

UNIT-11

s and p-Blocks

1. CHEMISTRY OF S AND P BLOCK ELEMENTS INCLUDING NOBLE GASES PROPERTIES AND APPLICATION OF MAIN GROUP ELEMENTS

Introduction:

The elements in the long form of the periodic table have been divided into four blocks — s, p, d and f- block elements. This classification is based on the type of the atomic orbital in which the outermost electron is located. The s orbital can accommodate two electrons, while the three p orbitals can accommodate a maximum of six electrons. Thus there are two groups of s - block elements — Groups 1 and 2 whose electronic configurations are represented as [Noble gas] ns^1 and [Noble gas] ns^2 respectively. There are six groups of p - block elements — Groups 13 to 18. The s and p block elements are collectively called the main – group elements or representative elements. The d and f - block elements are located between the s and p - block elements.

The s - block elements are located on the left of the periodic table and comprise of highly reactive metals. The p -block elements comprise of both metals and non-metals.

CLASSIFICATION OF PERIODIC TABLE :

Classification - 1			
s-Block Elements	p-Block Elements	d-Block Elements	f-Block Elements
Group 1 & 2	Group 3 to 12	Group 13 to 18	
Alkali and Alkaline Earth Metals		Transition Elements	Inner transition Elements
Classification - 2			
Inert Gases	s & p block elements	d-Block Elements	f-Block Elements
ns^2p^6	ns^1, ns^2, np^{1-5}	$(n-1)d^{1-9}ns^{1-2}$ exception Zn, Cd, Hg Group 12	$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$ 4f - Lanthanides 58 - 71 5f - Actinides 90-103
Inert Gases	Representative Elements	Transition Elements	Inner transition Elements

I. s - block elements:

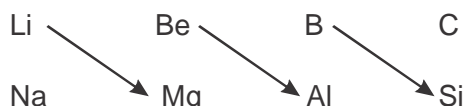
- The elements of groups 1 and 2 are called the s- block elements because the outermost electron(s) occupy the s -orbital.
- They are highly electropositive metals and form ionic compounds.
- They are referred to as alkali and alkaline- earth metals respectively. Due to their high reactivity the metals do not occur in the free state in nature but are present in form of halides, silicates, nitrates (Group1) and silicates, carbonates, sulphates and phosphates (Group 2).

The elements show similarities in physical and chemical properties within a group — however the first elements exhibit considerable differences from the rest of the elements of the same group. This anomalous behaviour is mainly due to the following factors —

- (1) Comparatively higher value of the first ionization energy and electronegativity
- (2) Small size
- (3) High polarizing power of the cation, consequently a greater tendency to form covalent compounds (Fajan's rules) and complexes,
- (4) Inability to display a coordination number exceeding 4 due to non-availability of d - orbitals in the valence shell.

Diagonal Relationship

A close similarity is observed in certain cases between the first element of a group with the second element of the following group. This is referred to as the diagonal relationship and is observed in the following pairs.



Reason

In a period the atomic size and electropositive character decreases. Ionisation potential and electronegativity increases.

Down a group atomic size and electropositive character increases. But Ionisation potential and electronegativity decreases.

On moving in a diagonal these properties cancel each other. Therefore, similarly in behaviour. [e.g.. ionic size of Li^+ =76pm & that of Mg^{2+} =72pm]

Group 1 — the Alkali Metals

- The elements in this group are lithium, sodium, potassium, rubidium, caesium and the radioactive, francium.
- They have one electron in their valence shell (ns^1 configuration).
- Due to similarity in electronic configuration, they exhibit similarities in chemical properties. They are soft, highly reactive, univalent metals, excellent conductors of heat and electricity and form colourless ionic compounds.
- Lithium shows considerable differences from the lower members and exhibits diagonal relationship with magnesium.

The physical properties of alkali metals are summarized in Table.

Table: Physical Properties of Group 1 Elements

Property	Li	Na	K	Rb	Cs
Atomic Number	3	11	19	37	55
Electronic Configuration	$[\text{He}]2s^1$	$[\text{Ne}]3s^1$	$[\text{Ar}]4s^1$	$[\text{Kr}]5s^1$	$[\text{Xe}]6s^1$
Covalent radius (pm)	123	156	203	216	235
Ionic radius (M^+) (pm)	60	95	133	148	169
Ionization Energy (KJmol^{-1})	520	496	419	403	376
Electron Affinity (KJmol^{-1})	60	53	48	47	46
Electronegativity	0.912	0.869	0.734	0.706	0.659
Melting Point ($^{\circ}\text{C}$)	180.5	97.8	63.2	39	28.5
Boiling Point ($^{\circ}\text{C}$)	1347	881	766	688	705
$E^{\circ} (M^+ \rightarrow M)$ (V) against S.H.E,	-3.04	-2.71	-2.92	-2.92	-2.92

General Group Trends

1. Size & Density

On moving down the group the size of the atom increases as additional shells are introduced to accommodate the electrons. This out-weighs the effect of increased nuclear charge. Formation of the cation involves removal of the outermost shell of electrons; the effective nuclear charge also increases and the electrons are held tightly. Thus the cation is smaller than the neutral atom. Even so, the cations are quite large and an increase in size is observed on descending the group. The atoms are large and the atomic mass is low; thus the Group 1 elements have low densities.

2. Ionization Energy

The first ionization energies of the atoms are the lowest in the corresponding period. The atoms are large and the outermost electron is loosely held. Moreover; loss of this electron gives a stable noble gas configuration. On moving down the group, the ionization energy decreases as the size increases.

The second ionization energy is extremely high as it is difficult to remove an electron from a cation having noble gas configuration. The elements form unipositive cations, they are highly electropositive and the metallic character increases down the group.

3. Melting and Boiling Points

These metals are soft and can be cut with a knife. At room temperature they adopt a body-centred cubic lattice. They have one electron that can participate in metallic bond formation and thus they have low cohesive energy, which is reflected in low melting and boiling points. On moving down the group, the metallic bonding becomes weaker and the melting and boiling points decrease.

4. Electronegativity and Type of Bond

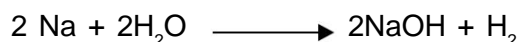
These elements have low electronegativity; consequently when they react with other elements a large electronegativity difference is possible and ionic bonds are formed.

5. Flame Colours

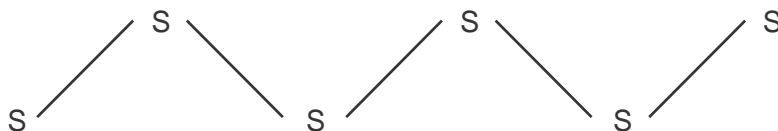
The alkali metal atoms have low ionization energy and may emit electrons when irradiated with light, hence they find use in photocells. Electrons may also be excited to higher energy levels, for example in the flame test. When an alkali metal salt is introduced to a Bunsen burner flame, a characteristic colour is observed. (Li – red, Na – golden- yellow, K – lilac). The colour arises from electronic transitions, which occur due to excitation of electrons from valence shell to higher excited state energy levels. When the excited electrons return to the original level, the extra energy is emitted and lies in the visible range of the electromagnetic spectrum.

Chemical Properties:

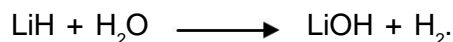
- The alkali metals are very similar in their chemical properties, which are governed by the ease with which they can lose their valence electron. They are excellent reducing agents and react with water forming hydrogen.



- The reaction is highly exothermic.
- They react with oxygen to form oxides, peroxides or superoxides depending on the metal. Lithium forms the oxide (Li_2O), sodium, the peroxide (Na_2O_2) while others form the superoxide (M O_2 , $\text{M} = \text{K, Rb, Cs}$). Lithium is the only element that forms a nitride by direct combination with nitrogen.
- Alkali metals react with sulphur forming sulphides e.g. Na_2S and polysulphides Na_2S_n where $n = 2$ to 6 . The polysulphides have zig – zag chain of sulphur atoms.



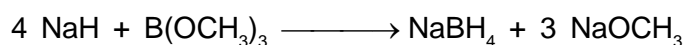
- The metals react with hydrogen forming ionic hydrides, $M^+ H^-$. The stability of the hydrides decreases down the group. The hydrides are ionic solids and are the only example of species containing H^- ion. During electrolysis hydrogen is liberated at the anode. They react with water liberating hydrogen.



Lithium hydride reacts with aluminum hydride to form lithium aluminium hydride, an excellent and useful reducing agent in organic chemistry



Sodium hydride reacts with trimethyl borate to form another useful compound, sodium borohydride



- The alkali metals react violently with halogens to form halides. The reactivity of an alkali metal towards a particular halogen increases down the group. The reactivity of halogen towards an alkali metal follows the order: $F_2 > Cl_2 > Br_2 > I_2$. The general reactions of alkali metals are summarized in Table.

Table: Reaction of Group 1 Metals

Reagent	Reaction	Remarks
O_2	$M + O_2 \rightarrow M_xO_y$	$x = 2, y = 1$ for Li (monoxide); $x = 2, y = 2$ for Na (peroxide) $x = 1, y = 2$ for others (superoxide)
S	$2M + S \rightarrow M_2S$	Polysulphides also formed
H_2O	$M + 2H_2O \rightarrow MOH + H_2$	Slow for Li, explosive for K
H_2	$2M + H_2 \rightarrow 2MH$	Ionic hydrides formed
X_2 (halogen)	$2M + X_2 \rightarrow 2MX$	All halogens react
N_2	$6Li + N_2 \rightarrow 2Li_3N$	Only Li reacts
ROH	$2M + 2ROH \rightarrow 2MOR + H_2$	Slow for Li, Vigorous for others
NH_3	$M + NH_3(e) \rightarrow [M(NH_3)_x]^+ + e^- (NH_3)$	Excellent reducing agents

Solvation of Alkali Metal Ions

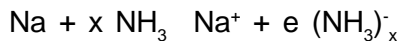
Solvent molecules always surround a metal ion in solution. This is referred to as solvation. If the solvent is water, then it is called hydration. The alkali metal ions are extensively hydrated. A small ion has high charge density and attracts the solvent molecules strongly, resulting in extensive hydration. The energy evolved during hydration is called hydration energy.

Li^+ being smallest is most heavily hydrated and has highest hydration energy. The extent of hydration decreases down the group. Hydration directly affects ionic mobility. Li^+ , the smallest ion is expected to be highly mobile, but in fact the reverse is true. This is because the hydrated radius of Li^+ is the largest and is least mobile and least conducting in solution.

The decrease in hydration from Li^+ to Cs^+ is revealed by the fact that most crystalline salts of lithium are hydrated. Most salts of alkali metals are soluble in water. For any substance to dissolve the hydration energy must exceed lattice energy.

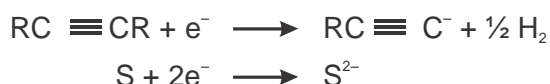
Solution of Metals in Liquid Ammonia

The alkali metals dissolve in liquid ammonia and other amines to give blue solution believed to contain solvated electrons.

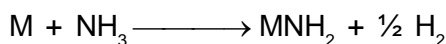


Due to the presence of these solvated electrons, dilute solution of alkali metals conduct electricity far better than completely dissociated electrolytes.

As the concentration of the metal increases the conductivity decreases initially and then increases. At sufficiently high concentrations the solution develops a bronze metallic luster and the conductivity approaches the value of a molten metal. The dilute solutions are paramagnetic but the paramagnetism decreases with increase in concentration. The blue colour is attributed to the solvated electrons. These solutions are excellent reducing agents.



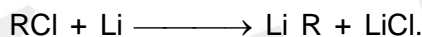
The solutions undergo slow decomposition to give amides.



The Group 2 metals and some lanthanides also dissolve in liquid ammonia.

Alkyls and Aryls

Lithium shows a stronger tendency to covalency than the other alkali metals. It forms covalent alkyls and aryls. These compounds are frequently tetrameric or hexameric and are made by reaction of lithium with the alkyl / aryl halide.



The methyl derivative is tetrameric $[(\text{LiCH}_3)_4]$, covalent and soluble in organic solvents. The four Li atoms occupy the corners of a tetrahedron with the methyl groups above the face of the tetrahedron. The classical theories of bonding cannot explain the formation of these compounds, which involve multi-centred bonds. These compounds are starting materials for synthesis of organometallic and organic compounds. The alkyls of Na, K, Rb and Cs are ionic.

Complexation Behaviour of Alkali Metals

The alkali metals generally have weak complexing ability. This is because the factors that favour complexation viz, small size, high nuclear charge and availability of empty orbitals of low energy are lacking in alkali metals.

Aqua complexes like $[\text{Li}(\text{H}_2\text{O})_4]^+$, $[\text{Cs}(\text{H}_2\text{O})_6]^+$ are known. A number of chelates are known e.g. those with salicylaldehyde and acetyl acetone.

An important development in the field of alkali metal chemistry is the discovery of complexes with cyclic ethers and cryptands (cryptates) i.e. with macro cyclic molecules containing nitrogen and oxygen. The cyclic ethers are called crown ethers; they have varying sizes of rings and form complexes with alkali metal ions by donating electron density through the oxygen atoms. Examples of such molecules are shown in Fig.

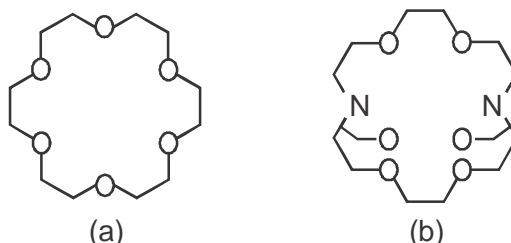


Fig.: a. A crown ether b. A cryptand

The cryptates are more selective and stronger complexing agents than the crown ethers, with eight donor atoms (nitrogen and oxygen) surrounding the metal ion completely. The ability of crown ether or a cryptands to trap a metal ion depends on the size of both the cavity and the metal ion.

Biological Importance

- Living organisms need about 15 metals for different biological processes. Some of the alkali metals are biologically active.
- Sodium and potassium ions act as charge carriers and are involved with balancing the electrical charges associated with negatively charged macromolecules in the cell.
- Na^+ is the major cation in the extra cellular fluid and its concentration is about 0.15 M, it is actively expelled from the cell where its concentration is about 0.01 M. K^+ is the major cation inside the cell (0.15 M) whereas its concentration in the extra cellular fluid is about 0.03 M. This uneven concentration of Na^+ and K^+ on either side of the cell wall is controlled by the sodium-potassium pump and a large amount of energy is needed to maintain this disequilibrium.
- The energy is provided by hydrolysis of ATP. Na^+ and K^+ are also involved in maintaining the osmotic pressure inside the cell, thereby keeping it turgid.
- The different ratio of Na^+ to K^+ inside and outside the cell produces a characteristic electrical potential across the cell membrane and muscle cells.
- They also activate specific enzymes. Lithium salts are used as anti-depressants. The exact mode of action is however not clear.

Group 2 — the Alkaline Earth Metals

This group comprises of six metallic elements – beryllium, magnesium, calcium, strontium and barium. Calcium and magnesium are amongst the most abundant elements in the earth's crust; strontium, barium and beryllium are less abundant. All isotopes of radium are radioactive (longest lived isotope, ^{226}Ra has half of 1600 years).

Selected physical properties of the alkaline earth metals are given in Table.

Table: Physical Properties of Group 2 Elements

Property	Be	Mg	Ca	Sr	Ba	Ra
Electronic Configuration	$[\text{He}]2s^2$	$[\text{Ne}]3s^2$	$[\text{Ar}]4s^2$	$[\text{Kr}]5s^2$	$[\text{Xe}]6s^2$	$[\text{Rn}]7s^2$
Ionic radius (pm)	31	65	99	113	135	–
Covalent radius (pm)	89	136	174	191	198	–
Ionization Energy (KJmol^{-1}) (I)	900	738	590	549	502	509
Electron Affinity (KJmol^{-1})	-50	-40	-30	-30	-30	-30
Melting Point ($^{\circ}\text{C}$)	1287	649	839	768	727	700*
Boiling Point ($^{\circ}\text{C}$)	2500	1105	1494	1381	1850*	1700*
Electronegativity	1.576	1.293	1.034	0.963	0.881	0.9
$E^{\circ} (\text{M}^{2+} + 2e^{-} \rightarrow \text{M})$ (V) Against S.H.E	-1.97	-2.36	-2.84	-2.89	-2.92	-2.92

* Approximate value

Physical Properties

The atoms have two electrons in their outermost shell. They are divalent, reactive metals, though less reactive than the elements of Group 1. The atoms of the Group 2 elements are smaller than the neighbouring Group 1 elements as a consequence of the greater nuclear charge of the former. As a result of their smaller size they are denser than the alkali metals and have greater ionization energy.

The Group 2 metals have two electrons, which can participate in metallic bond formation and thus have higher cohesive energy and much higher melting and boiling points than Group 1 metals. The melting points do not vary regularly as the metals adopt different crystal structures in the solid state.

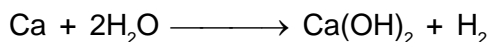
The metals of this group form ionic compounds. Beryllium, however, due to its small size and moderately higher value of electronegativity has a tendency to form covalent compounds. The general group trends in Group 2 are very similar to those in Group 1.

