NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 221

COURSE TITLE: ELEMENTS OF GROUPS 4, 5 AND 7

COURSE GUIDE

CHM 221
ELEMENTS OF GROUPS 4, 5 AND 7

Course Team
Dr. Isa Bello – LAUTECH
Dr. Bayo Oyewole – ABU
Mrs. Felicia Folaranmi – ABU
Dr. (Mrs.) Charity Okonkwo &
Dr. Makanjuola Oki (Course Developers/Writers)
Prof. J. Amupitan (Course Editor) – ABU
Prof. Femi Peters (Programme Leader) – NOUN
Mr. Adakole Ikpe (Course Coordinator) – NOUN

NATIONAL OPEN UNIVERSITY OF NIGERIA

National Open University of Nigeria
Headquarters
14/16 Ahmadu Bello Way
Victoria Island, Lagos

Abuja Office
5 Dar es Salam Street
Off Aminu Kano Crescent
Wuse II, Abuja

e-mail: centralinfo@nou.edu.ng
URL: www.nou.edu.ng

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INTRODUCTION

CHM 221: **ELEMENTS OF GROUP 4, 5 and 7** is a two- credit unit course designed for 200 Level undergraduates running the B.Sc degree in Chemistry.

This course guide tells you briefly what the course is all about, the course materials you will need and how you can derive maximum benefit from the customised self-instructional materials. It also provides hints on your Tutor-Marked Assignments, details of which will be given to you at your study centre. Tutorial sessions, where you can seek clarifications on the course materials will be arranged for you at your centre. It is in your own interest to attend the sessions! The time and venue will be made known to you at your centre.

The one-module course is designed to equip the students with the methods, approaches, and strategies required teaching some concepts of chemistry. The module introduces you to elements of Groups 4, 5 and 7 of the periodic table; where Occurrence, Extraction and Uses of these elements were clearly stated.

WHAT YOU WILL LEARN IN THIS COURSE

The overall aim of CHM 221- Elements of Groups 4, 5 and 7 is to introduce you to the families of groups of elements on the periodic table. During the course you will learn about the occurrence, extraction and uses of the elements of carbon, nitrogen and halogen families; and allotropy and different forms in which these elements exist.

You will learn the general characteristics of the elements of carbon, nitrogen and halogen and their reactions, catenation with special reference to carbon. You will also learn internal π-bonding and the concept of complex formation by elements of this group, the nature of bonding in carbides, the chemistry of halides, hydrides, oxides and oxoacids of these dements, the structure and uses of silicates and silicones, and the chemistry of divalent compounds of these element. In addition, you will understand the maintenance of nitrogen-nitrate balance through nitrogen cycle, atmospheric nitrogen fixation, the use of phosphorus in fertilisers. You will understand the isolation of fluorine, the chemistry and geometry of interhalogen compounds and polyhalides, and the anomalous behaviour of fluorine.

COURSE AIMS

The course aims to introduce groups of elements and compounds. The learners will learn the classical and modern ideas about the development of atomic structure. They will also learn the Occurrence, Extraction and Uses of elements of Groups 4, 5 and 7 in the periodic table. The course is also intended to make learners understand the General Characteristics of the elements.

COURSE OBJECTIVES

At the end of the course, you should be able to:

- explain the occurrence, extraction and uses of the elements of carbon, nitrogen and halogen families
- explain allotropy and describe different forms in which these elements exist
- list the general characteristics of the elements of carbon, nitrogen and halogen describe their reactions
- explain catenation with special reference to carbon
- describe internal π-bonding and the concept of complex formation by elements of this group
- explain the nature of bonding in carbides
- discuss the chemistry of halides, hydrides, oxides and oxoacids of these dements
- describe the structure and uses of silicates and silicones, and
- describe the chemistry of divalent compounds of these element
- explain how nitrogen-nitrate balance is maintained through nitrogen cycle
- explain how atmospheric nitrogen is fixed
- describe the use of phosphorus in fertilisers, and
- describe the isolation of fluorine
- describe the chemistry and geometry of interhalogen compounds and polyhalides, and
- explain the anomalous behaviour of fluorine.

WORKING THROUGH THIS COURSE

You are required to spend a lot of time and commitment to studying this course; you are required to read books and other materials. You will need to find out more about the examples given to explain certain concepts. You will need to spend three hours on each unit of this course.

We advise that you avail yourself of the opportunity of the tutorial sessions, where you benefit from clarifications from your course facilitators, and the interaction with your colleagues.

COURSE MATERIALS

You will be provided with the following materials:

a. Course Guide
b. Study Units
c. Textbooks
d. Assignment file
e. Presentation schedule

STUDY UNITS

The following are the study units contained in this course:

Module 1

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

Each study unit consists of three hours work and includes the specific objectives, direction for study, reading materials and other sources. Each unit consists of self-assessment exercises, which would test you on what you have read in the course material. The self-assessment exercises help you to assess your progress and to reinforce your understanding of the material. These exercises together with the tutor-marked assignments will assist you in achieving the stated objectives at the beginning of each unit.

TEXTBOOKS AND REFERENCES

The following textbooks are necessary for you. You should try to buy them yourself.

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

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

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

Puri, B. R. & Sharma, L. R. (1986). *Principles of Inorganic Chemistry.* New Delhi: Shoban Lal Nagin Chand & Co.

ASSIGNMENT FILE

You will find details of works you are to submit to your tutor for marking in your assignment file. The marks you obtain for your assignments will count towards the final mark you obtain for this course. Further information on assignments will be found in the assignment file itself and in the assessment section of this course guide. Each unit of this course has some assignments. These assignments are meant to help you understand the course and assess your progress.

ASSESSMENT

There are three aspects to the assessment for this course. The first is in form of the Self-Assessment Exercises, the second are the Tutor-Marked Assignments, and the third is the written examination/end of course examination.

You are advised to attempt the exercises with all sincerity as that will assist you greatly. In tackling the assignments, you are expected to apply the information, knowledge and techniques gathered during the course. The assignments must be submitted to your tutor/facilitator for formal assessment in accordance with the deadlines stated in the presentation schedule and the assignment file. The work you submit to your tutor for assessment will account for 30% of the total course score. At the end of the course, you will sit for a final or end of course examination of about three hours duration. This examination will form 70% of the total score for the course.

TUTOR-MARKED ASSIGNMENTS (TMAs)

The TMA is a continuous assessment component of your course. It accounts for 30% of the total score. You are required to submit at least four (4) TMAs before you are allowed to sit for the end of course examination. The TMAs would be given to you by your facilitator, and would be returned to you after they have been graded.

Assignment questions for the units in this course are contained in the assignment file. You will be able to complete your assignment from the information and materials contained in your study units and references. However, it is desirable to demonstrate that you have read and researched into other references; this will give you a wider view point and a deeper understanding of the subject.

Ensure that each assignment reaches your facilitator before the deadline in the presentation schedule and assignment file. If for any reason you cannot complete your work on time, contact your facilitator before the assignment is due, to discuss the possibility of extension. Extension sought after the due date, will not be granted.

FINAL EXAMINATION AND GRADING

The end of course examination for this course will be about three hours, and will account for 70% of the total course score. The questions will be fashioned after the self-testing, practice exercise and tutor-marked assignments that you have previously encountered during your course. All areas of the course will be examined.

Utilise the time between the last unit and the commencement of your examination to revise the whole course. You might find it useful to review your self-test, TMAs, and comments on them before the examination. The end of course examination covers information from all parts of the course material.

The time for the examination is not fixed, but you will be given adequate notice of the examination.

PRESENTATION SCHEDULE

Dates for prompt completion and submission of your TMAs and attendance of tutorials will be reflected in your course materials. You should remember to submit all assignments at the stipulated date and time. You should work as scheduled, and do not lag behind in your work!

COURSE MARKING SCHEME

Assessment	**Marks**
Assignments 1-4	The best three (3) of the four Assignments will be rated based on 10% each, making a total of 30% of the course marks.
End of course examination	70% of overall course marks.
Total	100%.

COURSE OVERVIEW

Unit	Title of Work	Weekly Activity	Assessment (End of Unit)
	Course Guide	1	
	Module 1		
1	Elements of Group 4	1	
2	Elements of Group 5	1	Assignment 1
3	Elements of Group 7	1	
Total		4	

HOW TO GET THE MOST FROM THIS COURSE

- In distance learning, the study units replace the university lectures. This is one of the great advantages of distance learning; you can read and work through specially designed study materials at your own pace, and at a time and place that suits you. Realise the fact that you are reading the lecture instead of listening to the lecturer. In the same way, a lecturer might assign you some reading materials. The study units tell you when to read, your text materials and recommended books for your further reading. You are provided exercises to attempt at appropriate point in time, just as a lecturer might give in a classroom situation.

- Each of the study units follows a common format. The first item is an introduction to the subject matter of the unit, and how a particular unit is integrated with other units, and the course as a whole. Next to this is a set of learning objectives. These objectives state the mental tasks you should be able to accomplish by the time you have completed the unit. These learning objectives are therefore, meant to guide your study. The moment a unit is finished, you must go back and check whether you have achieved the objectives. If this is made a habit, you will significantly improve your chances of passing the course.

- The main body of the unit guides you through the required reading from other sources; this is either from your references or a reading section.

- The following is a practical strategy for working through the course: If you run into any trouble, telephone your tutor or visit the study centre nearest to you. Remember, your tutor’s job is to help you. When you need assistance, do not hesitate to ask your tutor to provide it.

- Read this Course Guide thoroughly; this is your first assignment!

- Organise a Study Schedule; Design a 'Course Overview' to guide you through the course. Note the time you are expected to spend on each unit and how the assignments relate to the units. Important information, e.g. details of your tutorials, and the date of the first day of the semester is available at the centre. You need to gather all the information into one place, such as your diary or a wall calendar. Decide on whatever method you choose, and write in your own dates and schedule of work for each unit.

- Once you have created your own study schedule, do everything to stay faithful to it. The major reason why students fail is that they lag behind in their course work. If you get into difficulties with your schedule, please, let your tutor know before it is too late for help.

- Turn to unit 1, and read the instruction and the objectives for the unit.

- Assemble the study materials. You will need your references and the unit you are studying at any point in time.

- As you work through the unit, you will know what sources to consult for further information.

- Visit your study centre whenever you need up-to-date information.

- Before the relevant due dates (about 4 weeks before due dates), visit your study centre for your next required assignment. Keep in mind that you will learn a lot by doing the assignments carefully. They have been designed to help you meet the objectives of the course and, therefore, will help you pass the examination. Submit all assignments as at when due.

- Review the objectives for each study unit to confirm that you have achieved them. If you are not sure about any of the objectives, you can move to the next unit. Study unit by unit through the course, and try to space your study so that you can keep to the schedule.

- When you have submitted an assignment to your tutor for marking, do not wait for its return before starting the next unit. Keep to your schedule. When the assignment is returned, pay particular attention to tutor's comments, both on the tutor-marked assignment form and also the written comments on the ordinary assignments.

- After completing the last unit, review the course and prepare yourself for the final examination. Check that you have achieved the unit objectives (listed at the beginning of each unit), and the course objectives (listed in the Course Guide).

FACILITATORS/TUTORS AND TUTORIALS

There are some hours of tutorial provided in support of this course. You will be notified of the dates, times and venue of these tutorials, as well as the name, and phone number of your facilitator as soon as you are fixed in a tutorial group.

Your tutor or facilitator will mark and comment on your assignments. He/She keeps a close watch on your progress, so as to render necessary assistance when required. You mail your tutor-marked assignment to your tutor before the scheduled date. They will be marked by your tutor and returned to you as soon as possible.

Do not hesitate to contact your facilitator by telephone, e-mail, and discuss your problems for necessary assistance.

The following might be circumstances in which you would find help necessary. Contact your facilitator if you:

- do not understand any part of the study units of the assigned readings.
- have difficulty with the self-test or exercises.
- have a question or problem with an assignment or with the grading of an assignment.

You should try your best to attend the tutorials. This is the only chance for a face-to-face contact with your course facilitator, and to ask questions which are answered instantly. You can raise any problems encountered in the course of your study. To derive maximum benefit from course tutorials, prepare a list of questions before the tutorial session. You will learn a lot by your active participation in the discussion.

SUMMARY

This course intends to introduce you to the elements of Groups 4, 5 and 7 on the Periodic Table. Upon completing this course, you will be equipped with the occurrence, extraction and uses of the elements. By the time you complete this course, you will be able to answer some relevant questions.

MAIN COURSE

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MODULE 1

UNIT 1 ELEMENTS OF GROUP 4

CONTENTS

1.0 INTRODUCTION

In CHM 121 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

At the end of 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 π-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 dements
- describe the structure and uses of silicates and silicones
- describe the chemistry of divalent compounds of these element.

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 this unit, you will study the occurrence, extraction and uses of elements of Group 4.

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, $4Ag_2S.GeS_2$, in germanite, $Cu_3(Ge,Fe)S_4$, and as a mixture in zinc and tin ores. Tin occurs mainly as cassiterite or tin stone, SnO_2 and lead as galena, 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 (Figures 1.l 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 (Figure 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 α-tin, which is a semimetallic form, stable below 286 K, and white or β-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 β-tin, 7.31 x 10^3 kgm^{-3}, is considerably higher than that of α-tin, 5.75 x 10^3 kgm^{-3}. The two forms are interconvertible as shown in following equilibrium:

Grey (α-tin) White (β-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 ~2775/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 incidently won the 19% Nobel Prize in Chemistry jointly. Detailed information of the discovery, properties and uses of fullerenes has been given in App.-.I.

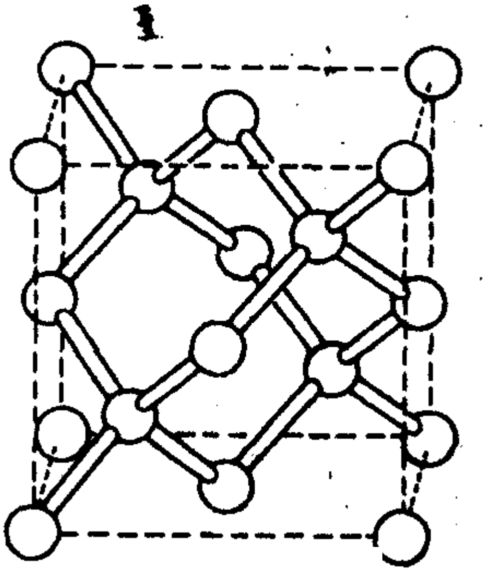


Fig. 1.1: Structure of Diamond

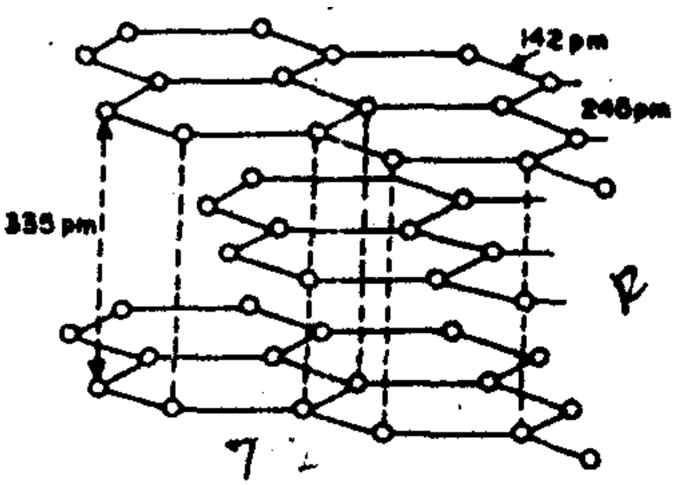


Fig. 1.2: Structure of Graphite

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.

$$SiO_2 + 3C \xrightarrow{-2CO} [SiC] \xrightarrow{2775K} Si_{(g)} + C\ (graphite)$$

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 SiO_2 with C or CaC_2 in an electric furnace. High purity silicon is obtained either from $SiCl_4$ or from $SiHCl_3$. 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 GeO_2 with C or H_2. Tin is obtained by the reduction of its oxide with carbon. Lead is normally obtained from 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 tit 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 aluminum. 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, 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 3.4.5) 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 $PbSO_4$, 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, Et_4Pb and tetramethyllead, Me_4Pb, 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 PbO_2 as the oxidising agent and spongy Pb as the reducing agent. The electrolyte is dilute H_2SO_4.

