main Content
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### 1.0 INTRODUCTION

In CHM 111 you studied the periodic table which gives the classification of elements into various periods and groups. You have seen that in any period the element in Group 1 is the most electropositive and metallic in nature. As we go across a period from Group 1 to Group 7 of the main group elements, nonmetallic nature, ionisation energy, electron affinity and electronegativity increase, reaching a maximum at Group 7. In this way, at one extreme we have Group 1 comprising alkali metals and at the other we have Group 7 comprising non-metals, namely, fluorine, chlorine, bromine, iodine and astatine, collectively called the halogens. Halogens derive their name from the Greek words, halos + gens meaning salt producers, as they form salts in combination with metals. The most common of these salts is sodium chloride or the common salt. Halogens find a wide variety of uses in everyday life. In view of their nature and usefulness, it will be interesting to study the chemistry of halogens.

## 2.0 OBJECTIVES

After studying this unit, you should be able to:

- explain the occurrence, extraction and uses of halogens;
- describe the isolation of fluorine;
- list the general characteristics of halogens and describe their reactions;
- describe the chemistry of hydrogen halides, halogen oxides and oxoacids;
- describe the chemistry and geometry of interhalogen compounds and polyhalides; and
- explain the anomalous behaviour of fluorine.

### How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

## 3.0 MAIN CONTENT

### 3.1 Occurrence, Extraction and Uses

Chemistry of halogens is very interesting and has varied applications in our daily life. Due to their high reactivity, halogens do not occur free in nature. In the combined form, however, they are fairly abundant. In this section you will study their occurrence, extraction and some important uses.

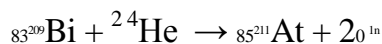
#### 3.1.1 Occurrence

Fluorine is the first element of this group; it constitutes nearly 0.054% of earth's crust, where it occurs as fluorspar ( $\text{CaF}_2$ ), cryolite ( $\text{AlF}_3 \cdot 3\text{NaF}$ ) and fluorapatite [ $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$ ].

Chlorine, which forms 0.013% of earth's crust, occurs mainly as chlorides of sodium and other alkali and alkaline earth metals in salt mines as well as in sea water. Sea water is almost a 3% solution of various salts, of which sodium chloride forms ~8.3%. Bromine, as bromides, occurs in sea water and dry salt lakes and constitutes about  $2.0 \times 10^{-4}\%$  of earth's crust. Iodine is the rarest of all the halogens, forming only  $4.6 \times 10^{-5}\%$  of earth's crust. Its main source used to be kelp, or the ash obtained on burning sea weeds, and Chile saltpetre in which it occurs as iodates. However, now it is mostly extracted from brine. Astatine is a radioactive element. The naturally occurring isotopes of astatine have half-lives of less than one minute.



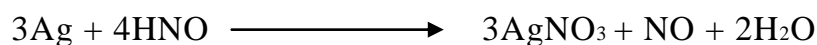
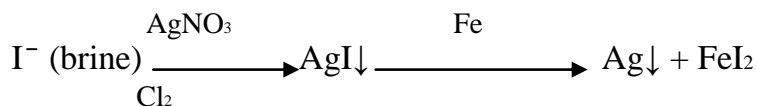
Therefore, it occurs in negligible amounts in nature. The isotope  $^{211}\text{At}$  having the longest half-life of 7.21 hours, is made by bombarding bismuth with  $\alpha$  particles.



### 3.1.2 Extraction

The only practicable method of preparing fluorine gas is Moissan's original procedure based on the electrolysis of KF dissolved in anhydrous HF. The details of this method along with some other methods for the isolation of fluorine have been given separately in Section 4.2.3. You have already studied in Unit 3 that chlorine is obtained as a byproduct along with hydrogen in the manufacture of sodium hydroxide by electrolysis of brine. Electrolysis of molten sodium chloride also gives chlorine and sodium. In some, parts of the world, it is produced by the electrolysis of aqueous HCl. Bromine is made on an industrial scale by reaction of bromides with chlorine. A mixture of air and chlorine is blown through an aqueous solution of a bromide at a pH of 3.5. Chlorine displaces bromine and air blows it out of the solution.

Iodine can also be prepared similarly by the oxidation of iodides by chlorine. Iodine is also prepared by treating brine with  $\text{AgNO}_3$  to precipitate  $\text{AgI}$ . This is possible because  $\text{AgI}$  is the least soluble of all the silver halides. Precipitated  $\text{AgI}$  is treated with clean scrap iron or steel to form metallic silver and a solution of  $\text{FeI}_2$ . This solution is then treated with chlorine to liberate  $\text{I}_2$ . Precipitated silver is redissolved in dil.  $\text{HNO}_3$  to give  $\text{AgNO}_3$  which is used again to precipitate  $\text{AgI}$ .



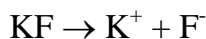
### 3.1.3 Preparation of Fluorine

Isolation of fluorine presented a tough problem to chemists for about a century. Though its existence was first shown by Davy in 1813, yet it could not be isolated before 1886. All attempts at isolation of fluorine failed due to the following reasons:

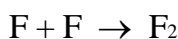
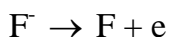
- i) High chemical reactivity of fluorine towards other elements.
- ii) It attacked the apparatus whether made of glass, carbon, platinum or any other metal in which its preparation was tried.
- iii) In view of fluorine being the most powerful oxidant, no oxidising agent could be available which could bring about the oxidation of HF to  $\text{F}_2$ . Therefore, the only method available was that of electrolysis.
- iv) The method of electrolysis was not fruitful. Aqueous HF on electrolysis yielded hydrogen and oxygen. On the other hand anhydrous HF was found to be a nonconductor of electricity.

- v) Exceedingly poisonous and corrosive character of anhydrous HF proved fatal to early chemists.

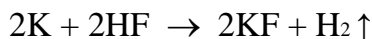
All the above mentioned reasons were very disheartening. However, Moissan picked up courage and entered this field. He electrolysed a cooled solution of KF in anhydrous liquid HF at 250 K using platinum-iridium electrodes sealed with fluorspar caps in a platinum U-tube. In this reaction, the actual electrolyte is KF while HF acts as an ionising solvent, F<sub>2</sub> is evolved at the anode and H<sub>2</sub> at the cathode as indicated below:



At the anode,



At the cathode



Potassium fluoride thus formed again undergoes electrolysis. As the hydrogen fluoride is used up, more is added to prevent the melting point of the mixture from rising. The outgoing gases, F<sub>2</sub> and H<sub>2</sub>, are not allowed to mix up in the electrolytic cell. The fluorine gas is collected in plastic receivers.

Moissan's original method has been modified. In place of the expensive Pt/Ir alloy, cells made of copper, steel or Monel metal, which is a nickel-copper alloy, has been used. These get covered by a thin protective film of the fluoride just as aluminium is protected by the thin film of oxide. Anode is a carbon rod impregnated with copper to render it inert and cathode is made of steel or copper. A mixture of KF and HF in the molar ratio of 1:1 or 1:2 is used as electrolyte giving a working temperature of 515 K or 345 K, respectively.

### 3.1.4 Uses

The main use of halogens is in the halogenation of organic and inorganic compounds. You must have heard of or used the tincture of iodine (iodine dissolved in alcohol) as an antiseptic. Iodine is present in the thyroid hormone. A deficiency of iodine causes goitre and leads to stunted growth and cretinism. To prevent this, common salt is routinely iodised. You must have used toothpastes containing fluorides in order to prevent tooth decay by dental caries. You are aware that naturally occurring uranium is a mixture of two isotopes <sup>238</sup>U (99.3%) and <sup>235</sup>U (0.7%). Of the two, the latter is fissionable and is used for the generation of nuclear power. Fluorine is used for the production of uranium hexafluoride, the compound used for separation of <sup>235</sup>U and <sup>238</sup>U isotopes by gaseous diffusion method. Besides this, liquid fluorine was used as an oxidant in rocket fuels but this has now been discontinued. Teflon, so familiar to modern housewife in the form of its coating on kitchenware to make

them nonsticking, is a polymer of fully fluorinated ethylene. You have earlier studied the use of chlorofluorocarbons or CFCs as refrigerants, in aerosol sprays and in micro-electronics. Freons, e.g.,  $\text{CCl}_2\text{F}_2$  (Freon-12) and  $\text{CCl}_3\text{F}$  (Freon-11) used as refrigerants also contain fluorine. Bleaching powder,  $\text{CaOCl}_2$ , is used for bleaching paper pulp and textiles. Bleaching powder or liquid chlorine is used for disinfection of water on a large scale. Chlorine was used in the chemical warfare in World War I. The most important use of chlorine is in the manufacture of polyvinylchloride or PVC, which because of its non-inflammability and insulating properties is used as an electrical insulator, for covering electric wires, making conduit pipes, etc.