Chemical Properties

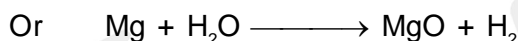
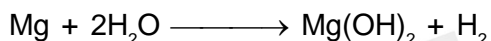
The elements, with the exception of beryllium have very similar chemical properties. Much of their chemistry is governed by their tendency to form M^{2+} ions, which have noble gas configuration.

They are good reducing agents. The reduction potential of beryllium is less than those for the rest of the group. This indicates that beryllium is less electropositive (metallic) than others.

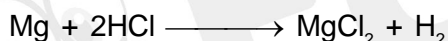
The heavier members react with water to evolve hydrogen and form metallic hydroxides.



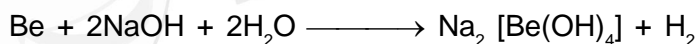
Magnesium is less reactive and decomposes hot water



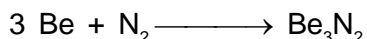
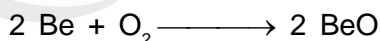
The hydroxide of beryllium is amphoteric while the other hydroxides are basic and basic character increases down the group as the metallic character increases. The metals react with acids forming hydrogen.



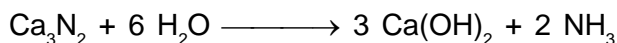
Beryllium reacts slowly and is rendered passive by concentrated nitric acid as a protective oxide film coats it. It is amphoteric and reacts with strong bases to evolve hydrogen.



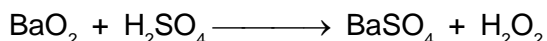
The elements burn in air to form the corresponding oxides and nitrides.



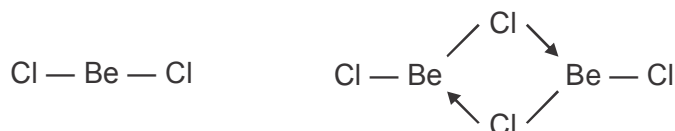
Beryllium nitride is covalent. All nitrides decompose to its elements on heating and react with water to give ammonia.



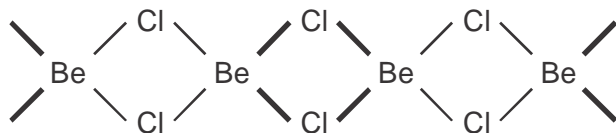
The tendency to form peroxides increase with the size of cation. This is because a large cation is stabilized by a large anion which gives rise to a species with high lattice energy. The peroxides contain the O^{2-} ion and liberate hydrogen peroxide with acids.



The halides are formed by direct combination or by action of halogen acids or metals. The halides of beryllium are hygroscopic and fume in air due to hydrolysis. Anhydrous beryllium halides are polymeric. Beryllium chloride in the vapour state contains both the monomer and the dimer.

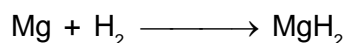


In the solid-state beryllium chloride has a polymeric structure containing bridging chlorine atoms.

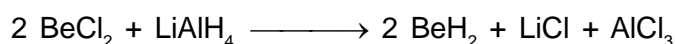


The halides are deliquescent and form hydrates. Calcium chloride is widely used as a drying agent.

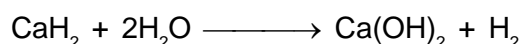
All the group 2 metals except beryllium combine with hydrogen at high temperature to form hydrides, MH_2



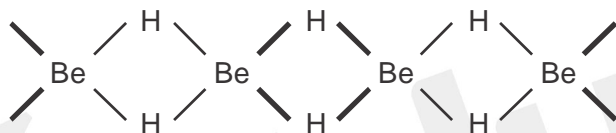
Beryllium hydride can be obtained by reducing beryllium chloride with lithium aluminum hydride.



The hydrides are reducing agents and react with water and acids to produce hydrogen.

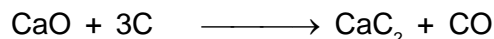
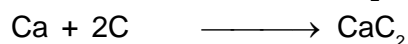
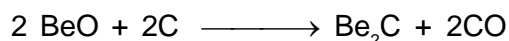


The hydrides of calcium, strontium and barium are ionic and contain the hydride ion (H^-). The hydrides of beryllium and magnesium are covalent and polymeric $(BeH_2)_n$. has a chain structure containing chains with hydrogen bridges between beryllium atoms



Each beryllium atom is bonded to two hydrogen atoms and each hydrogen atom to two beryllium atoms. Now, beryllium has only two valence electrons and hydrogen only one, it is apparent that there are not sufficient electrons to form so many electron pair bonds. The monomeric BeH_2 , if formed with normal bonds, would have only four electrons in the valence shell of the beryllium atom and would be electron deficient and unstable. It polymerizes to remedy the electron deficiency. The bonds formed cannot be explained by the classical theories of bonding. They are "banana shaped" molecular orbitals holding three atoms $Be \cdots H \cdots Be$ together and are called 3 centred – 2- electron ($3c - 2e$) bonds. It is an example of a cluster compound.

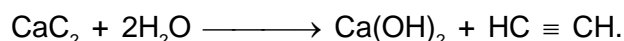
The metals and their oxides directly combine with carbon forming carbides.



Be_2C is ionic and hydrolyses to give methane



The other carbides produce ethyne



The general reactions of Group 2 metals are summarized in Table.

Table: Reaction of the Group 2 metals

Reagent	Reaction	Remarks
O ₂	2M + O ₂ → 2MO	All metals react at high temperature, Ba also forms BaO ₂
X	M + X → MX	All metals undergo this reaction
H ₂ O	M + 2H ₂ O → M(OH) ₂ + H ₂	Be reacts with steam, Mg with hot H ₂ O, others with cold H ₂ O
HCl	M + 2HCl → MCl ₂ + H ₂	All metals liberate hydrogen from acids
H ₂	M + H ₂ → MH ₂	M = Ca, Sr, Ba
N ₂	3M + N ₂ → M ₃ N ₂	All metal reacts at high temperature
X ₂	M + X ₂ → MX ₂ (X = F, Cl, Br, I)	Halides are formed by all metals

Solubility, Lattice Energy and Hydration Energy

Interesting trends are observed in solubility of many Group 2 compounds. The metal ions are easily hydrated eg. MgCl₂. 6H₂O, CaCl₂. 6H₂O, BaCl₂. 2H₂O. Because of small size and high nuclear charge, Group 2 cations have higher hydration energy than Group 1 cations (Table). The lattice energies of many compounds are high.

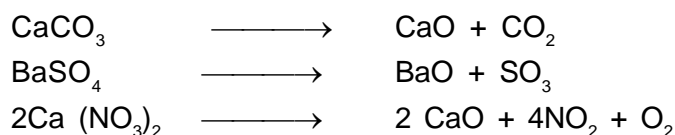
Table: Enthalpies of Hydration of M²⁺ ions & Lattice Energies of some compounds (KJ mol⁻¹)

	ΔH _{hyd} M ²⁺	MO	MCO ₃	MF ₂
Be	-2494	-	-	-
Mg	-1921	-3923	-3178	-2906
Ca	-1577	-3517	-2986	-2610
Sr	-1443	-3312	-2718	-2459
Ba	-1305	-3120	-2614	-2367

To predict the solubility of a substance in water it is necessary to know the relative values of hydration energy and lattice energy. Both hydration energy and lattice energy decrease with increase in size of metal ion. Decrease in lattice energy favours solubility whilst decrease in hydration energy disfavors solubility. If on descending the group the hydration energy decreases more rapidly than the lattice energy, the solubility decreases; this is observed in most cases, except for fluorides and hydroxides. The solubility of the sulphates decreases down the groups. This is because the sulphate anion is large and relatively small variation in size of the cation does not significantly alter the lattice energy. Due to small size Be²⁺ and Mg²⁺ have high hydration energies and BeSO₄ and MgSO₄ are soluble in water. CaSO₄ is slightly soluble whereas SrSO₄ and BaSO₄ are almost insoluble.

Thermal Stability of Oxo-salts

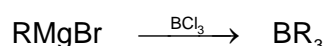
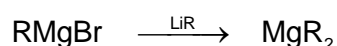
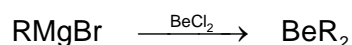
The thermal stability of the oxo salts like carbonates, sulphates and nitrates increase on moving down the group i.e. with increase in electro positive character. The carbonates, sulphates and nitrates all decompose give the corresponding oxides.



Organometallic Compounds

Beryllium and magnesium form an appreciable number of compounds with the M—C bond. The most important organomagnesium compounds are the Grignard Reagents represented by the formula RMgX (R= alkyl or aryl). They are made by the slow addition of an alkyl or aryl halide to a continuously stirred mixture of magnesium turnings in dry diethyl ether in the absence of air. These are versatile reagents and are widely used to synthesize a vast range of organic compounds like alcohols, aldehydes, ketones, carboxylic acids, esters and amines.

They are also good starting materials for synthesis of many organometallic compounds. Some examples are: -

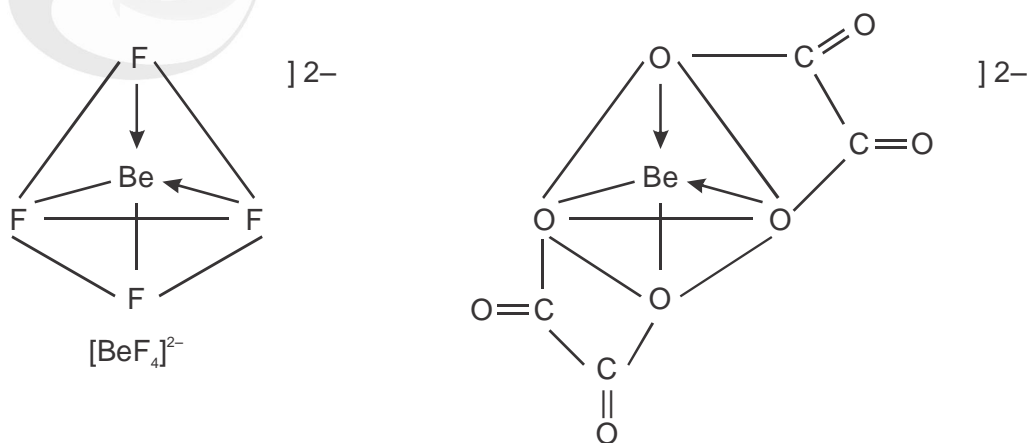


Grignard reagents cannot be stored. They are made and used as and when needed without isolating them.

All metals of this group form dialkyls and diaryls of the formula MR_2 . The dimethyl derivative of beryllium is dimeric in the vapour state and polymeric in the solid state having a chain structure like the hydrides. The bonding too is similar involving three-centred -two electron bonds.

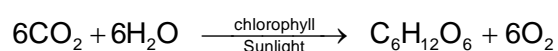
Complexes

Due to smaller size and higher nuclear charge, the Group 2 metals form more complexes compared to their Group 1 counterparts. Beryllium being smaller forms a greater number of complexes than the heavier members; the complexes are tetrahedral in structure with beryllium displaying a coordination number of 4. This is understandable as beryllium does not have vacant d orbitals and cannot expand its octet. Among the best known complexes of beryllium are the tetrafluoroberyllates $[\text{BeF}_4]^{2-}$ and dioxalatoberyllate $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$



In hydrated salts like $\text{BeCO}_3 \cdot 4\text{H}_2\text{O}$ and $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, beryllium exists as the tetraaquaberyllium ion, $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$.

The most important compound of magnesium containing organic species is chlorophyll, which is responsible for life on earth. It is a green pigment in plants that absorbs sunlight and makes energy available for photosynthesis. It converts carbon dioxide in presence of water to glucose in sunlight.



The magnesium is coordinated to four cyclic nitrogen atoms in a reduced porphyrin ring system (Fig.)

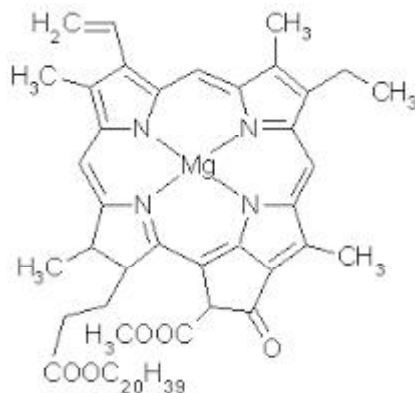


Fig.: Chlorophyll

Calcium and the lower members form complexes with strong complexing agents like ethylenediamine-tetraacetic acid (EDTA). EDTA forms complexes with coordination number six with both calcium and magnesium; this fact is utilized in estimation of hardness of water. The amount of Ca²⁺ and Mg²⁺ (responsible for harness) is determined by titration with EDTA. They also form complexes with polyphosphates that is used in water softening. Stable solid complexes with crown ethers and crypts have been isolated.

Biological Importance

Mg²⁺ and Ca²⁺ are important in biology. Mg²⁺ is an essential constituent of chlorophyll. Mg²⁺ ions are present in animal cells whilst Ca²⁺ ions are present in the extra cellular fluid. Calcium salts are quite insoluble and hence calcium is found in hard tissues — nails, bone and teeth. Mg²⁺ ions form a complex with ATP and are constituents of enzymes for reactions involving ATP. They are also involved for transmission of nerve impulses. Ca²⁺ ions are involved in blood clotting and muscle-contraction and maintain correct rhythm of the heartbeat.

2. P-BLOCK ELEMENTS

General Trend

- The elements in which the outermost electron enters one of the p-orbitals are referred to as p-block elements.
- There are six groups of p-block elements (Groups 13, 14, 15, 16, 17 and 18).
- The general outer electronic configuration is $ns^2 np^{1-6}$.
- The covalent radii and metallic character increase on moving down the group and decrease on moving across a period.
- The ionization enthalpy, electronegativity and oxidizing power increase across a period and decrease down the group.
- Unlike the s-block elements, which are all reactive metals, the p-block elements comprise of both metals and non-metals.
- Since the chemical behavior of metals and non-metals vary, a regular gradation of properties is not observed in p-block elements.

Difference in Chemical Behaviour of the First Element

It is interesting to note that the first member of each group differs in many respects from the other members. These differences are quite striking in Groups 13-16. The cumulative effects of small size, high electro-negativity and non-availability of d-orbitals for the first member are responsible for these differences.

Due to non-availability of d-orbitals, the first member can display a maximum coordination number of 4, whereas the others can display higher coordination numbers. Hence we come across species like $[\text{SiF}_6]^{2-}$, PCl_5 , PF_5 , SF_6 , but analogous species for carbon, nitrogen and oxygen are not known. The first member, by virtue of having small size and high electronegativity, can form $p\pi - p\pi$ bonds with itself or other elements e.g. $\text{C} = \text{C}$, $\text{C} \equiv \text{C}$, $\text{N} \equiv \text{N}$, $\text{C} = \text{O}$, $\text{C} \equiv \text{N}$, $\text{N} = \text{O}$ etc. The heavier members do not display $p\pi - p\pi$ multiple bonding but can show $p\pi - d\pi$ bonding.

Inert Pair Effect

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

Group-wise systematic study of p-block elements

Group-13

- The elements in this group are boron, aluminium, gallium, indium and thallium.
- The general electronic configuration is ns^2np^1 .
- Boron is a non-metal while the others are fairly reactive metals.

Physical Proportion

Some important physical constants of the Group 13 elements are shown in table.

Table: Physical properties of Group 13 Elements

Property	B	Al	Ga	In	Tl
Electronic Configuration	[He] $2s^22p^1$	[Ne] $3s^23p^1$	[Ar] $3d^{10}4s^24p^1$	[Kr] $4d^{10}5s^25p^1$	[Xe] $4f^{14}5d^{10}6s^26p^1$
Atomic radius (pm)	85	143	135	167	170
Ionization Energy (I) (KJmol ⁻¹)	801	578	579	558	589
Electronegativity	2.05	1.61	1.75	1.65	1.79
Melting Point (°C)	2180	660	29.8	157	304
Boiling Point (°C)	3650	2467	2403	2080	1457

The elements of Group 13 have smaller atomic radii and higher electronegativities as compared to s-block elements. However, these properties do not vary in a regular manner. The atomic radius of gallium (135 pm) is slightly less than that of aluminum (143 pm). This is because Ga follows the d-block elements and the inner core of Ga contains ten 'd' electrons that do not shield the nuclear charge efficiently. Therefore, the effective nuclear charge of Ga is more than that of Al so that the outer electrons are attracted towards the nucleus and the size is smaller than expected.

The electronegativity and ionization energy consequently are higher than expected. Similarly, the inclusion of fourteen *f* electrons on the inner core affect the size and ionization energy of Tl.

Oxidation states and Bond Type

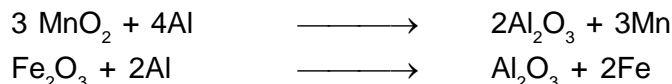
- The common oxidation states are +3 and +1.
- The stability of the +1 oxidation state, due to inert pair effect, increases down the group. Compounds of Ga (I), In (I) and Tl (I) are known Tl (I) compounds are more stable than Tl (III) and the latter are oxidizing in nature. Ga (I) compounds are reducing indicating that Ga (III) is more stable.
- The higher oxidation state is generally covalent. Boron is always covalent and does not form B^{3+} ion. Some compounds of Al and Ga like $AlCl_3$ and $GaCl_3$ are covalent in the anhydrous state.
- However the M^{3+} ions are associated with high hydration energies, which compensate the high ionization energies, and hydrated cations are known.