SELF-ASSESSMENT EXERCISE

Tick √ on the correct answer:

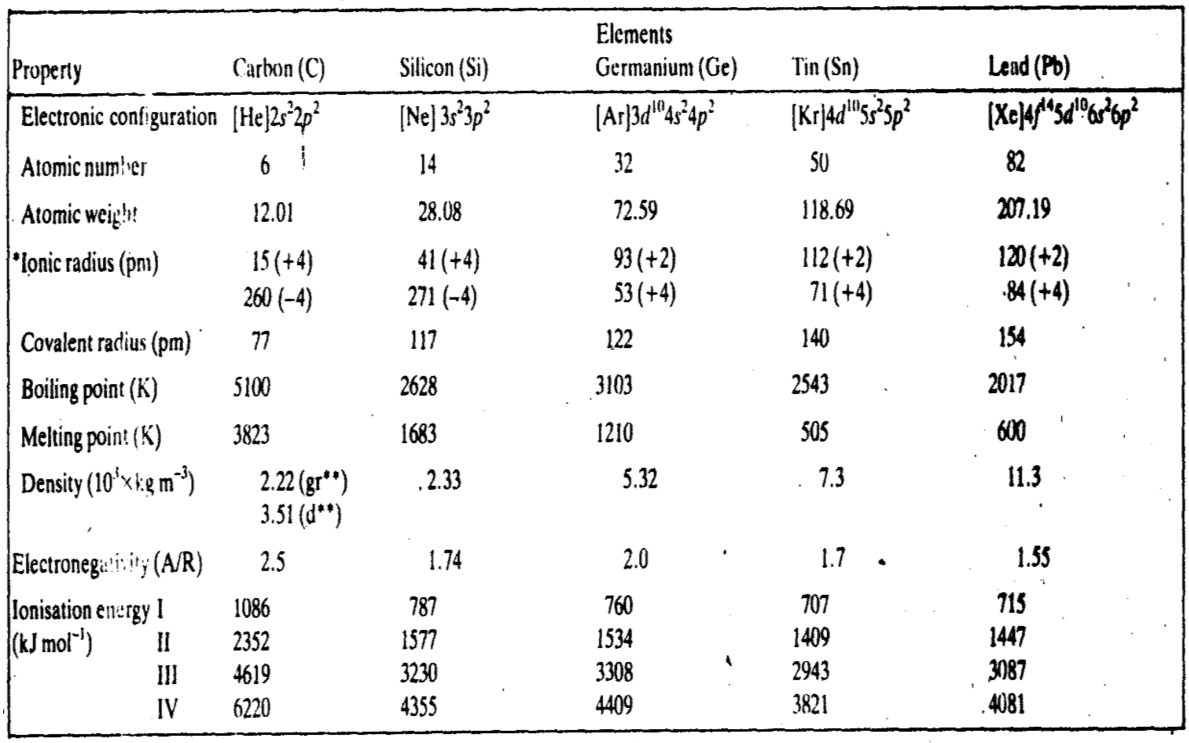
Diamond is not a conductor of electricity because:

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



			Elements		
Property	Carbon (C)	Silicon (Si)	Germanium (Ge)	Tin (Sn)	Lead (Pb)
Electronic configuration	[He]$2s^2 2p^2$	[Ne] $3s^2 3p^2$	[Ar]$3d^{10} 4s^2 4p^2$	[Kr]$4d^{10} 5s^2 5p^2$	[Xe]$4f^{14} 5d^{10} 6s^2 6p^2$
Atomic number	6	14	32	50	82
Atomic weight	12.01	28.08	72.59	118.69	207.19
*Ionic radius (pm)	15 (+4) 260 (–4)	41 (+4) 271 (–4)	93 (+2) 53 (+4)	112 (+2) 71 (+4)	120 (+2) 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 ($10^3 \times$ kg m^{-3})	2.22 (gr**) 3.51 (d**)	2.33	5.32	7.3	11.3
Electronegativity (A/R)	2.5	1.74	2.0	1.7	1.55
Ionisation energy I	1086	787	760	707	715
(kJ mol^{-1}) II	2352	1577	1534	1409	1447
III	4619	3230	3308	2943	3087
IV	6220	4355	4409	3821	4081

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

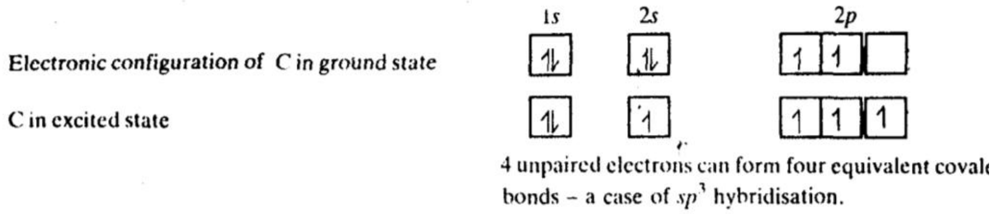
3.2.1 Physical Properties

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	-1
Alkali metals (Group 1)	+1
Alkaline earth metals (Group 2)	+2
Sum of all oxidation numbers in a neutral molecule	0

The ionisation energies (Table1.1) indicate that a very large amount of energy is required to form a M^{4+} 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 tetracovalency. 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.



4 unpaired electrons can form four equivalent coval
bonds – a case of sp^3 hybridisation.

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 state. This is reflected in the oxidising power of their tetravalent compounds. For example, CO_2, SiO_2 and GeO_2 do not act as oxidants; SnO_2 is a mild oxidising agent while 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; PbF_2 and $PbCl_2$ are well defined ionic compounds.

Lead (IV) oxide converts hot HCl to Cl_2:

$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2 \uparrow$

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

$2PbO_2 \longrightarrow 2PbO + O_2$

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, R_4Pb, compared to the dialkyllead species, R_2Pb, 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 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 of the kind C^{2-}, in acetylidcs and C^{4-} in methanides, while the other elements in the group are unable to do so. When we see the electronegativity 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.

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 4*s* electrons offered by the 3*d* 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 4*f* 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

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

CH_4, $CHCI_3$, CH_2CI_2 and CH_3Cl.

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3.2.3 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 ($>C=C<$), alkynes($-C\equiv C-$), imines ($>C=N-$), nitriles ($-C\equiv N$), ketones ($>C=O$), 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 $>Si=Si<$ and $>Si=C<$ double bonds, but their details are beyond the scope of this course. Stoichiometric analogues like SiO_2, SnO_2 and $(Me_2SiO)_n$ 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 π bond is formed by the lateral overlap of two dumb-hell shaped orbitals, e.g. *p*π -bond can be represented as:

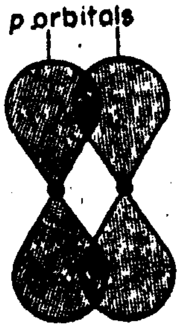


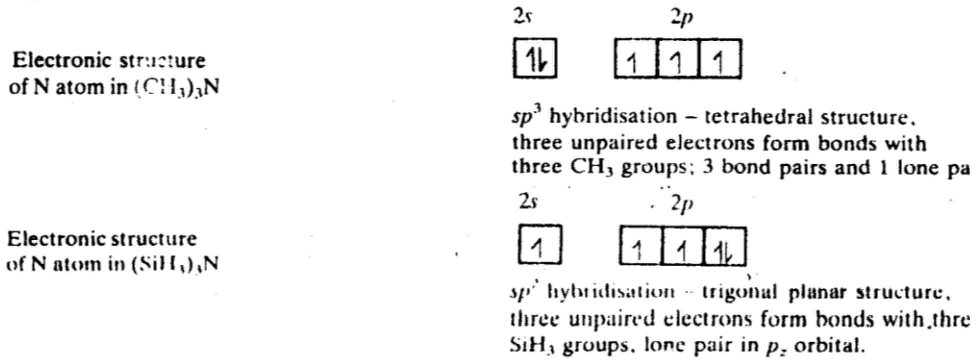
Table 1.3: Bond Energies of Group 4 Elements (kJmol^{-1})

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

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

pπ-dπ Bonding

You are familiar with a *π* bond formed by the lateral overlap of *p* orbitals. It is called a *pπ-pπ* bond. A lateral overlap of *p* and *d* orbitals under favourable conditions can also lead to the formation of a π bond. Such a π bond formation is called *pπ-dπ* bond. Let us understand this in case of C and Si compounds with nitrogen as the central atom, e.g., in trimethyl amine, $(CH_3)_3N$, and trisilyl amine, $(SiH_3)_3N$, (Figure1.3). 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, $(SiH_3)_3N$, 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 $(CH_3)_3N$

sp^3 hybridisation – tetrahedral structure, three unpaired electrons form bonds with three CH_3 groups; 3 bond pairs and 1 lone pa

Electronic structure of N atom in $(SiH_3)_3N$

sp^2 hybridisation – trigonal planar structure, three unpaired electrons form bonds with thre SiH_3 groups, lone pair in p_z orbital.

In case of $(SiH_3)_3N$, the p_z orbital of N with a lone pair overlaps with the empty d-orbital of silicon and forms a π bond. It may be noted that p_z orbital of N has energy comparable to d-orbital of Si. This kind of a π bond is called *pπ -dπ* bond. Since donation of lone pair is within the molecule, this is called internal π-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 *pπ-dπ* overlap is indicated in the Figure 1.3.

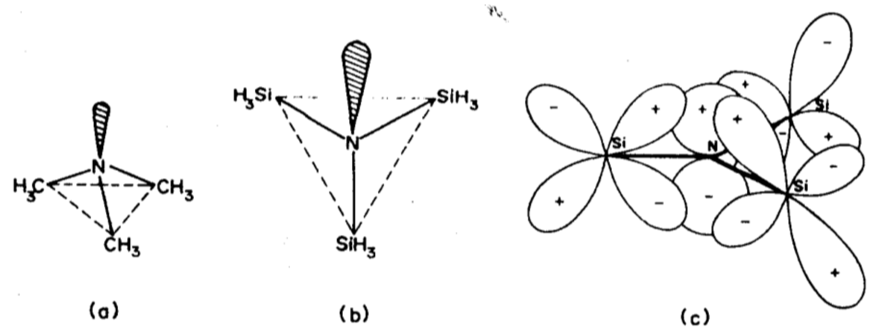


Fig. 1.3: (a) Structure of Trimethylamine
(b) Structure of Trisilylamine
(c) *pπ-dπ* Bond between N and Si in Trisilylamine

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 C_nH_{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 Si_nH_{2n+2}, but n does not exceed 8. Its halides also show catenation and have a general formula Si_nX_{2n+2}, where if X = F, n = l-14; if X = Cl, Br or I, n = 1-10. Germanium forms germanes, with general formula $Ge_nH_{2n+}2$, where n = l-9. Germanium halides form dimers, e.g., Ge_2Cl_6. Hydrides of Sn and Pb are much less stable, while SnH_4 and Sn_2H_6 have been prepared, analogous methods fail for the preparation of PbH_4. No catenated halides are known for Sn and Pb.

SELF-ASSESSMENT EXERCISE

Discuss briefly in the given space why tin and lead compounds do not show *pπ -dπ* bonding.

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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., $CaC_{2,}$ $A1_4C_3$, Be_2C, 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., salt-like or ionic carbides, interstitial carbides and covalent carbides.

a) Salt-like or Ionic Carbides

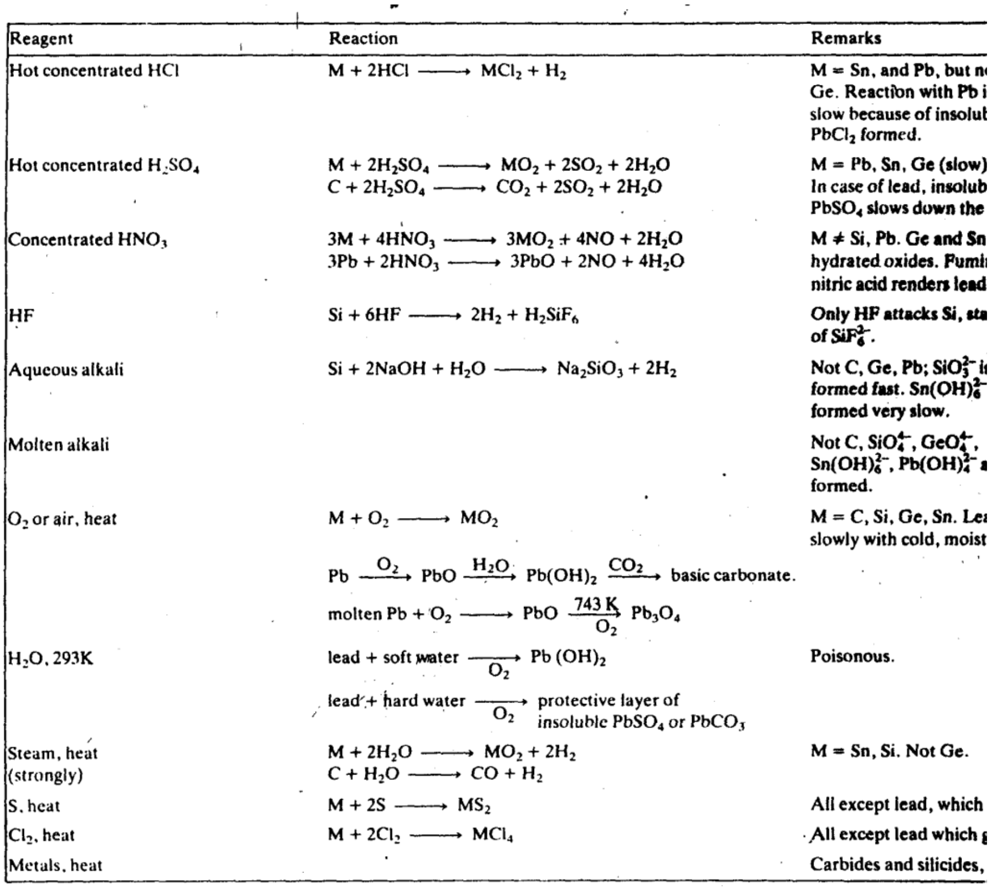
Ionic carbides are formed by elements of groups 1, 2, 3, 11, 12 and 13 except boron. Most of these are colourless and non-conducting in the solid state. These carbides are decomposed by water and dilute acids liberating either acetylene or methane. They are named as acetylides and methanides, respectively.

$CaC_2(s) + 2H_2O(l) \longrightarrow C_2H_2(g) + Ca(OH)_2(s)$
(Calcium acetylide)

$Al_4C_3(s) + 12H_2O(l) \longrightarrow 3CH_4(g) + 4Al(OH)_3(s)$
(Aluminium methanide)

Most of the acetylides have cubic structure similar to the podium chloride structure. One cell axis is, however, elongated to accommodate the $(C=C)^{2-}$ ion making the symmetry of the crystal tetragonal and not cubic. In Figure 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 n Ge. Reaction with Pb i slow because of insolub $PbCl_2$ 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) In case of lead, insolub $PbSO_4$ slows down the
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 hydrated oxides. Fumi nitric acid renders lead
HF	$Si + 6HF \longrightarrow 2H_2 + H_2SiF_6$	Only HF attacks Si, sta of SiF_6^{2-}.
Aqueous alkali	$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$	Not C, Ge, Pb; SiO_3^{2-} i formed fast. $Sn(OH)_6^{2-}$ formed very slow.
Molten alkali		Not C, SiO_4^{4-}, GeO_4^{4-}, $Sn(OH)_6^{2-}$, $Pb(OH)_4^{2-}$ a formed.
O_2 or air, heat	$M + O_2 \longrightarrow MO_2$	M = C, Si, Ge, Sn. Le slowly with cold, moist
	$Pb \xrightarrow{O_2} PbO \xrightarrow{H_2O} Pb(OH)_2 \xrightarrow{CO_2}$ basic carbonate.	
	molten $Pb + O_2 \longrightarrow PbO \xrightarrow[O_2]{743\ K} Pb_3O_4$	
H_2O, 293K	lead + soft water $\xrightarrow[O_2]{}$ $Pb(OH)_2$	Poisonous.
	lead + hard water $\xrightarrow[O_2]{}$ protective layer of insoluble $PbSO_4$ or $PbCO_3$	
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
Cl_2, heat	$M + 2Cl_2 \longrightarrow MCl_4$	All except lead which
Metals, heat		Carbides and silicides,

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

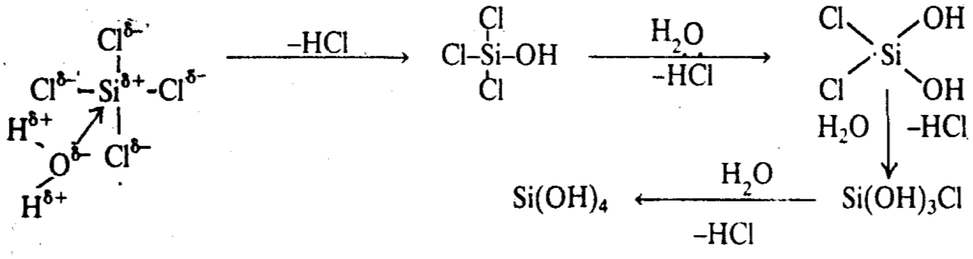
These are formed by combination of carbon with elements of almost equal electrondgativity like boron and silicon. Silicon carbide, SiC, known as carborundum and boron carbide, $B_{12}C_3$ are giant macromolecules having covalent bonding all through. Both carbides are very hard, infusible and chemically 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 Figure 1.l.

