

(iii) Octahedral complexes involving chelate groups like acetyl acetone, oxalates and 8-hydroxy quinoline.

COMPARATIVE STUDY OF ELEMENTS OF CARBON FAMILY

General Characteristics. The elements carbon, silicon, germanium, tin and lead belong to group IV A or 14 of the periodic table. Their general electron configuration is $ns^2 np^2$ and hence all are tetravalent. These belong to p -block of the periodic table.

Their general characteristics are given in the following table 3.5.

Table 3.5 Some physical properties of group IV A Elements.

Property ↓	Elements, Carbon, C →	Silicon, Si	Germanium, Ge	Tin, Sn	Lead, Pb
Atomic number	6	14	32	50	82
Electronic configuration	$[\text{He}]^2 2s^2 2p^2$ (+ II), + IV	$[\text{Ne}]^{10} 3s^2 3p^2$ (+ II), + IV	$[\text{Ar}]^{18} 3d^{10} 4s^2 4p^2$ (+ II), + IV	$[\text{Kr}]^{36} 4d^{10} 5s^2 5p^2$ + II, + IV	$[\text{Xe}]^{54} 4f^{14} 5d^{10} 6s^2 6p^2$ + II, (+ IV)
Oxidation states*					
Ionisation energies kcal/mole	1st 260 2nd 562 3rd 1103 4th 1486 Total 3411	188 377 772 1040 2377	182 367 789 1053 2391	169 337 707 939 2152	171 347 746 967 2225
Density (gm/ml)	3.51 (diamond) 2.25 (graphite)	2.35	5.36	6.00	11.34
Melting point (°C)	= 3750	1423	960	231.19	327
Boiling point (°C)	3800	2680	2380	268.7	1751
Electronegativity (Pauling scale)	2.5	1.8	1.8	1.8	1.8
Atomic radii (Å)	0.77	1.17	1.22	1.41	1.54
Ionic radii (Å) of M^{4+}	0.16	0.52	0.53	0.71	0.84
Atomic weight	12.011	28.09	72.60	118.70	207.21

ANOMALOUS BEHAVIOUR OF CARBON

Carbon differs from rest of the elements in group 14 because of its smaller size, higher electronegativity and non-availability of d -orbitals. Thus :

(i) Maximum coordination number shown by carbon is 4 because of non-availability of d -subshell in its penultimate shell. Other elements of group 14 show coordination number 4 and 6. e.g., CCl_4 , SiCl_4 , $[\text{SiF}_6]^{2-}$, $[\text{SnCl}_6]^{2-}$. etc.

(ii) Carbon forms multiple bonds such as $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$, $\text{C}=\text{O}$, $\text{C}=\text{S}$ etc. due to its small size. Other elements of group 14 usually do not show multiple bond.

(iii) Carbon has a great tendency to **catenation** (i.e. tendency to form long chains). This tendency of carbon is related to the strength of bond (in kJ mol^{-1}). The bond strength in kJ mol^{-1} of some bonds in group 14 elements is :

$\text{C}-\text{C}$ (348); $\text{Si}-\text{Si}$ (222); $\text{Ge}-\text{Ge}$ (167) and $\text{Sn}-\text{Sn}$ (155). Since $\text{C}-\text{C}$ bond strength is more, carbon shows the property of catenation.

PERIODICITY IN PROPERTIES OF GROUP 14 ELEMENTS

From the electron configuration of these elements, it is clear that C and Si have noble gas kernel beneath their valence shell while Ge, Sn and Pb have 18 electrons in their penultimate shell. Lead has even 32 electron in its ante-penultimate shell. So, there is regular gradation in properties of these elements down the group.

1. **Size of atom (atomic radii and atomic volume).** Both atomic radii and atomic volume increase down the group as shown below :

Atomic radii (pm)	C	Si	Ge	Sn	Pb
	72.2	117.6	122.3	140.5	146
Atomic volume (cm^3)	5.4	11.4	13.6	16.3	18.27

*Uncommon oxidation states are given in brackets.

The reason is that as we go down the group, the screening effect of the new added shells is greater than the effective nuclear charge of the elements.

2. **Ionisation energy.** The ionisation energy to form M^{4+} ions in group 14 elements has the following order:
 $C > Si < Ge > Sn < Pb$.

The order of I.E. of C and Si is same as expected.

However in case of germanium, the filling of $3d$ subshell increase the nuclear charge and provides poorly shielding d -electrons. Similarly in case of tin and lead, the filling of $4f$ and $5f$ subshells increases the nuclear charge and provides poorly shielding f -electrons. This explains the above irregular order of ionisation energies.

3. **Metallic and non-metallic character.** A metal has a tendency to lose electrons and become electro positive. ($M \rightarrow M^+ + e^-$). Smaller the value of ionisation energy of an element, greater the ease with which it will lose electron and greater will be its metallic character. The decrease in ionisation energy on moving down the group from Si to Ge and further to Sn and Pb is comparatively smaller. Thus C and Si are non-metals, germanium is metalloid while tin and lead are metals. The increase in metallic character is exhibited in the following characters.

(i) Malleability, ductility and electrical conductivity nature. (ii) Structure and appearance of elements

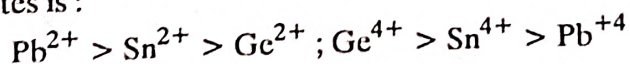
(iii) Increase in basic character, decrease in acidic character of their oxides and hydroxides and increased tendency to form M^{2+} ions down the group.

4. **Electronegativity values.** The electronegativity value of these elements do not decrease in a regular way. For example ; (C = 2.5), Si (1.8), Ge (1.8), Sn (1.8), Pb (1.9). It is probably due to the filling of d and later f -orbitals of elements down the group.

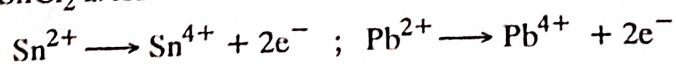
5. **Oxidation states.** (a) **Carbon.** C^{4-} (Ne gas configuration formation) is energetically unfavourable because very high energy will be required to add four electrons to C-atom. However, C^{4-} ion is thought to exist in Be_2C and Al_4C_3 . Also C^{4+} ion (He gas configuration) formation is energetically unfavourable because very high energy (1411 kcal/mole) is required to remove four electrons from neutral gaseous carbon atoms. ${}_6C$ (excited) is $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$. It undergoes sp^3 hybridisation and forms four equivalent hybrid orbitals which are directed towards the four corners of a regular tetrahedron. Thus, it shows a covalency of four. Divalent carbon compounds are unstable but are known in organic reactions in which transient carbene intermediates like $:CH_2$ and $:CF_2$ are known.

(b) **Silicon.** Its ionisation energies to form Si^{4+} ion are much less than C^{4+} ion and shows covalency of four in $SiCl_4$.

(c) **Germanium, tin and lead.** All these elements exhibit +2 and +4 oxidation states. As we go from Ge to Pb, the stability of +2 oxidation state increases while that of +4 oxidation state decreases. It is due to the increasing stability of inert pair of s -electrons in the valence shell. Thus, the decreasing order of stability of +2 and +4 oxidation states is :

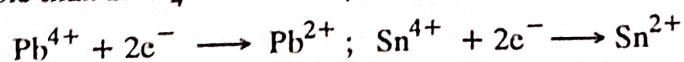


It indicates that (1) $SnCl_2$ is less stable and hence better reducing agent than $PbCl_2$



Since Sn^{4+} ion is more stable than Pb^{4+} ion, Sn^{2+} ion is better reducing agent than Pb^{2+} ion.