Dichlorodiphenyltrichloroethane (DDT) is used widely as an insecticide. Methyl bromide is the most effective nematocide known. It is also used as a general pesticide. The use of silver bromide in making photographic plates or films is a common knowledge.

### SELF ASSESSMENT EXERCISE 1

Give three reasons why isolation of fluorine was very disheartening

## 3.2 General Characteristics

All elements of Group 7 have seven electrons in their outermost shells, with configuration  $ns^2, np^5$ . Thus, they are just one electron short of the electronic configuration of noble gases. The single unpaired electron in  $p$ -orbital is responsible for chemical bonding with other elements. Let us now discuss some of their physical and chemical properties.

### 3.2.1 Physical Properties

Halogens exist as non-polar diatomic molecules which are coloured. Fluorine is pale yellow, chlorine is yellowish green, bromine is brown and iodine is violet in the gaseous state. Solid iodine is almost black with a shiny metallic lustre. Except iodine which has some useful biological applications, halogens are very hazardous and toxic, fluorine being the most. Their vapours produce a choking sensation when inhaled.

Some of the physical properties of the halogens are listed in Table 4.1

Table 3.1: Some physical properties of halogens

Property	Fluorine F	Chlorine Cl	Bromine Br	Iodine I
Atomic number	9	17	35	53
Electronic configuration	[He]2s <sup>2</sup> 2p <sup>5</sup>	[Ne]3s <sup>2</sup> 3p <sup>5</sup>	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>5</sup>	[Kr]4d <sup>10</sup> 4s <sup>2</sup> 4p <sup>5</sup>
Atomic weight	18.9984	35.453	79.909	126.904
Density (liquid) (10 <sup>3</sup> x kgm <sup>-3</sup> )	1.11	1.56	3.12	4.94
Ionic radius X <sup>-</sup> (pm)	136	181	195	216
Covalent radius (pm).	64	99	114	133
Melting point (K)	53	172	266	386
Boiling point (K)	85	238.5	332	456
Enthalpy of fusion (kJ mol <sup>-1</sup> )	0.26	3.2	5.27	7.8
Enthalpy of vaporisation (kJ mol <sup>-1</sup> )	of 3.27	10.2	15	30
Enthalpy of atomisation (kJ mol <sup>-1</sup> )	79.1	122	111	106
Enthalpy of hydration X <sup>-</sup> (g) (kJ mol <sup>-1</sup> )	460	385	351	305
Electronegativity (A/R)	4.10	2.85	2.75	2.20
Ionisation energy (kJ mol <sup>-1</sup> )	1681	1255	1142	1007
Electron affinity (kJ mol <sup>-1</sup> )	333	348	340	297
Electrode potential $\frac{1}{2}X_2(g) + e \rightarrow X(aq)$	+2.87	+1.36	+1.07	+0.54
Oxidation states	-I	-I,I,III	-I,I,III,V	I,I,III,V,VII
Lattice energy (kJ mol <sup>-1</sup> ) (Potassium salt)	817	718	656	615
Bond dissociation energy (XX) (kJmol <sup>-1</sup> )	158	244	192	152

Physical properties like melting and boiling points are related to the sizes and masses of the molecules as well as intermolecular attraction. The effects of size and mass, which gradually increase as we go down the group, is easy to understand. As for the intermolecular attraction in non-polar homonuclear diatomic molecules like halogens, which do not have any permanent polarity, the only forces of attraction are the weak van der Waals forces. The polarisability of halogens increases as we go down the group, and its maximum in iodine and least in fluorine. So, Van der Waals forces of attraction are maximum in iodine and least in fluorine, with bromine and chlorine coming in between.

As a consequence of this, fluorine and chlorine are gases at ordinary temperatures, bromine is a liquid and iodine a solid. This is also reflected in the trends observed in their enthalpies of fusion and vaporization. (Table 4.1)

You have already learnt in CHM 111 that as we move along a period, the effective nuclear charge increases reaching a maximum at the noble gases. Halogens which immediately precede the noble gases have a very high effective nuclear charge coupled with small sizes and thus have the highest ionisation energies in the respective periods, next only to the noble gases. Like the trend in other groups, utilisation energy of halogens also decreases in going down the group from fluorine to iodine.

Halogens have seven electrons in their valence shells, they have a very strong tendency of gaining an electron to acquire a stable noble gas configuration. Therefore, they have very high electron affinities. In fact, their electron affinities are the highest in their respective periods. Their electron affinity follows the order  $\text{Cl} > \text{F} > \text{Br} > \text{I}$ . As explained earlier, the smaller electron affinity of fluorine than that of chlorine is a consequence of its small size.

You know that as we go across the *p*-block elements in a period, the electronegativity increases reaching a maximum at the halogen group. Thus, halogens are the most electronegative elements in their respective periods. Electronegativity decreases on moving down a group, making fluorine the most and iodine the least electronegative among the halogens.

In going down the group from chlorine to iodine, the X-X bond dissociation energy gradually decreases (Table 3.1). This is easily explained by considering once again the size factor. In the chlorine molecule;-which is the smallest of the three, viz.,  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ , the two bonding electrons are nearer to both the nuclei and are held strongly, while in bromine and iodine, the distance of the bonding electrons from the nuclei gradually increases resulting in lesser attraction and consequent weakening of the bond. Furthermore, as the size of the atom increases, it results in a less effective overlap of the orbitals and therefore, progressively weaker bonds are formed as we go down the group. The bond dissociation energy increases in the order  $\text{I}_2 < \text{Br}_2 < \text{Cl}_2$  and if this trend was to continue, you should expect the F-F bond dissociation energy to be greater than the bond energy of chlorine,  $244 \text{ kJ mol}^{-1}$ . But this is not so. The actual bond dissociation energy of fluorine molecule is, however, surprisingly low and has the value of  $158 \text{ kJ mol}^{-1}$  only. The anomalously low bond dissociation energy of fluorine molecule is attributed to the fact that fluorine atom is very small and the non-bonding electrons on fluorine are nearer to each other, resulting in a much greater lone pair-lone pair repulsion, which weakens the covalent bond and lowers its dissociation energy. This repulsion is not so great in relatively larger halogen molecules like chlorine, bromine and iodine where the lone pairs are at a greater average distance from each other.

## SELF ASSESSMENT EXERCISE 2

Fill the name of the appropriate halogen in the space provided against each of the following:

Which of the halogens

- has two complete electron shells below the valence shell
- is solid at room temperature
- has highest electronegativity value
- lowest ionisation energy

### 3.2.2 Oxidation States

Fluorine is always univalent. Since it is the most electronegative element, it always has the oxidation number, 1. Fluorine has no *d*-orbital in its valence shell, hence it cannot have any excited states or any other oxidation number.

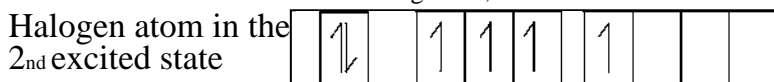
Oxidation state of -1 is the most common and stable one for other halogens also. However, consistent with the decreasing electronegativity, -1 oxidation state becomes gradually less stable in going down the group. As chlorine, bromine and iodine are less electronegative than fluorine and oxygen, they exhibit an oxidation state of +1 in their fluorides and oxides. In addition, except fluorine all the other halogens exhibit oxidation states of +3, +5 and +7 due to the availability of vacant *d*-orbitals as shown below:



Oxidation state =  $\pm 1$   
 e.g. HCl, HBr & HI  
 (oxidation = -1),  
 HClO, HBrO & HIO  
 (oxidation state = + 1)



Oxidation state = + 1  
 e.g. ClF<sub>3</sub>, BrF<sub>3</sub>



Oxidation state = + 5  
 e.g. HClO<sub>3</sub>, HBrO<sub>3</sub>, HBrO<sub>3</sub>, HIO<sub>3</sub>

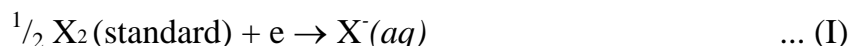


Oxidation state = + 5  
 e.g. HClO<sub>4</sub>, HIO<sub>4</sub>

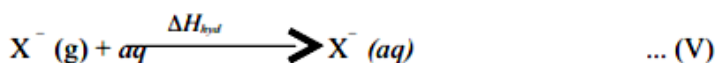
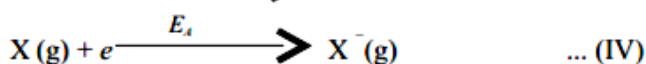
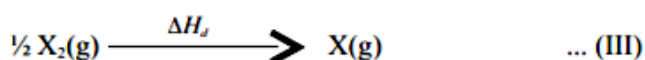
Chlorine and bromine also exhibit oxidation state + 4 (ClO<sub>2</sub> and BrC<sub>2</sub>) and + 6 (Cl<sub>2</sub>O<sub>6</sub> and BrO<sub>3</sub>). Iodine exhibits an oxidation state + 4 in I<sub>2</sub>O<sub>4</sub>.