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 $PbBr_4$ and 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 $SiCl_4$ gets readily hydrolysed to give silicic acid:

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{Silicic acid}}{Si(OH)_4} + 4HCl$$

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 $SiCl_4$ can be illustrated as given below:



Hydrolysis in the presence of alkali will be faster because of the stronger nucleophile, i.e., 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 3.5.

Fluorocarbons

Fluorocarbons are the synthetic equivalents of hydrocarbons in which some or all of the hydrogens have been replaced by fluorine atoms, e.g. CF_4, C_2F_4, C_2F_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 $kJmol^{-1}$ compared with C-H bond energy of 414 $kJmol^{-1}$. Fluorocarbons are resistant to attack by acids, alkalis, oxidising 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 CoF_3, AgF_2 and MnF_3:

$$C_8H_{18} + 9F_2 \longrightarrow C_8F_{18} + 18HF$$

$$C_6H_6 + 6F_2 \longrightarrow C_6F_{12} + 12HF$$

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.

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, C_2F_6, is analogous to ethane, C_2H_6. Tetrafluoroethene, C_2F_4 can be polymerised thermally or in aqueous emulsions to a chemically inert plastic, polytetrafluoroethene (PTFE), commercially known as **Teflon**.

$$nC_2F_4 \longrightarrow (\text{- } CF_2.CF_2 \text{ -})_n$$

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 CCl_2F_2, $CFCl_3$ and CF_3Cl 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. $CF_3CHBrCl$ 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 CH_4 and other alkanes are stable compounds, 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 stable except for PbO_2, the reason being an increase in stability of +2 oxidation state down the group (see sub-section 3.2.1). Acidic character of the dioxides decreases down the group; CO_2 and SiO_2 are acidic oxides, while GeO_2, SnO_2 and PbO_2 are amphoteric. Carbon is exceptional in forming gaseous mono and dioxides, CO and CO_2.

Carbon monoxide is obtained on passing steam over red hot coke. The product, a mixture of CO and H_2, is called **water gas** and is used as a fuel.

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

The electronic structure of 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 $C^{\delta-}$-$O^{\delta+}$ 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 CO is the most stable diatomic molecule, with the highest bond energy of 1071 $kJmol^{-1}$.

$${}^{x}_{x}C\underset{\leftarrow}{{}^{x}_{x}}:O:\text{usually written as }:\underset{\leftarrow}{C}= O \text{ or } {}^{-}C\equiv O^{+}$$

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. $CaCO_3$, in the form of marble chips is usually taken:

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2 \uparrow$$

Increase in the concentration of CO_2 in the atmosphere has recently been causing concern, wrapping of earth's thermal radiation by CO, 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_2 is a colourless gas with a faint smell. Its structure can be represented by O=C=O. It can be easily liqujfied by application of pressure even at the ordinary ambient temperatures. If liquid CO_2 is allowed to expand rapidly, solid CO_2 is obtained. Solid CO_2 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:

$$2NaOH(aq) + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

$$Na_2CO_3(aq) + H_2O + CO_2 \longrightarrow NaHCO_3(aq)$$

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 earlier on. Being a non-supporter of combustion, CO_2 is used in fire extinguishers.

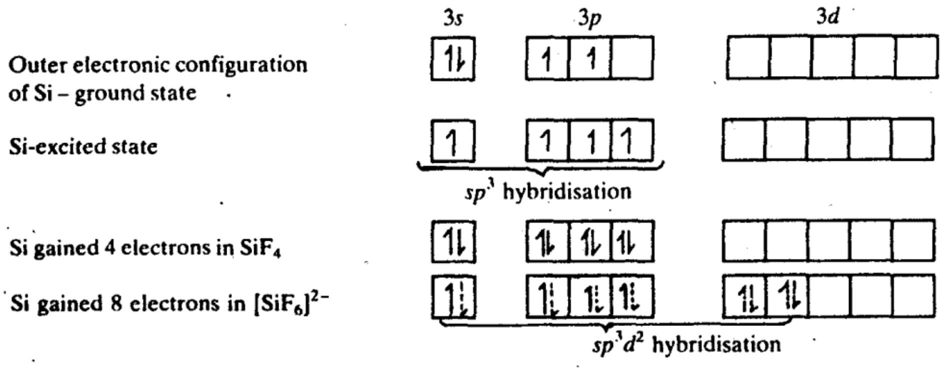
Silicon forms an important acidic oxide, silicon dioxide discussed in detail in Section 3.4 and an unstable monoxide, SiO. Germanium and tin form amphoteric oxides. GeO_2 is mainly acidic, while SnO and SnO_2 are amphoteric in nature, dissolving both in alkalis and acids. As explained in sub-section 3.2.1, PbO_2 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_3O_4 or $2PbO{\cdot}PbO_2$, also called '**red lead**':

$$6PbO + O_2 \longrightarrow 2Pb_3O_4$$

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^- 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.,

$$GeF_4 + 2NMe_3 \longrightarrow [GeF_4(NMe_3)_2]$$

$$SnCl_4 + 2Cl^- \longrightarrow [SnCl_6]^{2-}$$

SELF-ASSESSMENT EXERCISE

i. Why is C-H bond essentially non-polar? Explain in the space given below.

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ii. Using the concept of hybridisation, predict the shape of $[SiF_6]^{2-}$ ion.

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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 out:

- Carbon has a maximum covalency of 4 and is not able to form complex compounds.
- Carbon is the only element in the group to form stable derivatives with double and triple bonds, which show special characteristics.
- Carbon forms gaseous oxides, i.e., CO and CO_2 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, 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.

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 \longrightarrow SiO_2$$

Silica is insoluble in water and acids except hydrofluoric acid with which it forms volatile silicon tetrafluoride, SiF_4. When passed in water, SiF_4 is hydrolysed to give soluble H_2SiF_6 and silicic acid as an insoluble white solid:

$$SiF_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HF$$

$$2SiF_4 + 4HF \longrightarrow 2H_2SiF_6$$

$$3SiF_4 + 4H_2O \longrightarrow 2H_2SiF_6 + Si(OH)_4\uparrow$$

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

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_2 + H_2O$$

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

SiO_2 differs from CO_2 in an important respect that it is a solid at room temperature whereas CO_2 is a gas. You know that 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, 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 atom, in turn, is bonded to two silicon atoms (Figure 1.5). However, the overall stoichiometry or the silicon-oxygen ratio remains the same, i.e. SiO_2.

Silica is the chief constituent of glass. **Silica gel** is an amorphous form of 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):

$$SiO_2 + Na_2CO_3 \longrightarrow Na_2SiO_3 + CO_2$$

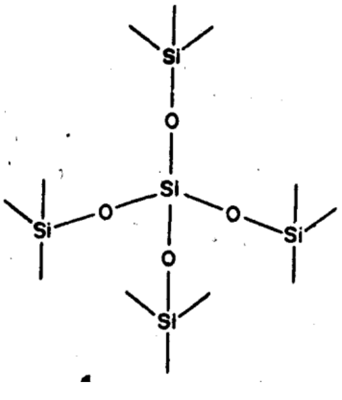
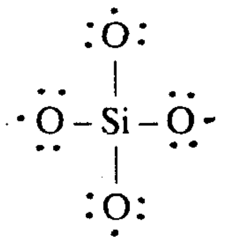


Fig. 1.5: Structure of Silicon Dioxide

3.4.2 Silicates

Silicates are regarded as the salts of silicic acid, H_4SiO_4. All the silicates are comprised of SiO_4 units. These units have a tetrahedral structure formed as a result of *sp*^{2} hybridisation (cf. SiF_4, Sub-sec. 3.2.5). 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 $(SiO_4]^{4-}$. 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 $[SiO_4]^{4-}$



The $[SiO_4]^{4-}$ tetrahedra can be represented in three ways as shown in Figure 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, H_4SiO_4, and contain the orthosilicate ion, $[SiO_4]^{4-}$, e.g. $Zr^{4+}SiO^{4-}$.

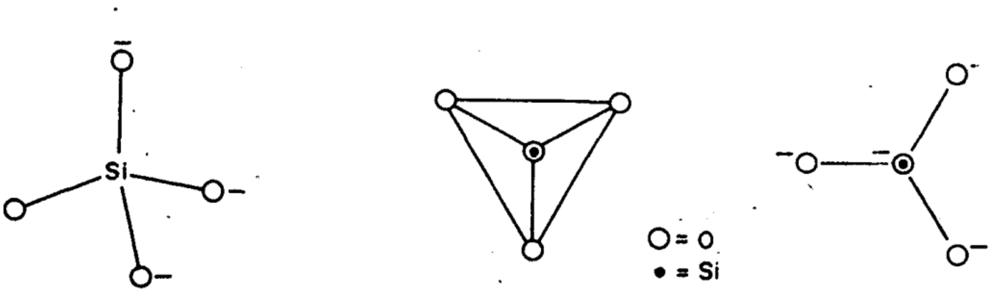


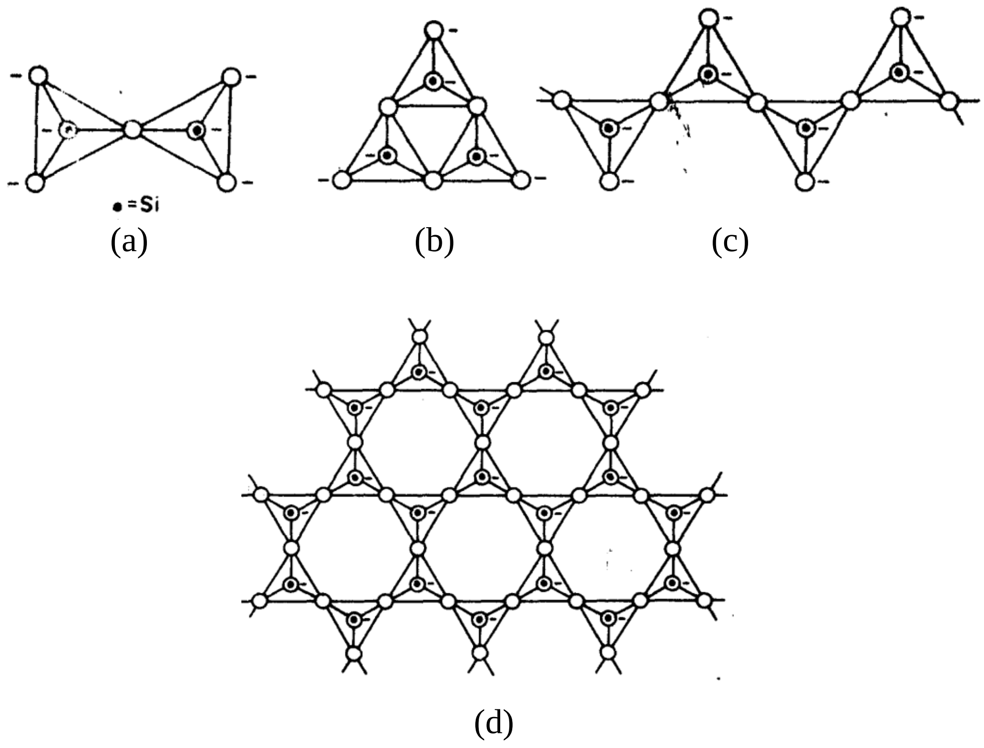
Fig. 1.6: Representations of SiO^{4-} Tetrahedra.

In some silicates, the oxygen atoms of 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 Li^+, Na^+, K^+,

Ca^{2+}, Al^{3+} etc. Depending upon the way these SiO_4 units are linked, silicates of different structure and complexity are obtained. Some representative types are given in Figure 1.7.

In addition to the types where linkages between SiO_4 units are two-dimensional, complex silicates result from three dimensional linkages between 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 manufactured. Let us study, in brief the uses of some mineral silicates.



Flg. 1.7: Structure of (a) Pyrosilicates, e.g., Thorteveltlte, $Sc_2Si_2O_7$

(b) Cyclic silicates, e.g., Wollastonite, $Ca_2(Si_3O_9)$

(c) Chain silicates, e.g., Spodumene, LiAl $(SiO_3)_2$

(d) Sheet Silicates, e.g., Talc, $Mg_3(OH)_2(Si_2O_5)_5$

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, Si^{4+} ion in the lattice is replaced by 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 alkalis 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 clay 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 clay 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 Ca^{2+} and Mg^{2+} ions from hard water.

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

$$Na_2Z + Ca \longrightarrow CaZ + 2Na^+ \text{ (Water softening)}$$

$$CaZ + 2Na^+ \longrightarrow Na_2Z + Ca^{2+} \text{ (recharging or regenerating)}$$

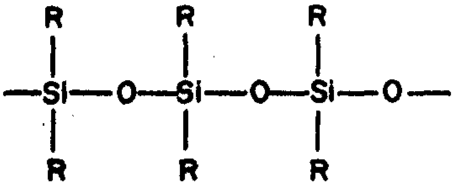
The calcium and magnesium salts of permutit can be converted back into the sodium salt by treatment with a concentrated solution of sodium chloride.

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.

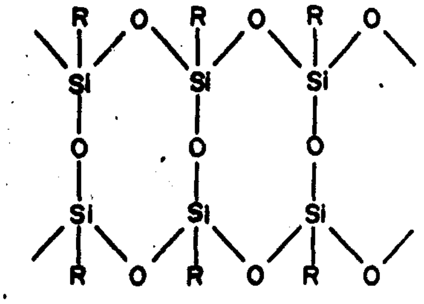
When a mixture of silicates mainly of sodium and calcium is melted and then supercooled, i.e. cooled immediately to a low temperature, a transparent solid is obtained which is called glass. There are different varieties of glass but most of them are a mixture of either only different silicates or mixture 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 Cu_2O, Fe_2O_3, U_3O_8, MnO_2, NiO, Co_2O_3, etc. giving red, green, yellow, violet, black and blue colours to the glass, respectively.

3.4.3 Silicones

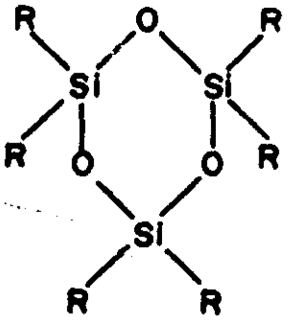
Silicones are a group of organosilicon polymers. Unlike $SiCl_4$ which on complete hydrolysis gives SiO_2, alkylsubstituted chlorosilanes on hydrolysis do not give the expected silicon compound analogous to ketone but get hydrolysed to long chain polymers or silicones. While the hydrolysis of trialkylmonochlorosilane yields Linear gilicone 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 up to ~500K, water repellent, good-electrical insulators and show little viscocity change with temperature. They are used as lubricants, insulators, protective coating and heating oils.



Linear Silicone Polymer



Cross linked Silicone Ploymer



Cyclic Silicone

SELF-ASSESSMENT EXERCISE

Which silicon compound is used as a:

i. dehydrating agent
ii. cation exchanger
iii. lubricant
iv. thermal insulator

3.5 Chemistry of Divalent Silicon, Germa-Nium, 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 on going from silicon to lead while that of oxidation state II increases. This is reflected in a decrease in the reducing property of the *+2* state and an increase in the oxidising property of +4 state. Ge(Il) is a strong reducing agent, Sn(IV) 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. 3.2. 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, MX_2. This is expected since both metals are weakly electropositive, tin less than lead. $SnCl_2$ is, in fact, soluble in organic solvents and does not conduct electricity in the molten state, whereas $PbCl_2$ is only sparingly soluble in alcohol and molten $PbCl_2$ is a good conductor. Thus $SnCl_2$ is best regarded as covalent and $PbCl_2$ 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 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, 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.

$$GeX_4 + Ge \longrightarrow 2GeX_2$$

GeF_2 and $GeCl_2$ react exothermically with solutions of alkali metal halides to give the hydrolytically stable $[GeX_3]^-$ ion.