Chemical Proportion

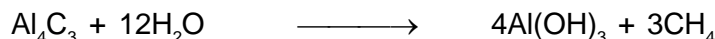
Boron's chemistry is so different from that of the other elements in this group that it deserves separate discussion.

Chemically boron is a non-metal, it has a tendency to form covalent bonds and displays similarities with silicon, which will be discussed later.

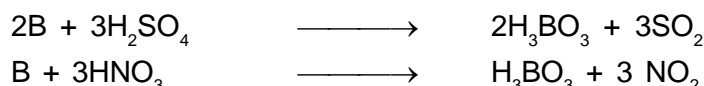
All elements except thallium when treated with halogens, oxygen or sulphur form halides (MX_3) oxides (M_2O_3) and sulphides (M_2S_3). Thallium forms TlX , Tl_2O and Tl_2S . Aluminum has a very high affinity for oxygen (enthalpy of formation of Al_2O_3 is $-1676 \text{ KJ mol}^{-1}$) and is used to remove oxygen from other metal oxides. This forms the basis of the Thermite process for extracting many metals from their oxides.



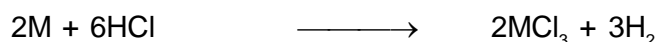
Boron and aluminium form nitrides by direct combination with nitrogen at very high temperature. They form carbides on heating with carbon. Aluminium carbide (Al_4C_3) on hydrolysis given methane.



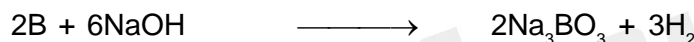
Boron carbide (B_2C_3) is a hard, high melting, inert compound used as an abrasive. Boron combines with many metals to form borides e.g. MgB_2 , VB , Fe_2B where it displays negative oxidation state. The reactions of the elements with acids differ. Boron reacts only with oxidizing acids to form boric acid



Boric acid is better represented as $B(OH)_3$ and does not contain replaceable hydrogen. The other elements react with dilute mineral acids to evolve hydrogen



Al is rendered passive with concentrated nitric acid. Boron liberates hydrogen when fused with alkali.



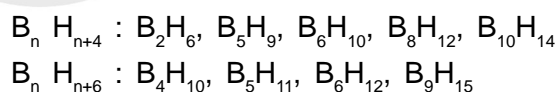
Aluminium and gallium dissolve in alkali to form tetrahydroxoaluminate (III) and tetrahydroxogallate (III) respectively.



Thus, we see that elements of Group 13 are quite reactive. We will now study some important compounds.

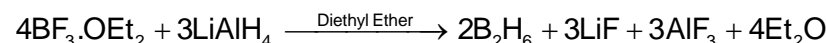
Hydrides

The elements form tri-hydrides (MH_3), the stability decreases on moving down the group. They are electron deficient compounds. Boron forms a series of volatile hydrides called boranes (by analogy with alkanes and silanes). They fall into two series:

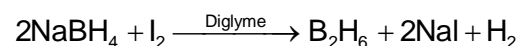


They are named by indicating the number of boron atoms. If two or more boranes have the same number of B atoms, then the H atoms are also specified, e.g. B_5H_9 and B_5H_{11} are named pentaborane – 9 and pentaborane – 11 respectively.

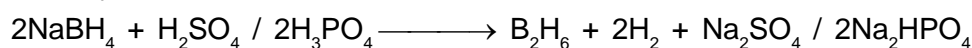
Diborane is the simplest and most extensively studied hydride. It is an important reagent in synthetic organic chemistry. It may be prepared by various ways:



Boron tri-fluoride etherate

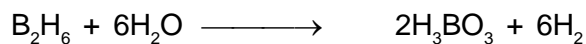


Sodium borohydride

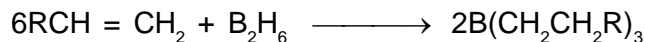


It is a colourless gas, which burns in air and is readily hydrolyzed.

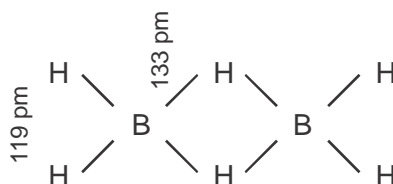




Diborane undergoes addition reaction with alkenes and alkynes in ether at room temperature to form organo-boranes.



This is known as hydroboration reaction. The structure of diborane is of great interest as it is an electron deficient compound having only twelve electrons, which are insufficient to form the required number of bonds. Each boron has three electrons and can form a BH_3 unit each but how will the two units be held together?



Diborane is found to have a bridge structure in which each B atom is bonded to two H atoms (called terminal H atom) by regular electron pair bonds. The resulting two BH_2 units are bridged by two H atoms (the bridge H atoms), which are at a plane perpendicular to the rest of the molecule and prevent rotation between the two B atoms. The structure has been confirmed by electron diffraction, infrared and Raman spectroscopic methods. Four hydrogen atoms are in an environment different from the other two – this is confirmed by Raman spectra and by the fact that diborane cannot be methylated beyond the tetra methyl derivative without breaking the molecule into BMe_3 .

The terminal B-H bond distances are the same as in non-electron deficient compounds. These are normal two centre - two – electron bonds (2c-2e). Electron deficiency is thus associated with the bridge bonds. The four bridge bonds involve only four electrons – a pair of electrons is involved in binding three atoms – B, H and B. These bonds are called three-centre-two-electron-bonds (3c-2e).

Each B atom is sp^3 hybridized giving four sp^3 hybrid orbitals. B has three valence electrons so three orbitals are filled singly. Two of the sp^3 hybrid orbitals on each B overlap with the 1s orbitals of H forming four 2c – 2e bonds.

Then one singly filled sp^3 hybrid orbital on one B atom, and one vacant sp^3 hybrid orbital on another B atom overlap with a singly filled 1s orbital on one H atom to form a bonding orbital shaped like a banana embracing all three nuclei. Another 3c – 2e bond is formed similarly (fig.)

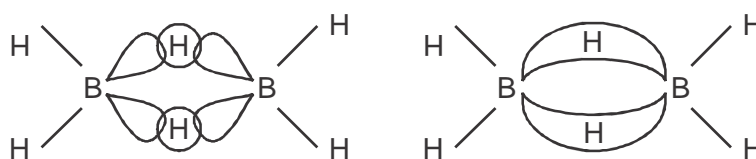


Fig. : Formation of banana-shaped three-centre-two-electron bond in Diborane

Most syntheses of the higher boranes involve heating B_2H_6 , sometimes with hydrogen. Most of the higher boranes are liquids but B_6H_{10} and $\text{B}_{10}\text{H}_{14}$ are solids. They were considered to be potential rocket fuels, but interest in this was soon diverted as it was found that on combustion they formed a polymer, which blocked the nozzles.

The higher boranes have an open cage structure (fig). The structures involve 2c – 2e bonds between B and H and B – B and 3c – 2e bonds involving B-H-B and B-B-B. Closed 3c-2e bonds of the type are also known.

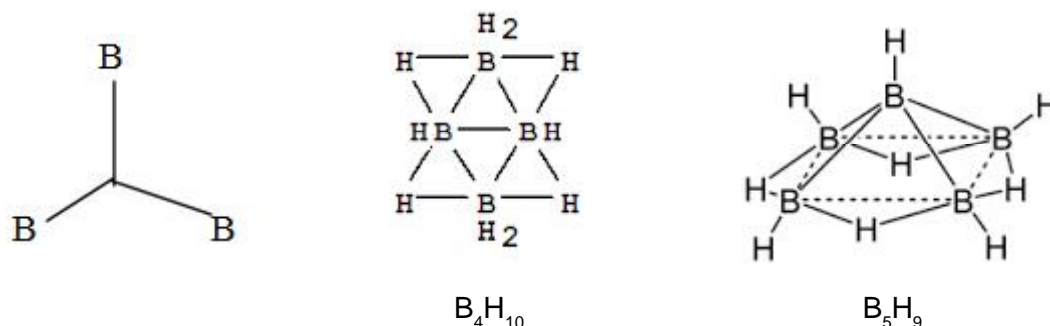
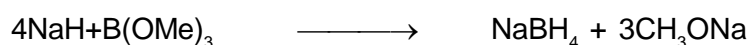


Fig. : Structures of Some Boranes

Borohydrides

Borohydrides like $NaBH_4$, $Al(BH_4)_3$ contain the tetrahydroborate (III) anion, BH_4^- . In these compounds boron has a complete octet and thus they are more stable than the boranes. Sodium borohydride is obtained by the reaction between sodium hydride and methyl borate.



Other borohydrides may be obtained from $NaBH_4^-$. The BH_4^- ion has a tetrahedral structure, $NaBH_4$ is a useful reagent used in reduction of aldehydes and ketones.

Hydrides of other members

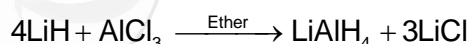
Other members of Group 13 form a few hydrides which are polymeric in nature e.g. $(AlH_3)_n$, $(GaH_3)_n$ and $(InH_3)_n$ and contain M-H-M bridges. Their stability decreases on moving down the group. $(AlH_3)_n$ is the best known and is prepared by the action of pure H_2SO_4 or $AlCl_3$ on lithium aluminium hydride in ether.



It is a colourless and thermally unstable solid and reacts violently with water.



A complex hydride of aluminium, lithium aluminium hydride is well known. It is prepared from lithium hydride and aluminium chloride in ether.



It is a powerful reducing agent and is widely used in organic chemistry. The borohydrides of aluminium, beryllium and the transition metals are covalent. In $Al(BH_4)_3$ each BH_4^- unit forms two hydrogen bridges while in $Be(BH_4)_2$ each BH_4^- unit forms three hydrogen bridges (Fig.)

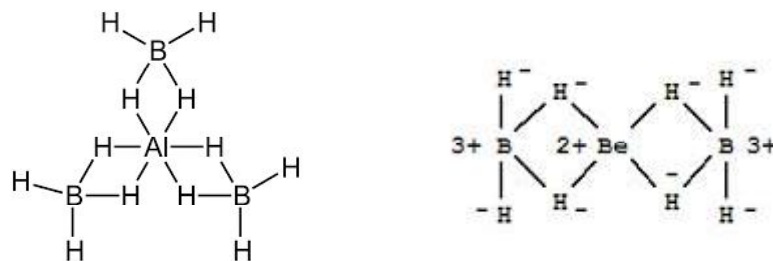
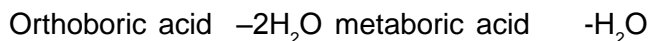
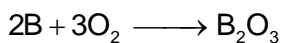


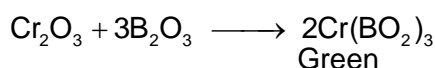
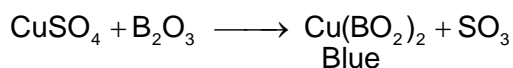
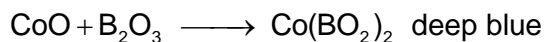
Fig: Structures of (a) $Al(BH_4)_3$ (b) $Be(BH_4)_2$

Oxides, oxoacids and hydroxides

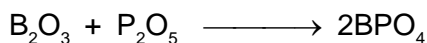
Trioxides of all elements (M_2O_3) are known. Thallium forms the monoxide. On moving down the group, the basicity of the oxide increases along with increase in metallic character of the element. Thus B_2O_3 is acidic, Al_2O_3 and Ga_2O_3 amphoteric while In_2O_3 and Tl_2O_3 are basic. Tl_2O is strongly basic; it dissolves in water forming $TlOH$, which is as strong a base as KOH . B_2O_3 is obtained by direct combination or by dehydration of boric acid.



Being the oxide of a non-metal it is acidic in nature. It is the anhydride of boric acid. When fused with metal oxides or salts it forms metaborates. The metaborates of transition metals have characteristic colours and form the basis of borax-bead test of identification of metals.



However when B_2O_3 is treated with strongly acidic compounds like phosphorus pentoxide, it is forced to behave as a base.

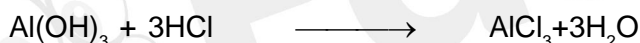


Aluminium oxide occurs in nature as bauxite and corundum and also as gemstones – ruby, emerald, sapphire etc. the colour is due to transition metal ions like iron, chromium, titanium etc. Anhydrous aluminium oxide exists in two forms- $\alpha\text{-Al}_2O_3$ and $\gamma\text{-Al}_2O_3$. $\gamma\text{-Al}_2O_3$ is obtained by dehydration of $Al(OH)_3$ below $450^\circ C$ and unlike $\alpha\text{-Al}_2O_3$ it is soluble in acids, absorbs water and is used in chromatography.

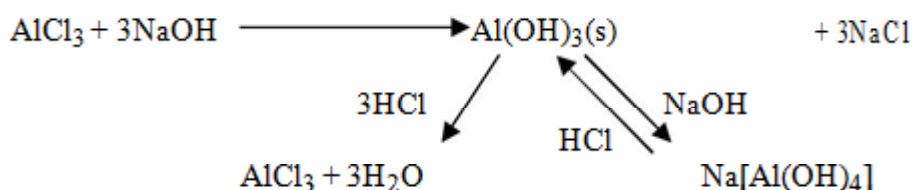


On heating to $1250^\circ C$ it changes to the α form which high melting, hard and inert.

Aluminium hydroxide is amphoteric and dissolves in both acids and bases.



In sodium hydroxide it forms sodium tetrahydroxoaluminate (III), commonly referred to as sodium aluminate. If this solution is acidified $Al(OH)_3$ is reprecipitated. The sequence of reactions may be represented as



The structure of sodium aluminate is complicated and varies with pH and concentration. Polymeric species with OH bridges are formed between pH 8-12. Above pH13, the tetrahedral $[Al(OH)_4]^-$ ion exists in dilute solutions while dimeric species are found in concentrated solutions (fig.)

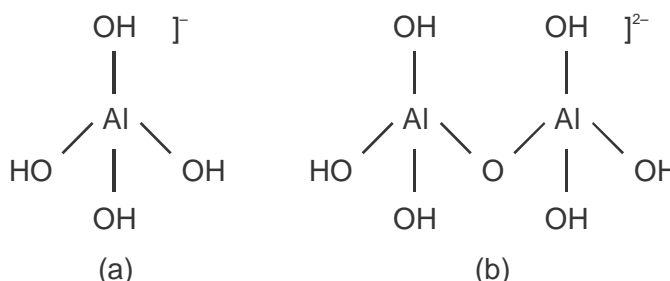


Fig: Hydro complexes of Aluminium at (a) pH8-12 (b) above pH 13

Ga_2O_3 and $\text{Ga}(\text{OH})_3$ are amphoteric like Al_2O_3 and $\text{Al}(\text{OH})_3$. In_2O_3 , Ti_2O_3 and Ti_2O are basic. When a metal exists in two oxidation states, the lower oxidation state is more basic. Thus TlOH is a stronger base than $\text{Tl}(\text{OH})_3$.

The most common oxo acid of boron is orthoboric acid which is a flaky solid having a two-dimensional layer structure (fig.). The BO_3 units are linked by hydrogen bonds and individual layers are held by weak forces, making the substance flaky and waxy.

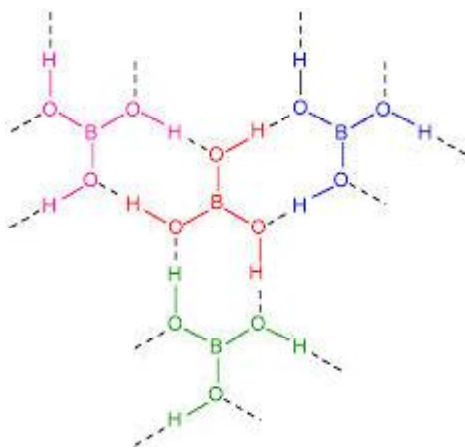
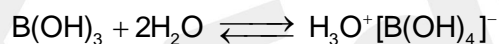
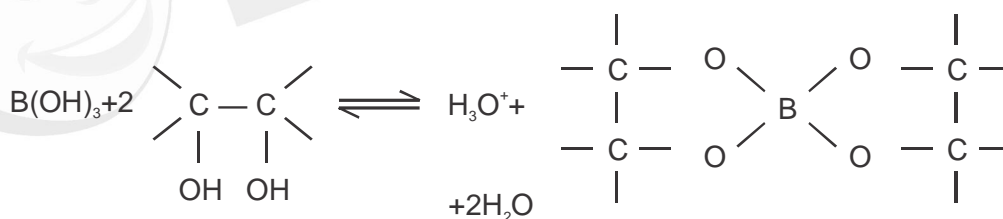


Fig: Hydrogen bonded structure of Boric acid

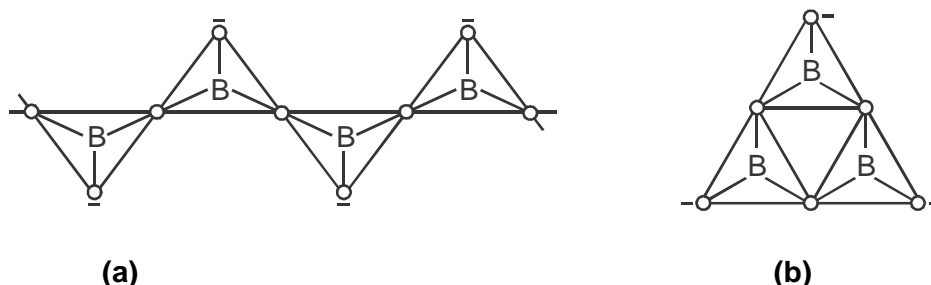
It is a very weak monobasic acid ($\text{pK}_a = 9.25$). It is not a proton donor but an OH^- acceptor - thus it acts as a Lewis acid. It is frequently represented as $\text{B}(\text{OH})_3$



Its acid strength is enhanced in presence of cis-diols like glycerol, mannitol and sorbitol. The cis-diols form stable complexes with the metaborate ion, this shifts the equilibrium to the right making boric acid ionize to its full capacity.