### 3.2.3 Oxidation Power

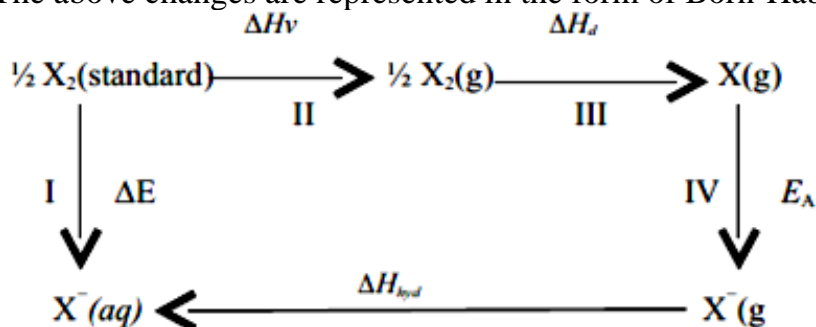
Oxidation may be regarded as the removal of electrons, so that the oxidising agent gains electrons. Since halogens have a greater tendency to pick up electrons, they act as strong oxidising agents. Their oxidising power, however, decreases on moving down the group. The strength of an oxidising agent or its ability to accept electrons depends on several energy terms. The reaction,



Representing the oxidising action of a halogen is actually a complicated process. It involves the following steps:



The above changes are represented in the form of Born-Haber cycle, as shown below:



Evidently, since energy is invariably absorbed in steps (II) and (III), enthalpy of vapourisation,  $\Delta H_v$  and enthalpy of dissociation,  $\Delta H_d$ , always have positive values. However, energy is released in steps (IV) and (V), hence, electron affinity,  $E_A$ , and enthalpy of hydration,  $\Delta H_{hyd}$  are negative. Consequently, from Hess's law, the net enthalpy change,

$\Delta E$  for the reduction reaction (I) is given by the expression:

$$\Delta E = \Delta H_v + \Delta H_d + E_A + \Delta H_{hyd}$$

Hess's Law:

The amount of heat evolved in a chemical process is always the same irrespective of whether the process goes as a one or many step reaction.

For fluorine and chlorine which are gases at room temperature, the enthalpy of evaporation is omitted. Enthalpy changes associated with each of the above steps and the net enthalpy change,  $\Delta E$  are given in Table 4.2.

You can see from Table 4.2 that  $\Delta E$ , or the net enthalpy change associated with the reaction (I) decreases from fluorine to iodine. Considering that the difference in entropy changes are small and mainly enthalpy changes determine the free energy change, it can be inferred that the free energy change for reaction (I) becomes less negative on descending the group. In other words, fluorine is the strongest oxidising agent of the four. Thus, you may note that despite the electron affinity of chlorine being highest, fluorine is the strongest oxidising agent because of its low enthalpy of dissociation and high enthalpy of hydration.

Thus, it is the total enthalpy change and not the electron affinity which controls the strength of an oxidising agent.

Table 3.2: Enthalpy values for  $1/2 X_2 \rightarrow X^-(aq)$

Molecule	Enthalpy of vapourisation $\Delta H_v$ kJ mol <sup>-1</sup>	Enthalpy of dissociation, $\Delta H_d$ kJ mol <sup>-1</sup>	Enthalpy of affinity, $E_A$ kJ mol <sup>-1</sup>	Enthalpy of hydration $\Delta H_{hyd}$ kJ mol <sup>-1</sup>	$\Delta E$ kJ mol <sup>-1</sup>
F <sub>2</sub>	-	+79.2	-333	-460	-714
Cl <sub>2</sub>	-	122.0	-348	-385	-611
Br <sub>2</sub>	15	96.0	-340	-351	-580
I <sub>2</sub>	30	76.0	-297	-305	-496

The oxidising power of the halogens in the solid state reactions also shows the same order. This is because lattice energies of the ionic halides (Table 3.1) follow the same order as the hydration energy; fluorides having the highest and iodides the lowest lattice energy.

Another important factor which makes fluorine the strongest oxidising agent is the high element-fluorine covalent bond energy as shown in Table 3.3.

Table 3.3: Halogen-element Bond Energy, kJ mol<sup>-1</sup>

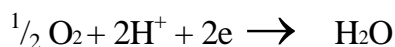
Molecule	Enthalpy of vapourisation $\Delta H_v$ kJ mol <sup>-1</sup>	Enthalpy of dissociation, $\Delta H_d$ kJ mol <sup>-1</sup>	Enthalpy of affinity, $E_A$ kJ mol <sup>-1</sup>	Electron hydration $\Delta H_{hyd}$ kJ mol <sup>-1</sup>	Enthalpy of kJ mol <sup>-1</sup>	$\Delta E$ kJ mol <sup>-1</sup>
F <sub>2</sub>	-	+79.2	-333	-460	-714	
Cl <sub>2</sub>	-	122.0	-348	-385	-611	
Br <sub>2</sub>	15	96.0	-340	-351	-580	
I <sub>2</sub>	30	76.0	-297	-305	-496	

You will notice that the values in the first row representing fluorine-element bond energy are highest except in the case of fluorine-fluorine bond energy; the reasons for which you have studied earlier in Section 3.3. Thus fluorine forms a very strong bond with almost all other elements. A consequence of this is that fluorine is able to form compounds with other

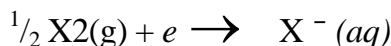


elements in their higher oxidation states. The order of the ability of the halogens to combine with elements in higher oxidation states is  $F > Cl > Br > I$ .

A comparison of the reduction potential of halogens with that of oxygen can indicate which of them would oxidise water to oxygen. The standard electrode potential for reduction of oxygen to water in acid solution is 1.23 volts:



The standard reduction potential of the halogen half cell reaction,



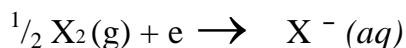
is +2.87 volts in the case of fluorine and +1.36 volts in the case of chlorine (Table 3.1). These are more positive than that for reduction of oxygen to water. These two halogens can, therefore, oxidise water to oxygen. Fluorine does so readily but chlorine reacts rather slowly, at first giving HClO which later decomposes to oxygen and HCl. The electrode potentials of bromine and iodine are less than that of oxygen, therefore, they are not able to oxidise water to oxygen.

To sum up, the main thermodynamic factors responsible for making fluorine so uniquely highly oxidising and reactive are:

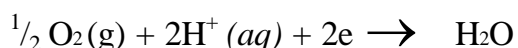
- high hydration energy of the fluoride ion
- high lattice energy of ionic fluorides
- low F-F bond energy and
- high element fluorine bond energy.

### SELF ASSESSMENT EXERCISE 3

Table 3.1 lists the standard reduction potential for the half cell reaction,



and the standard potential for the reaction,



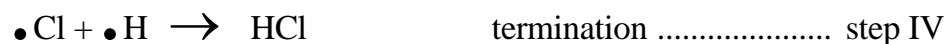
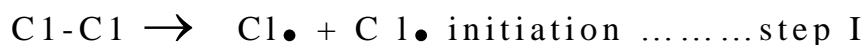
is 1.23V. What reaction do you predict between bromine and water and iodine and water on this basis?

#### 3.2.4 Chemical Properties

All the halogens are very reactive. Fluorine is the most reactive of all the halogens, combining directly with every other element except oxygen and some of the noble gases. Therefore, it is also called a super halogen. You have also seen that the reactivity decreases

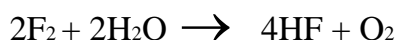
from  $F_2$  to  $I_2$ . In displacement reactions we find that fluorine displaces all the remaining three halogens from their salts, chlorine displaces bromine and iodine, while bromine displaces only iodine. Halogens react with each other to form interhalogen compounds, brief description of these is given in Section 3.4.4. Halogens, in general, react with most metals, though bromine and iodine do not react with some noble metals like Ag, Au. Halogens also react with many non-metals to form halides.