(2) $PbCl_4$ is less stable than $SnCl_4$. Thus $PbCl_4$ is better oxidising agent than $SnCl_4$

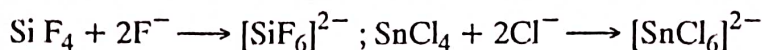


Types of compounds. M^{2+} ions are bigger in size and smaller in the amount of charge than M^{4+} ions. Thus M^{2+} ions and M^{4+} ions are expected to form ionic and covalent compounds respectively. Hence, as we go down the group, the tendency to form ionic compounds increases. However, the oxides and fluorides of tin and lead, viz SnO_2 , SnF_4 , PbO_2 , and PbF_4 are ionic in nature.

6. Melting point, boiling point and heat of atomisation. As we go down the group, the inter-atomic force decreases. As a result, the melting point, boiling point and heat of atomisation decrease.

7. Formation of complexes. The tendency of an element to form complexes is favoured by its small size, high charge and availability of vacant orbitals of right energy in it. Since ${}_6\text{C}$ [$(\text{He})^2 2s^2 2p^2$] has no d -orbital, so it cannot extend its octet. It is only tetravalent (e.g., CH_4 , CCl_4) and does not form any complex compound.

Silicon and other members of the group have vacant $(n - 1)$ d subshells. So, these can extend their octet and form complex compounds having coordination number 4 and more than 4. For example, it is 6 for Si, $(\text{SiF}_6)^{2-}$ and Ge, $[\text{GeCl}_6]^{2-}$ and 8 for Sn and Pb.



In these complexes, the central atom Si and Sn form four covalent and two coordinate bonds through sp^3d^2 hybridisation as shown in fig. 3.18. $(\text{SiF}_6)^{2-}$ and $(\text{SnCl}_6)^{2-}$ both have octahedral structure.

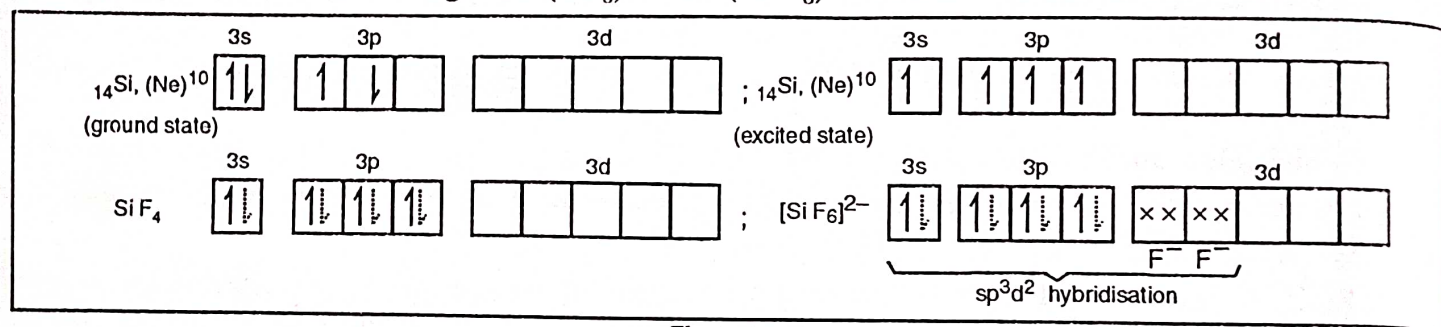


Fig. 3.18.

8. formation of tetra-alkyls. These elements form tetra-alkyls e.g. silicon forms tetraethylsilicon, $\text{Si}(\text{C}_2\text{H}_5)_4$ and lead forms tetra ethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4$

9. Hydrides. All the group 14 elements form covalent hydrides. The number formed and the ease of their formation decreases as we go down the group.

(a) **Carbon** forms a large number of chain and ring compounds including alkanes ($\text{C}_n\text{H}_{2n+2}$), alkenes (C_nH_{2n}), alkynes ($\text{C}_n\text{H}_{2n-2}$) and aromatic compounds due to catenation. Here, the limit of 'n' is not known.

(b) **Silicon** forms a limited number of saturated hydrides, $\text{Si}_n\text{H}_{2n+2}$ (straight or branched chains) called silanes. Here n is from 2 to 6. Their limited number is due to weak Si-Si bond.

(c) **Germanium** hydrides behave similarly as silicon. But germanium hydrides, GeH_4 (germane), Ge_2H_6 (digermane), Ge_3H_8 (trigermane) etc. are less readily hydrolysed and are less inflammable.

(d) **Tin.** It forms two hydrides : stannane (SnH_4) and distannane (Sn_2H_6). SnH_4 is less stable but can be prepared by reducing SnCl_4 with $\text{Li}(\text{AlH}_4)$ in ether at -30°C .

(e) **Lead.** It forms plumbane, PbH_4 . It is less stable than stannane and is difficult to be prepared. It has, however, been prepared by the cathodic reduction and has been detected by mass spectrometer.

From above we see that the number formed and ease of formation of hydrides decrease as we move down the group.

Stability of hydrides. As we go down the group, the stability of hydrides goes on decreasing. It is explained as follows :

(i) In hydrides of carbon, the electronegativity difference between C(2.5) and H(2.1) is extremely small. Thus H-atom in C-C-H bond does not withdraw electronic charge to much extent. As a result, the strength of C-C bond is not affected and hydrides are most stable than alkanes.

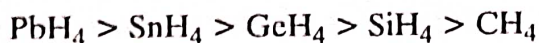
(ii) In hydrides of silicon, the electronegativity of H(2.1) is more than Si(1.8). Thus, H-atom withdraws electric charge from Si-H bond and makes Si-Si bond weak. Thus silanes are less stable than alkanes.

(iii) In hydrides of Ge, Sn and Pb, there is a large difference in the sizes of metals and hydrogen. As a result M-H covalent bond is very weak due to poor overlap of orbitals. Thus, the stability of hydrides decreases down the group.

Reducing nature. All the hydrides act as reducing agents. Since the decreasing order of stability of hydrides is



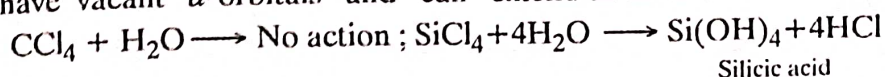
the decreasing order of reducing power is :



10. Halides. (i) All the group IVA or 14 elements form **tetrahedral covalent halides**.

(ii) Carbon halides are saturated compounds. Since carbon atoms has no *d*-orbital, it cannot increase its co-ordination number.

(iii) Except carbon halides, halides of other group IVA or 14 elements undergo hydrolysis. It is because these elements have vacant *d*-orbitals and can extend their co-ordination number beyond four



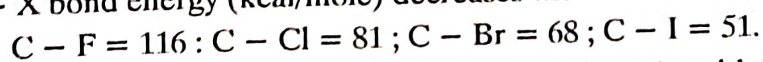
The hydrolysis involves following steps :

(a) Oxygen atom (donor) of $\text{H}_2\ddot{\text{O}}$: forms co-ordinate bond with central atom.