Divalent tin halides, SnF_2 and $SnCl_2$, are important compounds.
When Sn is heated with gaseous HF or HCl, SnF_2 or $SnCl_2$ is obtained. SnF_2 is less soluble in water. SnO_2 hydrolyses in water to the basic chloride. However, if a slightly acidic solution of $SnCl_2$ is taken, $SnCl_2.2H_2O$ crystallises out. It is soluble in organic solvents, which shows its covalent nature. Despite their covalent nature, in aqueous halide solutions, SnF_2 and $SnCl_2$, like the corresponding germanium halides, give complex ions, $[SnX_3]^-$. 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.

$$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$$

$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$$

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

Categorise the following compounds into oxidising and reducing agents: CO, GeO, PbO_2, $SnCl_2$ and $PbCl_4$

……………………………………………………………………………
……………………………………………………………………………
……………………………………………………………………………

4.0 CONCLUSION

In this unit, we have discussed the occurrence, extraction and uses of Group 4 elements. General characteristics such as physical properties, multiple bonding, catenation, chemical properties of Group 4 elements were examined. Complex formation, anomalous behaviour of carbon, silica and silicates were discussed. The chemistry of divalent silicon, germanium, tin and lead compounds were explained.

5.0 SUMMARY

Let us recollect what we have studied in this unit, 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 Irom 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 arc supposed to have internal π-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 tctrahalides. They can also be divalent forming compounds containing the ions Sn^{2+} and 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

i. Diamond and graphite both are allotropic forms of carbon; still only graphite is used as a lubricant. Why?
ii. What are the properties responsible for the anomalous behaviour of carbon?
iii. Why are tin and lead incapable of showing the property of catenation?
iv. Why is trisilylamine a very weak and trimethylamine a good Lewis base?
v. Give reactions to show that CO_2 is an acidic oxide and SnO_2 is an amphoteric oxide.
vi. Explain the following briefly:
    a. SiC is as hard as diamond.
    b. CCl_4 is not hydrolysed while $SiCl_4$ or $SnCl_4$ get hydrolysed easily.
    c. $PbBr_4$ and PbI_4 do not exist.
    d. SiO_2 is a solid whereas CO_2 is a gas.

7.0 REFERENCES/FURTHER READING

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UNIT 2 ELEMENTS OF GROUP 5

CONTENTS

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

At the end of 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 formed by these 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
- list the differences of nitrogen from rest of the Group 5 elements.

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 (1.9×10^{-3}%) in the crustal rocks and soils of earth. A few major minerals are saltpetre, KNO_3 and Chile saltpetre, $NaNO_3$. 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, $Ca_5(PO_4)_3X$ and the common members are fluorapatite, $Ca_5(PO_4)_3F$, chlorapatite, $Ca_5(PO_4)_3Cl$ and hydroxyapatite, $Ca_5(PO_4)_3OH$. In addition, there are vast deposits of amorphpus phosphate rock, phosphorite, $Ca_3(PO_4)_2$. 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 $Ca_3(PO_4)_2$ is also present in bones and teeth. Arsenic, antimony and bismuth are comparatively less abundant in the earth's crust, their abundances being 1.8×10^{-4}%, 2.0×10^{-5}% and 8.0×10^{-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 2×10^4 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 (Figure 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.

$$2Ca_3(PO_4)_2 + 6SiO_2 \rightarrow 6CaSiO_3 + P_4O_{10}$$

$$P_4O_{10} + 10C \rightarrow P_4 + 10CO$$

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.

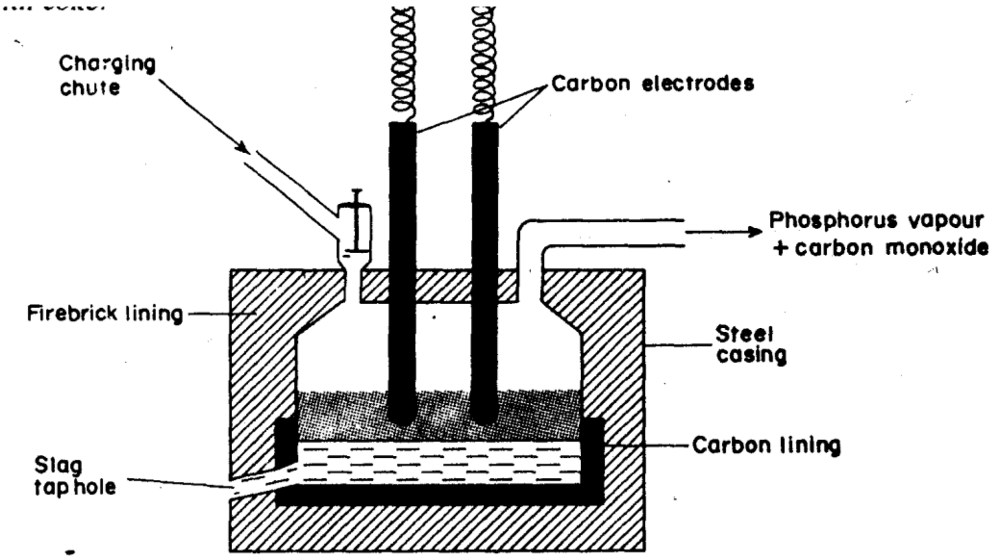


Fig. 2.1: Electric Furnace for Extracting Phosphorus

3.1.3 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 materials like meat, preservation of biological specimens and for in-transit refrigeration.

Red phosphorus is used in matches, fireworks 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 NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, 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 NH_4NO_3, explosives like nitroglycerine, nitrocellulose and TNT. Hydrazine, N_2H_4 and its methyl derivatives, $MeNHNH_2$ and Me_2NNH_2, are used as rocket fuels. Nitrous oxide, N_2O, is used as an anaesthetic.

Sulphides of phosphorus, P_4S_3 and P_4S_{10} are used in match industry. Phosphoric acid is used in fertilisers, cleaning of metals, rust proofing, pharmaceuticals, etc. Disodium hydrogen phosphate, Na_2HPO_4, is widely used as an emulsifier in the manufacture of pasteurised cheese. Sodium dihydrogen phosphate, NaH_2PO_4, is used as a constituent in the undercoat for metal paints. Calcium phosphates are used in baking powders and tooth-pastes. Synthetic $Ca_5(PO_4)_3OH$ (1 - 2%) is added to table salt to impart free flowing properties. Sodium tripolyphosphatc, NaP_3O_{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, As_2O_5, is used to decolourise bottle glass. Antimony compound, antimonial lead, is used in storage batteries. Compounds of antimony with aluminium, gallium and indium, AlSb, GaSb and 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 $d^{10}f^{14}$. This is reflected in the properties of these elements which we will discuss below.

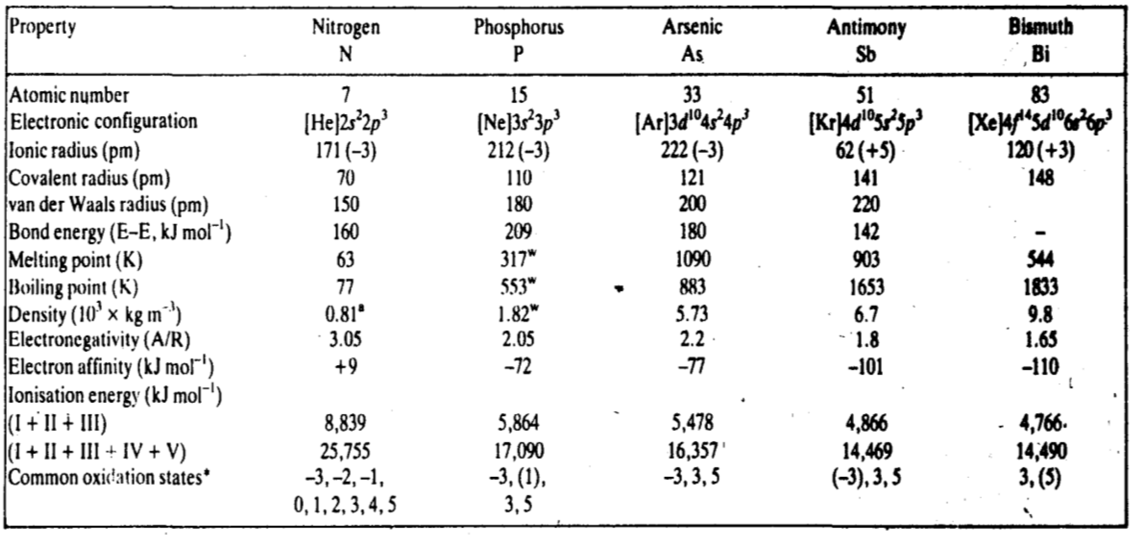
3.2.1 Physical Properties

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=N. This is due to the very high bond energy of the N=N bond, 946 $kJmol^{-1}$, which is nearly six times the N-N bond energy, 160 $kJmol^{-1}$. On the contrary $P \equiv P$ bond is quite weak; its energy of 490 $kJmol^{-1}$ is only ~ 2.5 times the P-P bond energy, 209 $kJmol^{-1}$. 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 sub-section.

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, 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 shells; 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 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.l: 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	$[He]2s^22p^3$	$[Ne]3s^23p^3$	$[Ar]3d^{10}4s^24p^3$	$[Kr]4d^{10}5s^25p^3$	$[Xe]4f^{14}5d^{10}6s^26p^3$
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^{-1})	160	209	180	142	–
Melting point (K)	63	317^w	1090	903	544
Boiling point (K)	77	553^w	883	1653	1833
Density ($10^3 \times$ kg m^{-3})	0.81^a	1.82^w	5.73	6.7	9.8
Electronegativity (A/R)	3.05	2.05	2.2	1.8	1.65
Electron affinity (kJ mol^{-1})	+9	−72	−77	−101	−110
Ionisation energy (kJ mol^{-1})					
(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*	−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^{3-}) is rare. 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_3N, Be_3N_2, Mg_3N_2, Ca_3N_2. 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 *spd*-orbitals in P, As, Sb and Bi, within which these elements can attain sp^3d and sp^3d^2 hybridisations, e.g., in $PC1_5$ and PCl_6^-, 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., $NH_3.BF_3$, $CaCl_2.4NH_3$, etc.

Nitrogen forms strong pπ-pπ **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 *pπ-pπ* multiple bonding include nitrates, NO_3^-, nitrites, NO_2, azides, N_3^-, cyanides, $O=N^-$, oxides of nitrogen, etc. Thus, the oxides N_2O_3 and N_2O_5 are monomeric due to the presence of multiple bonds but analogous P_2O_3 and P_2O_5 exist as dimers, P_4O_6 and P_4O_{10}. 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_4 molecules in the gaseous and liquid states and also in the solid state as white phosphorus. Because of angular strain in the P_4 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 some time, 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 (Figure 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 kJmol^{-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 H_3PO_4, H_3AsO_3 (arsenious acid), $Sb_2(SO_4)_3$ and $Bi_2(SO_4)_3$, respectively. With nitric acid, phosphorus forms phosphoric acid, arsenic forms arsenious and arsenic acids, antimony and bismuth form Sb_2O_5 and $Bi(NO_3)_3$, respectively.
- The action of alkalies is different on different elements — phosphorus forms alkali hypophosphites and phosphine, arsenic forms alkali $_3$arsenites. AsO^{3-}, whereas antimony and bismuth remain unaffected.

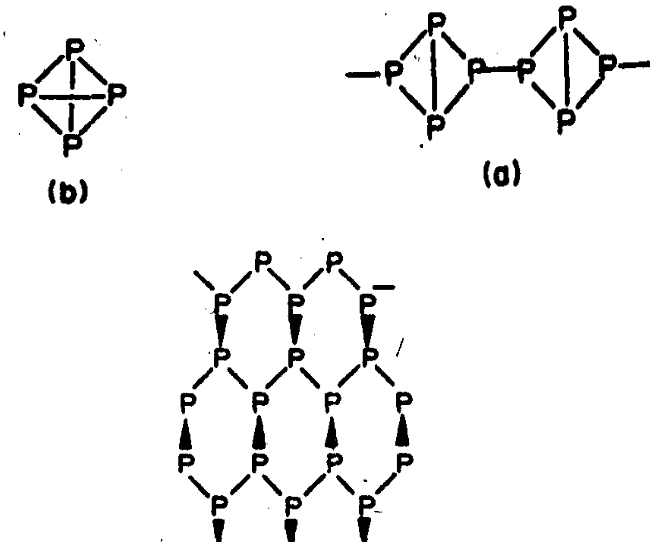


Fig. 2.2: Allotropes of Phosphorus:
(a) Red Phosphorus
(b) White Phosphorus and
(c) Black Phosphorus.

These reactions are summarised in Table 2.2.

Table 2.2: Some Reactions of Group 5 Elements

$E + O_2 \xrightarrow{\text{Heat}} E_xO_y$	Nitrogen forms NO when a mixture of N_2 and air is passed through an electric arc; P gives P_2O_3 and P_2O_5; As, Sb and Bi yield As_2O_3 and Bi_2O_3.
$E + F_2 \longrightarrow E_xF_y$	Not N and P; As, Sb and Bi form AsF_5, SbF_5 and BiF_3, respectively.
$E + X_2 \longrightarrow E_xX_y$ (X = Cl, Br, I)	Not N; P gives PX_3 and PX_5; As, Sb and Bi form EX_3.
$E + S \longrightarrow E_xS_y$	Not N; P gives P_4S_3; As, Sb and Bi form As_2S_3, Sb_2S_3 and Bi_2S_3, respectively.
$P + KOH + H_2O \longrightarrow PH_3 + KH_2PO_2$	Not N, Sb and Bi; As reacts with fused alkalies to form Na_3AsO_3 and H_2.
$As + H_2SO_4 \longrightarrow H_3AsO_3$ hot & conc.	Not N; P forms H_3PO_4 whereas Sb and Bi yield $Sb_2(SO_4)_3$ and $Bi_2(SO_4)_3$, respectively.
$As + HNO_3 \longrightarrow H_3AsO_3$ dil	Conc. HNO_3 oxidises P, As, Sb and Bi to H_3PO_4, H_3AsO_4, Sb_2O_5 and $Bi(NO_3)_3$, respectively.

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

SELF-ASSESSMENT EXERCISE

Explain briefly in the space given below, why

i. Nitrogen exists as N_2 whereas phosphorus exists as P_4 molecules in the gaseous state.
…………………………………………………………………
…………………………………………………………………

ii. 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 NH_3, and phosphorus gives PH_3 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. 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 ($kJmol^{-1}$)	389	322	297	255	-
Bond angle	$106^o47'$	$93^o30'$	92^o	$91^o30'$	-
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, (Figure 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 decrease in the bond angles which become close to 90° (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, NH_3 readily forms ammonium salts with H^+. Phosphonium salts are formed with H^+ only under anhydrous conditions but other hydrides, AsH_3, SbH_3 and BiH_3 do not form such salts. Let us now discuss the hydrides of nitrogen in brief.

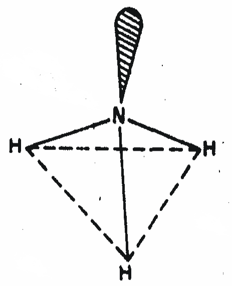


Fig. 2.3: Structure of Ammonia

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:

$$2NH_4Cl \quad + \quad Ca(OH)_2 \;\rightarrow\; CaCl_2 + 2NH_3 + 2H_2O$$

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 atmospheres and at a temperature of 800 K in the presence of a finely divided catalyst.

$$N_2 \;+ 3H_2 \rightleftharpoons \quad 2NH_3, \quad \Delta H^o \;=\; - 92.0\ \text{kJmol}^{-1}$$

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 Mg, K and Al. The above pressure and temperature is optimum to give about 15% yield of NH_3. The unreacted gases are recycled.

A mixture of carbon monoxide and hydrogen, obtained from methane, CH_4, naphtha, C_7H_{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 NH_3(aq), NH_4(aq) and OH^-(aq) ions:

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The equilibrium constant K for the above reaction is only 1.81×10^{-5}. This value is quite low, suggesting that the aqueous solution is a weak alkali. Ammonia solution, in the presence of NH_4C1, 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 HCl in your school chemistry.

As we have discussed earlier, NH_3 molecule has a pyramidal structure, having a lone pair of electrons at the apex. The ammonium ion formed on reaction with 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., $[Cu(NH_3)_4]^{2+}$, $[Ag(NH_3)_2]^+$, $[Ni(NH_3)_6]^{2+}$, 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:

$$2NH_3 \rightleftharpoons NH_4 + NH_2$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

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., HCl, HNO_3 are acids in water and NaOH, $_+$Ca(OH)$_2$ are bases. Similarly, all those substances $_-$which dissolve in liquid ammonia to give NH_4 ions are acids and those which give amide ions, NH_2, are bases. Thus, NH_4Cl, NH_4NO_3 are acids and $NaNH_2$ 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.