Halogens react with hydrogen to form hydrides which are called hydrogen halides. Fluorine and chlorine react with hydrogen with explosive violence; fluorine-hydrogen mixture explodes even in the dark. Chlorine-hydrogen mixture does so only in presence of light. This is called a photochemical reaction. It has been shown that this reaction starts with the formation of halogen free radicals. It is not surprising in view of the lower X-X bond energy as compared to H-H bond energy. Reactions of bromine and iodine with hydrogen are slow, the latter being reversible.



Such reactions are called Chain Reactions since after the initiation of the reaction, the propagation steps II and III are repeated in sequence till the reactants are consumed. The reaction gets terminated when free radicals start combining with each other as in step IV.

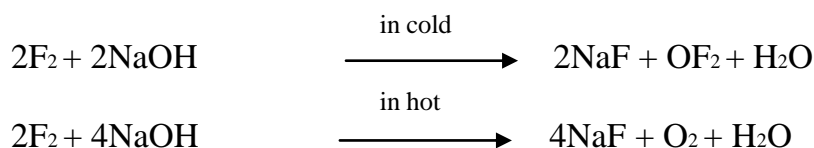
Fluorine reacts vigorously with water to form hydrofluoric acid and oxygen:



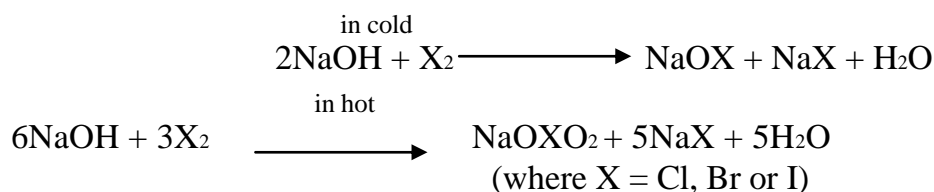
The other halogens are sparingly soluble in water ( $Br_2 > Cl_2 > I_2$ ) and react partly to give a mixture of hydrohalic and hypohalous acids:



Halogens react with aqueous alkali, the reactivity decreasing from fluorine to iodine. Fluorine behaves differently from other halogens. It reacts with alkalis violently forming fluorides and fluorine oxides or oxygen as shown below:

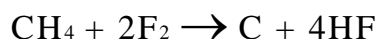


Other halogens react with alkalis in cold to give hypohalites ( $XO^-$ ) and in hot to form halates ( $XO_3^-$ ):



Hypohalites are oxidising agents. Bleaching powder  $\text{CaCl}(\text{OCl})$  owes its bleaching action to its oxidising properties.

All halogens react with hydrocarbons but reactivity decreases with the increase in atomic number. Fluorine is the most reactive and brings about decomposition of the hydrocarbons:



Chlorine and bromine substitute hydrogen atoms, reaction with bromine being slower, iodine has little or no reaction:



Some more reactions of halogens are summarised in Table 3.4:

Table 3.4: Some Reactions of Halogens

General Reaction	Remarks
$n\text{X}_2 + 2\text{M} \rightarrow 2\text{MX}_n$	$\text{F}_2$ , $\text{Cl}_2$ with practically all metals; $\text{Br}_2$ , $\text{I}_2$ with all except noble metals.
$\text{X}_2 + \text{H}_2 \rightarrow 2\text{HX}$	Reaction with iodine reversible.
$3\text{X}_2 + 2\text{P} \rightarrow 2\text{PX}_3$	Similar reactions with As, Sb, Bi.
$5\text{X}_2 + 2\text{P} \rightarrow 2\text{PX}_5$	With excess $\text{X}_2$ , but not with $\text{I}_2$ ; $\text{SbF}_5$ , $\text{SbCl}_5$ , $\text{AsF}_5$ , $\text{AsCl}_5$ and $\text{BiF}_5$ may be prepared similarly.
$\text{X}_2 + 2\text{S} \rightarrow \text{S}_2\text{MX}_n$	With $\text{Cl}_2$ , $\text{Br}_2$ .
$n\text{X}_2 + 2\text{M} \rightarrow 2\text{MX}_n$	Not with $\text{F}_2$ .
$n\text{X}_2 + 2\text{M} \rightarrow 2\text{MX}_n$	$\text{F}_2$ rapidly, $\text{Cl}_2$ and $\text{Br}_2$ slowly in sunlight.
$n\text{X}_2 + 2\text{M} \rightarrow 2\text{MX}_n$	$\text{X}_2 = \text{Cl}_2, \text{Br}_2$ .
$n\text{X}_2 + 2\text{M} \rightarrow 2\text{MX}_n$	$\text{X}_2 = \text{F}_2, \text{Cl}_2$ .
$n\text{X}_2 + 2\text{M} \rightarrow 2\text{MX}_n$	Formation of interhalogen compounds (all except $\text{IF}$ ).
(X and Y are Two different halogens)	

### 3.2.5 Basic Properties of Halogens

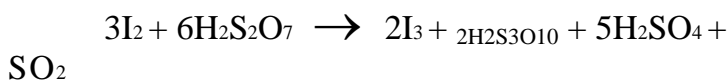
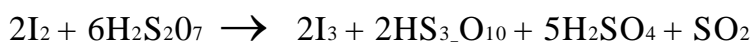
In general, the basic or metallic nature of elements increases as we descend down a group. Thus, you have seen in preceding units that the last member of each of the Groups 14, 15

and 16, i.e., Pb, Bi and Po, respectively, is definitely metallic in character. But, this trend is not so well marked in the elements of Group 7 because very little is known about the last member of the group, astatine. There is, however, definite evidence to show the existence of halogen cations in media which are weakly nucleophilic.

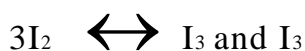
Fluorine is the most electronegative element and has no basic properties. Chlorine shows a slight tendency to form cations. For example,  $\text{ClF}$  ionises to form  $\text{Cl}^+$  and  $\text{F}^-$  due to the higher electronegativity of fluorine. Bromine cation,  $\text{Br}^+$ , exists in complexes such as  $\text{Br}(\text{pyridine})^+\text{NO}_3$ , electrolysis of  $\text{ICN}$  in pyridine solution gives iodine at the cathode.

This indicates that  $\text{ICN}$  ionises to  $\text{I}^+$  and  $\text{CN}^-$ . Many pyridine complexes, e.g.  $[\text{I}(\text{pyridine})]^+\text{NO}_3$ ,  $[\text{I}(\text{pyridine})_2]^+\text{ClO}_4$  and  $[\text{I}(\text{pyridine})]^+\text{CH}_3\text{COO}$  are known.

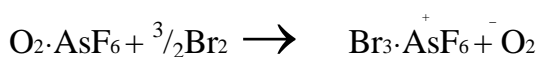
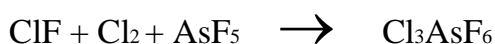
Iodine dissolves in oleum giving a bright blue solution which has been shown to have  $\text{I}_2$  and  $\text{I}_3$ :



Electrical conductivity of molten iodine is due to the presence of  $\text{I}_3^+$  and  $\text{I}_3^-$  species produced by the self ionisation of iodine:



The cations,  $\text{Cl}_3^+$  and  $\text{Br}_3^+$  are formed in the following reactions:

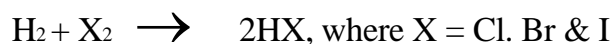


### 3.3 Compounds of Halogens

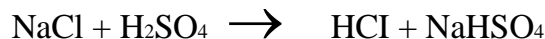
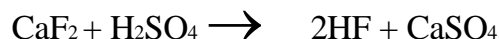
In the preceding section you have learnt that the halogens form a variety of compounds with other elements. In this section, you will study the salient features of the chemistry of some of these compounds, viz, hydrogen halides, halogen oxides, oxoacids of halogens and the interhalogen compounds.