(b) HX gas (X = halogen atom), then goes out.

(iv) Except carbon halides, all group IVA or 14 halides act as **strong Lewis acids**. It is because these elements have vacant *d*-orbitals and can extend their coordination number beyond four.

(v) Stability of CX_4 (X = halogen) decreases with increase in the molecular weight of halogen. It is because, the C - X bond energy (kcal/mole) decreases with increase in atomic weight of halogen e.g.



(vi) Volatility of group IVA or 14 halides decreases regularly with increase in the molecular weight of tetrahalides.

(vii) Since Br_2 and I_2 are weak oxidants, these are unable to oxidise Pb^{2+} to Pb^{4+} . Hence PbBr_4 and PbI_4 are unknown.

11. Oxides. Elements of group IVA form monoxides and dioxides. Oxides of carbon differ from oxides of other elements because these contain $p\pi - p\pi$ multiple bonds between carbon and oxygen. Various oxides of carbon are CO , CO_2 , C_3O_2 , C_5O_2 and C_{12}O_9 . We shall discuss CO , CO_2 and oxides of other elements of group IVA. The tendency to form monoxide increases down the group.

(vi) **Nature of bonding in oxides** (i) CO_2 . X-ray analysis of solid carbon dioxide shows that it is of molecular lattice type in which each CO_2 molecule occupies an independent position in the geometric pattern. CO_2 molecules are held together by **weak polar intermolecular attractions**.

(vii) SiO_2 . X-ray analysis shows that SiO_2 has an **infinite three dimensional structure**. In SiO_2 , silicon and oxygen atoms are held together by **strong covalent forces** in a continuous chain. Here each silicon atom is bonded tetrahedrally to four oxygen atoms. Also each oxygen atom is common to two tetrahedra (Fig. 3.19).

CO_2 is a gas but other oxides of group IVA or 14 elements are solids. Carbon as well as oxygen atoms are small in size and form **multiple covalent bonds**. CO_2 has linear structure with zero dipole moment. Hence CO_2 molecules are held together at room temperature by weak intermolecular forces. Thus CO_2 is a gas. Other elements of this group are of large size and are unable to form multiple bonds. The $\text{Si} = \text{O}$, $\text{Ge} = \text{O}$, $\text{Sn} = \text{O}$ and $\text{Pb} = \text{O}$ bonds do not exist. As a result, oxides of group IVA elements are **non-gaseous but are solids**.

Catenation. Carbon and silicon atoms have the property of catenation (*i.e.*, property to join with one another in large number) to form straight chain and ring compounds. This property is more marked in carbon than in silicon.

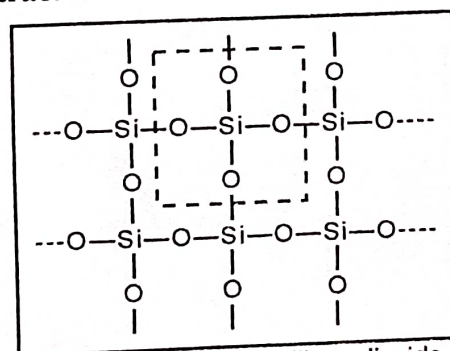


Fig. 3.19 Structure of silicon dioxide.

CARBON AND TIN

Both show similarity in the formation of allotropic forms as shown below :

Allotropy. Various forms of the same element having same chemical properties but different physical properties are called allotropic forms and the phenomenon is called allotropy. Carbon as well as tin show allotropy. These are explained below :

I. Allotropy of carbon. Two main allotropic forms of carbon are **diamond and graphite.**

(i) **Graphite.** Each carbon atom in graphite is sp^2 hybridised. It is bonded to three other carbon atoms through covalent bonds forming *hexagonal rings in two dimensions*. Thus it has two dimensional sheet like polymeric rings. Any two successive sheets (layers) are about 3.35 \AA apart and are held by weak van der Waal's forces. It is due to these forces that graphite layers slip easily over each other.

As a result, graphite is very soft to touch and has lower density (2.2 gm/c.c.).

Good Conductivity. Each carbon in graphite is sp^2 hybridised. Thus one valence electron of each carbon atom is free to move from one point to other. The unhybridised orbitals containing one electron each overlap laterally to form π -bonds between adjacent layers.

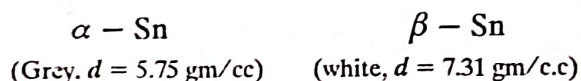
These electrons are delocalised and are quite free to move under the influence of heat and electric field. Thus, graphite is good conductor of heat and electricity.

(ii) **Diamond.** Each carbon atom in diamond is sp^3 hybridised. It is bonded tetrahedrally to other four carbon atoms by covalent bonds. Thus, it has a **three dimensional network of strong covalent bonds**. Thus, it is the **hardest substance known** (m.p. = 3570°C).

Since no electron is left unpaired in its formation, it is a **bad conductor of heat and electricity**. Each C-C bond length is 1.54 \AA and bond angle is $109^\circ 28'$ or 109.5° .

(i) **Allotropy of tin.** Allotropic forms of tin are : (i) α or grey tin and (ii) β or white tin.

The two forms co-exist as follows :



(i) **Grey tin.** It exists in powder form. It lacks metallic properties and is a poor conductor of electricity. It is stable below 13.2°C and consists of interlocking tetrahedral units.

Bond length, Sn-Sn = 2.80 \AA and density = 5.75 gm/cc .

(ii) **White tin.** It exists in the form of metal. It is soft, ductile and good conductor of heat and electricity. It changes to grey tin at low temperature. It has cubic close packed lattice.

NITROGEN FAMILY

The elements belonging to group V A or 15 or pnictogens are given in table 3.6.

Table 3.6 Some physical properties of group VA elements.

Property ↓	Element Nitrogen, → N	Phosphorus, P	Arsenic, As	Antimony, Sb	Bismuth, Bi
Atomic number	7	15	33	51	83
Electronic configuration	$[\text{He}]^2 2s^2 2p^3$	$[\text{Ne}]^{10} 3s^2 3p^3$	$[\text{Ar}]^{18} 3d^{10} 4s^2 4p^3$	$[\text{Kr}]^{36} 4d^{10} 5s^2 5p^3$	$[\text{Xe}]^{54} 4f^{14} 5d^{10} 6s^2 6p^3$
Oxidation states	0, -I, -II, -III, +I, +II, +III, +IV, +V	+III, (+IV), +V	+III, +V	+III, +V	+III, +V
Atomic weight	14.008	30.975	74.91	121.76	208.98
Ionisation energies in kcal/molecule	1st 335	253	226	190	168
	2nd 683	463	466	429	385
	3rd 1487	695	629	572	589
	4th 1784	1184	1155	1018	1044
	5th 2256	1499	1443	1284	1291
Total	6545	4094	3919	3502	3477

Atomic Volume, ml	17.3	1.70 (white P ₄)	13.1	18.2	20.9
Density g/cm ³ solid	0.95	1.82 (white P ₄)	5.72	6.69	9.86
Melting point (°C)	-210	44 (white P ₄)	817 (36 mm)	630.5	271
Boiling point (°C)	-195.8	280 (white P ₄)	613	1337	1559
Electronegativity (Pauling scale)	3.0	2.1	2.0	1.9	1.9
Atomic radii (Å) X ³⁻	0.74	1.10	1.21	1.41	1.52
Atomic radii (Å) X ³⁺	1.71	1.12	2.22	2.45	-
Ionic radii (Å) X ³⁻	-	-	0.69	0.90	1.52
X ³⁺	0.11	0.34	0.47	0.62	0.74
Heat of atomisation, ΔH° (kcal/mole)	1.12	79.8	69.4	47.5	47.5

GENERAL CHARACTERISTICS

(a) **Physical properties.** Some physical properties of group VA elements are given in table 3.6. These properties are discussed below:

1. **Electronic configuration.** The electronic configuration of these elements (table 3.6) shows the presence of five electrons ($ns^2 np^3$) in their valence shell.