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

$$NaNH_2 \longrightarrow Na^+ + NH_2$$

$$NH_4Cl + NaNH_2 \xrightarrow{NH_3} NaCl + 2NH_3$$

$$HCl + NaOH \xrightarrow{H_2O} NaCl + H_2O$$

Similarly,

$$2NH_4Cl + \underset{\text{Lead imide}}{PbNH} \xrightarrow{NH_3} PbCl_2 + 3NH_3$$

$$3NH_4Cl + \underset{\text{Aluminium nitride}}{AlN} \xrightarrow{NH_3} AlCl_3 + 4NH_3$$

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 (pka = 5) but will function as a strong acid in liquid ammonia:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

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

$$ZnCl_2 + 2NaOH \xrightarrow{\text{water}} Zn(OH)_2 \xrightarrow[\text{NaOH}]{\text{excess}} [Zn(OH)_4]^{2-}$$

precipitate soluble complex

$$ZnCl_2 + 2NaNH_2 \xrightarrow{\text{Liquid } NH_3} \quad \xrightarrow{\text{excess}} Zn(NH_2)_2$$

$[Zn(NH_2)_4]^{2-}$

precipitate $NaNH_2$ soluble complex

As you have learnt earlier on, 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_2H_4

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:

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$$

$$NH_3 + NH_2Cl + NaOH \longrightarrow NH_2NH_2 + NaCl + H_2O$$

$$N_2H_4 + 2NH_2Cl \longrightarrow N_2 + 2NH_4Cl \text{ (side reaction)}$$

$$3NH_2Cl + 2NH_3 \longrightarrow N_2 + 3NH_4Cl \text{ (side reaction)}$$

Anhydrous hydrazine may be obtained by distillation over NaOH or by precipitating $N_2H_6SO_4$, which is then treated with liquid NH_3 to precipitate $(NH_4)_2SO_4$:

$$N_2H_4(aq) + H_2SO_4(aq) \longrightarrow N_2H_6SO_4 \xrightarrow{2NH_3} N_2H_4 + (NH_4)_2SO_4$$

Hydrazine is a colourless, fuming liquid. It forms a dihydrate, N_2H_4-$2H_2O$ and two series of salts, e.g., N_2H_5Cl and $N_2H_6Cl_2$. Hydrazine burns in air giving nitrogen and water. As this reaction is highly exothermic ($\Delta H^o = -622$ kJ), hydrazine is used as **a rocket fuel** along with liquid air or oxygen as an oxidant.

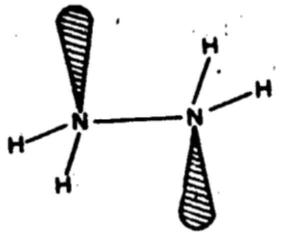


Fig. 2.4: Structure of Hydrazine

Hydrazine has a structure (Figure 2.4) 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 Co^{2+}, 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 N_2, NH_3 and H_2 at 500 K.

3.3.3 Hydrazoic Acid, HN_3, and Azides

Hydrazoic acid is also known as hydrogen azide. It is a colourless, highly explosive liquid. When sodamide is reacted with N_2O at 450 K, sodium azide is formed which on treatment with sulphuric acid gives hydrazoic acid:

$$2NaNH_2. + N_2O \longrightarrow NaN_3 + NaOH + NH_3$$

$$2NaN_3 \quad + H_2SO_4 \longrightarrow 2HN_3 + Na_2SO_4$$

It is a weak acid and dissociates only slightly in water. With electropositive metals it forms azidcs. $Pb(N_3)_2$ is covalent and explosive in nature and it is used as a **detonator.** NaN_3 is ionic and non-explosive. For the azide ion, N_3, three resonance structures can be drawn:

$$:\underset{\cdot\cdot}{\bar{N}}=N^{+}=\underset{\cdot\cdot}{N}: \longleftrightarrow\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}{}^{2-} - N^{+}\equiv N: \longleftrightarrow\ :N\equiv N^{+} - \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}{}^{2-}:$$

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.

$$HN=N^{+}=\underset{\cdot\cdot}{N}: \qquad \overset{\cdot\cdot}{\underset{\cdot\cdot}{H}}N - N^{+}\equiv N: \qquad HN\equiv N^{+} - \overset{\cdot\cdot}{.N}{}^{2-}:$$

Not possible

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

3.3.4 Phosphine, PH_3

Phosphine, PH_3, is the most stable hydride of phosphorus. It is intermediate. 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_3P_2:

  $$Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$$

- Pyrolysis of phosphorus acid at 480 - 485 K:

$$4H_3PO_3 \longrightarrow PH_3 + 3H_3PO_4$$

- Alkaline hydrolysis of phosphonium iodide:

$$PH_4I + KOH \longrightarrow PH_3 + KI + H_2O$$

- Alkaline hydrolysis of white phosphorus (industrial process):

$$P_4 + 3KOH + 3H_2O \longrightarrow PH_3 + 3KH_2PO_2$$

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, to protonate in water. However, it does react with HI to form phosphonium iodide:

$$PH_3 + HI \longrightarrow PH_4I$$

Pure phosphine ignites in air at about 435 K, but when contaminated with traces of P_2H_4 it is spontaneously inflammable:

$$PH_3 + 2O_2 \longrightarrow H_3PO_4$$

3.3.5 Arsine, Stibine and Bismuthine

AsH_3, SbH_3 and BiH_3 are exceedingly poisonous, thermally unstable, colourless gases whose physical properties are compared with those of NH_3 and PH_3 in Table 2.3. As pointed out earlier, the thermal stability and basic character of these hydrides decrease from NH_3 to BiH_3.

The thermal instability of AsH_3 is realised in the detection of arsenic poisoning.

AsH_3 and SbH_3 can be prepared by acid hydrolysis of arsenides and antimonides of electropositive elements like Na, Mg, Zn, etc.:

$$Mg_3As_2 + 6HCl \longrightarrow 2AsH_3 + 3MgCl_2$$

$$Zn_3Sb_2 + 6HCl \longrightarrow 2SbH_3 + 3ZnCl_2$$

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

$$3MeBiH_2 \longrightarrow 2BiH_3 + BiMe_3.$$

SELF-ASSESSMENT EXERCISE

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 5 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 Trihalldes

All the elements of Group 5 form trihalides, MX_3. Of all nitrogen halides, only NF_3 is stable due to strong N-F bonds. All other trihalides of nitrogen, NCl_3, NBr_3 and NI_3 are unstable. Of these, NCl_3 is explosive and NBr_3 and NI_3 exist only as their ammoniates, i.e., as ammonia adducts and detonate on removing ammonia.

Except NX_3, all the trihalides hydrolyse rapidly to either hydrated oxides, e.g., $As_2O_3 \cdot nH_2O$ or acids, H_3PO_3 or oxochloride, SbOCl and BiOCl. NCl_3 on hydrolysis gives NH_3 and HOCl instead of HNO_2 (nitrous acid) and HCl:

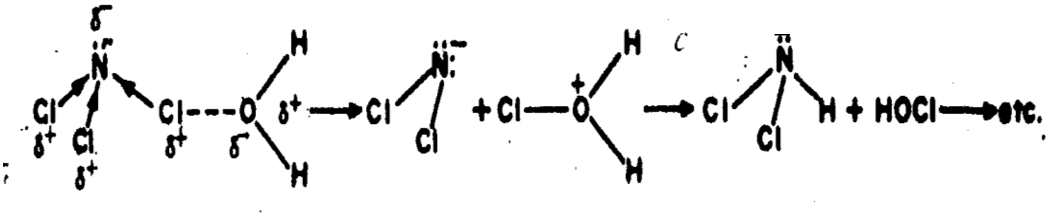
$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$$

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

$$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$$

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

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 $H_2O \rightarrow PCl_3$. The formation of this type of intermediate is impossible for nitrogen because of the non-availability of *d*-orbitals. 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 Cl_2N^- anion then generates one molecule of HOCl and $NHCl_2$ each. Replacement of two more chlorine atoms with hydrogen produces the NH_3 molecule:



The trihalides, except NX_3, act as Lewis acids, i.e. electron pair acceptors, forming haloanions, $\overline{S}bCl_4$, $BiCl_4$, etc. The trihalides can be oxidised to pentahalides. The ease of oxidation decreases from PX_3 to BiX_3. However, NX_3 is not oxidised at all. The trihalides function as halogenating agents. PCl_3 reacts with NH_3, halogens, HI, S, O_2 and AgNCO to give $P(NH_2)_3$, PX_2Cl_3, PI_3, $PSCl_3$, $POCl_3$ and $P(NCO)_3$, respectively. The following chemical equations represent these reactions:

$$PCl_3 + 3NH_3 \longrightarrow P(NH_2)_3 + 3HCl$$

$$PCl_3 + Br_2 \longrightarrow PBr_2Cl_3$$

$$PCl_3 + HI \longrightarrow PI_3 + 3HCl$$

$$PCl_3 + S \longrightarrow PSCl_3$$

$$2PCl_3 + O_2 \longrightarrow 2POCl_3$$

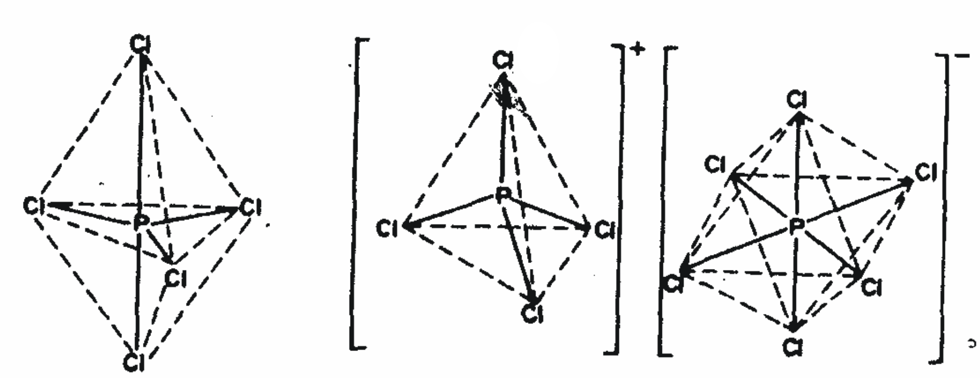
$$PCl_3 + 3AgNCO \longrightarrow P(NCO)_3 + 3AgCl$$

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 NH_3. The trihalides of heavier elements, e.g., BiF_3, are ionic in nature.

3.4.2 Pentahalldes

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 oxidising than those of the element following it in the group. All the pentahalides have trigonal bipyramidal structure in the gas phase (Figure 2.5). However, their structures differ in the solid state, e.g., PCl_5 splits into $[PC1_4][PCl_6]^-$ 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:

$$PX_3 + X_2 \rightleftharpoons PX_5$$



(a) (b)

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:

$$ROH + PCl_5 \longrightarrow RCl + POC1_3 + HCl$$

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

They hydrolyse to give either oxoacids like H_3PO_4, H_3AsO_4 or hydrated oxides like $Sb_2O.nH_2O$ or oxohalidcs like BiOCl; partial hydrolysis of $PC1_5$ gives $POC1_3$. Almost all pentahalides can accept an electron pair and act as Lewis acids, as in PF_6, PF_5, etc.

SELF-ASSESSMENT EXERCISE

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.

3.5.1 Oxides of Nitrogen

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
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 pentoxidc	Colourless	Unstable as gas; ionic solid
NO,N_2O_6			Not well characterised and quite unstable

Preparation

N_2O is obtained generally by heating NH_4NO_3:

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

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:

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

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

$$2NaNO_2 + 2NaI + 4H_2SO_4 \longrightarrow 4NaHSO_4 + 2NO + I_2 + 2H_2O$$

As you will study later, NO is formed as an intermediate in the manufacture of nitric acid by oxidation of NH_3.

N_2O_3 is obtained as an intense blue liquid or a pale blue solid on cooling an equimolar mixture of NO and NO_2:

$$NO + NO_2 \longrightarrow N_2O_3$$

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

NO_2 can be prepared by reduction of conc. HNO_3 with Cu or by heating heavy metal nitrates:

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

N_2O_5 is an anhydride of HNO_3. It is best prepared by dehydrating HNO_3 with P_4O_{10} at low temperatures:

$$4HNO_3 + P_4O_{10} \xrightarrow{250\ K} 2N_2O_5 + 4HPO_3$$

N_2O is also known as laughing gas because it induces laughter. Mixed with N_2, it is used as an anaesthetic by dentists.

Properties and Structure

Oxides of nitrogen are all oxidising agents, N_2O 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_2O and NO are neutral oxides, while the other oxides are acidic.

N_2O is isoelectronic with CO_2 and also has a linear structure. However, unlike CO_2, N_2O has a small dipole moment. The resonance structures of the molecule are given in Figure 2.6.

$$:\underset{\cdot\cdot}{N}^{-}=N^{+}=\underset{\cdot\cdot}{O}: \quad \text{————} \quad :N\equiv N^{+}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}^{-}:$$

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 (Figure 2.7) are formed cancelling out the magnetic effect of unpaired electrons.

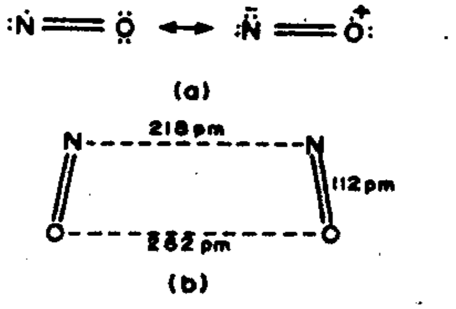


Fig. 2.7: (a) Resonance Structures of Nitric Oxide, and
(b) Molecular Structure of Crystalline Nitric Oxide

The bonding in NO is best described by the molecular orbital theory. Molecular orbital electronic configuration of NO molecule can be represented as $\sigma s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p^2, \sigma 2p^2, \pi 2p^2 \equiv \pi 2p^2., \pi^* 2p^1$ This gives a bond order of 2.5. If the unpaired electron occupying the antibonding π^*2p_y orbital is removed, nitrosonium ion, 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 NO^+. Nitrosonium ion is stable and forms salts like NO^+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, $[Fe(H_2O)_5NO]^{2+}$.

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. NO_2 molecule is angular with ONO angle of 134°. 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 (Figure 2.8).

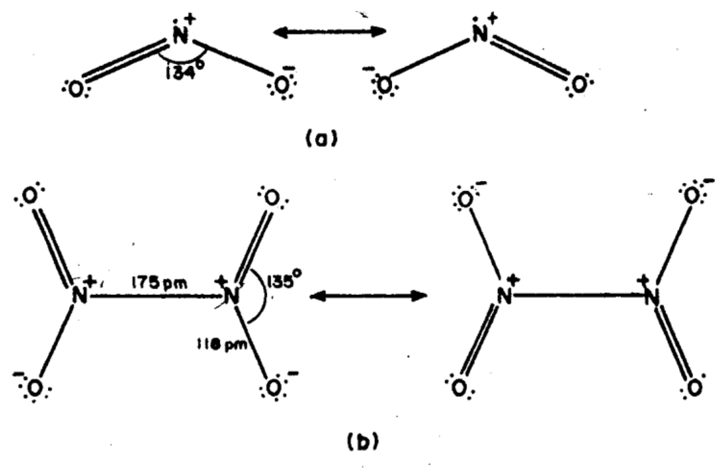


Fig. 2.8: Resonance Structure of (a) NO_2, and (b) N_2O_4

Liquid N_2O_4 undergoes self-ionisation to form NO^+ and NO_2 ions and therefore, it has been extensively studied as a non-aqueous solvent. Resonance structures of N_2O_3 are shown in Figure. 2.9(a).

Solid N_2O_5 exists in the ionic form, NO_2NO_3. In the gaseous form, the discrete N_2O_5 molecules have an N-O-N bond angle close to 180°, Figure. 2.9(b).

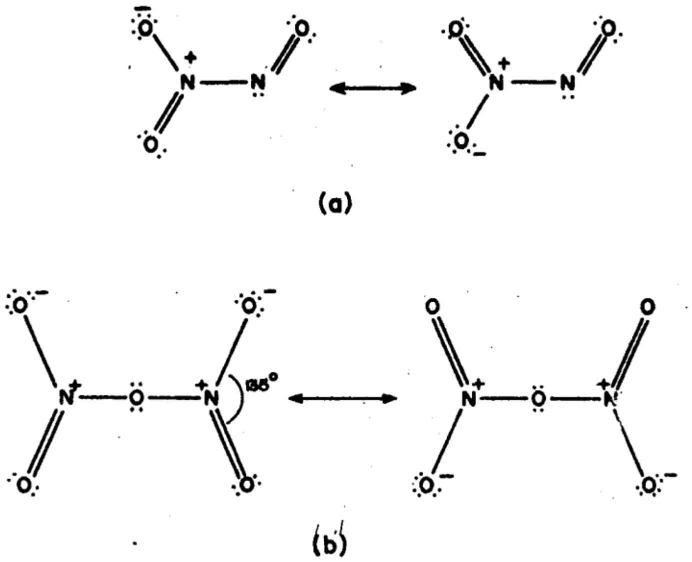


Fig. 2.9: Resonance Structures of (a) N_2O_3, and (b) N_2O_5

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, Bi_2O_3 is known. Remember the stability of higher oxidation states decreases on going down the group. Except Bi_2O_3 others exist in dimeric form. Structures of oxides of phosphorus are shown in Figure 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.