#### 3.3.1 Hydrogen Halides

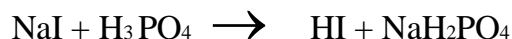
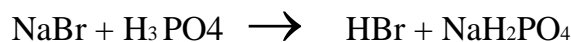
You have studied in the preceding section that all the halogens combine with hydrogen and form volatile hydrides of the type  $\text{HX}$ , which are also known as hydrogen halides. The reaction of fluorine with hydrogen is very violent whereas bromine and iodine react with hydrogen only at elevated temperatures and in the case of iodine the reaction does not proceed to completion:



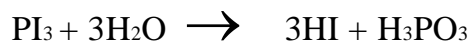
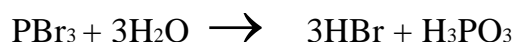
Hydrogen fluoride and hydrogen chloride are obtained by the action of concentrated sulphuric acid on fluorides and chlorides:



Since concentrated sulphuric acid partially oxidises HBr and HI to Br<sub>2</sub> and I<sub>2</sub>, these are prepared by the action of concentrated orthophosphoric acid on bromides and iodides:



Hydrogen bromide and hydrogen iodide are usually prepared in the laboratory by the hydrolysis of PBr<sub>3</sub> and PI<sub>3</sub>:



Under ordinary conditions HCl, HBr and HI are gases while HF is a liquid, due to strong hydrogen bonding. Their melting and boiling points show a gradual increase in the order HCl < HBr < HI, but H-F does not follow the trend and has unexpectedly higher values. This is because of strong hydrogen bonding in H-F molecules about which you have studied in CHM 111. Due to hydrogen bonding HF<sub>2</sub> ion is stable and gives salts like KHF<sub>2</sub>.

Hydrogen halides are covalent compounds with varying degree of polarity of the H-X bond depending upon the electronegativity of the halogen atom. Thus, H-F bond is most polar and the decreasing order of polarity is H-F > H-Cl > H-Br > H-I as shown by the percent ionic character in these bonds.

Some physical properties of the hydrogen halides are listed in the Table 3.5

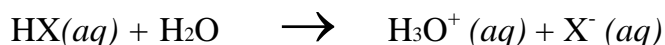
Table 3.5: Physical Properties of Hydrogen Halides

	Physical state	Colour	B.P. (K)	M.P. (K)	% dissociation at 373 K	Per cent ionic Character
HF	Liquid	Colourless	293	190	Very slight	44
HCl	Gas	''	188	159	0.0014	17
HBr	Gas	''	208	186	0.5	11
HI	Gas		237	222	33	5

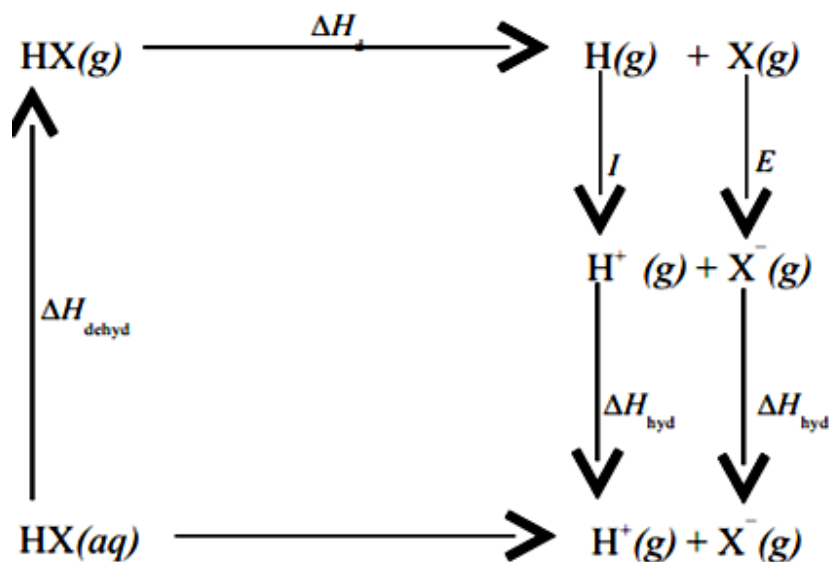
The thermal stability of hydrogen halides decreases from HF to HI. Thus hydrogen fluoride is the most stable whereas hydrogen iodide is the least stable. This can be seen from their percentage dissociation data (Table 3.5). For example, while HF and HCl are not appreciably dissociated even at 1473 K, HBr is dissociated to the extent of 0.5% and HI is dissociated to the extent of 33% at 373 K.

### Hydrohalic Acids

Aqueous solutions of hydrogen halides are called hydrohalic acids, viz., hydrofluoric, hydrochloric, hydrobromic and hydriodic acid. Hydrohalic acids form constant boiling point mixtures with water. The aqueous solutions of acids ionise as follows:

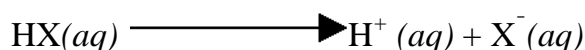


Their acid strength follows the order  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ . Acid strength is in general the tendency of  $\text{HX}(aq)$  to give  $\text{H}_3\text{O}^+(aq)$  and  $\text{X}^-(aq)$ . The enthalpy changes associated with the dissociation of hydrohalic acids can be represented with the help of Born-Haber cycle in its simplest form as given below:



A constant boiling point mixture is a mixture of two or more with a definite composition, which boils at a specific temperature at a specific pressure. HCl, for example forms a constant boiling point mixture containing 20.24% HCl with a boiling point 383 K.

The acid strength depends upon the sum of all enthalpy terms for various stages indicated in the Born Haber cycle. Of these the most marked change is in the enthalpy of dissociation of H-X bond, which decreases in the order  $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$  and the enthalpy of hydration of  $\text{X}^-$ , which decreases from  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ . The total enthalpy change becomes more negative, i.e., the reaction,



becomes more exothermic from HF to HI. As expected, acid strength varies in the reverse order, HI being the strongest acid and HF the weakest acid.

### SELF ASSESSMENT EXERCISE 5

Explain briefly in the space given below, why HF is the weakest acid.

### 3.3.2 Oxides

All halogens form oxides. Numerous halogen oxides have been reported although many of them are unstable. These are listed in Table 1.6. Halogen-oxygen bonds are largely covalent because of the similarities in electronegativity of halogens and oxygen. Fluorine is more electronegative than oxygen, hence compounds of fluorine with oxygen are considered as fluorides of oxygen rather than oxides of fluorine.

I<sub>2</sub>O<sub>5</sub> is the only halogen oxide which is stable with respect to dissociation into elements. Chlorine oxides decompose violently while the bromine oxides are the least stable among the halogen oxides. Of these only Cl<sub>2</sub>O and ClO<sub>2</sub> find some practical importance as bleaching agents in paper pulp and flour industries, I<sub>2</sub>O<sub>5</sub> is used in the estimation of CO.

Table 3.6: Oxides of Halogens

Fluorides		Oxides					
Compound	Oxidation Number	Chlorine Compound	O.N	Bromine Compound	O.N	Iodine Compound	O.N
OF <sub>2</sub>	-1	Cl <sub>2</sub> O	+1	Br <sub>2</sub> O	+1		
O <sub>2</sub> F <sub>2</sub>	-1	ClO <sub>2</sub>	+4	BO <sub>2</sub>	+4	I <sub>2</sub> O <sub>5</sub>	+5
		Cl <sub>2</sub> O <sub>6</sub>	+6	BO <sub>3</sub>	+6		
		Cl <sub>2</sub> O <sub>7</sub>	+7				

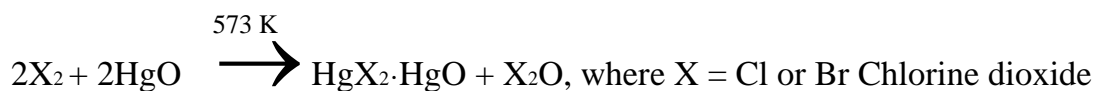
#### Preparation of Halogen Oxides

Oxygen difluoride is prepared by passing fluorine into a 2% NaOH solution:

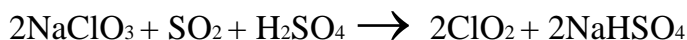


It is a stable colourless gas. It reacts vigorously with metals, sulphur, phosphorus and halogens and gives fluorides and oxides. It reacts with bases to give F<sup>-</sup> ion and free oxygen.

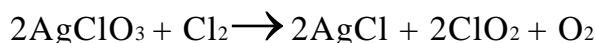
Cl<sub>2</sub>O and Br<sub>2</sub>O are prepared by heating freshly precipitated mercuric oxide with the halogen



(ClO<sub>2</sub>) is also prepared by the following reactions:



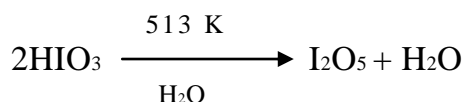
It is also obtained by treating silver chlorate with dry chlorine at 363 K:



Chlorine dioxide is a gas at normal temperature, b.p. 284 K. It is a powerful oxidising and chlorinating agent. It reacts with alkalis to form chlorites and chlorates:



Iodine pentoxide (I<sub>2</sub>O<sub>5</sub>) is prepared by dehydration of iodic acid at 513 K:



It is a white solid which decomposes to iodine and oxygen above 573 K. I<sub>2</sub>O<sub>5</sub> is a good oxidising agent, it oxidises H<sub>2</sub>S to sulphur and HCl to chlorine.