2. **Oxidation states.** These elements attain inert gas configuration by the following two different methods:

(a) **By transfer of electrons.** Nitrogen as well as phosphorus atoms form triply charged negative ions (N^{3-} , P^{3-}) but As, Sb and Bi have little or no tendency to form such ions.

The reasons are: (i) As we move down the group, the size of the element increases and attraction of the nucleus for the newly added electrons decreases.

(ii) More the negative charge on the ion, more it becomes susceptible to polarisation.

(iii) A large sized anion cannot fit well in a lattice of small cations.

N^{3-} ions form stable ionic compounds with strong electropositive metals like Li, Mg and Al, e.g., Li_3N , Mg_3N_2 and AlN . P^{3-} ions behave similarly but less effectively.

-3 oxidation state is exhibited by N and P atoms through the transfer of electrons from metal atoms to N and P-atoms.

+3 and +5 oxidation states. +3 and +5 states are shown by oxides of the type M_2O_3 and M_2O_5 respectively.

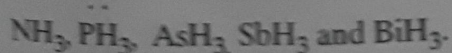
M^{5+} ions are rare. It is due to following reasons:

(i) The size of M^{5+} ion is extremely small and its ionisation energy will be abnormally high.

(ii) M^{5+} ions are hydrolysed in aqueous solution.

M^{3+} ions are common. As we move down the group, the inert pair effect increases regularly. Thus, the stability of +3 oxidation state (by the loss of three p electrons) increases while that of +5 decreases.

(b) **By sharing of electrons.** All these elements have three unpaired electrons in their valence shell. Thus, these form three covalent bonds by sharing these electrons with electrons of other atoms e.g.,:



Maximum covalency of N is 4 and those of others is 5 and 6. N-atoms (${}^7N = 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$) has one lone pair of electrons ($2s^2$) in its valence shell. When it donates its lone pair to H^+ -ion, NH_4^+ ion is

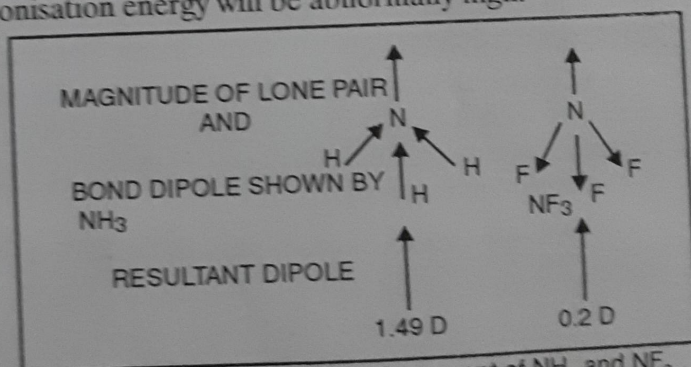


Fig. 3.20 Comparison of dipole moment of NH_3 and NF_3 molecules.

*Uncommon oxidation states are in brackets.

Atomic Volume, ml	17.3	1.70 (white P ₄)	13.1	18.2	21.3
Density gm/ml solid	0.95	1.82 (white P ₄)	5.72	6.69	9.80
Melting point (°C)	-210	44 (white P ₄)	817 (36 mm)	630.5	271
Boiling point (°C)	-195.8	280 (white P ₄)	613	1337	1559
Electronegativity (Pauling scale)	3.0	2.1	2.0	1.9	1.9
Atomic radii (Å) X ³⁻	0.74	1.10	1.21	1.41	1.52
Ionic radii (Å) X ³⁺	1.71	1.12	2.22	2.45	-
X ⁵⁺	-	-	0.69	0.90	1.52
Heat of atomisation, 25°C (kcal/mole)	0.11	0.34	0.47	0.62	0.74
	1.12	79.8	69.4	47.5	47.5

GENERAL CHARACTERISTICS

(a) **Physical properties.** Some physical properties of group VA elements are given in table 3.6.

These properties are discussed below :

1. Electronic configuration. The electronic configuration of these elements (table 3.6) shows the presence of five electrons ($ns^2 np^3$) in their valence shell.

2. Oxidation states. These elements attain inert gas configuration by the following two different methods:

(a) **By transfer of electrons.** Nitrogen as well as phosphorus atoms form triply charged negative ions (N^{3-} , P^{3-}) but As, Sb and Bi have little or no tendency to form such ions.

The reasons are : (i) As we move down the group, the size of the element increases and attraction of the nucleus for the newly added electrons decreases.

(ii) More the negative charge on the ion, more it becomes susceptible to polarisation.

(iii) A large sized anion cannot fit well in a lattice of small cations.

N^{3-} ions form stable ionic compounds with strong electropositive metals like Li, Mg and Al, e.g., Li_3N , Mg_3N_2 and AlN . P^{3-} ions behave similarly but less effectively.

-3 oxidation state is exhibited by N and P atoms through the transfer of electrons from metal atoms to N and P-atoms.

+3 and +5 oxidation states. +3 and +5 states are shown by oxides of the type M_2O_3 and M_2O_5 respectively.

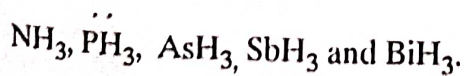
M^{5+} ions are rare. It is due to following reasons :

(i) The size of M^{5+} ion is extremely small and its ionisation energy will be abnormally high.

(ii) M^{5+} ions are hydrolysed in aqueous solution.

M^{3+} ions are common. As we move down the group, the inert pair effect increases regularly. Thus, the stability of +3 oxidation state (by the loss of three p electrons) increases while that of +5 decreases.

(b) **By sharing of electrons.** All these elements have three unpaired electrons in their valence shell. Thus, these form three covalent bonds by sharing these electrons with electrons of other atoms e.g. :



Maximum covalency of N is 4 and those of others is 5 and 6. N-atoms (${}_{7}N = 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$) has one lone pair of electrons ($2s^2$) in its valence shell. When it donates its lone pair to H^+ -ion, NH_4^+ ion is

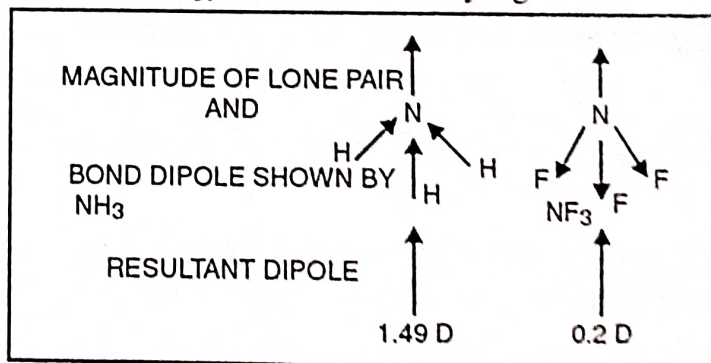


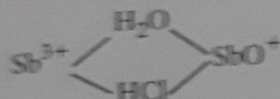
Fig. 3.20 Comparison of dipole moment of NH_3 and NF_3 molecules.