As^{III} is quantitatively oxidised to As^{V} by I_2. Therefore, As_2O_3 is used as a primary standard in iodimetric titrations.

$$\tfrac{1}{2}As_2O_3 + I_2 + H_2O \longrightarrow \tfrac{1}{2}As_2O + 2H^+ + 2I^-$$

SELF-ASSESSMENT EXERCISE

Explain briefly why NO is paramagnetic whereas NO$^+$ is diamagnetic.

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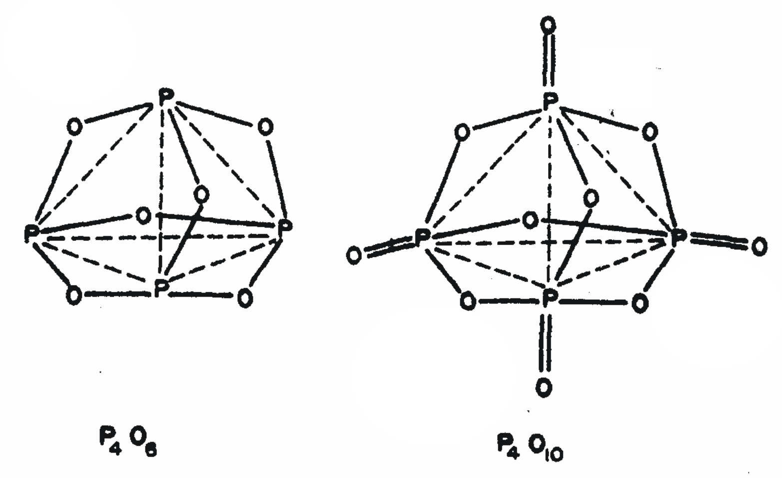


Fig. 2.10: Structures of Oxides of Phosphorus

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., CI-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 unit.

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_2

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_2 into water:

$$Ba(NO_3)_2 + H_2SO_4 \longrightarrow 2HNO_2 + BaSO_4\downarrow$$

$$NO + NO_2 + H_2O \longrightarrow 2HNO_2$$

On trying to concentrate, the acid decomposes:

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

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.

$$2KI + 2HNO_2 + 2HCl \longrightarrow 2H_2O + 2NO + 2KCl + I_2$$

With strong oxidising agents, like $KMnO_4$, nitrous acid and nitrites function as reducing agents and get oxidised to NO_3 ions:

$$2KMnO_4 + 5KNO_2 + 6HCl \longrightarrow 2MnCl_2 + 5KNO_3 + 3H_2O + 2KCl$$

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

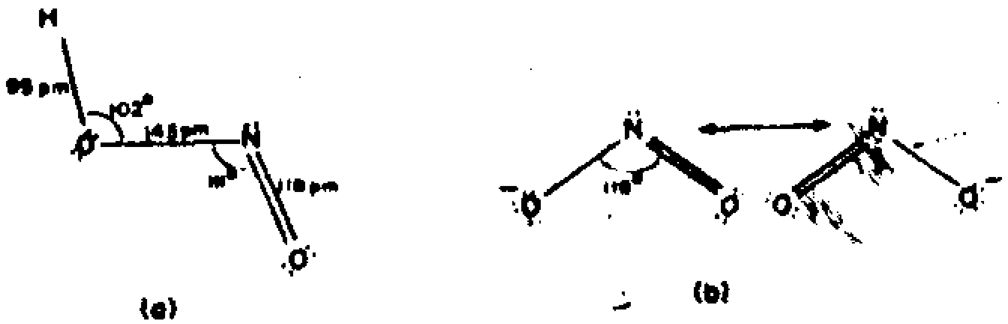


Fig. 2.11: (a) Molecular Structure of HNO_2; (b) Resonance Structures of Nitrite Ion

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←NO_2 and M←ONO structures. Analogous organic derivatives are also known, the nitrites, R←ONO and the nitro compounds, R-NO_2 where R is any alkyl or aryl group. Such ligands which can coordinate in two different ways are called ambidentate.

Nitric Acid, HNO_3

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_3 is now almost exclusively manufactured by Ostwald process. In this process NH_3 is catalytically oxidised to give NO:

$$4NH, + 5O_2 \xrightarrow{\text{Pt-Rh catalyst}} 4NO + 6H_2O, \Delta H = -904\ kJmol^{-1}$$

In the above reaction, about 96-98% of NH_3 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_2 to give NO_2 which is absorbed in water to give HNO_3 and NO, which is then recycled. The following equations represent various steps in this process:

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

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 HNO_3 with metals is of, particular interest because of the great variety of products obtained, e.g., H_2, N_2, NH_4NO_3, N_2O, NO and 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:

$$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2 \uparrow$$

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 NH_3, N_2O or N_2. Thus, Zn reacts with dilute HNO_3 in cold giving N_2O or N_2 according to the following equations:

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 4$$

$$2HNO_3 + 8H \longrightarrow N_2O + 5H_2O$$

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 5$$

$$2HNO_3 + 10H \longrightarrow N_2 + 6H_2O$$

$$5Zn + 12HNO_3 \longrightarrow 5Zn(NO_3)_2 + N_2 + 6H_2O$$

Very dilute HNO_3 reacts with Zn to give NH_3, which is of course neutralised to form NH_4NO_3:

$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 4$

$HNO_3 + 8H \longrightarrow NH_3 + 3H_2O$

$HNO_3 + NH_3 \longrightarrow NH_4NO_3$

$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$

Similarly, iron and tin also give NH_4NO_3 with dilute 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_2 depending upon whether the acid is dilute or concentrated. For instance, Cu, Ag, Hg and Bi react with dilute acid liberating NO:

$3Cu + 2HNO_3 \longrightarrow 3CuO + 2NO + H_2O$

$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O] \times 3$

$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

With concentrated acid NO_2 is given off:

$Cu + 2HNO_3 \longrightarrow CuO + 2NO_2 + H_2O$

$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$

$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$

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_3 and conc. HC1 known as **aqua regia** dissolves Au and Pt as it contains free chlorine:

$HNO_3 + 3HCl \longrightarrow 2H_2O + 2Cl + NOCl$

$Au + 3C1 + HCl \longrightarrow HAuCl_4$

$$Pt + 4C1 + 2HCl \longrightarrow H_2PtCl_6$$

Conc. HNO_3 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_3PO_4, arsenic acid, H_3AsO_4, antimony pentoxide, Sb_2O_5, sulphuric acid, H_2SO_4, iodic acid, HIO_3 and metastannic acid, H_2SnO_3, respectively, e.g.,

$$2HNO_3 \longrightarrow [2NO_2 + H_2O + O] \times 10$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Dilute nitric acid also acts as an oxidising agent. Hence, reducing agents, such as, H_2S, HI and $FeSO_4$ are oxidised to S, I_2 and $Fe_2(SO_4)_3$; respectively:

$$4HNO_3 \longrightarrow 4NO + 2H_2O + 3O_2$$

$$2H_2S + O_2 \longrightarrow [2S + 2H_2O] \times 3$$

$$2HNO_3 + 3H_2S \longrightarrow 2NO + 4H_2O + 3S$$

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:

$$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$$

This process known as nitration is of great industrial importance because of usefulness of nitro compounds. Nitronium ion, NO_2^+, which is formed in the presence of the conc. H_2SO_4, is believed to be the active nitrating agent:

$$HNO_3 + H_2SO_4, \rightleftharpoons NO_2 + HSO_4 + H_2O$$

The molecular structure of nitric acid is shown in Figure 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.

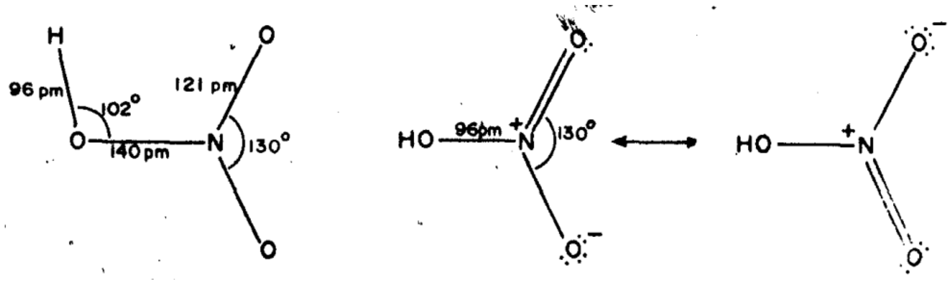


Fig. 2.12 (a) Molecular Structure of HNO_3 2.12 (b) Resonance Structures of HNO_3

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

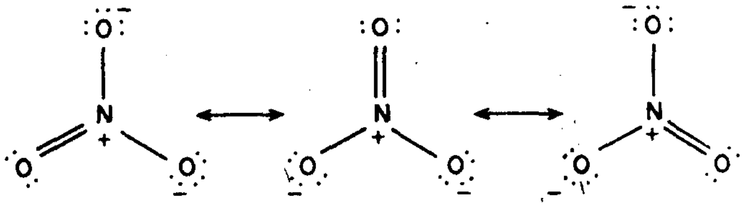


Fig. 2.13: Resonance Structures of Nitrate Ion

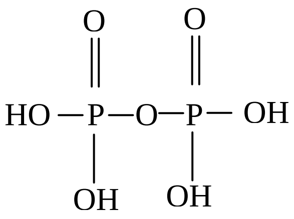
3.6.2 Oxoacids of Phosphorus, Arsenic and Antimony

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

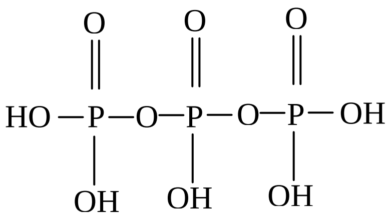
Acid	Nature	Preparation	Anion	Remarks
H_3PO_2 or $H_2PO(OH)O$ Hypophosphorous	Crystalline white solid	White P_4 + alkali	$H_2PO_2^-$ Hypophosphite	Strongly reducing monobasic pK~ 2
$H_3P_2O_3$ or HPO(OH) Orthophosphorous	Delinquescent colourless solid	P_4O_6 or PCl_3 + H_2O	$H_2PO_3^-$, $H_2PO_3^{2-}$ Phosphate	Reducing, but sliw, 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 oxidising, tetrabasic $pK_1 – 2$
H_3PO_4 Orthophosphoric	White solid	P_4O_{10} + H_2O	$H_2PO_4^-$, HPO_4^{2-} PO_4^{6-}, 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	Delinquescent 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 P-O-P linkages, e.g. di or pyrophosphoric acid, $H_4P_2O_7$ and triphosphoric acid, $H_5P_3O_{10}$:



$$HO-\underset{OH}{\overset{O}{\overset{\|}{P}}}-O-\underset{OH}{\overset{O}{\overset{\|}{P}}}-OH$$

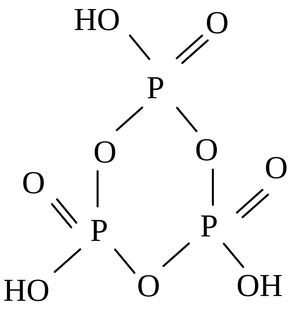
Diphosphate acid



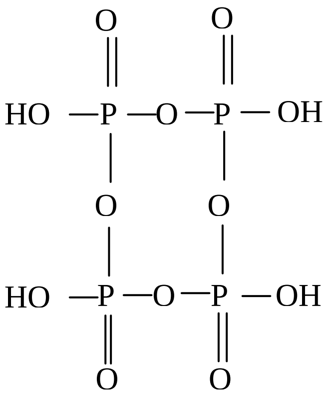
$$HO-\underset{OH}{\overset{O}{\overset{\|}{P}}}-O-\underset{OH}{\overset{O}{\overset{\|}{P}}}-O-\underset{OH}{\overset{O}{\overset{\|}{P}}}-OH$$

Triphosphoric acid

Sodium salt of triphosphoric acid, $Na_5P_3O_{10}$, 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 HPO_3 is in fact a mixture of cyclo-polyphosphoric acids containing -P-O-P-O- linkages. Two important cyclo-polyphosphoric acids are cyclotriphosphoric acid, $H_3P_3O_9$ and cyclo-tetraphpsphoric acid, $H_4P_4O_{12}$.



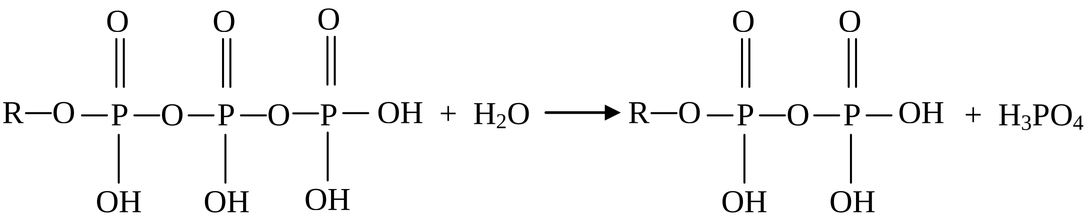
Cyclo-triphosphoric acid



Cyclo-tetraphosphoric acid

Salts of cyclo-polyphosphpric acids having 3-8 phosphorus atoms are known. Sodium cyclo-hexaphosphate, $Na_6P_6O_{18}\cdot 6H_2O$, 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, P-O-P, is very important in biological systems, as it is supposed to be the prime store of energy. The energy of the bond (29 $kJmol^{-1}$) is released to the system when needed, by enzyme catalysed hydrolysis of the phosphate link in adenosine triphosphate (ATP), the high energy molecule:



$$\mathrm{R{-}O{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}OH + H_2O \longrightarrow R{-}O{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}OH + H_3PO_4}$$

Adenosine diphosphate (ADP) **Adenosine triphosphate (ATP)**

SELF-ASSESSMENT EXERCISE

i. Write one reaction each showing oxidising and reducing properties of HNO_2.

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ii. Describe briefly the manufacture of nitric acid.
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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 gels converted to nitric oxide and then to nitric acid. This nitric add 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 x 10^6 tonnes of nitrogen is fixed biologically per year. The comparable figures for industrial fixation are about 85 x 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.

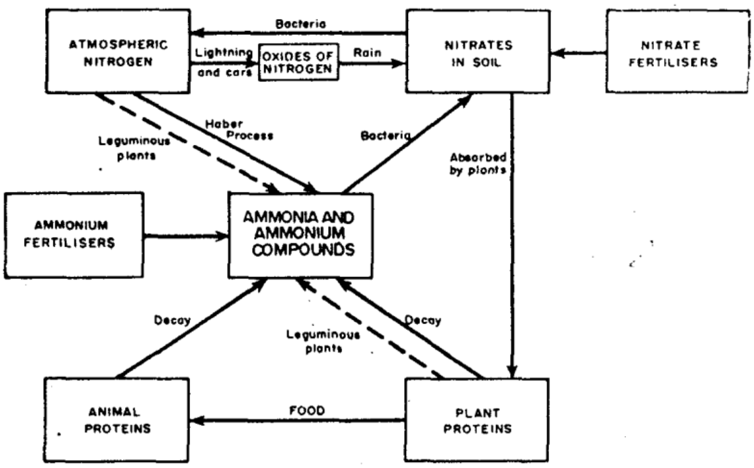

Fig. 2.14: Nitrogen Cycle in Nature

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 (Figure 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 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 N_2 over calcium carbide at 1400 K.

$$CaC_2 + N_2 \xrightarrow{1400\text{ K}} CaCN_2 + C$$

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

$$CaCN_2 + 5H_2O \longrightarrow CaCO_3 + 2NH_4OH$$

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 $Ca_3(PO_4)_2$ has a very low solubility it is able to deliver phosphate only slowly and in small amounts. However, treatment of $Ca_3(PO_4)_2$ with dilute sulphuric acid gives a fertiliser known as superphosphate of lime, a mixture of $CaSO_4$ and $Ca(H_2PO_4)_2$:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow Ca(H_2PO_4)_2 + 2(CaSO_4 \cdot 2H_2O)$$

↓
Superphosphate of lime

Because $Ca(H_2PO_4)_2$ 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 $(NH_4)_2HPO_4$ and $CaHPO_4$. In the manufacture of steel, a by-product phosphatic slag is obtained. This slag is also a very good fertiliser.