Salts of boric acid are called the borates. Orthoborates contain discrete BO_3^{3-} units where the boron atom is sp^2 hybridized. In metaborates the simple units join together to give chain and ring structure. The most common borate is borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (Sodium metaborate). The structures of some borates are shown in Fig.



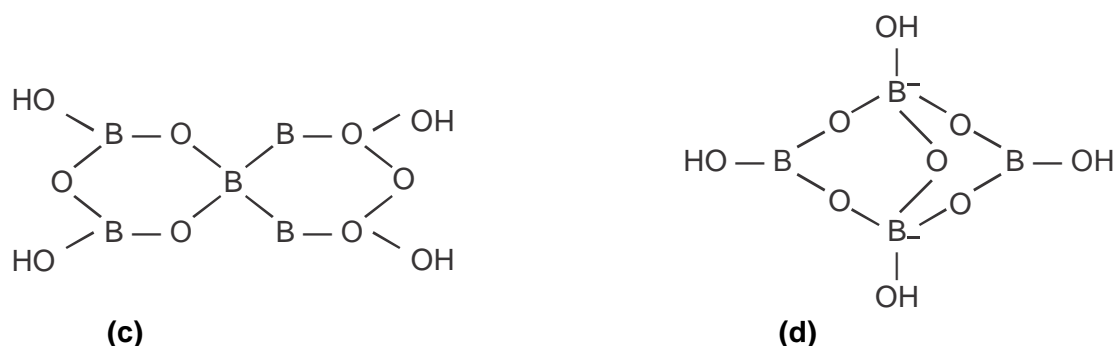
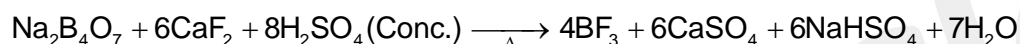
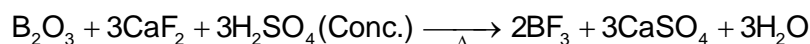


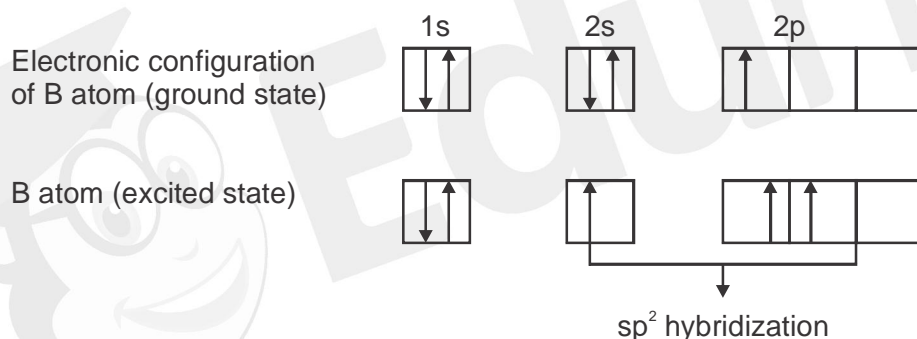
Fig. : Structures of (a) Metaborate chain (b) Metaborate ring
(c) Complex metaborate (d) Borax

Halides

Tri-halides (MX_3) are known for all elements except TlI_3 . Due to inert pair effect $Tl(I)$ is stable and $Tl(III)$ is oxidizing in nature. It oxidizes iodide to iodine. Thallium (III) chloride and bromide are also unstable. The halides of boron are covalent. BF_3 is the most important halide and is prepared by the following reaction:



BF_3 is an electron deficient compound and boron has a sextet of electrons around itself (instead of an octet) VSEPR theory predicts a planar triangle structure with bond angle of 120°



The B-F bond lengths (130 pm) are shorter than the sum of covalent radii of B (80 pm) and F (72pm). The bond energy is also higher than that of a single bond. This implies development of double bond character in the B-F bond. The vacant 2p orbital on B overlaps with one of the filled 2p orbital of fluorine to form a dative π bond ($p\pi - p\pi$ bond) fig.

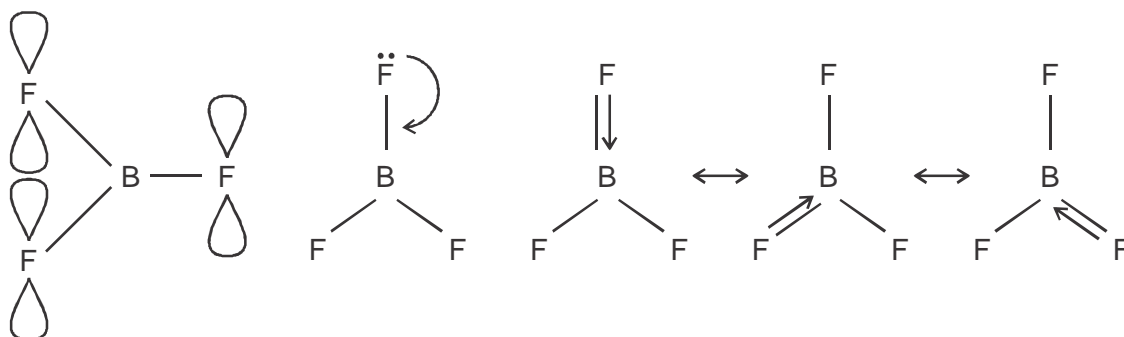
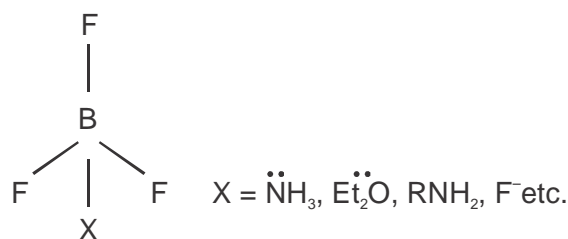


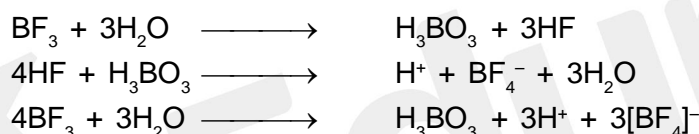
Fig. : Structure of BF_3

As a result of this π bond formation, the boron atom attains an octet of electrons and remedies the electron deficiency. All bond lengths are identical indicating resonance between three forms (fig.). As may be expected from their electron deficient nature, the tri-halides of boron act as Lewis acids and

accept electron pairs from Lewis bases like ammonia, amines and ethers. The electrons are donated to the vacant 2p orbital and the resultant adducts have tetrahedral structure.



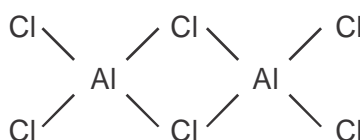
In these compounds the B-F bond length is longer than that in BF_3 as there is no vacant 2p orbital on B and the dative bond cannot be formed. Fluorine is the most electro-negative halogen and the order of acid strength of BX_3 is expected to be $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3 > \text{BI}_3$ but the reverse is true. These compounds act as Lewis acids because of their electron deficiency. We have seen that an internal compensation of electron deficiency is achieved by dative bond formation. In order to form a strong dative bond, it is essential that the orbitals of the combining atoms be matched in size so as to allow effective overlap. The 2p orbital of fluorine is matched in size with the 2p orbital of boron resulting in a strong bond and reduction of electron deficiency on boron. As the size of the halogen increases, the orbitals become larger and more diffuse to allow effective overlap with the 2p orbital of boron. Thus the electron deficiency on boron increases and the relative acid strength follows the order: $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$. The boron halides undergo hydrolysis; the hydrolysis of BF_3 is partial and the hydrolysis products, boric acid and hydrogen fluoride, combine to give fluoroborate ion



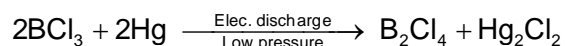
The other tri-halides are hydrolyzed completely to give boric acid and the corresponding hydrogen halide.



The fluorides of the other elements are ionic and high melting solids. The other halides are largely covalent; the trichlorides of aluminium and gallium exist as bridged dimers.

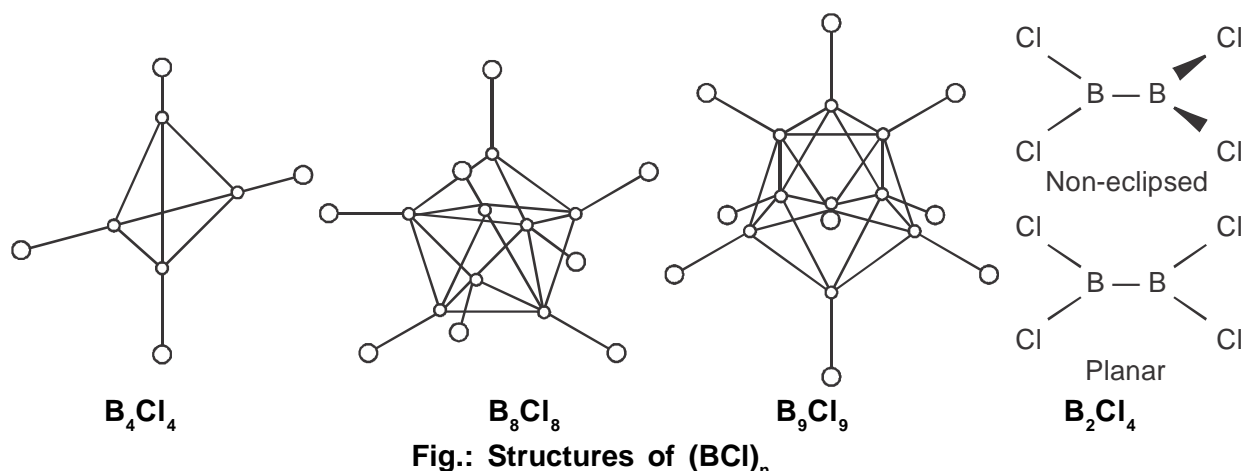


Each aluminium atom acquires an octet by accepting an unshared electron pair from the other AlCl_3 molecule. However, these dissolve in water, the high hydration enthalpy allows the formation of $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ and 3 Cl^- ions. Anhydrous aluminium chloride is used as a catalyst in Friedel-Craft's reaction. TlI_3 is an unusual compound where in Tl is present in +I oxidation state and it is bound to the linear triiodide ion (I_3^-). It is represented as Tl^+I_3^- . Boron forms dihalides of the formula B_2X_4 , the dichloride is obtained from BCl_3



It exists in non-eclipsed and planar conformations with free rotation about the B-B bond (fig.) Gallium and indium form di-halides, GaCl_2 and InCl_2 they are better represented as $\text{M}^+ [\text{MCl}_4]^-$, i.e. they contain M(I) and M(III).

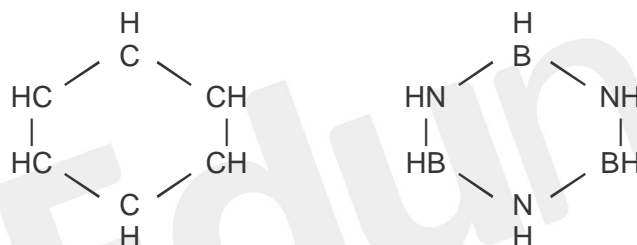
Boron forms some monohalides which are polymeric and are represented as $(\text{BX})_n$, Chlorides with $n=4, 8, 9, 10, 11$ and 12 are reported, B_4Cl_4 , B_8Cl_8 are crystalline solids having closed cage of boron atoms (fig.)



Each boron atom is bonded to three other boron atoms and one chlorine atom by multi-centred bonding.

Boron-nitrogen compounds

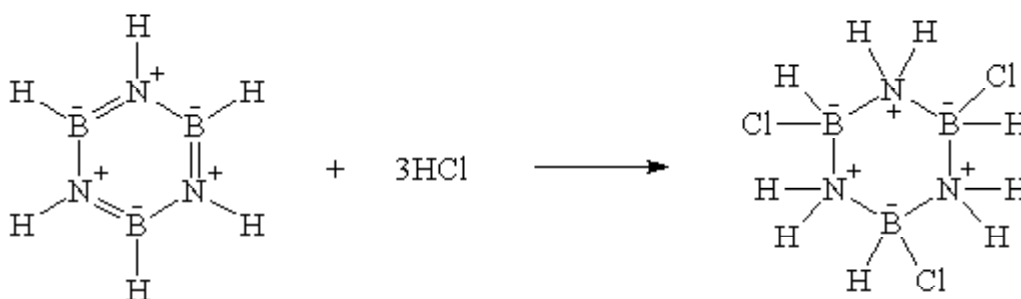
The B-N bond is isoelectronic with the C-C bond and parallels between boron-nitrogen compounds with organic compounds are known. One of the best known of these pairs is benzene and the isoelectronic borazine also known as inorganic benzene, B₃N₃H₆



The compounds are structurally similar and also exhibit similar physical properties. However, the chemical properties are widely different. The nature of the π -bond in borazine and benzene differ. In benzene the π -bond is formed by sideways overlap of the 2p orbitals of carbon atoms and the two atoms involved in π bond formation do not differ in electro negativity. In borazine the nitrogen atom donates an unshared electron pair to a vacant p orbital on B, thereby forming a π bond



The polarity of the B-N bond is less than what is expected on basis of electro negativity difference between boron and nitrogen. This is because during σ -bond formation the electron density shifts towards the more electronegative atom, nitrogen while the reverse happens during π bond formation. The molecule however is polar and undergoes addition reactions.



This is in sharp contrast to benzene, which does not undergo addition reaction.

Another interesting compound is boron nitride, BN. Like carbon it exists in two forms – a diamond – like form and another form like graphite, which comprises of six-membered rings fused together (Fig.)

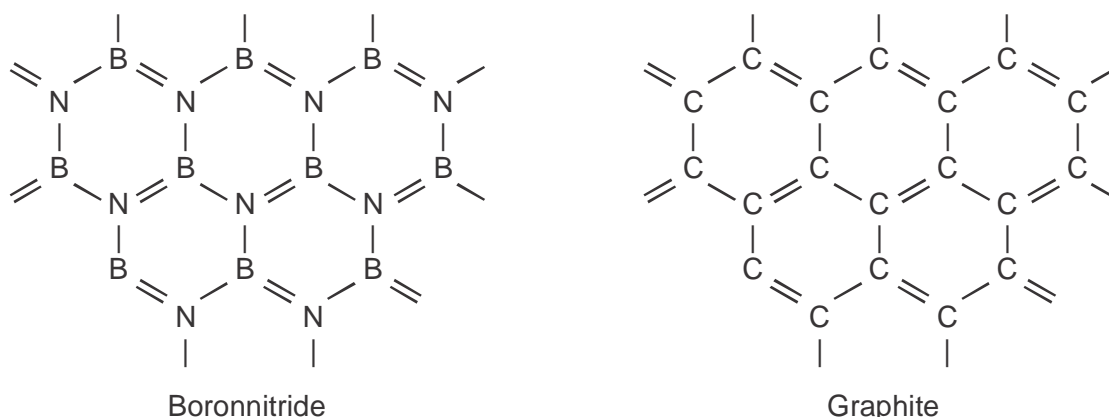
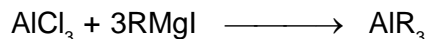


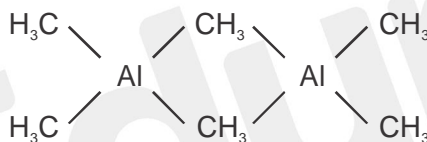
Fig. : Similarity in structures of Boron Nitride and Graphite

Organometallic compounds

Tri-alkyl and tri-aryl derivatives of boron, aluminium, gallium and indium are known. The tri-alkyl derivatives of aluminium are important and are obtained by treating aluminium chloride with the appropriate Grignard reagent.



These are electron deficient compounds and exists as bridged dimers



The terminal Al-C bond lengths are shorter than the bridge Al – C bond lengths. The bridge bonds are three – centre – two – electron bonds.

Aluminium tri-ethyl is referred to as Ziegler catalyst and is used to carry out polymerization of ethene to give polythene. Polymerization is quicker if TiCl_4 (Natta Catalyst) is used along with Ziegler catalyst and the reaction does not require high pressure.

Complex formation

The Group 13 elements form complexes more readily than the s-block elements. Because of lack of d orbitals, boron exhibits a coordination number of 4 and forms tetrahedral complexes like NaBH_4 , HBF_4 , $\text{BF}_3 \cdot \text{NH}_3$ etc. The lower members form octahedral complexes also e.g. $[\text{AlCl}_6]^{2-}$, $[\text{GaCl}_6]^{2-}$ etc.