*Uncommon oxidation states are in brackets.

formed. In NH_4^+ ion nitrogen shows a consistency of four. Since N-atom has no *d*-orbital, it is unable to extend its coordination number beyond 4. Hence, nitrogen does not form NF_5 or NCl_5 . It may be noted that nitrogen also exhibits 0, -1, -2, -3, +1, +2 and +4 oxidation states in N_2 , NH_2OH , N_2H_4 , NH_3 , N_2O , NO and NO_2 respectively.

P, As, Sb and Bi have available *d*-orbitals and can extend their coordination number to 5 or 6 e.g. PF_5 , $[SbF_6]^-$, $[PCl_6]^-$

Fluorides of these elements (NF_3 , PF_3 , AsF_3 , SbF_3 , BiF_3) exist as ionic solids. The M^{3+} ion undergoes hydrolysis in H_2O to form SbO^+ and BiO^+ . The change can be reversed by adding 5M HCl.

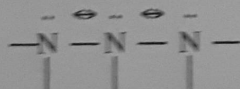


3. Metallic and non-metallic character. As we move down the group, there is a decrease in the values of electronegativity and heat of atomisation. As a result, there is an increase in metallic character down the group. Thus N and P are non-metals, As and Sb are metalloids while bismuth is a true metal. This character is indicated in their oxides. For example, the normal oxides of N and P are strongly acidic, those of As and Sb are amphoteric while that of Bi are strongly basic

4. Ionisation energy. As we go down the group, the screening effect of new shells becomes greater than effective nuclear charge. As a result, the energy required to remove valence electron becomes less and less. Thus the first ionisation energy goes on decreasing down the group. However, the first ionisation energy of VA group elements is much higher (than expected) than IVA elements. This trend is explained on the basis of (i) increased nuclear charge and (ii) increased stability of half-filled *p*-orbitals.

5. Catenation (Self-linkage). The property of catenation in group VA elements is less than that of group IVA elements. For example, two N-atoms are bonded together in hydrazine, $H_2N - NH_2$ while three N-atoms are bonded in hydrazoic acid, $H - N = N = N$ and azide ions, N_3^-

Reason. The lesser tendency of catenation is due to the weakness of N-N bond strength (31 kcal/mole) as compared to C-O bond (84 kcal/mole). This trend is attributed to the repulsion between non-bonding lone pair of electrons on N-atoms.



The tendency of catenation decreases down the group. It is due to decreasing M-M bond energies and hence decreasing tendency to form chains. For example, P and As form P_2H_4 and As_2H_4 respectively.

6. Thermal and electrical conductivity. The thermal and electrical conductivity of group VA elements increases with increase in atomic number down the group. It is due to the increasing delocalisation of electrons in moving from nitrogen ($:N \equiv N:$), (co-ordination number, 1) to bismuth (having metallic crystal co-ordination number, 6).

7. Atomic radius, ionic radius [X^{3-} , X^{3+} , X^{5+}] atomic volume, atomic weight, density, melting point (except Bi) and boiling point. These properties increase as we move down the group.

The difference in the size of Sb (1.41 Å) and Bi (1.52 Å) is less than expected. It is because the filling of 4*d*-sub-shell in Sb increases the nuclear charge due to poorly shielding effect of 4*d*-electrons. The 5 additional protons in Bi-nucleus have a deciding effect in pulling various shells close to the nucleus. As a result, the six shells of Bi occupy a little more volume than five shells of Sb. Due to the same reason, there is sharp increase in the density of Bi (9.8 gm/cc) than Sb (6.7 gm/cc).

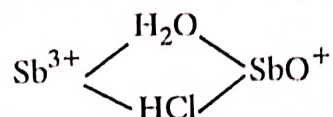
Melting point of Bi is less than that of Sb. It is because of comparatively less availability of pair of electrons in bismuth due to inert pair effect. The inert pair effect increases down the group.

8. Volatile nature. Group VA elements are more volatile than their immediate neighbours. It is because these elements have five electrons ($ns^2 np_x^1 np_y^1 np_z^1$) in their valence shell. This arrangement

formed. In NH_4^+ ion nitrogen shows a covalency of four. Since N-atom has no d -orbital, it is unable to extend its coordination number beyond 4. Hence, nitrogen does not form NF_5 or NCl_5 . It may be noted that nitrogen also exhibits 0, -1, -2, -3, +1, +2 and +4 oxidation states in N_2 , NH_2OH , N_2H_4 , NH_3 , N_2O , NO and NO_2 respectively.

P, As, Sb and Bi have available d -orbitals and can extend their coordination number to 5 or 6 e.g. PF_5 , $[\text{SbF}_6]^-$, $[\text{PCl}_6]^-$

Fluorides of these elements (NF_3 , PF_3 , AsF_3 , SbF_3 , BiF_3) exist as ionic solids. The M^{3+} ion undergoes hydrolysis in H_2O to form SbO^+ and BiO^+ . The change can be reversed by adding 5M HCl.

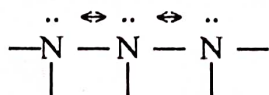


3. Metallic and non-metallic character. As we move down the group, there is a decrease in the values of electronegativity and heat of atomisation. As a result, there is an increase in metallic character down the group. Thus N and P are non-metals, As and Sb are metalloids while bismuth is a true metal. This character is indicated in their oxides. For example, the normal oxides of N and P are strongly acidic, those of As and Sb are amphoteric while that of Bi are strongly basic

4. Ionisation energy. As we go down the group, the screening effect of new shells becomes greater than effective nuclear charge. As a result, the energy required to remove valence electron becomes less and less. Thus the first ionisation energy goes on decreasing down the group. However, the first ionisation energy of VA group elements is much higher (than expected) than IVA elements. This trend is explained on the basis of (i) increased nuclear charge and (ii) increased stability of half-filled p -orbitals.

5. Catenation (Self-linkage). The property of catenation in group VA elements is less than that of group IVA elements. For example, two N-atoms are bonded together in hydrazine, $\text{H}_2\text{N} - \text{NH}_2$ while three N-atoms are bonded in hydrazoic acid, $\text{H} - \overset{+}{\text{N}} = \overset{-}{\text{N}} = \overset{-}{\text{N}}$ and azide ions, N_3^-

Reason. The lesser tendency of catenation is due to the weakness of N-N bond strength (38 kcal/mole) as compared to C-O bond (84 kcal/mole). This trend is attributed to the repulsion between non-bonding lone pair of electrons on N-atoms.



The tendency of catenation decreases down the group. It is due to decreasing M-M bond energies and hence decreasing tendency to form chains. For example, P and As form P_2H_4 and As_2H_4 respectively.