SELF-ASSESSMENT EXERCISE

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, N=N, whereas other elements exist as solids. In the gaseous state, P, As and Sb exist in the form of tetra-atomic molecules, P_4, As_4 and Sb_4. This is due to the fact that bond energy of triply bonded nitrogen is much greater than that of phosphorus, i.e., $E_{N=N} >> E_{P=P}$; but the reverse is true for the single bonds $E_{P-P} >> E_{N-N}$.
- Nitrogen is very inert as a consequence of the high bond strength of N=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 NF_3, the halides of nitrogen, NCl_3, NBr_3, 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 PF_5, PF_6 have no nitrogen analogues. This has other effects also on the chemistry of nitrogen; for example, hydrolysis of NCl_3 is slow and yields a different product from the hydrolysis of 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

In this unit you have learnt the occurrence, extraction and uses of group 5 elements. The general characteristics, physical properties, allotropic forms of phosphorus and chemical properties were discussed. You also learnt the hydrides ammonia, hydrazine, hydrazoic acid HN_3, and azides phosphine arsine. Halides, Trihalides, Pentahalides and oxides of nitrogen and phosphorus were examined.Oxoacids of nitrogen, phosphorus, arsenic and antimony were discussed. Nitrogen cycle, nitrogen fixation and phosphate fertilisers and anomalous behaviour of nitrogen were also explained.

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 MOX, phosphorus forms oxohalides of the type 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 (P_4O_6) and +5 (P_4O_{10}). Arsenic, antimony and bismuth also form +3 oxides (As_4O_6, Sb_4O_6 and Bi_2O_3) and +5 oxides (As_2O_5 and Sb_2O_5).
- The most important oxoacid of nitrogen is nitric acid, 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 are 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

i. Write the electronic configurations of nitrogen and phosphorus in the ground state.
Point out the major difference between the two, which is responsible for differences in various properties.
ii. Explain why nitrogen is chemically less reactive.
iii. Explain why NF_3 is stable, while NCl_3 and NI_3 are explosives.
iv. Why are PBr_5 and PI_5 less stable despite the fact that phosphorus (V) is not an oxidising state?
v. Why are the oxides of nitrogen so different from those of phosphorus?
vi. For the three hydrides, NH_3, PH_3 and AsH_3.
   a) Give the shape of the molecule and state how the bond angle varies from $NH_3 \rightarrow PH_3 \rightarrow AsH_3$.
   b) State which is the strongest and which is the weakest base. 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.
vii. Explain briefly why the hydrolysis of NCl_3 and PCl_3 yields different types of products.

7.0 REFERENCES/FURTHER READING

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UNIT 3 ELEMENTS OF GROUP 7

CONTENTS

1.0 INTRODUCTION

In CHM 101 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 the 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

At the end of 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
- explain the anomalous behaviour of fluorine.

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 (CaF_2), cryolite ($AlF_3 \cdot 3NaF$) and fluorapatite [$CaF_2.3Ca_3(PO_4)_2$].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 2.0×10^{-4}% of earth's crust. Iodine is the rarest of all the halogens, forming only 4.6×10^{-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}At having the longest half-life of 7.21 hours, is made by bombarding bismuth with α particles.

$$^{209}_{83}Bi + ^{4}_{2}He \longrightarrow ^{211}_{85}At + 2^{1}_{0}n$$

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 3.1.3. You have already studied earlier on 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 $AgNO_3$ to precipitate AgI. This is possible because AgI is the least soluble of all the silver halides. Precipitated AgI is treated with clean scrap iron or steel to form metallic silver and a solution of FeI_2. This solution is then treated with chlorine to liberate N. Precipitated silver is redissolved in dilute HNO_3 to give $AgNO_3$ which is used again to precipitate Agl.

$$I^{-} \text{(brine)} \xrightarrow{AgNO_3} AgI\downarrow \xrightarrow{Fe} Ag\downarrow + FeI_2$$

$$FeI_2 \xrightarrow{Cl_2} FeCl_2 + I_2$$

$$3Ag + 4HNO \longrightarrow 3AgNO_3 + NO + 2H_2O$$

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 F_2. Therefore, the only method available was that of electrolysis.

iv) The method of electrolysis was not fruitful. Aqueous HF on electrolysis yields 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_2 is evolved at the anode and H, at the cathode as indicated below:

$$KF \longrightarrow K^+ + F^-$$

At the anode

$$F^- \longrightarrow F + e$$
$$F + F \longrightarrow F_2$$

At the cathode

$$K^+ + e \longrightarrow K$$

$$2K + 2HF \longrightarrow 2KF + H_2 \uparrow$$

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, $F_2$and H_2, 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 aluminum 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 ^{238}U (99.3%) and ^{235}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 hexaflouride, the compound used for separation of ^{235}U and ^{238}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 already learnt about the use of chlorofluorocarbons or CFCs as refrigerants, in aerosol sprays. Freons, e.g., CCl_2F_2 (Freon-12) and CCl_3F(Freon-11) used as refrigerants also contain fluorine. Bleaching powder, $CaOCl_2$, 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

Why can't fluorine be obtained by electrolysis of an aqueous solution of NaF?

…………………………………………………………………………

…………………………………………………………………………

…………………………………………………………………………

3.2 General Characteristics

All elements of Group 7 have seven electrons in their outermost shell, 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 4.1: Some Physical Properties of Halogens

Property	**Fluorine F**	**Chlorine Cl**	**Bromine Br**	**Iodine I**
Atomic number	9	17	35	53
Electronic configuration	[He]$2s^2 2p^5$	[Ne]$3s^2 3p^5$	[Ar]$3d^{10} 4s^2 4p^5$	[Kr]$4d^{10} 4s^2 4p^5$
Atomic weight	18.9984	35.453	79.909	126.904
Density (liquid) (10^3 x kgm^{-3})	1.11	1.56	3.12	4.94
Ionic radius X-(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 ($kJmol^{-1}$)	0.26	3.2	5.27	7.8
Enthalpy of vaporisation ($kJmol^{-1}$)	3.27	10.2	15	30
Enthalpy of atomisation ($kJmol^{-1}$)	79.1	122	111	106
Enthalpy of hydration X^-(g) ($kJmol^{-1}$)	460	385	351	305
Eleclronegativity (A/R)	4.10	2.85	2.75	2.20
lonisation energy ($kJmol^{-1}$)	1681	1255	1142	1007
Electron affinity ($kJmol^{-1}$)	333	348	340	297
Electrode potential	+2.87	+ 1.36	+ 1.07	+0.54
½X_2 (g) + e → X *(aq)* Oxidation states	-I	-I,I,III	-I,I,III,V	-I,I,III,V,VII
Lattice energy ($kJmol^{-1}$) (Potassium salt)	817	718	656	615
Bond dissociation energy (XX) ($kJmol^{-1}$)	158	244	192	152

Physical properties like melting and boiling points are related to the size and mass of the molecules as well as intermolecular attraction. The effect 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, begin maximum in iodine and least in fluorine. So, van der Waals forces of attraction are high 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 temperature; bromine is a liquid and iodine a solid. This is also reflected in the trends observed in their enthalpies of fusion and vaporisation. (Table 4.1).

You have already learnt in CHM 121 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 size and thus have the highest ionisation energies in the respective periods, next only to the noble gases. Like the trend in other groups, ionisation 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 affinities follow the order Cl > F > Br > I. As explained in unit 2, 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. This is easily explained by considering once again the size factor. In the chlorine molecule;-which is the smallest of the three, viz., Cl_2, Br_2, 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 $I_2 < Br_2 < Cl_2$ 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 kJmol^{-1} But this is not so. The actual bond dissociation energy of fluorine molecule is, however, surprisingly low and has the value of 158 kJmol^{-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

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

Which of the halogens:

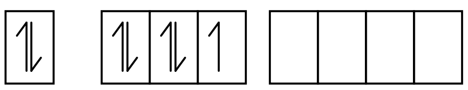
i. has two complete electron shells below the valence shell? ....
ii. is solid at room temperature? ....
iii. has highest electronegativity value?..
iv. lowest ionisation energy?..

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.

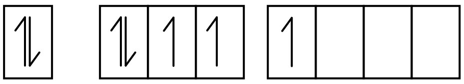
Oxidation state of -1 is the most common and stable one for other halogens also. However, consistent with the decreasing electronegativity, -1 oxidation state becomes gradually less stable in going down the group. As chlorine, bromine and iodine are less electronegative than fluorine and oxygen, they 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:

Halogen (except F)
atom in ground state



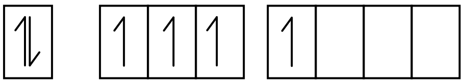
Oxidation state = ± 1
e.g. HCl, HBr & HI
(oxidation = -1),
HClO, HBrO & HIO
(oxidation state = + 1)

Halogen atom in 1st excited state



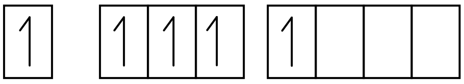
Oxidation state = + 1
e.g. ClF_3, BrF_3

Halogen atom in the 2nd excited state



Oxidation state = + 5
e.g. $HClO_3$, $HBrO_3$, HFO_3, HIO_3

Halogen atom in the 3rd excited state



Oxidation state = + 5
e.g. $HClO_4$, HIO_4

Chlorine and bromine also exhibit oxidation state + 4 (ClO_2 and BrC_2) and + 6 (Cl_2O_6 and BrO_3). Iodine exhibits an oxidation state + 4 in I_2O_4.

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,

$$\tfrac{1}{2}X_2\text{ (standard)} + e \longrightarrow X^-(aq) \qquad \text{... (I)}$$

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

$$\tfrac{1}{2}X_2\text{(standard)} \xrightarrow{\Delta Hv} \tfrac{1}{2}X_2(g) \qquad \text{... (II)}$$

$$\tfrac{1}{2}X_2(g) \xrightarrow{\Delta H_d} X(g) \qquad \text{... (III)}$$

$$X(g) + e \xrightarrow{E_A} X^-(g) \qquad \text{... (IV)}$$

$$X^-(g) + aq \xrightarrow{\Delta H_{hyd}} X^-(aq) \qquad \text{... (V)}$$

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

$$\begin{tikzcd}
\frac{1}{2}X_2(\text{standard}) \arrow[r, "\Delta Hv", "\text{II}"'] \arrow[d, "\text{I}"', "\Delta E"] & \frac{1}{2}X_2(g) \arrow[r, "\Delta H_d", "\text{III}"'] & X(g) \arrow[d, "\text{IV}"', "E_A"] \\
X^-(aq) & & X^-(g \arrow[ll, "\Delta H_{hyd}"', "\text{V}"]
\end{tikzcd}$$

Evidently, since energy is invariably absorbed in steps (II) and (III), enthalpy of vapourisation, ΔH_v and enthalpy of dissociation, ΔH_d, always have positive values. However, energy is released in steps (IV) and (V), hence, electron affinity, E_A, and enthalpy of hydration, ΔH_{hyd} are negative. Consequently, from Hess's law, the net enthalpy change, ΔE 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 irrespetive 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, ΔE are given in Table 4.2.

You can see from Table 4.2 that ΔE, 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 4.2: Enthalpy values for ½ $X_2 \longrightarrow X^-$ *(aq)*

Molecule	Enthalpy of vapourisation ΔH_v $kJmol^{-1}$	Enthalpy of dissociation, ΔH_d $kJmol^{-1}$	Electron affinity, E_A $kJmol^{-1}$	Enthalpy of hydration ΔH_{hyd} $kJmol^{-1}$	ΔE $kJmol^{-1}$
F_2	-	+79.2	-333	-460	-714
Cl_2	-	122.0	-348	-385	-611
Br_2	15	96.0	-340	-351	-580
I_2	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 4.1) 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 4.3.

Table 4.3: Halogen-Element Bond Energy, $kJmol^{-1}$

Element	B	C	N	O	F	Si	P	S	Cl	H
F	644	489	286	213	158	598	498	285	251	565
Cl	433	326	192	205	251	402	331	272	244	431
Br	368	272		201	251	331	268	213	209	364
I	272	238			243	234	184		209	299

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 4.3. 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 in 1.23 volts:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e \longrightarrow H_2O$$

The standard reduction potential of the halogen half cell reaction,

$$½X_2(g) + e \longrightarrow X^-(aq)$$

is +2.87 volts in the case of fluorine and +1.36 volts in the case of chlorine (Table 4.1). 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

Table 4.1 lists the standard reduction potential for the half cell reaction,

$$½X_2 (g) + e \longrightarrow X^-(aq)$$

and the standard potential for the reaction

$$½O_2 (g) + 2H^+ (aq) + 2e \longrightarrow H_2O$$

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

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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 and bromine displaces only iodine. Halogens react with each other to form interhalogen compounds, brief description of these is given in section 3.3.4. 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.

$Cl\text{-}Cl \longrightarrow Cl + Cl$ initiation ……….. step I

$Cl + H\text{-}H \longrightarrow HCl + H$ propagation ……….. step II

$H + Cl\text{-}Cl \longrightarrow HCl + Cl$ propagation ……….. step III

$Cl + H \longrightarrow HCl$ termination ……….. step IV

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:

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

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:

$$X_2 + H_2O \rightleftharpoons HX + HOX$$

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:

$$2F_2 + 2NaOH \xrightarrow{\text{in cold}} 2NaF + OF_2 + H_2O$$

$$2F_2 + 4NaOH \xrightarrow{\text{in hot}} 4NaF + O_2 + H_2O$$

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

$$2NaOH + X_2 \xrightarrow{\text{in cold}} NaOX + NaX + H_2O$$

$$6NaOH + 3X_2 \xrightarrow{\text{in hot}} NaOXO_2 + 5NaX + 5H_2O$$

(where X = Cl, Br or I)

Hypohalilcs are oxidising agents. Bleaching powder CaCl (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:

$$CH_4 + 2F_2 \longrightarrow C + 4HF$$

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

$$CH_4 + 4X_2 \longrightarrow CX_4 + 4HX, \quad \text{where X = Cl or Br}$$

Some more reactions of halogens are summarised in table 4.4:

Table 4.4: Some Reactions of Halogens

General Reaction	**Remarks**
$nX_2 + 2M \rightarrow 2MX_n$	F2, Cl_2 with practically all metals; Br_2, I_2 with all except noble metals.
$X_2 + H_2 \rightarrow 2HX$	Reaction with iodine reversible.
$3X_2 + 2P \rightarrow 2PX_3$	Similar reactions with As, Sb, Bi.
$5X_2 + 2P \rightarrow 2PX_5$	With excess X_2, but not with I_2; SbF_5, $SbCl_5$, AsF_5, $AsCl_5$ and BiF_5 may be prepared similarly.
$X_2 + 2S \rightarrow S_2MX_n$	With Cl_2, Br_2.
$nX_2 + 2M \rightarrow 2MX_n$	Not with F_2.
$nX_2 + 2M \rightarrow 2MX_n$	F_2 rapidly, Cl_2 and Br_2 slowly in sunlight.
$nX_2 + 2M \rightarrow 2MX_n$	$X_2 = Cl_2, Br_2$.
$nX_2 + 2M \rightarrow 2MX_n$	$X_2 = F_2, Cl_2$.
$nX_2 + 2M \rightarrow 2MX_n$	Formation of interhalogen compounds (all except 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, ClF ionises to form Cl^+ and F^- due to the higher electroncgativity of fluorine. Bromine cation, Br^+, exists in complexes such as Br $(pyridine)^+NO_3$, Electrolysis of ICN in pyridine solution gives iodine at the cathode.

This indicates that ICN ionises to I^+ and CN^-. Many pyridine complexes, e.g. $[I\ (pyridine)]^+NO_3$, $[I\ (pyridine)_2]^+ClO_4$ and $I\ (pyridine)^+CH_3COO$ are known**.**

Iodine dissolves in oleum giving a bright blue solution which has been shown to have I_2^+ and I_3^+:

$$2I_2 + 6H_2S_20_7 \longrightarrow 2I_3 + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

$$3I_2 + 6H_2S_2O_7 \longrightarrow 2I_3 + \overset{-}{2}H_2S_3O_{10} + 5H_2SO_4 + SO_2$$

Electrical conductivity of molten iodine is due to the presence of $I_3^+ + I_3^-$ species produced by the self ionisation of iodine:

$$3I_2 \underset{+}{\rightleftharpoons} I_3^{++} \text{ and } I_3^-$$

The cations, Cl_3^+ and Br_3^+ are formed in the following reactions:

$$ClF + Cl_2 + AsF_5 \longrightarrow Cl_3AsF_6$$

$$O_2^+\cdot AsF_6 + {}^3/_2Br_2 \longrightarrow Br_3^+\cdot AsF_6^- + O_2$$

SELF-ASSESSMENT EXERCISE

Complete the following reactions:

i. $I_2 + IF_2 \longrightarrow$ ……...
ii. $Cl_2 + H_2O \longrightarrow$ ……..................... + ...
iii. $Cl + 2NaOH \longrightarrow$ .... + ... + ...
iv. $Cl_2 + H_2S \longrightarrow$ ……..................... + ...
v. $CH_4 + 4Br_2 \longrightarrow$ ……..................... + ...