Apart from complexes, aluminium forms double sulphates (alums) of the general formula $\text{M}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ where M is a monovalent metal or ammonium eg. $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ is potash alum. Aluminium can be replaced by cations of comparable size and charges like iron, chromium etc.

Group 14

The elements in this group range from a non-metal, carbon to the metals tin and lead, with the intervening element – germanium showing semi metallic behaviour. Carbon has been known from pre history as the charcoal resulting from partial combustion of organic matter. Carbon is an essential constituent of all living matter. Silicon is the second most abundant element in the earth's crust; tools made of flint (a form of SiO_2) were used in the Stone Age. Tin and lead have also been known since ancient times. Germanium was a "missing element" in Mendeleev's periodic table. He named this element as "ekasilicon" and predicted its properties that later matched with those of germanium. All the elements have an outer electronic configuration of $ns^2 np^2$ and some important physical constants are summarized in Table.

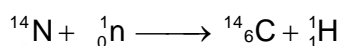
Table: Physical properties of Group 14 elements

Property	C	Si	Ge	Sn	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
Covalent radius (pm)	77	118	122	140	146
Ionization Energy (I) (KJmol ⁻¹)	1086	786	762	709	716
Electronegativity	2.54	1.92	1.99	1.82	1.85
Melting Point (°C)	4100	1420	945	232	327
Boiling Point (°C)	Sublimes	3280	2850	2623	1751
M – M bond energy (KJmol ⁻¹)	348	297	260	240	-

The general trends observed in size and ionization energy follow the same order as in group 13.

The main isotope of carbon present in the earth is ¹²C (in the modern system of atomic mass this is taken as the standard), two other isotopes ¹³C and ¹⁴C are also known. ¹³C NMR spectroscopy is common for characterization of organic compounds.

¹⁴C is obtained from nitrogen in the atmosphere by thermal neutrons in presence of cosmic radiation.



The ¹⁴C produced is oxidized to ¹⁴CO₂ which is radioactive and this alongwith non-radioactive CO₂ is incorporated into plants by photosynthesis. The ratio of ¹⁴C to ¹²C in a living plant is the same as that in the atmosphere. When the plant dies the amount of ¹⁴C diminishes by radioactive decay and this loss is not compensated by assimilation of ¹⁴CO₂ from the atmosphere. The ratio of ¹⁴C to ¹²C decreases. The half-life of ¹⁴C is 5730 years and by measuring the remaining amount of ¹⁴C it is possible to know the age of the substance (i.e. time of its death). This is called "radiocarbon dating".

Allotropy of Carbon

Until 1985, only two allotropes of carbon were known – diamond and graphite. Diamond is the hardest substance known, having a very rigid structure. Each carbon atom is sp³ hybridized and linked to four other atoms. Graphite has a layer – structure in which weak van der Waal's forces hold individual layers of fused six membered rings together. The carbon atoms are sp² hybridized and out of four valence electrons, three are involved in σ-bond formation the fourth electron is involved in delocalized π-bonding. The layers slide over one another and the π electrons move within each layer making graphite a conductor of electricity and conferring lubricating properties. Some physical properties in table.

Table: Physical properties of Diamond and Graphite

Property	Diamond	Graphite
Density (gcm ⁻³)	3.51	2.26
Electrical Resistivity (Ωm)	1 × 10 ¹¹	1.3 × 10 ⁻⁵
C-C distance (pm)	154.4	141.5 (Intra Layer) 335.4 (Inter Layer)

At room temperature graphite is thermodynamically more stable and can be converted to diamond at high pressure and temperature. Artificial diamonds are prepared from graphite.

A fascinating discovery was the synthesis of spheroid carbon- cage molecules called fullerenes. These were first prepared by evaporation of graphite using laser. A more practical method is to heat graphite in an electric arc in an inert atmosphere (helium or argon). A sooty material so formed consists of C_{60} with smaller amounts of C_{70} and other fullerenes containing even number of carbon atoms. Unlike diamond and graphite fullerenes dissolve in organic solvents like toluene. C_{60} is the most stable fullerene containing twenty six-membered rings and twelve five-membered rings. The six- membered rings are fused to other six membered and five- membered rings while five- membered rings are connected to only six- membered rings(Fig.). Two types of bond lengths are noted, the C-C bond lengths at fusion of two six membered rings is 135.5 pm while the C-C distances at fusion of five and six membered rings is 146.7 pm. Thus there is greater π character in the bonds obtained by fusion of six membered rings.

The smallest known fullerene is C_{20} obtained from the hydrocarbon $C_{20}H_{20}$ by a two- step reaction. First, the hydrogens are replaced by bromine, this is followed by debromination. The Nobel Prize for Chemistry (1996) was shared by R.F. Curl, H. Kroto and R.E. Smalley for the discovery of fullerenes.

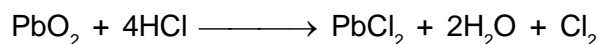
Silicon and germanium predominantly crystallize in diamond structure and both are semiconductors. Tin exists in a diamond form (α) and metallic form (β) while lead is metallic.



Fig. : Diamond, Graphite, Fullerenes

Oxidation states and Bond Type

The commonly observed oxidation states in this group are +4 and +2. Carbon and silicon are generally tetravalent but on descending the group the stability of the +4 oxidation state decreases due to inert pair effect. The +2 oxidation state becomes important progressively and lead is predominantly divalent. Therefore $Pb(IV)$ compounds like $PbCl_4$ and PbO_2 are highly oxidizing and PbO_2 may oxidize hydrochloric acid to chlorine.

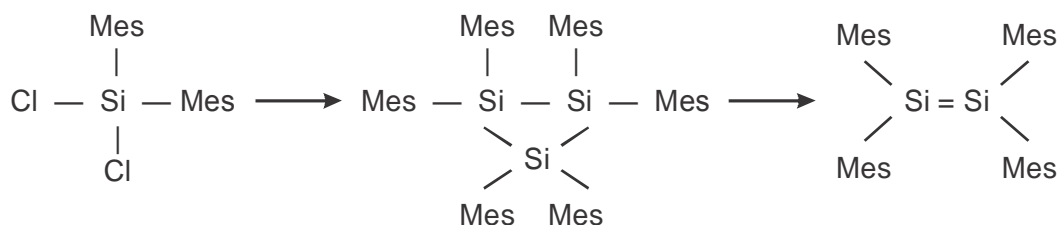


The lower oxidation state is more ionic as M^{4+} is smaller than M^{2+} and covalency is favoured by large charge on cation and small size. In tetravalent compounds the Group 14 element is sp^3 hybridized. Carbon has greater electronegativity and may form carbide ion, C^{4-} and C_2^{2-}

Catenation and multiple bond formation

Carbon has a remarkable property of forming long chains and rings when bound to itself. This is called catenation and is attributed to the strength of the C-C bond, The M – M bond strength decreases down the group and tendency for catenation also decreases. Carbon also forms $p\pi - p\pi$ bonds with itself and other electronegative elements e.g. $C=C$, $C\equiv C$, $C=O$, $C=S$ and $C\equiv N$ linkages are known. The other elements do not form such bonds. The reluctance of the silicon atom to form multiple bonds is revealed by the fact that silicon adopts a diamond – like structure and not graphite – like structure; CO_2 is a gas comprising of discrete stable $O=C=O$ units whilst SiO_2 is a high-melting solid having a net-work three-dimensional structure of Si-O-Si linkage.

Chemists have been exploring the tendency of the silicon atom to form multiple bonds. Transient reaction species containing the Si = C bond have been known since 1966 and the first such species, $\text{Me}_2\text{Si} = \text{CHMe}$ was isolated a decade later. In view of the extensive chemistry of alkenes it was natural to search for analogous compounds containing the $> \text{Si} = \text{Si} <$ bond. The first such compound, tetramesityldisilene, was isolated in 1981 as orange crystals following photolysis of cyclotrisilane.



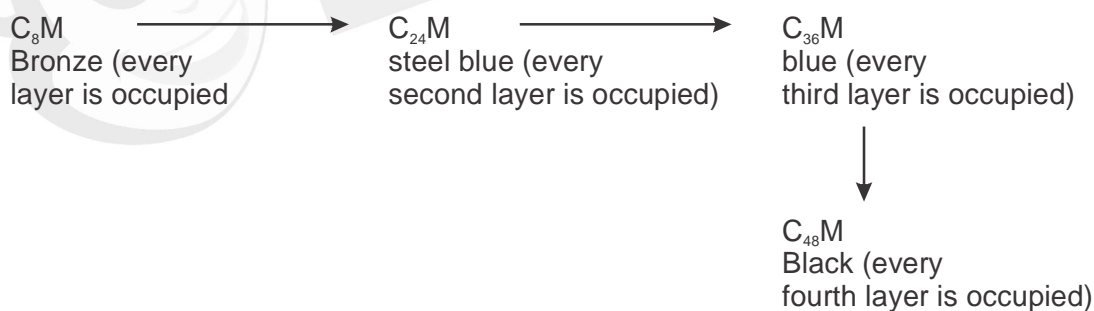
where, Mes = Mesityl

The Si = Si distance in such compounds lies in the range 214 to 216pm considerably shorter than the normal single bonded Si—Si distance. Disilenes are chemically very reactive and it is possible to add reagents like halogens, HX and EtOH across the Si = Si double bond. The 3p orbitals of Si are larger and more diffused than the 2p orbitals of C; therefore the π -bond formed between the Si atoms is weaker than that between the C atoms.

Intercalation compounds

The structure of graphite indicates loosely bound layers separated by a large distance. Many molecules can be inserted in the space between the layers forming intercalation compounds of varying composition. The interlayer distance increases in these compounds. If the graphite sheets remain flat, then the new compound retains the structure and conductivity of graphite. If the attacking species add electrons, the conductivity increases.

Heating graphite 300° C in presence of vapors of K, Rb and Cs gives bronze coloured compounds C_8M , on heating further at reduced pressure, some of the metal is lost and intercalation compounds are formed which vary in colour, depending on the number of layers invaded by the metal.



Intercalation compounds of graphite are known with FeCl_3 , chlorine, bromine, some metal oxides and sulphides. The intercalated compounds exhibit interesting properties.

Chemical properties

The chemical reactivity increases down the group. Some reactions of Group 14 elements are shown in table.

Table : Some Reactions of Group 14 Elements

HCl (hot, concentrated)	$M + 2HCl \rightarrow MCl_2 + H_2$	M = Sn, Pb
H_2SO_4 (hot, concentrated)	$M + 2H_2SO_4 \rightarrow MO_2 + 2SO_2 + 2H_2O$	M = Sn, Pb, C slow for Ge
HNO_3 concentrated	$3M + 4HNO_3 \rightarrow 3MO_2 + 4NO + 2H_2O$ $3Pb + 2HNO_3 \rightarrow 3PbO + 2NO + 4H_2O$	M = Ge, Sn
NaOH (aq)	$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$	-
O_2 / air (heat)	$M + O_2 \rightarrow MO_2$ $2Pb + O_2 \rightarrow 2PbO$	M=C, Si, Ge, Sn
Cl_2 (heat)	$M + 2Cl_2 \rightarrow MCl_4$ $Pb + Cl_2 \rightarrow PbCl_2$	M=C, Si, Ge, Sn

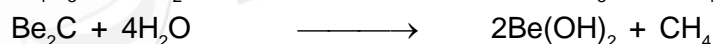
Compounds

Carbides

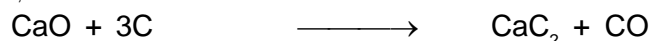
Compounds of carbon with a less electronegative element are called carbides. This excludes binary compounds of carbon with N, P, O, S and halogens. Depending on the bond – type carbides are classified as – ionic, interstitial or covalent.

(a) Ionic (salt – like) carbides

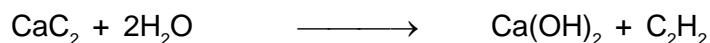
These are formed with electropositive metals and may contain different carbide anions. The bonding is predominantly ionic with some covalent character. The most well characterized carbide ions are C^{4-} and C_2^{2-} . Species containing C^{4-} are represented by Al_4C_3 and Be_2C . These are called methanides as they hydrolyze to give methane.



The C_2^{2-} ion is found in CaC_2 , carbides of Cu, Ag, Au and some lanthanides. The most important carbide is CaC_2 , which is obtained by strongly heating lime with coke. It is structurally similar to NaCl (Fig.)



It is called acetylide as it yields ethyne on hydrolyses



The C_3^{4-} ion is found in Mg_2C_3 , which yields propyne ($H_3C - C \equiv CH$) on hydrolysis.

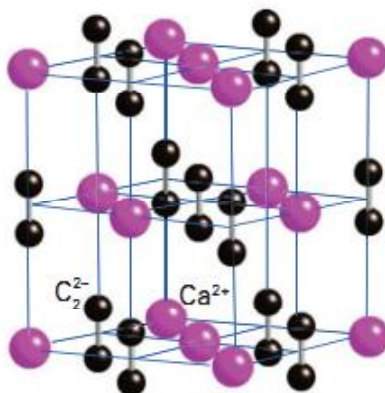


Fig: Structure of Calcium carbide

(b) Interstitial carbides

They are formed with transition metals like Cr, Mn, Fe, Co, Ti and W and with some lanthanides. They are generally high melting and hard. The C atoms occupy octahedral voids in the metal lattice and do not affect the conductivity of the metal. The ability of carbon atoms to enter the metal lattice without distortion indicates that the interstices should be fairly large (possible if atomic radius of metal > 135 pm). For smaller metals i.e. those of the 3d series, inclusion of carbon results in distortion of the lattice, giving rise to complicated structures.

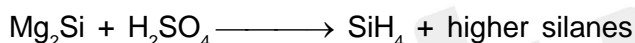
(c) Covalent carbides

These are formed when carbon combines with an element of comparable electro-negativity e.g. SiC and B₄C. SiC (Carborundum) is very hard, un-reactive and a good refractory material. B₄C is better represented as B₁₂C₃. They are hard, infusible and inert macromolecules.

Hydrides

All the elements form covalent hydrides but the number of hydrides formed, their stability and ease of formation decreases down the group. Carbon forms a large number of hydrides involving chains, rings and multiple bonds between carbon atoms. These hydrides form the basis of organic chemistry.

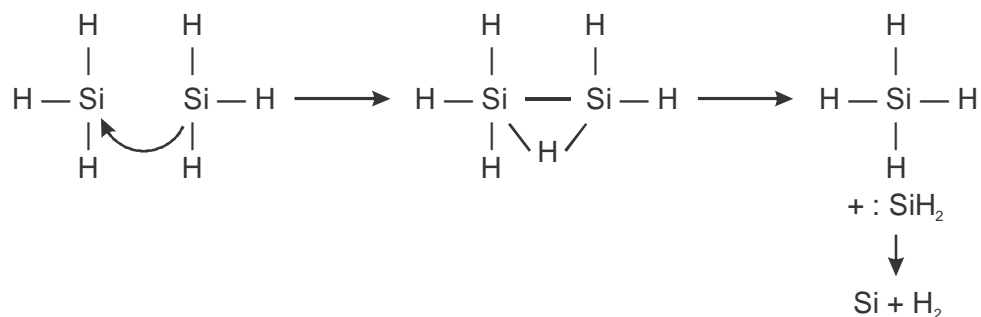
Silicon forms a limited number of hydrides, the silanes (represented by the formula Si_nH_{2n+2}). Monosilane, SiH₄, is the most stable and is tetrahedral, like methane. Silanes containing up to eight silicon atoms have been synthesized but their stability decreases with increase in chain – length. The hydrides are prepared as a mixture when magnesium silicide is treated with dilute acids.



Monosilane can be prepared by reaction of SiCl₄ with lithium aluminium hydride or sodium hydride



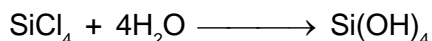
Silanes are more reactive than the corresponding alkanes. Various reasons are attributed to this. The Si – Si bond is slightly weaker than the C – C bond (bond energies are 340 & 368 KJmol⁻¹ respectively). The Si – H bond is weaker than the C – H bond (bond energies 393 & 435 KJmol⁻¹). The electronegativity values of Si, C and H are 1.8, 2.5 and 2.1 respectively so the polarity of Si – H and C – H bonds differ and are depicted as Si – H and C – H. Silicon is more susceptible to nucleophilic attack than carbon as the larger size of silicon provides greater surface area for the nucleophile to attack. Silicon has vacant low-lying d orbitals, which can accept electron pairs from nucleophiles and form reactive intermediates. Silanes decompose to give silicon of high purity by elimination of SiH₂. The following mechanism has been suggested.