6. Thermal and electrical conductivity. The thermal and electrical conductivity of group VA elements increases with increase in atomic number down the group. It is due to the increasing delocalisation of electrons in moving from nitrogen ($:\text{N} \equiv \text{N}:$), (co-ordination number, 1) to bismuth (having metallic crystal co-ordination number, 6).

7. Atomic radius, ionic radius [X^{3-} , X^{3+} , X^{5+}] atomic volume, atomic weight, density, melting point (except Bi) and boiling point. These properties increase as we move down the group.

The difference in the size of Sb (1.41 Å) and Bi (1.52 Å) is less than expected. It is because the filling of $4d$ -sub-shell in Sb increases the nuclear charge due to poorly shielding effect of $4d$ -electrons. The 32 additional protons in Bi-nucleus have a deciding effect in pulling various shells close to the nucleus. As a result, the six shells of Bi occupy a little more volume than five shells of Sb. Due to the same reason, there is sharp increase in the density of Bi (9.8 gm/cc) than Sb (6.7 gm/cc).

Melting point of Bi is less than that of Sb. It is because of comparatively less availability of pair of electrons in bismuth due to inert pair effect. The inert pair effect increases down the group.

8. Volatile nature. Group VA elements are more volatile than their immediate neighbours. It is because these elements have five electrons ($ns^2 np_x^1 np_y^1 np_z^1$) in their valence shell. This arrangement is

conductive to form discrete molecules. Since the attraction among such molecules is very small, less energy is required to separate them. Hence these elements are much volatile.

Elemental state. (a) Nitrogen is small sized atom (${}_{7}\text{N} = 1s^2 2s^2 2p^3$). It contains only $1s^2$ electrons in its inner core. When N-atoms come close, these do not encounter any repulsion from $1s^2$ electrons. Thus, atoms form $p\pi - p\pi$ multiple bonds by the lateral overlap of p - orbitals. Hence nitrogen exists as a diatomic molecule ($\text{N} \equiv \text{N}$) or N_2 . Since the forces holding discrete nitrogen molecules are weak van der Waal forces, nitrogen exists as a gas.

(b) P, As and Sb are large sized atoms. The atoms of these elements cannot approach close enough because of **increased repulsions from the non-bonding electrons of the inner core**. Thus these elements are unable to form $p\pi - p\pi$ multiple bonds. As a result, these do not exist as diatomic molecules. On the other hand, each element shares its three unpaired electrons with other three elements to form tetrahedral molecules, P_4 , As_4 and Sb_4 . As we move down the group, the giant lattices of P, As, Sb and Bi show a gradual trend from covalent to metallic bonding. For example :

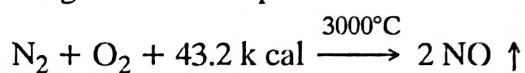
- (i) Red and violet phosphorus form **layered structure** with co-ordination number three.
- (ii) Arsenic and antimony form more closely packed layers having intermediate covalent-metallic structures, and
- (iii) Bismuth involves such a packing of atoms that the bonding is purely metallic.

Inert nature of nitrogen. ${}_{7}\text{N}$ -atoms ($1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$) shares its three unpaired electrons with three unpaired electrons of another N-atom to form $p\pi - p\pi$ multiple bond. As a result, both N-atoms attain neon gas (stable) configuration and form $\text{N} \equiv \text{N}$ molecule. The bond length is very short (1.094 \AA) and bond dissociation energy (225 k cal per mole) is very high. Thus :

(i) At room temperature, strong bonding in N_2 molecule is not disturbed by collision among molecules. Thus, it is not reactive at room temperature.

(ii) At very high temperature, the N_2 molecules acquire high kinetic energy. The triple bond in N_2 , thus gets broken (into atoms) by the collision among molecules. The atoms so formed have high electronegativity and exhibit high chemical reactivity.

(iii) The formation of most of nitrogen compounds involve endothermic nature. This is also one of the causes of inert nature of nitrogen. For example :



CHEMICAL PROPERTIES

1. **Hydrides.** The elements of group VA form volatile hydrides of the type MH_3 . N, P and As also form hydrides of the type M_2H_4 . Nitrogen also forms hydrazoic acid, HN_3 . Some hydrides are given in the following table 3.7.

Table 3.7 Hydrides of group VA elements,

MH_3 type	M_2H_4 type	M_3H type
NH_3 Ammonia	N_2H_4 Hydrazine	N_3H Hydrazoic acid
PH_3 Phosphine	P_2H_4 Diphosphine	
AsH_3 Arsine	As_2H_4 Diarsine	
SbH_3 Stibine	Sb_2H_4 distibine	
BiH_3 Bismuthine		

(a) Hydrides of MH_3 type are discussed below :

Structure. These hydrides (MH_3) have **pyramidal** structure. The bond angle, bond energy, electronegativity and atomic radii of these hydrides are given in the following table 3.8.

Table 3.8 Some character of group VA elements.

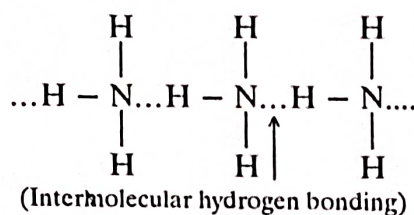
Bond angle	Bond energy M-H (kcal/mole)	Electronegativity	Atomic radius (Å)
HNH (106° .45')	N-H = 93	N = 3.0	N = 0.74
HPH (94°)	P-H = 77	P = 2.1	P = 1.10
HAsH (91° .48')	As-H = 59	As = 2.0	As = 1.21
HSbH (91° .18')	Sb-H = 61	Sb = 1.9	Sb = 1.41

In all these hydrides, the central atom involves sp^3 hybridisation and forms four sp^3 hybrid orbitals. One sp^3 -hybrid orbital contains a lone pair of electrons. Rest sp^3 hybrid orbitals overlap with s -orbitals of H-atoms. As a result, MH_3 attains pyramidal structure.

The H-N-H bond angle is slightly less than tetrahedral angle (109° .28'). The bond angle in rest hydrides is considerably less (table 3.8). It is because as we go down the group, the electronegativity of the central atom goes on decreasing. As a result, lone pair-bond pair and bond-pair-bond pair repulsion decreases regularly. Thus, the bonding electrons in MH_3 are drawn farther and farther away from M and closing up of bond angles takes place.

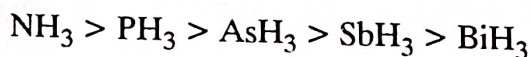
(iii) **Properties.** (a) **Covalent nature.** As we move down the group, the electronegativity difference between group VA elements and hydrogen goes on decreasing. Thus, polar character goes on decreasing and covalent character goes on increasing.

(b) **Hydrogen bonding.** The small size and high electronegativity of nitrogen atom results in intermolecular hydrogen bonding in ammonia molecules.

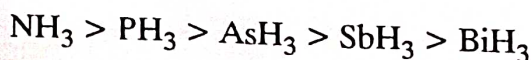


Thus, ammonia (NH_3) is a liquid. Since high energy is required to break hydrogen bonding, NH_3 has high boiling point and heat of vaporisation. As we move down the group, the size of central atom goes on increasing while the electronegativity goes on decreasing. Thus these elements are unable to form intermolecular hydrogen bonding. So, PH_3 , AsH_3 , SbH_3 and BiH_3 are gases.