### Properties of Halogen Oxides

All oxides of halogens have positive free energies of formation except F<sub>2</sub>O and are thus unstable with respect to dissociation into elements. F<sub>2</sub>O is stable upto 475 k. A combination of kinetic and thermodynamic factors leads to the generally decreasing order of stability I > Cl > Br. The higher oxides tend to be more stable than the lower. Except for that of iodine all oxides tend to be explosive. Iodine pentoxide, I<sub>2</sub>O<sub>5</sub>, is white solid stable upto 575 K. Because of their oxidising properties, chlorine oxides, Cl<sub>2</sub>O and ClO<sub>2</sub> are used as bleaching agents and as germicides. I<sub>2</sub>O<sub>5</sub> quantitatively oxidises CO into CO<sub>2</sub> and therefore, is used in the estimation of CO.

### Structure of Oxides of Halogens

Structures of only OF<sub>2</sub>, Cl<sub>2</sub>O, Br<sub>2</sub>O, Cl<sub>2</sub>O<sub>7</sub> and I<sub>2</sub>O<sub>5</sub> are definitely known. Structures of the monoxides can be explained on the basis of VSEPR theory about which you have already studied in CHM 101. These oxides have tetrahedral structure with two lone pairs on oxygen. Thus, the molecule is V shaped or angular in shape. The bond angle EOE varies in the order FOF < ClOCl < BrOBr. This is because electrons in the case of OF<sub>2</sub> are nearer to fluorine due to high electronegativity of F compared to Cl or Br. The bonded electron pairs in Cl<sub>2</sub>O and Br<sub>2</sub>O are closer to oxygen making the repulsion between them more and thereby reducing the lone pair - lone pair repulsion on oxygen to some extent. Also due to the bulkiness of Cl and Br, the angles ClOCl and BrOBr



increase to such an extent that they are greater than  $109^{\circ}28'$ , the tetrahedral angle. Fig. 4.1 shows some of the structures of halogen oxides.

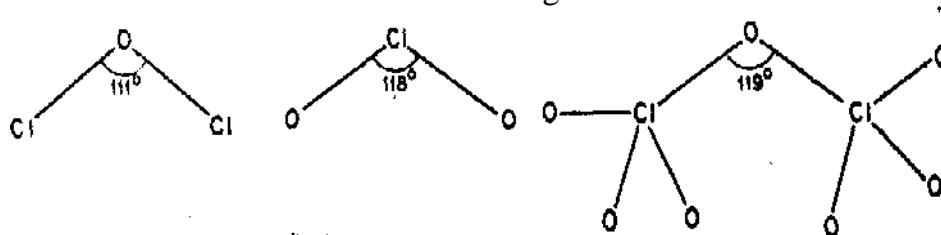


Fig. 4.1: Structures of some Oxides of Halogens

### 3.3.3 Oxoacids of Halogens

Oxoacids of halogens have oxygen attached to the halogen atom. They have the general formula  $\text{HOX}(\text{O})_n$  where  $n = 0, 1, 2$  or  $3$ . The oxoacids are named as hypohalous acid ( $\text{HOX}$ ), halous acid ( $\text{HOXO}$ ), halic acid ( $\text{HOXO}_2$ ) and perhalic acid ( $\text{HOXO}_3$ ), in which the oxidation state of the halogen is  $+1, +3, +5$  and  $+7$ , respectively. Most of the oxoacids are known only in solution or as salts. Fluorine being more electronegative than oxygen does not form oxoacids except the unstable  $\text{HOP}$ . Some important oxoacids of halogens are given in Table 4.7.

Table 4.7: Important Oxoacids of Halogens

Names of The acid and their salts	Oxidation state of halogen in the acid	Oxoacids Of			Structure
		Cl	Br	I	
Hypohalous, Hypohalites	+1	* $\text{HOCl}$ Hypochlorous acid	* $\text{HOBr}$ Hypobromous acid	* $\text{HOI}$ Hypoiodous acid	$\text{H-O-X}$
Halous, Halites	+3	* $\text{HOClO}$ Chlorous acid	* $\text{HOBrO}$ Bromous acid		$\text{H-O-X-O}$
Halic, Halaies	+5	* $\text{HOClO}_2$ Chloric acid	* $\text{HOBrO}_2$ Bromic acid	$\text{HOIO}_2$ Lodic acid	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{H-O-X-O} \end{array}$
Perhalic, Perialals	+7	$\text{HOClO}_3$ , Perchloric acid	* $\text{HOBrO}_3$ Perbromic acid	$\text{HOBrO}_3$ Periodic acid	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{HO-X-O} \\ \downarrow \\ \text{O} \end{array}$

\* Stable only in solution

The oxoacids containing higher number of oxygen atoms, i.e., having halogens in higher oxidation state are thermally more stable and are known in pure state. You may compare this with the increased, stability in case of higher oxides of halogens. However, the thermal stability decreases with increase in the atomic number of the halogen. Thus, HOCl is the most stable and HOI the least stable among the hypohalous acids.

Acid strength of oxoacids increases with increase in the oxidation number of the halogen. This can be explained as follows. Because oxygen is more electronegative than halogens (consider only Cl, Br and I), the terminal oxygen atom pulls the electrons of O-X bond towards itself, leaving a slight positive charge on the halogen atom. The halogen atom then draws the electrons of X-OH bond towards itself. This oxygen atom in turn pulls the electrons of O-H bond towards itself, leaving hydrogen atom slightly positively charged and making the O-H bond more easily ionisable. This makes the compound more acidic.

It is obvious from the above that higher the oxidation number of the halogen, higher is the number of oxygen atoms attached to the halogen, more effective is the displacement of shared electrons towards the terminal oxygen atoms and more acidic is the oxoacid.

Acid strength of oxoacids with halogen in the same oxidation state decreases as we go down the group. Thus HOCl is the strongest and HOI is the weakest amongst these acids. Hypoiodic acid is amphoteric and may be regarded as iodine hydroxide, IOH, in many reactions. Decrease in acid strength of corresponding oxoacids down the group may be explained on the basis of decreasing electronegativities of the halogens.

NaOCl is one of the important salts of hypochlorous acid and is used in bleaching cotton fabrics, wood pulp and also as a disinfectant.

Anhydrous perchloric acid,  $\text{HClO}_4$ , is an extremely powerful oxidising agent which explodes when in contact with organic matter and sometimes on its own. Periodic acid,  $\text{HIO}_4$ , is extensively used in organic chemistry for oxidation of alkenes to glycols.

### SELF ASSESSMENT EXERCISE 6

Arrange the following in the order of increasing acid strength: HOCl,  $\text{HOCIO}_2$ ,  $\text{HOCIO}_3$  and HOClO.

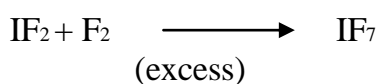
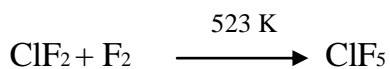
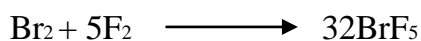
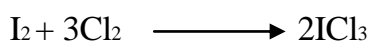
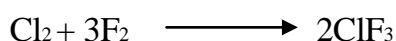
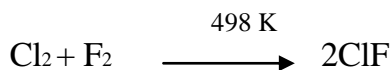
### 3.3.4 Interhalogen Compounds

Compounds formed by the interaction of one halogen with other halogens are called interhalogen compounds. Such compounds are either binary, formed by a combination of two halogens or ternary, formed by a combination of three halogens. The binary compounds are of four types, viz., XY,  $\text{XY}_3$ ,  $\text{XY}_5$  and  $\text{XY}_7$  where X and Y are the two halogens and Y is more electronegative than X. Interhalogen compounds are named as the halides of less electronegative halogen. Thus ClF is called chlorine monofluoride and not fluorine monochloride. Ternary interhalogen compounds were unknown until recently except as polyhalide anions or polyhalonium cations, but now some compounds, e.g.,

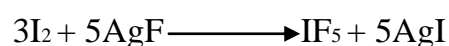
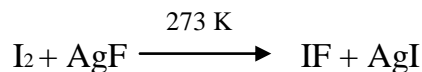
$\text{IFCl}_2$  and  $\text{IF}_2\text{Cl}$  have been prepared. The interhalogen compounds with fluorine are more common.

The stability of interhalogen compounds depends on the electronegativity difference of the two halogens. The greater the difference, the more polar is the bond and therefore, the greater is the thermal stability and the higher their melting and boiling points.