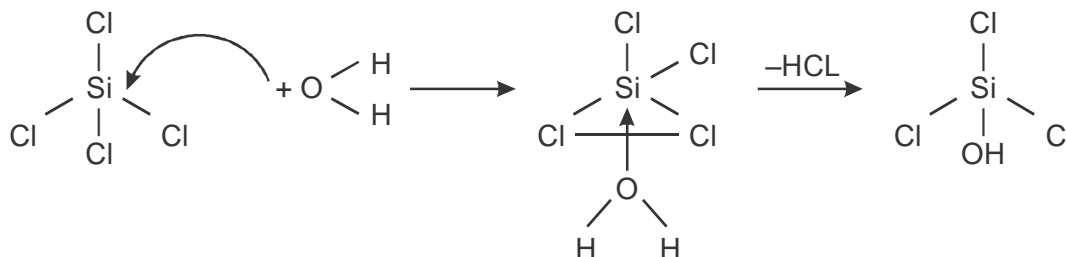
Germanes containing up to five germanium atoms and represented by the formula Ge_nH_{2n+2} are known. They are less stable than the silanes. Tin forms only two hydrides SnH₄ and Sn₂H₆ while lead forms the unstable PbH₄.

Halides

Tetra-halides (MX_4) of all elements are known; but Pb (IV) readily oxidizes iodide and hence the compound PbI_4 is not known. The stability of the tetra-halides decreases down the group. The fluorides, by virtue of high electronegativity of fluorine, are the most ionic. SnF_4 and PbF_4 are high melting solids; the others are covalent, tetrahedral and volatile. The halides of carbon are inert towards water, however the halides of silicon readily hydrolyze.



The hydrolysis proceeds via an intermediate where silicon has a coordination number of five.



This process continues till Si-OH bonds replace all the Si-Cl bonds. Since carbon does not have d orbitals it cannot form such an intermediate and therefore tetra-halides of carbon do not hydrolyze.

Germanium, tin and lead form both tetra-halides and di-halides. The tetra-halides have a tendency to hydrolyze, but the hydrolysis can be suppressed by adding the appropriate halogen acid

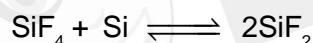


The halides of Si, Ge, Sn and Pb can increase the coordination number to 6 by forming complexes like $[SiF_6]^{2-}$, $[SnCl_6]^{2-}$ etc where the vacant d orbitals are used.

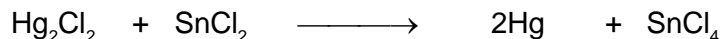
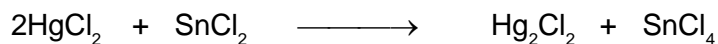
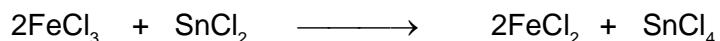
There is an increase in stability of dihalides on moving down the group



SiF_2 can be made at high temperature by the reaction



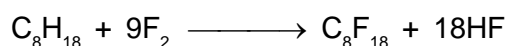
Divalent germanium halides are stable. GeF_2 is polymeric having fluorine bridges. Tin (II) halides are well – characterized and the most important one is $SnCl_2$. it undergoes partial hydrolysis and is soluble in organic solvents. It is a mild reducing agent as shown by the following reactions:



Lead (II) halides are the most stable di-halides of this group. In fact, lead is the only element of this group with well- defined cation, Pb^{2+} . All lead halides are insoluble in water. In qualitative analysis Pb (II) is precipitated in group I of qualitative analysis as $PbCl_2$ and is confirmed as the yellow PbI_2 (s).

Fluorocarbons

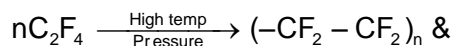
Fluorocarbons are the equivalents of hydrocarbons where some or all hydrogen atoms are replaced by fluorine eg. CF_4 , C_2F_4 etc. Replacement of hydrogen by fluorine increases the thermal stability and chemical inertness as the C-F bond is much stronger than the C-H bond (bond energies 489 and 414 $KJ\ mol^{-1}$). The fluorocarbons are prepared by treating the corresponding hydrocarbons with fluorine.



Fluorinating agents like CoF_3 , AgF_2 and MnF_3 may also be used. Fluorocarbons of chain length of several hundred-carbon atoms are known. They are resistant to attack by acids, alkalis, oxidizing and

reducing agents. They are attacked by molten sodium. On burning they split at the C-C bond and not at C-F bond.

The best-known fluorocarbon is polytetrafluoroethylene (Teflon).



Teflon has a low coefficient of friction. It is thermally and chemically inert and a good insulator. It is used as a coating material in non-stick utensils, razors and bearings.

Mixed chlorofluorocarbons eg. CFCl_3 , CF_2Cl_2 and CF_3Cl are called Freons. They are inert and non-toxic and widely used as refrigerants and propellants in aerosol. Their use in aerosols has been banned as they cause considerable environment damage. They persist unchanged on the atmosphere for a considerable period of time and are known to damage the ozone layer. Freons are also responsible for the 'greenhouse effect' alongwith carbon dioxide.

Oxides

The oxides of carbon involve $p\pi-p\pi$ bonding between carbon and oxygen. The two important oxides of carbon are carbon monoxide (CO) and carbon dioxide (CO_2). Both are colourless and odourless gases. Carbon monoxide is obtained when carbon is burnt in a limited supply of air and by the dehydration of formic acid by concentrated sulphuric acid



It is a neutral oxide of carbon and is highly toxic as it binds to haemoglobin in preference to oxygen. Thus haemoglobin cannot act as an oxygen carrier and oxygen is not available to tissues.

Carbon monoxide evolves a considerable amount of heat on burning and is an important fuel,



Producer gas, water gas and coal gas contain carbon monoxide. Carbon monoxide is an important ligand and forms carbonyl complexes with many transition metals in low oxidation states e.g. $\text{V}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, $\text{Co}_2(\text{CO})_8$, $\text{Ni}(\text{CO})_4$ etc. The metal-carbon σ -bond involves donation of an electron pair from CO to the metal, $\text{M} \text{C} \equiv \text{O}$. This σ -bond is strengthened by formation of a back bond by overlap of filled orbital of the metal with the vacant π^* molecular orbital of carbon monoxide. In carbonyls CO acts as both an electron donor i.e. Lewis base (σ -bond formation) and electron acceptor i.e. Lewis acid (π -bond formation). A schematic representation of the orbital overlaps leading to M – CO bonding is depicted in Fig.

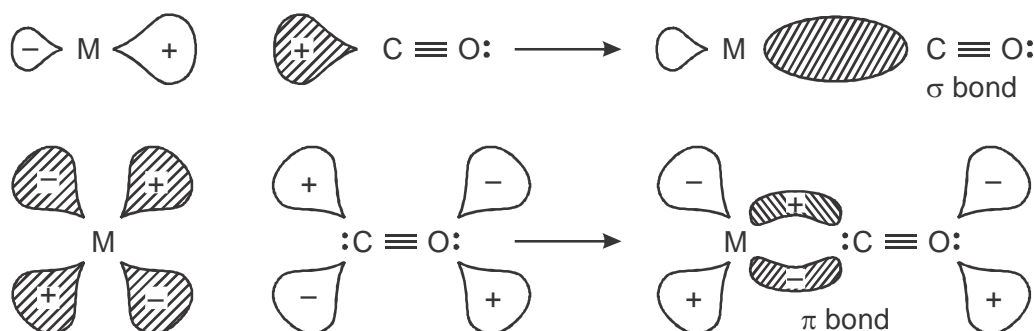
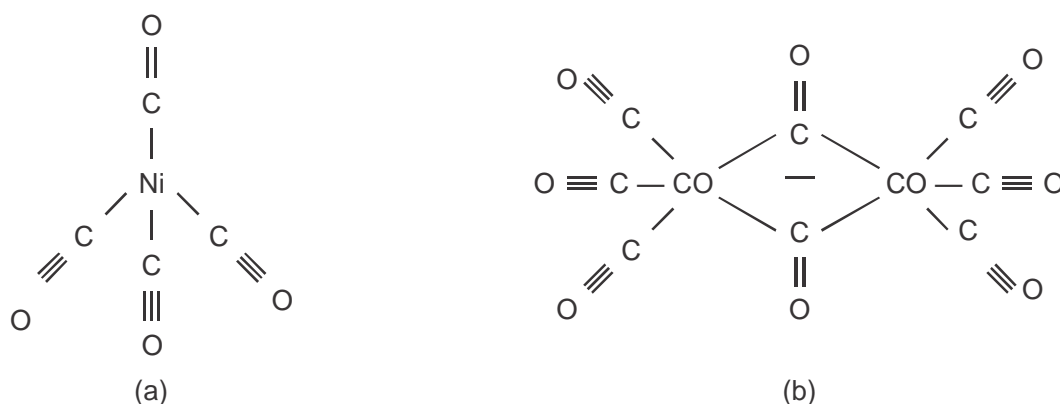


Fig: Schematic representation of Orbital overlaps in metal carbonyls. The σ -bond is formed by overlap of filled orbital on CO with vacant orbital on M. The π -bond involves overlap of filled orbital on M with vacant orbital on CO.

Carbon monoxide acts as a terminal ligand when bonded to only one metal, the $\text{M}-\text{C} \equiv \text{O}$ bond is linear. It can also act as a bridging ligand and be bonded to two different metal atoms simultaneously. **(Fig.)**



**Fig: Structures of (a) $\text{Ni}(\text{CO})_4$ – only terminal CO groups are present
(b) $\text{Co}_2(\text{CO})_8$ – having both terminal and bridging CO groups**

Carbon dioxide is familiar as a compound in the earth's atmosphere. It has been recognized as a "greenhouse gas", responsible for global warming. It can be liquefied under pressure and the solid form is called "dry ice" which is used as a fire extinguisher. It is an acidic oxide of carbon. Plants to synthesize carbohydrates in the process of photosynthesis use carbon dioxide.

Carbon dioxide exhibits unique properties and behaves as a supercritical fluid above its critical temperature and pressure (31.1°C and 73 atm respectively). It expands to fill a container like a gas but the density is like that of a liquid. Supercritical carbon dioxide is becoming an important commercial and industrial green solvent as it is non-toxic and is a byproduct of other industrial processes. It is used as a solvent in "dry cleaning" of textiles instead of the toxic tetrachloroethylene. It is also used as an extraction solvent in the perfumery industry. The relatively low supercritical temperature and reactivity of carbon dioxide allows the fragrance compounds to be extracted without denaturing and thereby not affecting their odours. Due to its non-toxicity coffee manufacturers use it as a decaffeinating solvent.

Si, Ge, Sn and Pb all form dioxides (MO_2). Silicon dioxide (silica) exists as an infinite three-dimensional network of silicon and oxygen atoms linked by a single bond. Each silicon atom is tetrahedrally surrounded by four oxygen atoms (fig.). The network structure of SiO_2 arises due to silicon's inability to form $p\pi-p\pi$ bond. Silica is a high-melting solid existing in three crystalline forms—quartz, tridymite and cristobalite.

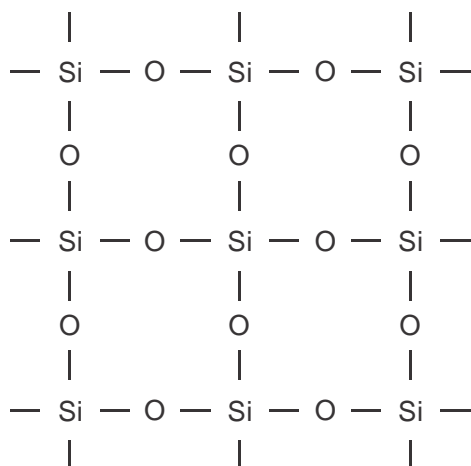
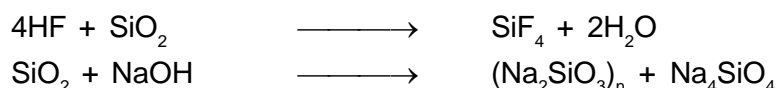


Fig: Two-dimensional structure of SiO_2

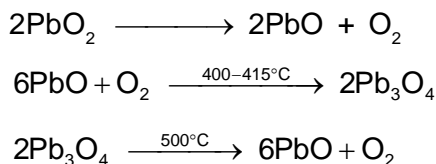
Silica is very unreactive. It reacts only with HF and caustic alkali.



The last reaction illustrates its acidic nature. Quartz is important as a piezo-electric material and is used in gramophone pick-ups, cigarette and gas-lighters and for making crystal oscillators in radios and computers.

The dioxides of Ge, Sn and Pb are solids and the basicity increases on moving down the group. GeO_2 is acidic, SnO_2 amphoteric and PbO_2 basic. PbO_2 contains Pb(IV) and is an oxidizing agent.

The lower oxides GeO , SnO and PbO are more basic and ionic than the higher oxides. Lead also forms a mixed oxide, Pb_3O_4 (red lead). It is represented as $2\text{PbO} \cdot \text{PbO}_2$ and contains Pb (II) and Pb (IV). The interconversion of various oxides of lead is shown by the following chemical reactions :



Silicates

Silicates are important rock forming minerals and comprise of tetrahedral SiO_4 units linked together by sharing corners and edges. Due to the great strength of the Si-O bond, these minerals are insoluble. The main structural principles of silicates have been determined by X-ray crystallography. The electro negativity difference between oxygen and silicon suggests that the bonds are 50% ionic and 50% covalent. The radius ratio $\text{Si}^{4+} : \text{O}^{2-}$ is 0.29 suggesting that silicon adopts a coordination number of four and is sp^3 hybridized giving SiO_4^{4-} units. These may exist as discrete units or polymerize by sharing oxygen atoms. Some silicon atoms may be replaced by aluminium to give aluminosilicates.

Silicates are classified on the basis of the number of oxygen atoms shared per SiO_4^{4-} tetrahedron. The classification of silicates alongwith some important examples are shown in table while some structures are depicted in Fig.

Table: Classification of Silicates

Type	General Formula	Examples	Remarks
Orthosilicates	SiO_4^{4-}	$\text{M}_2 [\text{SiO}_4]$, M=Zn, Willemite M=Be, Phenacite M=Mg, Forsterite $\text{M}[\text{SiO}_4]$ M=Zr, Zircon	No corners shared; Discrete tetrahedral units
Pyrosilicates	$\text{Si}_2\text{O}_7^{6-}$	$\text{Se}_2\text{Si}_2\text{O}_7$ Thortveitite	2 tetrahedra linked by one oxygen
Cyclic Silicates	$(\text{SiO}_3)_n^{2n-}$	$\text{Ca}_3[\text{Si}_3\text{O}_9]$ Wollastonite Ba, Ti $[\text{Si}_3\text{O}_9]$ Benitonite $\text{Be}_3\text{Al}_2 [\text{Si}_6\text{O}_{18}]$ Beryl	2 oxygen atoms per tetrahedron are shared
Chain Silicates a) pyroxene b) Amphibole	$(\text{SiO}_3)_n^{2n-}$ $(\text{Si}_4\text{O}_{11})_n^{6n-}$	Spodumene $\text{LiAl} (\text{SiO}_3)_2$ Enstatite $\text{Mg}_2 (\text{SiO}_3)_2$ Tremolite $\text{Ca}_2\text{Mg}_5 (\text{Si}_4\text{O}_{11})_2 (\text{OH})_2$ Crocidolite $\text{Na}_2\text{Fe}_3^{\text{II}}\text{Fe}_2^{\text{III}}$ $(\text{Si}_4\text{O}_{11})_2 (\text{OH})_2$ (Asbestos)	2 oxygen atoms per tetrahedron shared – single chain structures Some tetrahedra share 2 oxygens, some 3; double chain fibrous minerals
Sheet Silicates	$(\text{Si}_2\text{O}_5)_n^{2n-}$	Clay, White asbestos, Mica, Talc	3 oxygen atoms per tetrahedron shared minerals are soft & cleave into sheets
3 dimensional silicates	-	Feldspar, Zeolite, ultramarine	4 oxygen atoms per tetrahedron shared. Some Si atoms replaced by Al