(c) **Thermal Stability.** As we move down the group, the size of central atom goes on increasing. Thus, the extent of overlapping of sp^3 -hybrid orbital of central atom with s -orbitals of small H-atoms goes on decreasing. As a result, the strength of M-H bond goes on decreasing. Hence, the thermal stability of group VA hydrides goes on decreasing as shown below :

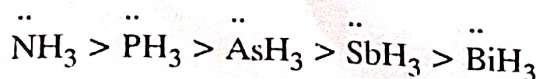


(d) **Reducing nature.** The thermal stability of hydrides of group VA elements goes on decreasing in the following order :



It is because, as we go down the group, the strength of M-H bond goes on decreasing (Also see thermal stability concept above). Hence the reducing character of hydrides goes on increasing.

(e) **Basic nature.** The basic nature of the hydrides of group VA elements is due to the lone pair of electrons present on central atom. The decreasing order of basicity of these hydrides is



Reason. Nitrogen is small sized atom. Lone pair of electrons, is thus concentrated on small region. As we move down the group, the size of central atom goes on increasing. The electron cloud (of lone pairs)

diffuses over larger and larger volume. As a result, the electron density in the sp^3 -hybrid orbitals goes on decreasing and hence electron donor capacity (basic strength) goes on decreasing.

2. Halides. Group VA elements form halides of the type MX_3 and MX_5 .

(a) **Trihalides of nitrogen.** These are predominantly covalent. The ionic character increases down the group and thus, $BiCl_3$ is ionic.

NF_3 is very stable gas and is inert in nature. It can be explained on the basis of its strong N-F bond. Also, its heat of formation, $\Delta H_f^\circ = -26$ kcal/mole is very high.

NCl_3 is explosive. NCl_3 is unstable or explosive. It is because of its high positive heat of formation, $\Delta H_f^\circ = +55.4$ kcal/mole. It undergoes hydrolysis to form ammonia and hypochlorous acid (HOCl):

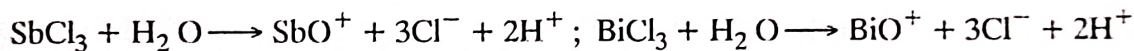
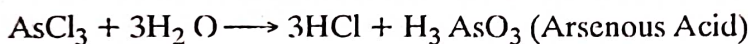
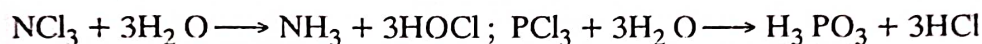


NF_3 has very low dipole moment and also does not act as Lewis acid. NF_3 has pyramidal structure. Since F-atom is small sized highly electronegative atom, it withdraws lone pair of electrons of sp^3 -hybrid orbital of N-atom strongly towards itself. Thus, N-atom is devoid of its electron donor character and does not act as Lewis base. Due to the same reason, the resultant dipole-moment of NF_3 becomes less than NH_3 in which H-atom has comparatively less electronegativity (Fig. 3.20).

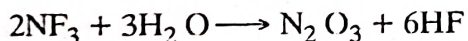
Trihalides of phosphorus. (a) PF_3 is stable and does not undergo hydrolysis because of strong P-F bond.

Also, P-F bond is stronger than P-O bond due to high electronegativity of fluorine. Thus during hydrolysis of PF_3 , P-O bonds are not formed and PF_3 does not undergo hydrolysis.

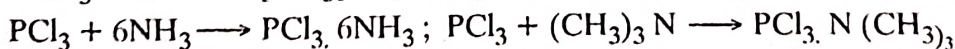
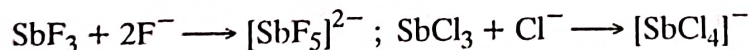
The hydrolysis of trichlorides of these elements is shown below. The product depends upon the nature of the element. For example :



NF_3 reacts with water only when electric spark is passed through the mixture :

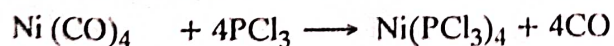


(b) **Trifluorides and trichlorides of phosphorus and antimony also act as Lewis acids,** (i.e., tendency to accept lone pair of electrons). It is because of the tendency of these elements to accept lone pair of electrons in their vacant d -orbitals. For example :



Trimethyl amine

PCl_3 also acts as Lewis base (electron donor nature) because P-atom is able to donate its lone pair of electrons to the vacant d -orbitals of other elements like nickel. for example :



Nickel carbonyl Lewis base

(c) **Pentahalides of group VA elements.** (i) N-atom does not have d -orbital. Thus, it cannot expand its octet to accept lone pair of electrons from other halogen atoms. So, nitrogen pentahalides are not possible.

(ii) **Phosphorous, arsenic and antimony form pentahalides.** It is because these elements have d -orbitals. Thus, these elements are able to expand their octet and can accept lone pair of electrons from other halogen atoms especially fluorine to form pentahalides.

(iii) **Bismuth pentahalide is not formed.** It is because the $6s$ electrons in bismuth element are reluctant to take part in bond formation due to inert pair effect.

(iv) **In solid state.** PCl_5 exists as ionic $[PCl_4]^+ [PCl_6]^-$. The $[PCl_4]^+$ is tetrahedral while $[PCl_6]^-$ is octahedral. In the gaseous and liquid state, it has trigonal bipyramidal shape. PBr_5 exists as $[PBr_4]^+$ and Br^-

(v) PI_5 does not exist. It is explained on the basis of large size of iodine atom and small electronegativity difference between P (2.1) and I-atom (2.2).

(vi) All pentahalides (except nitrogen) act as Lewis acids (electron pair acceptor). It is because the central atoms accept halide ions in their vacant d -orbitals and extend their coordination number to six. For example, in $[PCl_6]^-$, P-atom has coordination number six and the ion has octahedral structure.

(d) Bond angle in NF_3 (102.1°) is less than NH_3 ($106^\circ 45'$). F-atom in NF_3 is more electronegative (4.1) than H-atom (2.1) in NH_3 . Thus, F-atom reduces the size of bond pair of electrons in N-P bond. It causes lesser bond pair-bond pair repulsions than this type of repulsion in N-H bonds in NH_3 . Hence bond angle in NF_3 is less than that of NH_3 .

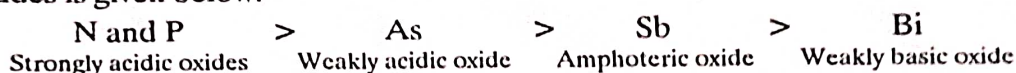
3. Oxides of group VA elements. The various oxides of group VA elements are given in the following table 3.9.

Table 3.9 Oxides of group VA elements.

Oxidation number of elements	Oxides of elements				
	N	P	As	Sb	Bi
+1	N_2O				
+2	NO				
+3	N_2O_3	P_4O_6	As_4O_6	Sb_4O_6	Bi_2O_3
+4	N_2O_4	P_4O_8	—	—	—
+5	N_2O_5	P_4O_{10}	As_2O_5	Sb_2O_5	—
+6	(NO ₃ , N ₂ O ₆) which are very unstable				

Nature of oxides. (i) For the same element, the oxides in the lower oxidation states are less acidic than those of higher oxidation state. For example, N_2O (oxidation state of N = + 1) is neutral while NO_2 (oxidation state of N = + 4) is acidic. It is because, the N^{4+} is smaller in size than N^+ and so interacts with water more strongly than N^+ . As a result, NO_2 shows acidic properties.