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 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:

$$H_2 + X_2 \longrightarrow 2HX, \text{ where } X = Cl, Br \text{ or } I$$

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

$$CaF_2 + H_2SO_4 \longrightarrow 2HF + CaSO_4$$

$$NaCl + H_2SO_4 \longrightarrow HCl + NaHSO_4$$

Since concentrated sulphuric acid partially oxidises HBr and HI to Br_2 and I_2, these are prepared by the action of concentrated orthophosphoric acid on bromides and iodides:

$$NaBr + H_3PO_4 \longrightarrow HBr + NaH_2PO_4$$

$$NaI + H_3PO_4 \longrightarrow HI + NaH_2PO_4$$

Hydrogen bromide and hydrogen iodide are usually prepared in the laboratory by the hydrolysis of PBr_3 and PI_3:

$$PBr_3 + 3H_2O \longrightarrow 3HBr + H_3PO_3$$

$$PI_3 + 3H_2O \longrightarrow 3HI + H_3PO_3$$

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 121. Due to hydrogen bonding HF_2 ion is stable and gives salts like KHF_2.

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 per cent ionic character in these bonds.

Some physical properties of the hvdrogen halides are listed in the table 4.5

Table 4.5: Physical Properties of Hydrogen Halides

	Physical state	**Colour**	**B.P. (K)**	**M.P. (K)**	**% dissoci-ation 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 4.5). 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:

$$\mathrm{HX}(aq) + \mathrm{H_2O} \longrightarrow \mathrm{H_3O}^+(aq) + \mathrm{X}^- (aq)$$

Their acid strength follows the order HI > HBr > HCl > HF. Acid strength is in general the tendency of HX *(aq)* to give H_3O^+*(aq)* and X^- *(aq)*. The enthalpy changes associated with the dissociation of hydrohalic acids can be represented with the help of Bom-Haber cycle in its simplest form as given below:

$$\begin{tikzcd}
\mathrm{HX}(g) \arrow[rrr, "\Delta H_{\mathrm{d}}"] & & & \mathrm{H}(g) \arrow[d, "I"] & + & \mathrm{X}(g) \arrow[d, "E"] \\
& & & \mathrm{H}^+ (g) \arrow[d, "\Delta H_{\mathrm{hyd}}"] & + & \mathrm{X}\ (g) \arrow[d, "\Delta H_{\mathrm{hyd}}"] \\
\mathrm{HX}(aq) \arrow[uu, "\Delta H_{\mathrm{dehyd}}"] \arrow[rrr] & & & \mathrm{H}^+(g) & + & \mathrm{X}^-(g)
\end{tikzcd}$$

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 presure. 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 HF > HCl > HBr > HI and the enthalpy of hydration of X^-, which decreases from F^- > Cl^- >Br^- > I^-. The total enthalpy change becomes more negative, i.e., the reaction,

$$\mathrm{HX}(aq) \longrightarrow \mathrm{H}^+(aq) + \mathrm{X}^-(aq)$$

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

SELF-ASSESSMENT EXERCISE

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

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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_2O_5 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_2O and ClO_2 find some practical importance as bleaching agents in paper pulp and flour industries, I_2O_5 is used in the estimation of CO.

Table 4.6: Oxides of Halogens

Fluorides		**Oxides**					
Compound	**Oxidation Number**	**Chlorine Compound**	**O.N**	**Bromine Compound**	**O.N**	**Iodine Compound**	**O.N**
OF_2	-1	Cl_2O	+1	Br_2O	+l		
O_2F_2	-1	ClO_2	+4	BO_2	+4	I_2O_5	+5
		Cl_2O_6	+6	BO_3	+6		
		Cl_2O_7	+7				

Preparation of Halogen Oxides

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

$$2F_2 + 2NaOH \longrightarrow 2NaF + H_2O + OF_2$$

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~ ion and free oxygen.

Cl_2O and Br_2O are prepared by heating freshly precipitated mercuric oxide with the halogen

$$2X_2 + 2HgO \xrightarrow{573\text{ K}} HgX_2 \cdot HgO + X_2O, \text{ where } X = Cl \text{ or } Br$$

Chlorine dioxide (ClO_2) is also prepared by the following reactions:

$$2NaClO_3 + SO_2 + H_2SO_4 \longrightarrow 2ClO_2 + 2NaHSO_4$$

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

$$2AgClO_3 + Cl_2 \longrightarrow 2AgCl + 2ClO_2 + O_2$$

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:

$$2ClO_2 + 2NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$$

Iodine pentoxide (I_2O_S) is prepared by dehydration of iodic acid at 513 K:

$$2HIO_3 \xrightarrow[H_2O]{513\ K} I_2O_5 + H_2O$$

It is a white solid which decomposes to iodine and oxygen above 573 K. I_2O_5 is a good oxidising agent, it oxidises H_2S to sulphur and HC1 to chlorine.

Properties of Halogen Oxides

All oxides of halogens have positive free energies of formation except F_2O and are thus unstable with respect to dissociation into elements. F_2O is stable up to 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_2O_5, is white solid stable up to 575 K. Because of their oxidising properties, chlorine oxides, Cl_2O and ClO_2 are used as bleaching agents and as germicides. I_2O_5 quantitatively oxidises CO into CO_2 and therefore, is used in the estimation of CO.

Structure of Oxides of Halogens

Structures of only OF_2, Cl_2O, Br_2O, Cl_2O7 and I_2O_5 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_2 are nearer to fluorine due to high electronegativity of F compared to Cl or Br. The bonded electron pairs in Cl_2O and Br_2O 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°28', the tetrahedral angle. Figure 4.1 shows some of the structures of halogen oxides.

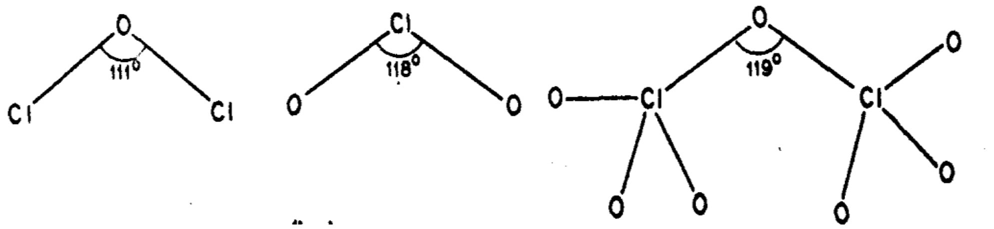


Fig. 4.1: Structures of Some Oxides of Halogens

3.3.3 Oxoacids of Halogens

Oxoacids of halogens have oxygen attached to the halogen atom. They have the general formula $HOX(O)_n$ where n = 0, 1, 2 or 3. The oxoacids are named as hypohalous acid (HOX), halous acid (HOXO), halic acid ($HOXO_2$) and perhalic acid ($HOXO_3$), 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 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	*HOCl Hypochlorous acid	*HOBr Hypobromous acid	*HOI Hypoiodous acid	H-O-X
Halous, Halites	+3	*HOClO Chlorous acid	*HOBrO Bromous acid	*HOIO Iodous acid	H-O-X→O
Halic, Halaies	+5	* $HOClO_2$ Chloric acid	*$HOBrO_2$ Bromic acid	*$HOIO_2$ Iodic acid	O ↑ H-O-X→O

Perhalic, Pertialalcs	+7	*$HOClO_3$ Perchloric acid	*$HOBrO_3$ Perbromic acid	*$HOBrO_3$ Periodic acid	O ↑ HO-X→O ↓ O

***** 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 the higher the oxidation number of the halogen the:

- 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, $HClO_4$, is an extremely powerful oxidising agent which explodes when in contact with organic matter and sometimes on its own. Periodic acid, HIO_4, is extensively used in organic chemistry for oxidation of alkenes to glycols.

SELF-ASSESSMENT EXERCISE

Arrange the following in the order of increasing acid strength: HOCl, $HOClO_2$, $HOClO_3$ 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, XY_3, XY_5 and 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 GIF 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., $IFCl_2$ and IF_2Cl 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. Greater the difference, more polar is the bond and therefore, greater is the thermal stability and 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:

- $Cl_2 + F_2 \xrightarrow{498\ K} 2ClF$
- $Cl_2 + 3F_2 \longrightarrow 2ClF_3$
- $I_2 + 3Cl_2 \longrightarrow 2ICl_3$
- $Br_2 + 5F_2 \longrightarrow 2BrF_5$
- $ClF + 2F_2 \xrightarrow{523\ K} ClF_5$
- $IF + \underset{\text{(excess)}}{3F_2} \longrightarrow IF_7$

Mono-and penta-fluorides of iodine are prepared by the action of AgF on I_2:

$$I_2 + AgF \xrightarrow{273\ K} IF + AgI$$

$$3I_2 + 5AgF \longrightarrow IF_5 + 5AgI$$

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 4.8.

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

$$XY + 2M \longrightarrow MX + MY$$

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.

$$2ICl_3 \rightleftharpoons ICl_2 + ICl_4$$

$$2BrF_3 \rightleftharpoons BrF_2 + BrF_4$$

Thus, the substances which furnish ICl_2^+ and BrF_2^+ behave as acids and those furnishing ICl_4^- and BrF_4^- behave as bases in ICl_3 and BrF_3 solvent systems, respectively.

Table 4.8: 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	ClF Chlorine fluoride	Gas, Colourless.	119	163
	BrF Bromine fluoride	Liquid below 293K pale-brown gas above 293 K	240	293
	$BrCl$ Bromine chloride	Liquid, reddish yellow	207	283
	ICl Iodine chloride	Solid, ruby red	.	310
	IBr Iodine bromide	Solid, brown like iodine	232	
XY_3	ClF_3 Chlorine trifluoride	Liquid below 261 K, Colourless gas above 261 K	197	261
	BrF_3 Bromine trifluoride	Liquid, Colourless	282	400
	$BrCl_3$ Bromine trichloride	Solid, Orange	374 (decomposes)	_
XY_5	ClF_5 Chlorine pentafluoride	Gas, Colourless	170	259
	BrF_5 Bromine pentafluoride	Liquid, Colourless	213	314
	IF_5 Iodine pentafluoride	Liquid, Colourless	283	314
XY_7	IF_7 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 4.9: 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_3	5	3	2	T-shaped
XY_5	6	5	1	Square pyramidal
XY_7	1	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 (Figure 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_3: 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 (Figure 4.3). Thus ClF_3, BrF_3 and ICl_3 have a T-shaped structure.

X atom in excited state

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

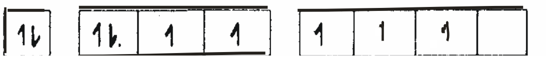
iii) Type XY_5: This type of compounds has a square pyramidal structure (Figure 1.4). The central atom X uses five of its seven valence electrons in forming five bonds with Y and two electrons remain as a lone pair. Thus X-atom in XY_5 molecule is *sp^3d* hybridised. The lone pair occupies the axial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

X atom in excited state

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 (Figure 4.5).

X alum in excited state



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:

X-Y

Fig. 4.2: Linear Structure of Interhalogen Molecule of the Type XY.

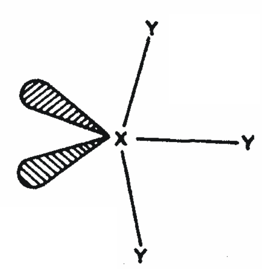


Fig. 4.3: T-shaped Structure of Interhalogen Molecules of the Type XY_3.

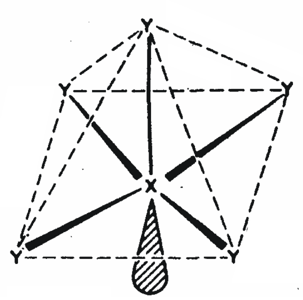


Fig. 4.4: Square Pyramidal Structure of Interhalogen Molecules of the Type XY_3

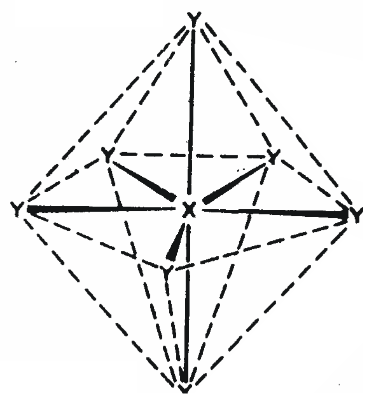


Fig. 4.5: Pentagonal bipyramidal Structure of Interhalogen Molecules of the Type XY_7

More complex ions of iodine, such as penta-iodide, I_5, heptaiodide, I_7 and nona-iodide, I_9 are also known.

These are generally found in the form of salts of large metal ions, e.g., $Rb^+I_9^-$, $2C_6H_6$ or large complex cations, e.g., $NH_4^+I_5$, $(C_2H_5)_4$ $N^+I_7^-$). A number of mixed polyhalide ions containing two or three different halogens are also known. E.g., ICl_2^-, $ICl_4^-$and $IBrF^-$ and $IBrCl^-$.

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 solution. Thus, the triiodidc being the most stable and Cl_3^- is the least. In non-aqueous solutions, polyhalides behave as mild halogenating agents.

You have learnt earlier on that polyhaloninm cations, e.g., ICl_2^+ and BrF_2^+ are formed as a result of autoionisation of ICl_3 and BrF_3. Other cations like Br_2^+, I_2^+, I_3^+, ClF_2^+, IF_2^+, IBr_2^+, $IBrCl^+$, ClF_4^+, BrF_4^+, IF_4^+, ClF_6^+, BrF_6^+, IF_6^+, etc. are also known. These are established by large anions like BF_4^-, PF_6^-, AsF_6^-, $AlCl_4^-$, $SbCl_6^-$, etc.

SELF-ASSESSMENT EXERCISE

Write 'T' for true and ‘F’ for false in the given boxes for the following statements about the 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 has square pyramidal structu ☐

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^-, 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_6.

- 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_7, 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.

$$2F_2 + 2H_2O \rightarrow 4HF + O_2$$

$$X_2 + H_2O \leftrightarrows HOX + HX$$

- Fluorine reacts with alkalis to yield the oxide, F_2O :

$$2F_2 + 2NaOH \rightarrow F_2O + 2NaF + H_2O$$

The other halogens react with alkalis 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 looked at occurrence, extraction and uses of halogens. The first one was fluorine, followed by chlorine, bromine and the last one was iodine. From these, we have been able to get the general characteristics of halogen which include; physical properties, oxidation states, oxidising power, chemical properties and basic properties of halogens.

Compounds of Halogens such as hydrogen halides, halogen oxides, oxoacids were aqlso discussed. Interhalogen compounds, polyhalides and polyhalonium ions, pseudohalogens and pseudohalides and anomalous behaviour of fluorine.

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^- 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 Cl^-, Br^-, 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 (OX_2 etc.), oxoacids like HOX, HOXO, $HOXO_2$ and $HOXO_3$ are interhalogen compounds of the type 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 leamt about the polyhalide ions. X_n^- and $XY_n^{\pm}$.

6.0 TUTOR-MARKED ASSIGNMENT

i. Fill the appropriate halogen in the following blanks:
   a) __________ displaces three halogens from their compounds.
   b) Cl_2 can be oxidised by ______________
   c) Br_2 can be reduced by ____________
   d) Fluorine and ……………... can oxidise water to oxygen.
   e) Oxidation of __________ and _________ by Cl_2 will give Br_2 and I_2, respectively.

ii. We have listed the physical properties of all the halogens except astatine. From your study of the periodicity in the properties of elements, predict the following for the astatine:
    a) Atomic number
    b) Molecular formula
    c) M.P., B.P:
    d) Physical state
    e) At-At bond energy
    f) Strength of aqueous hydroastatic acid.

iii. Why does fluorine combine with other elements in their higher oxidation states?

iv. Write the name of the following oxoacids and deduce the oxidation number of halogen atom in each.
    (i) HOCl (ii) HOClO (iii) HOBr
    (iv) $HOBrO_2$ (v) $HOIO_2$ (vi) $HOClO_3$

v. The bond dissociation energy increases from I_2 to $C1_2$. Thus, bond dissociation energy of F_2 should be higher than that of Cl_2. But it is not so, why?

vi. The solutions of the salts of hypohalous acids are alkaline, why?

7.0 REFERENCES/FURTHER READING

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