The interhalogen compounds can be prepared by direct combination of the halogens or by action of the halogen on a lower interhalogen compound. A few examples are given below:



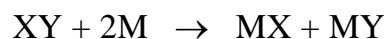
Mono- and penta-fluorides of iodine are prepared by the action of  $\text{AgF}$  on  $\text{I}_2$ :



## Properties

Some physical properties of the interhalogen compounds like colour are intermediate between those of the constituent elements but their melting and boiling points are higher than expected from interpolation of the melting and boiling points of the constituent halogens. Some properties of interhalogen compounds are given in Table 3.8.

Interhalogen compounds are generally more reactive than the halogens (except F) since  $\text{X}-\text{Y}$  bond is more polar than the  $\text{X}-\text{X}$  bond. They are hydrolysed by water or alkali to the halide ion of the lighter halogen ( $\text{Y}^-$ ) and the hypohalite ion of the heavier halogen ( $\text{OX}^-$ ). The interhalogen compounds react with alkenes and add across the double bond ( $\text{C}=\text{C}$ ). They are strong oxidising agents and are used to prepare metal halides. They convert metals into mixed halides:



Their most important use is as fluorinating agents. They are also used as non-aqueous solvents. Iodine trichloride and bromine trifluoride autoionise like water and ammonia to give polyhalide ions, e.g.



Thus, the substances which furnish  $\text{ICl}_2^+$  and  $\text{BrF}_2^+$  behave as acids and those furnishing  $\text{ICl}_4^-$  and  $\text{BrF}_4^-$  behave as bases in  $\text{ICl}_3$  and  $\text{BrF}_3$  solvent systems, respectively.

Table 3.8: Some interhalogen compounds

Type of interhalogen compound	Formulae and names of compounds	Physical state and colour at ordinary temperatures	Melting point (K)	Boiling point (K)
XY	$\text{ClF}$ Chlorine fluoride	Gas, Colourless.	119	163
	$\text{BrF}$ Bromine fluoride	Liquid below 293K pale-brown gas above 293 K	240	293
	$\text{BrCl}$ Bromine chloride	Liquid, reddish yellow	207	283
	$\text{ICl}$ Iodine chloride	Solid, ruby red	.	310
$\text{XY}_3$	$\text{BrI}$ Bromine iodide	Solid. brown like iodine	232	
	$\text{ClF}_3$ Chlorine trifluoride	Liquid below 261 K, Colourless gas above 261 K	197	261
	$\text{BrF}_3$ Bromine trifluoride	Liquid, Colourless	282	400
	$\text{BrCl}_3$ Bromine trichloride	Solid, Orange	374 (decomposes)	—

XY <sub>5</sub>	ClF <sub>5</sub> Chlorine pentafluoride	Gas. Colourless	170	259
	BrF <sub>5</sub> Bromine pentafluoride	Liquid, Colourless	213	314
	IF <sub>5</sub> Iodine pentafluoride	Liquid, Colourless	283	314
XY <sub>7</sub>	IF <sub>7</sub> Iodine heptafluoride	Gas, Colourless	279.5	

### Structure of Interhalogen Compounds

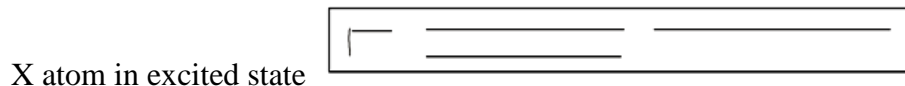
The interhalogen compounds are generally covalent in which the larger atom lies in the centre. Their shapes can be predicted by VSEPR theory about which you have already studied in CHM 101. Shapes of some of the interhalogen compounds are given in Table 4.9.

Table 3.9: Shapes of molecules of interhalogens predicted by VSEPR theory

Molecule	Total number of electron pairs around X	Bond pairs	Lone pairs	Shape
XY	4	1	3	Linear
XY <sub>3</sub>	5	3	2	T-shaped
XY <sub>5</sub>	6	5	1	Square pyramidal
XY <sub>7</sub>	7	7	0	Pentagonal bipyramidal

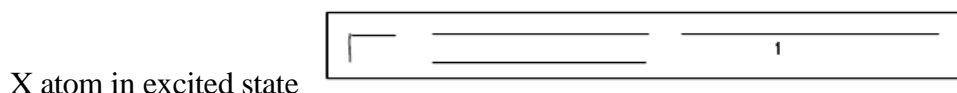
Structures of interhalogens can be explained with the help of Valence Bond Theory also in the following manner:

- i) Type XY: As expected, the compounds of the type XY are linear (Fig. 4.2). Thus ClF, BrF, BrCl, IBr and ICl all have a linear structure. In these compounds both the halogen atoms have an unpaired electron in the  $p_z$  orbital. Axial overlap of the  $p_z$  orbitals of the two halogen atoms results in a linear interhalogen molecule.
- ii) Type XY<sub>3</sub>: Structure of the interhalogens of this type can be explained on the basis of  $sp^3d$  hybridisation of the central halogen atom X. Three of the hybrid orbitals having an electron each are used in making three covalent bonds with three atoms of the other halogen atom. The remaining two orbitals accommodate the two lone pairs of the central atom. In order to minimise lone pair-lone pair and lone pair-bond pair repulsions, the lone pairs occupy the two equatorial sites around the central halogen atom, thereby giving a T-shape to the molecule (Fig. 3.3). Thus ClF<sub>3</sub>, BrF<sub>3</sub> and ICl<sub>3</sub> have a T-shaped structure.



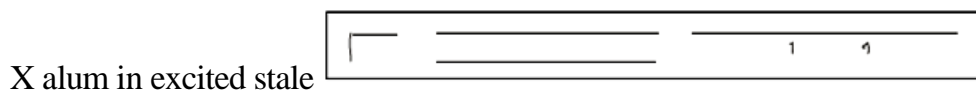
$sp^3d$  hybridisation - trigonal bipyramidal structure with two equatorial sites occupied by lone pairs.

iii) Type  $XY_5$ : This type of compounds has a square pyramidal structure (Fig. 1.4). The central atom X uses five of its seven valence electrons in forming five bonds with Y and two electrons remain as a lone pair. Thus X-atom in  $XY_5$  molecule is  $sp^3d$  hybridised. The lone pair occupies the axial hybrid orbital.



$sp^3d^2$  hybridisation - octahedral structure with one of the axial sites occupied by lone pair.

iv) Type  $XY_7$ : In these molecules, the central X atom uses all its seven valence electrons in forming seven X-Y bonds. Formation of this type of compounds can be explained on the basis of  $sp^3d^2$  hybridisation of the X atom. These compounds have a pentagonal bipyramidal structure with two axial X—Y bonds and five equatorial X—Y bonds (Fig. 3.5).



$sp^3d^3$  hybridisation - pentagonal bipyramidal structure.

### 3.3.5 Polyhalides and Polyhalonium Ions

Halide ions often associate with molecules of halogens or with interhalogen compounds to form polyhalide ions. For example, on addition of potassium iodide, the solubility of iodine in water is greatly enhanced due to the formation of the triiodide ion,  $I_3^-$



Fig. 3.2: Linear Structure of Interhalogen Molecule of the Type XY.

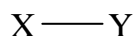


Fig. 3.3: T-shaped Structure of Interhalogen Molecules of the Type

$\text{XY}_3$ .

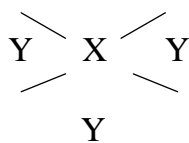


Fig. 3.4: Square Pyramidal Structure of Interhalogen Molecules of the type  $\text{XY}_5$ .

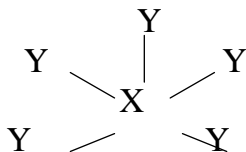
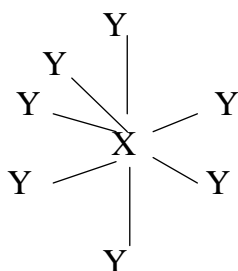


Fig. 3.5: Pentagonal bipyramidal structure of interhalogen molecules of the type  $\text{XY}_7$ .



More complex ions of iodine, such as penta-iodide,  $\text{I}_5$ , hepta-iodide,  $\text{I}_7$  and nona-iodide,  $\text{I}_9$  are also known.

These are generally found in the form of salts of large metal ions, e.g.,  $\text{Rb}^+\text{I}_9$ ,  ${}_{2\text{C}_6\text{H}_6}$  or large complex cations, e.g.,  $\text{NH}_4^+\text{I}_5$ ,  $(\text{C}_2\text{H}_5)_4\text{N}^+\text{I}_7$ .