(ii) As we move down the group, the metallic nature of the elements increases. Thus, the basicity of their oxides increases down the group. Except N_2O and NO (which are neutral), the decreasing order of acidity of oxides is given below.



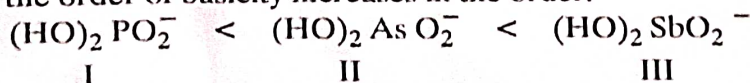
(iii) **Stability.** As we go down the group, the inert pair effect increases. Thus, the stability of oxides having elements of higher oxidation states decreases.

Oxyacids. Some important oxyacids of nitrogen, phosphorus and arsenic are stable. The oxyacids of antimony and bismuth are unstable. The oxyacids of N, P and As are formed by dissolving their oxides in water. All the oxyacids of phosphorus contain a tetrahedral phosphorus atom which is bonded to four atoms of oxygen through coordinate bond. All the acids contain atleast one P = O unit and one P-OH group.

Some phosphorus acids (e.g., H_3PO_2 , H_2PO_3 and $H_4P_2O_5$) are reducing agents because of H-atom in P-H bonds.

Order of basicity. As we go down the group ; (i) the atomic weight of central atom increases. (ii) X-O bond distance increases (X = central atom) (iii) the effectiveness of $p\pi-d\pi$ bonding decreases.

As a result, the order of basicity increases in the order.



Structure. (I) has

- | | |
|---------------------------------------|--|
| (a) smallest central atom | (b) smallest X-O bond distance |
| (c) most effective p-d- π bonding | (d) greatest amount of charge delocalisation |

Structure. (III) has

(a) largest central atom

(c) least effective $p-d\pi$ bonding

Thus, it is the **weakest base**.

(b) largest X – O bond distance

(d) least amount of charge delocalisation

Thus, it is the **strongest base**.

Allotropy. Various forms of the same element having same chemical properties but different physical properties are called allotropic forms and the phenomenon is called allotropy. Phosphorus, arsenic and antimony exhibit allotropy. These are discussed below.

1. Allotropy of phosphorus. There are five allotropic forms of phosphorus.

(i) White or yellow phosphorus
(ii) Red phosphorus

} Main forms

(iii) Black phosphorus

} Variety of white phosphorus

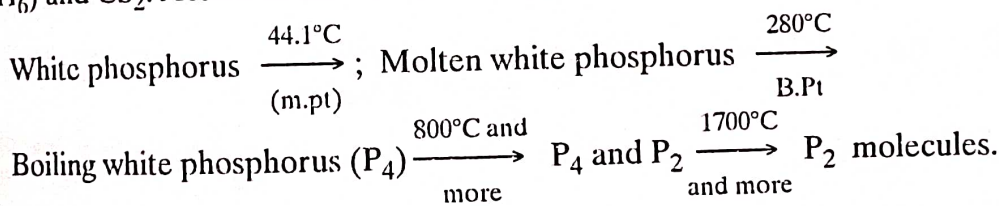
(iv) Scarlet phosphorus

} Variety of white phosphorus

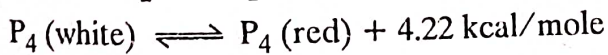
(v) Violet phosphorus

(a) **White phosphorus.** (i) Molecular weight data indicates that it exists as P_4 molecule (fig. 3.21).

(ii) Electron diffraction data indicates that P_4 is tetrahedral (Fig. 3.21). These molecules are held together by weak van der Waal forces. Thus, P_4 is solid. The PPP bond angle should be 90° but it is 60° . It indicates that P_4 molecule is under strain. And it is actually so. This strained nature is confirmed from its **high reactivity**. It requires very small energy for its decomposition. It is inflammable in air and is soluble in organic solvents like benzene (C_6H_6) and CS_2 . Action of heat is shown below.



(b) **Red phosphorus.** In this type, P atoms are bound together by covalent bonds to form long chained, giant molecular crystals (Fig. 3.22). It is prepared by heating white phosphorus at 400°C in an atmosphere of N_2 or CO_2 and a trace of iodine as catalyst.



It does not melt but sublimates on heating to give white phosphorus.

(c) **Black phosphorus or β -metallic phosphorus.**

It is prepared by heating white phosphorus at 200°C under a pressure of 12,000 to 13,000 kg/cm^3 . It is fairly good conductor of electricity.

Structure. It has double layered crystal lattice.

Each layer consists of adjacent zig-zag chains with PPP bond angle 99°

The distance of P-atoms (in one chain) which is bonded to two p-atoms in the same chain and one P-atom in a chain in the layer above or below, is same, i.e., 2.18 Å. The distance between two adjacent layers is 3.68 Å (Fig. 3.23).

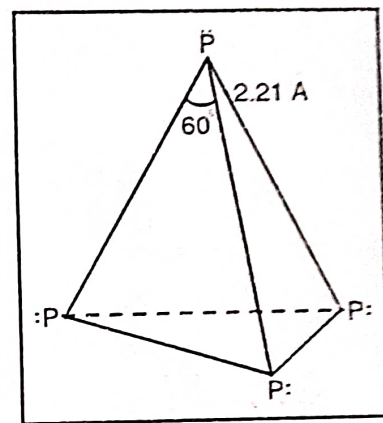


Fig. 3.21 Structure of P_4

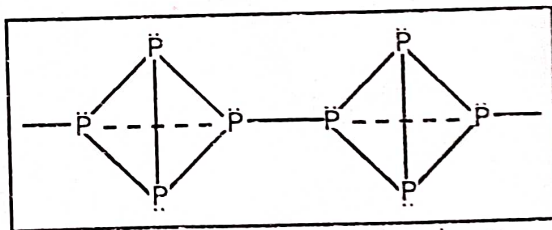


Fig. 3.22 Structure of red phosphorus.

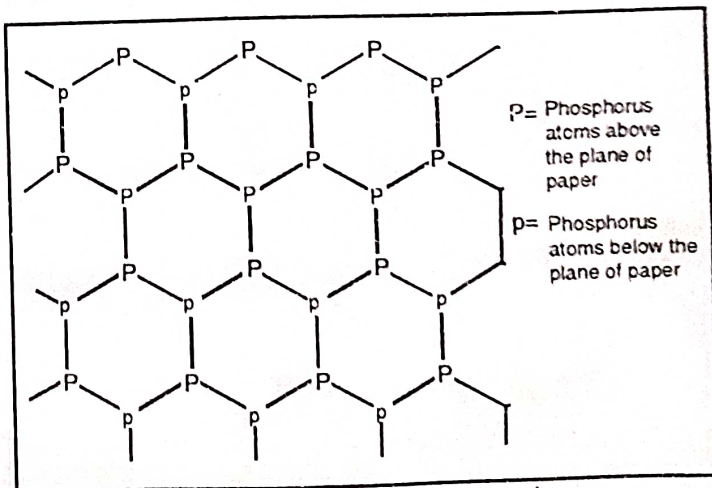


Fig. 3.23 Structure of black phosphorus.