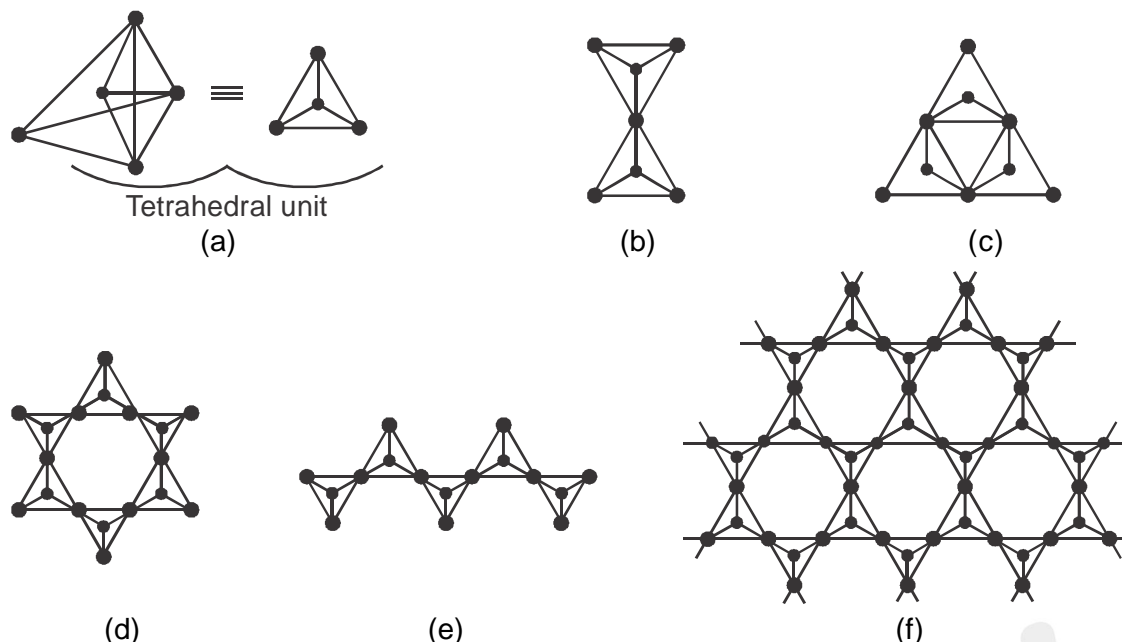


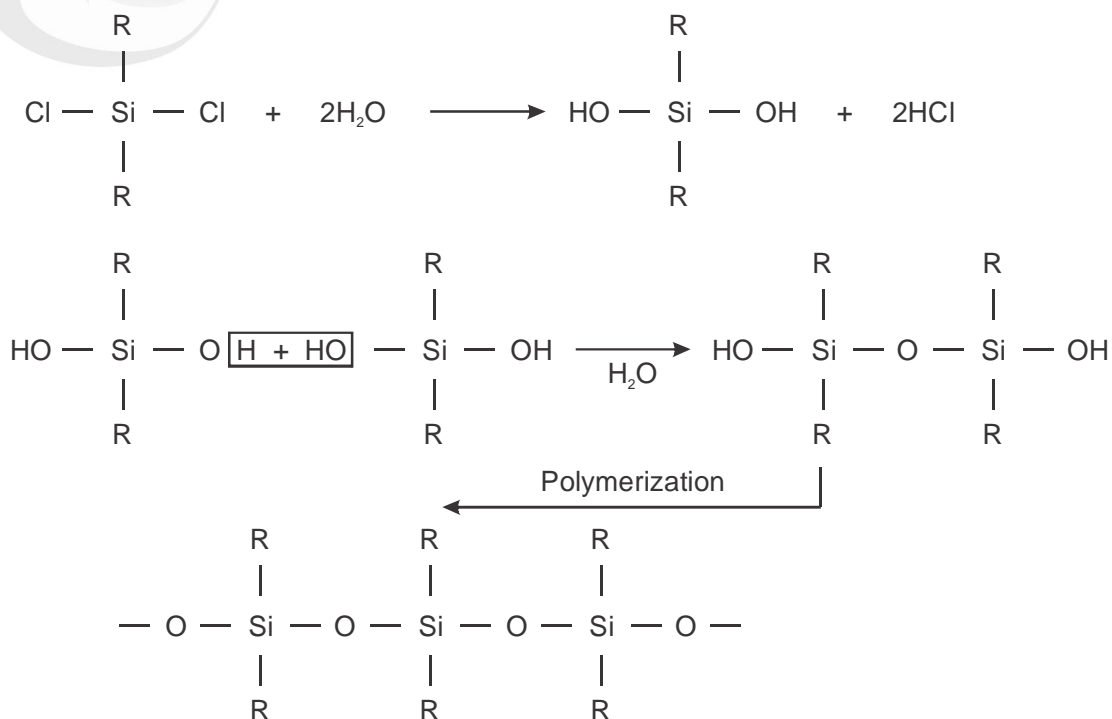
Fig: Some typical silicate structures (a) Orthosilicate SiO_4^{4-} (b) Pyrosilicate $\text{Si}_2\text{O}_7^{6-}$ (c-d) Cyclosilicates $(\text{SiO}_3)_n^{2n-}$ (e) Chain Silicate $(\text{SiO}_3)_n^{2n-}$ (f) Sheet Silicate $(\text{Si}_2\text{O}_5)_n^{2n-}$

The importance of silicates becomes apparent if we realize that asbestos, mica, zeolites, igneous rocks are all silicates. The cement, glass and ceramic industry are also based on silicates.

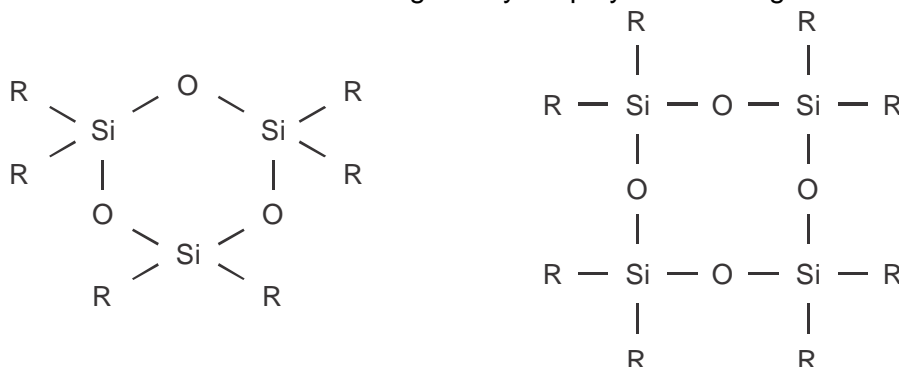
Organometallic compounds.

The elements have a fairly extensive organometallic chemistry. Due to inert pair effect the divalent state is more stable for the heavier members, however all organometallic compounds of tin and lead contain the element in the tetravalent state.

Alkyl silicon chlorides (RSiCl_3 , R_2SiCl_2 , R_3SiCl and SiR_4) are well – known. They are starting materials for an important class of organo silicon polymers referred to as silicones. Silicones contain long chains or rings of alternating silicon and oxygen atoms with alkyl or aryl groups attached to silicon. They are prepared by hydrolysis of alkyl substituted chlorosilanes or alkyl silicon chlorides.



The chain size can be limited by adding R_3SiCl . This hydrolyses to give R_3SiOH , which has only one active -OH group. It attaches itself to one side of the chain and since there is no functional -OH group on this side of the chain, the chain cannot grow at this end. Eventually the other end also gets blocked. Hydrolysis under controlled conditions gives cyclic polymers having three to six silicon atoms.



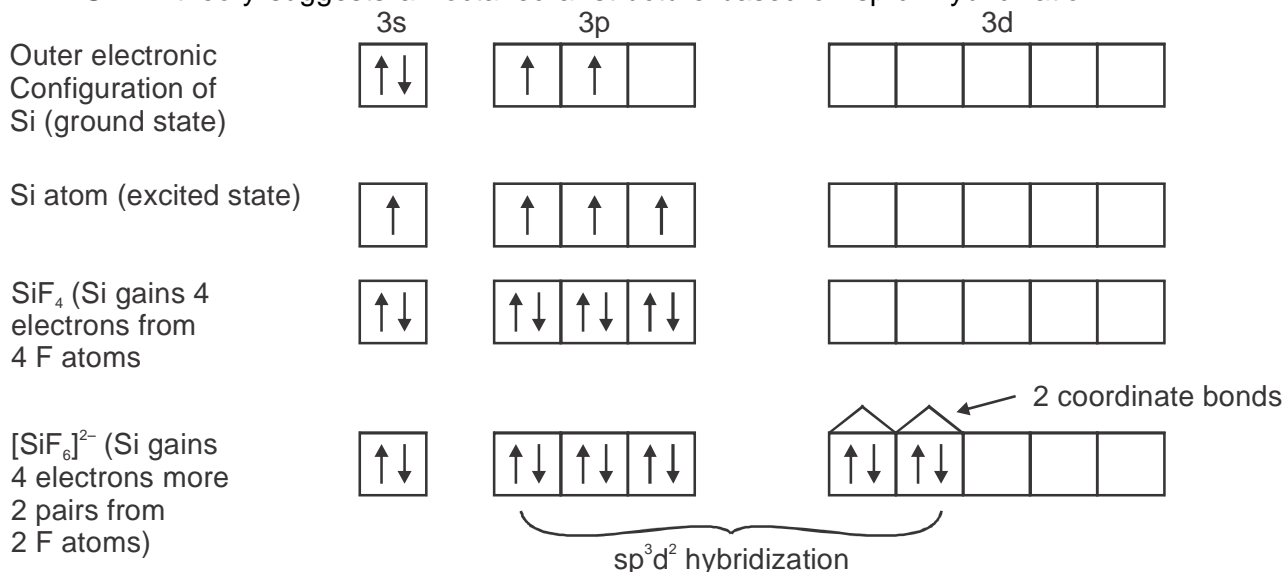
Cross-linked polymers are also known and are obtained when some $RSiCl_3$ is hydrolyzed along with R_2SiCl_2 .

Silicones are thermally and chemically inert due to stable Si-O linkage and a strong Si-C bond. They have oxidative stability, resistance to low and high temperature, excellent water repellency, good dielectric properties, desirable anti-foam and non-stick properties and physiological inertness. They can be made in the form of fluids, greases, emulsions, elastomers and resins (depending on chain length and extent of cross-linkage). They are used as water repellents for treating masonry, buildings and fabrics. Due to their anti-foam properties and non-toxicity they are used to reduce the froth in refining of cooking oil, fermentation processes, textile dyeing and sewage disposal. Other applications include their use as hydraulic fluids, light duty lubricants dielectric insulating material and non-stick coating material for utensils. Silicones are the most important inorganic polymers and their worldwide production is about 550,000 tons. Over 100 different silicone products are commercially available. Another important organometallic compound is tetraethyl lead $Pb(Et)_4$. This was used as an "anti-knock" agent to increase the octane number of petrol. Its use has been banned now as burning "leaded fuel" releases large amounts of toxic lead salts. Organotin compounds (R_2SnX_2 and R_3SnX) are used to stabilize PVC plastics and as fungicides and pesticides.

Complex formation

Carbon has a maximum coordination number of four and can accommodate eight electrons in the valence shell. It cannot increase its coordination number and forms no complexes. The other members have vacant d orbitals and can increase their coordination number to six and form complexes like $[SiF_6]^{2-}$, $[GeF_6]^{2-}$, $[GeF_4 \cdot (NMe_3)_2]$, $[SnCl_6]^{2-}$ and $[PbCl_6]^{2-}$.

VSEPR theory suggests an octahedral structure based on sp^3d^2 hybridization.

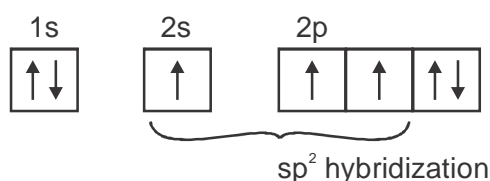


Internal π – bonding using d orbitals

Lateral overlaps of p orbitals give a $p\pi-p\pi$ bond. This is common for carbon and we have already seen that a few compounds containing $>Si=Si<$ are known. Under suitable conditions p and d orbitals undergo lateral overlap to give a $p\pi-d\pi$ bond. The compounds trimethylamine $(CH_3)_3N$ and trisilylamine $(SiH_3)_3N$ have similar formulae but their shapes are completely different (fig). The former has a pyramidal structure based on sp^3 hybridization of nitrogen. The electronic structure of N in trimethylamine is



The three unpaired electrons in 2p orbitals form bonds with $-CH_3$ groups. However trisilylamine has a planar structure based on sp^2 hybridization. The lone pair of electrons occupies a p orbital perpendicular to the plane of the molecule and overlaps with empty d orbital on the silicon atoms (fig). The electronic structure of N atom becomes



The unshared electron pair present in the 2p orbital of N is donated to a vacant 3d orbital on Si to form a $p\pi-d\pi$ bond. This is not possible in $(CH_3)_3N$ as carbon does not have d orbitals.

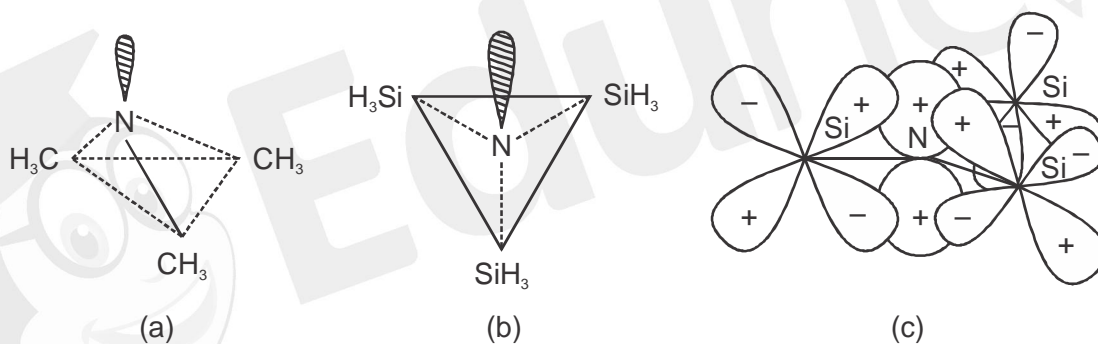


Fig: Shapes of (a) Trimethylamine (b) Trisilylamine (c) $p\pi-d\pi$ bonding in trisilylamine

Group 15

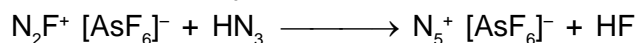
The elements in this group are nitrogen, phosphorous, arsenic, antimony and bismuth. Nitrogen is the most important component of the earth's atmosphere (78.1% by volume). Both nitrogen and phosphorous are essential constituents of plant and animal tissues. The last three elements had long been isolated and studied extensively by alchemists.

The elements span the range from non-metallic (nitrogen and phosphorous) to the metallic (bismuth). Arsenic and antimony have intermediate properties and are referred to as metalloids. The elements have five electrons in their outermost shell. Some selected physical properties are shown in table.

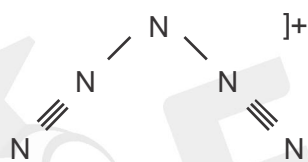
Table: Physical Properties of Group 15 Elements

Property	N	P	As	Sb	Bi
Atomic Number	7	15	33	51	83
Electronic Configuration	[He]2s ² 2p ³	[Ne]3s ² 3p ³	[Ar]3d ¹⁰ 4s ² 4p ³	[Kr]4d ¹⁰ 5s ² 5p ³	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ³
Covalent Radius (pm)	70	110	121	141	148
Ionization Energy (KJ mol ⁻¹)	1402	1012	947	834	703
Electron Affinity (KJmol ⁻¹)	-7	72	78	103	91
Electronegativity	3.06	2.05	2.21	1.98	2.01
Melting Point (°C)	-210	44	*	631	271
Boiling Point (°C)	-195.8	280.5	*	1587	1564

Nitrogen is a colourless diatomic gas having a triple bond, which confers unusual stability. For more than a century the only isolable chemical species containing only nitrogen were N₂ and the azide ion, N₃⁻. In 1999 the product N₅⁺ was reported to be formed in the following reaction.



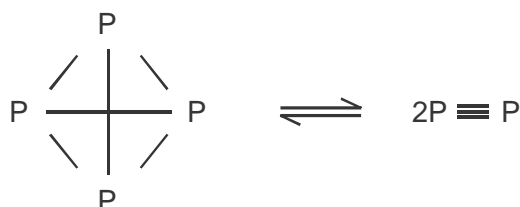
The N₅⁺ ion is stable below -78°C and has a V-shaped structure as shown



The N₂²⁻ ion has also been characterized in 2002. In SrN₂ the bond distance is 122.4 pm.

Allotropy

Phosphorous has many allotropes, the most common being white phosphorous existing as discrete tetrahedral P₄ molecules in the gaseous, liquid and solid states. It is soft, waxy and highly reactive and glows in moist air emitting a greenish – yellow light. This phenomenon is called phosphorescence and is the origin of the name of the element. It is stored under water. At very high temperature P₄ molecules dissociates to P₂:



Condensation of the vapours gives brown phosphorous, which probably contains P₂ molecules. If white phosphorous is heated in absence of air, red phosphorous is obtained. It exists in a variety of polymeric modifications. The most thermodynamically stable form is black phosphorous obtained by heating white phosphorous at high pressure. It is inert having a layer structure examples of these structures are shown in fig.

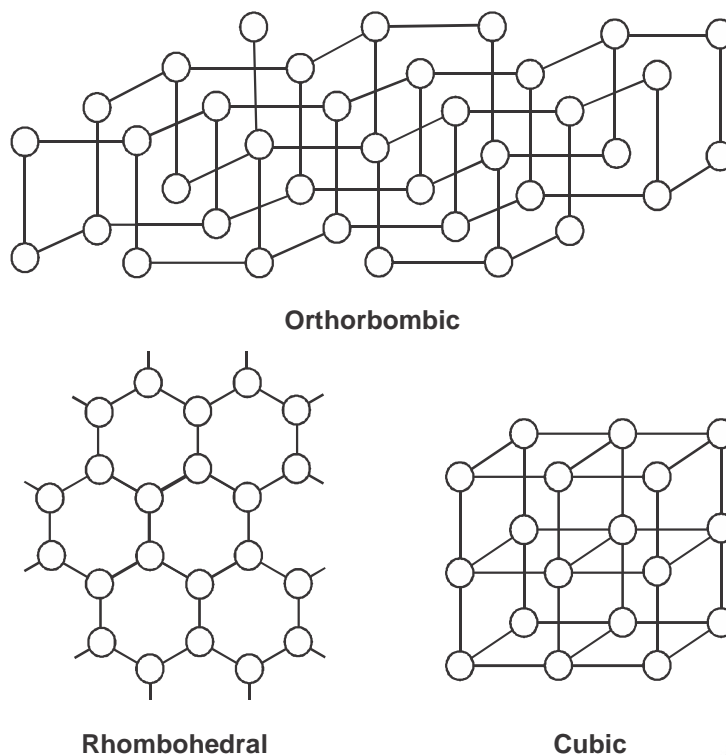


Fig: Allotropes of Phosphorus

Arsenic, antimony and bismuth exist in several allotropic modifications. Arsenic vapour contains tetrahedral As_4 molecules. In the solid state it exists in a yellow form comprising of As_4 molecules and a stable grey (α) form having a rhombohedral structure. Antimony exists in α form and another form having hexagonal close packed structure. Bismuth exists in α – form and a form having body-centred cubic structure.