A number of mixed polyhalide ions containing two or three different halogens are also known, e.g.,  $\text{ICl}_3^-$ ,  $\text{ICl}_4^-$  and  $\text{IBrF}_3^-$  and  $\text{IBrCr}_2^-$ .

All the polyhalides are hydrolysed to some extent in aqueous solution. The ease of hydrolysis increases with the introduction of the more electronegative halogen, into the ion. Thus, the triiodide being the most stable and  $\text{Cl}_3^-$  the least. In non-aqueous solutions, polyhalides behave as mild halogenating agents.

You have learnt earlier that polyhalonim cations, e.g.,  $\text{XYZ}_n^+$  and  $\text{XY}_n^+$  are formed as a result of autoionisation of  $\text{ICl}_3$  and  $\text{BrF}_3$ . Other cations like  $\text{Br}_2^+$ ,  $\text{I}_2^+$ ,  $\text{I}_3^+$ ,  $\text{ClF}_2^+$ ,  $\text{IF}_2^+$ ,  $\text{IBr}_2^+$ ,  $\text{IBrCl}^+$ ,  $\text{ClF}_4^+$ ,  $\text{BrF}_4^+$ ,  $\text{IF}_4^+$ ,  $\text{ClF}_6^+$ ,

$\text{BrF}_6^+$ ,  $\text{IF}_6^+$ , etc. are also known. These are established by large anions like  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{AlCl}_4^-$ ,  $\text{SbCl}_6^-$ , etc.

**SELF ASSESSMENT EXERCISE 7**

Write 'T' for true and 'F' for false in the given boxes for the following statements about interhalogen compounds.

- i) Interhalogen compounds are strong oxidising agents
- ii) Interhalogen compounds are strong reducing agents
- iii) X-Y bond is more polar than X-X and Y-Y bonds
- iv) Interhalogen compounds are ionic
- v)  $XY_3$  type of molecules have square pyramidal structure

**3.4 Pseudohalogens and Pseudohalides**

Some molecules like cyanogen,  $(CN)_2$ , thiocyanogen,  $(SCN)_2$  and selenocyanogen,  $(SeCN)_2$  have properties similar to those of the halogens. Therefore, these are called *pseudohalogens*. Pseudohalogens form hydro acids similar to the hydrohalic acids, e.g., H-CN. They also form anions such as cyanide,  $CN^-$ , cyanate,  $OCN^-$ , thiocyanate,  $SCN^-$ , selenocyanate,  $SeCN^-$ , tellurocyanate,  $TeCN^-$  and azide,  $N_3^-$ , which resemble the halide ions to some extent.

The best known pseudohalide is the cyanide,  $CN^-$ , which resembles  $Cl^-$ ,  $Br^-$  and  $I^-$  in following respects:

It can be oxidised to form a molecule,  $(CN)_2$ .

It forms an acid HCN similar to HCl, HBr, etc.

It forms insoluble salts with  $Ag^+$ ,  $Pb^{2+}$  and  $Hg^+$ .

Interpseudohalogen compounds ClCN, BrCN and ICN can also be formed.

Like AgCl, AgCN is insoluble in water but soluble in liquor ammonia.

It forms a large number of complexes similar to the halide complexes, e.g.,  $[Cu(CN)_4]^{2-}$  is similar to  $[CuCl]^{2-}$  and  $[Co(CN)_6]^{3-}$  is similar to  $[CoCl_6]^{3-}$ .

**3.5 Anomalous Behaviour of Fluorine**

Fluorine differs from other elements of the group because of its exceptionally small atomic and ionic size and low fluorine-fluorine bond dissociation energy. The result of these differences is that fluorine is the most electronegative element in the periodic table and is a powerful oxidant. Some differences between fluorine and other halogens are:



It is more reactive than other halogens because of low F-F bond energy, also due to its high electronegativity the bond between fluorine and other element is very strong so its compounds are more stable. Some of them are inert, e.g., SF<sub>6</sub>.

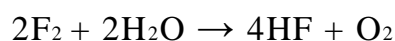
Fluorine is almost invariably monocoordinate (coordination number = 1) and is never more than mono covalent.

Fluorides are more ionic.

Fluorine forms strong hydrogen bonds resulting in the properties of hydrogen fluoride being anomalous.

Fluorine is the strongest oxidising agent and oxidises the elements to their highest oxidation state, for example in IF<sub>7</sub>, iodine has oxidation number seven.

The reactions of fluorine are also different from other halogens. Fluorine fumes in moist air and decomposes water to give oxygen, whereas other halogens are sparingly soluble in water and react partly to give hydrohalic and hypohalous acids.



Fluorine reacts with alkalies to yield the oxide, F<sub>2</sub>O :



The other halogens react with alkalies to yield a solution of hypohalite ions, which may disproportionate. The oxoacid of fluorine, HOF, prepared recently is very unstable. The oxides of fluorine are not acidic.

## 4.0 CONCLUSION

In this unit, we have successfully studied the Chemistry of the halogens. Halogen means salt producer. The most common of these salts is the common salt, NaCl. We can safely conclude that halogens find a wide variety of uses in everyday life.

## 5.0 SUMMARY

Let us now summarise what we have learnt in this unit.

- The halogens are only one electron short of the noble gas configuration. The elements form the anion X<sup>-</sup> or a single covalent bond. Their chemistry is completely non-metallic though there is some evidence of their forming cations.

Their chemical and the physical properties show variations according to the expected group trends.

Because of the extremely small size of fluorine, it exhibits anomalous behaviour in the F-F bond energy and electron affinity.

Fluorine is the strongest oxidising agent in the whole group. This is mainly because of very low F-F bond energy, very high F-element bond energy and the high hydration energy of the fluoride ion.

Fluorine can oxidise all the other halide ions like  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  to their respective elements. Because of its high oxidising power, fluorine forms compounds in which the other elements are in high oxidation states.

The oxidation state of fluorine is -1 while the other halogens exhibit variable oxidation states due to the availability of vacant *d* orbitals.

Halogens form a variety of compounds like, hydrohalic acids of the type HX, halogen oxides ( $\text{OX}_2$  etc.), oxoacids like HOX, HOXO, HOXO<sub>2</sub> and HOXO<sub>3</sub> and interhalogen compounds of the type  $\text{XY}_n$  where X and Y are two different halogens. The bond in interhalogen compounds is polar, with a positive charge on the heavier halogen. You have also learnt about the polyhalide ions.  $\text{X}_n^-$  and  $\text{XY}_n^\pm$ .

## 6.0 TUTOR MARKED ASSIGNMENT

- Fill the appropriate halogen in the following blanks:
  - \_\_\_\_\_ displaces three halogens from their compounds.
  - $\text{Cl}$  can be oxidised by \_\_\_\_\_
  - $\text{Br}_2$  can be reduced by \_\_\_\_\_
  - Fluorine and..... can oxidise water to oxygen.
  - Oxidation of \_\_\_\_\_ and \_\_\_\_\_ by  $\text{Cl}_2$  will give  $\text{Br}_2$  and  $\text{I}_2$ , respectively.
- We have listed the physical properties of all the halogens except astatine in an earlier table. From your study of the periodicity in the properties of elements, predict the following for the astatine:
  - Atomic number
  - Molecular formula
  - M.P., B.P:
  - Physical state
  - At-At bond energy
  - Strength of aqueous hydroastatic acid.
- Why does fluorine combine with other elements in their higher oxidation states?

4. Write the name of the following oxoacids and deduce the oxidation number of halogen atom in each.
- (i) HOCl            (ii) HOClO            (iii) HOBr  
(iv) HOBrO<sub>2</sub>        (v) HOIO<sub>2</sub>            (vi) HOClO<sub>3</sub>
5. The bond dissociation energy increases from I<sub>2</sub> to Cl<sub>2</sub>. Thus, bond dissociation energy of F<sub>2</sub> should be higher than that of Cl<sub>2</sub>. But it is not so, why?
6. The solutions of the salts of hypohalous acids are alkaline, explain why?

## 7.0 REFERENCES/FURTHER READINGS

*A New Concise Inorganic Chemistry*, J. D. Lee, ELBS, London, 3rd ed., 1977.

*Chemistry: Facts, Patterns and Principles*, W.R. Kneen, M.J.W. Rogers and P. Simpson, ELBS, London, 4th ed., 1984.

*Advanced Inorganic Chemistry*, F. A. Cotton and G. Wilkinson, Wiley Eastern Ltd.; New Delhi, 3rd ed., 1986.

*Principles of Inorganic Chemistry*, B. R. Puri and L. R. Sharma, Shoban Lal Nagin Chand & Co., New Delhi, 11th ed., 1986.