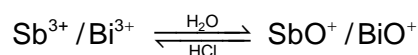
Bismuth is the heaviest element to have a stable, non-radioactive nucleus. All other heavier elements are radioactive. The liquid form of bismuth expands on solidification.

Oxidation states and bond type

The elements exhibit a maximum oxidation state of five towards oxygen by utilizing all valence electrons towards bond formation. Trivalency is important for heavier members (inert pair effect). They show oxidation states of three and five towards halogens and sulphur and three towards hydrogen. Nitrogen exhibits a range of oxidation states from -3 to +5 e.g. NH_3 (-3), N_2H_4 (-2), NH_2OH (-1), N_2 (0), N_2O (+1), NO (+2), HNO_2 (+3), NO_2 (+4) and HNO_3 (+5). It exists in three anionic forms N^{3-} (nitride), N^{3-} (azide) and N^{2-} . Nitrides are known for lithium, magnesium and aluminium. Phosphides and arsenides (Na_3P , Ca_3As_2) are also known.

Most compounds of this group are covalent. The electronic configuration is s^2p^3 and in compounds where the oxidation number is +3 e.g. NH_3 , the element has a lone pair of electrons, which can be donated, thus such compounds behave as Lewis bases.

The formation of M^{5+} ions is not energetically feasible but M^{3+} ions are known for Sb and Bi. The fluorides SbF_3 and BiF_3 are ionic solids. The M^{3+} ion in aqueous solution undergoes partial hydrolysis to give the oxoion.



Nitrogen cannot expand its coordination number beyond four, as only four orbitals are available in the valence shell. The other elements utilize d orbitals to form species like PCl_5 , PF_6^- etc. These are based on sp^3d and sp^3d^2 hybridization.

Nitrogen can form $p\pi-p\pi$ multiple bonds with itself or with oxygen and carbon. Hence it forms many compounds for which counterparts among the heavier members are not known. These include NO_3^- , NO_2^- , CN^- , N_3^- , N_2 , N_2O , NO and NO_2 . Because nitrogen can form multiple bonds, the oxides N_2O_3 and N_2O_5 exist as monomers while the analogous compounds of P, As and Sb exist as dimers.

Chemical properties

Nitrogen is rather unreactive. The other elements are fairly reactive and some reactions are shown in table.

Table: Some Reactions of Group 15 Elements

Reagent	Reaction	Remarks
O_2	$\text{M} + \text{O}_2 \xrightarrow{\Delta} \text{M}_x\text{O}_y$	N forms NO, P forms P_4O_6 & P_4O_{10} , As & Sb yield M_4O_6 while Bi forms Bi_2O_3
F_2	$\text{M} + \text{F}_2 \rightarrow \text{M F}_x$	M = As, Sb, Bi $x=5$ for As, Sb, $x = 3$ for Bi
X_2 (X=Cl, Br, I)	$\text{M} + \text{X}_2 \rightarrow \text{M X}_x$	M= P, As, Sb, Bi $x=3$ & 5 for P $x=3$ for Bi
S	$\text{M} + \text{S} \rightarrow \text{M}_x\text{S}_y$	M= P, As, Sb, Bi $x=4$ for P, 2 for others $y=5$ for P, 3 for others
KOH	$\text{P} + \text{KOH} + \text{H}_2\text{O} \rightarrow \text{KH}_2\text{PO}_2 + \text{PH}_3$	As reacts with fused KOH giving K_3AsO_3 & H_2 . others do not react
H_2SO_4 (conc.)	$\text{As} + \text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{AsO}_3$	P forms H_3PO_4 Sb & Bi form $\text{M}_2(\text{SO}_4)_3$

General trends are not as apparent as in other groups as one encounters with a variety of elements – non-metals, metalloids and metals.

Compounds

Hydrides

All elements form volatile hydrides of the formula MH_3 . Nitrogen also forms hydrazine, N_2H_4 and hydrazoic acid N_3H (fig.)

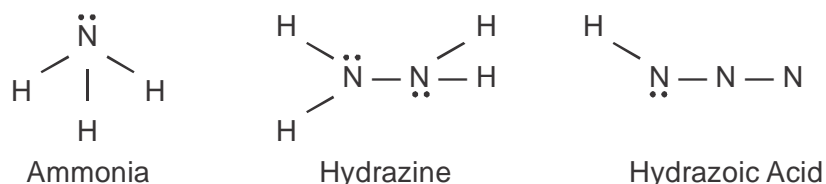


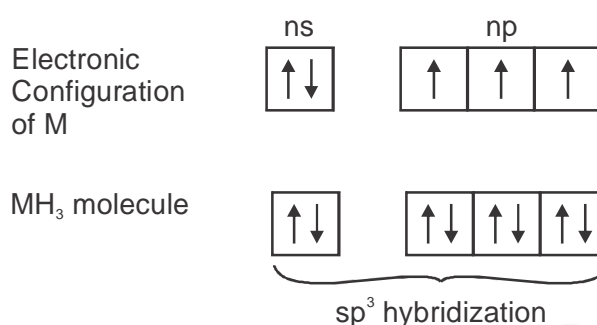
Fig: Some hydrides of Nitrogen

On moving down the group from NH_3 to BiH_3 , the central atom becomes larger and effective overlap with the small $1s$ orbital of hydrogen decreases. Thus the stability of the hydrides decreases down the group and their reducing power increases. The bond angle decreases down the group. Some properties of the hydrides are shown in Table.

Table: Some Properties of Group 15 Hydrides

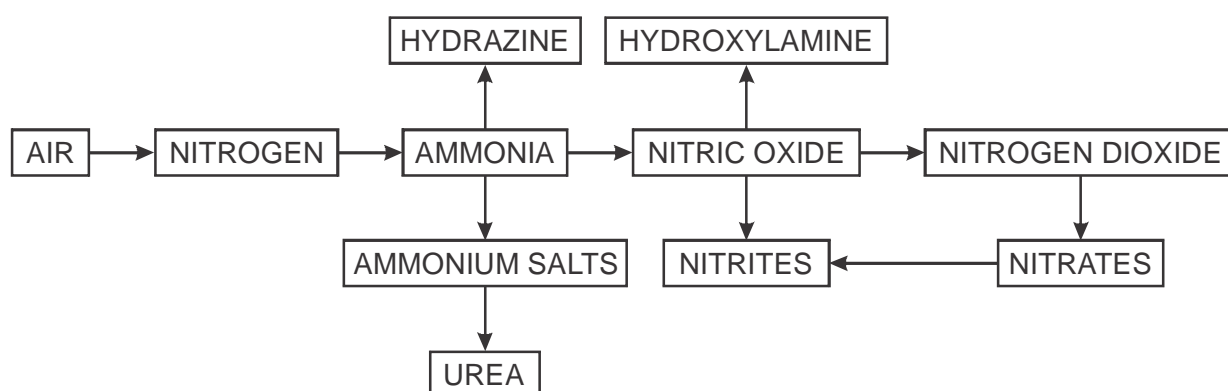
	m.p. ($^{\circ}\text{C}$)	b.p. ($^{\circ}\text{C}$)	Bond energy (KJmol^{-1})	Bond Angle	Bond length (pm)
NH_3	-77.8	-34.5	389	$107^{\circ}48'$	101.7
PH_3	-133.5	-87.5	318	$93^{\circ}36'$	141.9
AsH_3	-116.3	-62.4	247	$91^{\circ}48'$	151.9
SbH_3	-88	-18.4	255	$91^{\circ}18'$	170.7

VSEPR theory predicts pyramidal structure (sp^3 hybridization with lone pair on central atom).

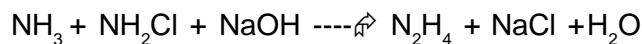
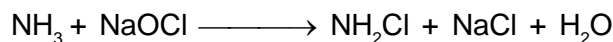


Due to the presence of the lone pair, the bond angle is less than the normal tetrahedral bond angle. On moving down the group, the electronegativity of the central atom decreases, the bond-pair tends to move away from the central atom, the lone pair is more tightly held causing greater distortion and is reflected by the decrease in bond angle down the group. The lone pair on the central atom can be donated and the elements act as Lewis bases. However, on descending the group, as the lone pair is more tightly held, the donor properties of the hydrides decreases. Thus phosphine is a much weaker base than ammonia.

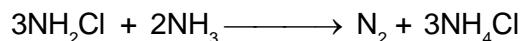
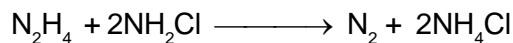
Ammonia is one of the most highly-produced inorganic chemicals. The Haber-Bosch Process manufactures most of it synthetically from nitrogen and hydrogen. A small amount is obtained during coal gas purification and during production of coke from coal. The worldwide production in 2004 was 109,000,000 tons, the chief producer being China followed by India. About 80% or more of the ammonia produced is used for fertilizing agricultural crops. The main fertilizers manufactured from ammonia are urea, ammonium nitrate, ammonium phosphate and ammonium sulphate. Ammonia is also used for the production of many inorganic and organic chemicals, plastics, fibres, explosives and intermediates for dyes and pharmaceuticals. Synthetic ammonia is the key to the production of most nitrogen compounds as shown below.



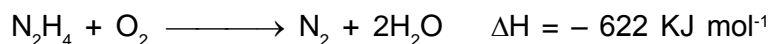
Hydrazine is prepared by the action of sodium hypochlorite on ammonia in presence of a small amount of glue or gelatin, which suppresses the side reactions:



Side reactions: Hydrazine

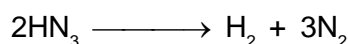


Oxidation of hydrazine is highly exothermic

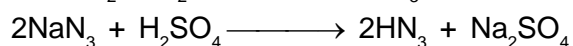
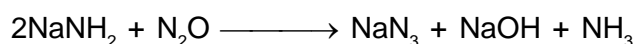


Advantage has been taken of this reaction in the major use of hydrazine and its methyl derivative, in rocket fuels. Hydrazine is a convenient reducing agent. It can also act as a coordinating ligand forming complexes with transition metals. Phosphorous forms an unstable hydride diphosphine, P_2H_4 , which has very little similarity with hydrazine.

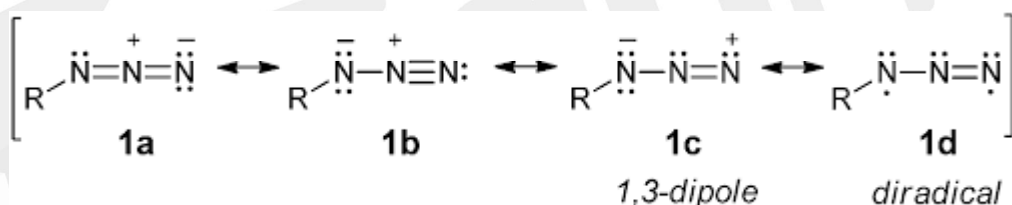
Hydrogen azide (hydrazoic acid HN_3) is an unstable compound, which decomposes on heating



It is slightly more stable in aqueous solution and behaves as weak acid forming salts known as azides. Sodium azide is obtained by reaction of sodamide with nitrous oxide.



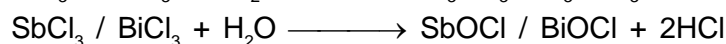
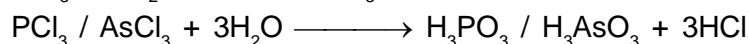
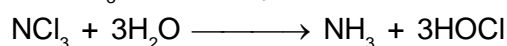
The acid and some its salts are explosive in nature. Ionic azides are more stable than covalent azides as a greater number of resonating structures can be drawn for the former.



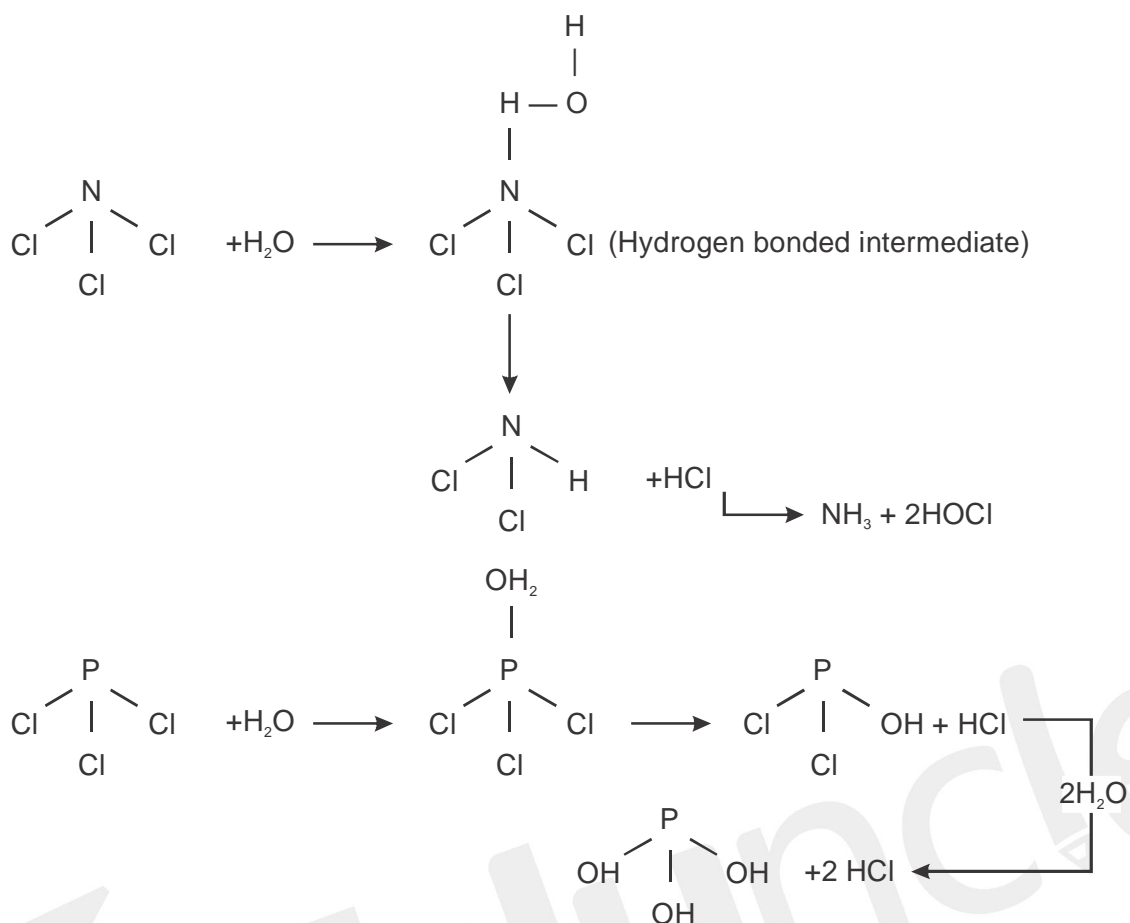
Halides

Two series of halides are known – the trihalides (MX_3) and pentahalides (MX_5). The trihalides are known for all the elements and can be prepared by direct combination. But if the halogen is in excess than the pentahalide is formed in addition. The trihalides are all covalent apart from BiF_3 that is ionic. SbF_3 and the other halides of bismuth have partial ionic character. The central atom is sp^3 hybridized and the shape is pyramidal (like NH_3).

Apart from NF_3 that is very stable the trihalides hydrolyze but the products vary.



The different products obtained in case of hydrolysis of NCl_3 and PCl_3 is due to a difference in mechanism, which results in formation of different intermediates.



In a case of SbCl_3 and BiCl_3 the hydrolysis is incomplete and may be reversed on adding HCl.

Nitrogen does not form pentahalides due to non-availability of d orbitals. Due to inert pair effect pentahalides of bismuth are less stable and only BiF_5 is known. The pentahalides of phosphorous are well characterized. In the gaseous phase they have trigonal bipyramidal structure (fig.)

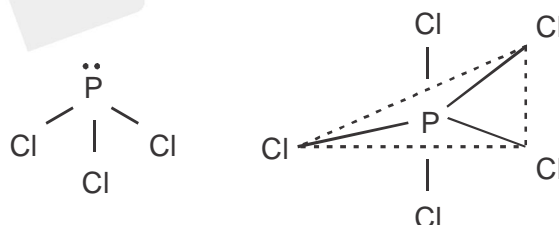
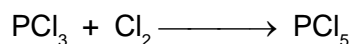


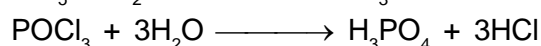
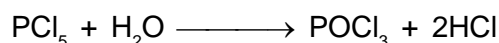
Fig: Structures of PCl_3 and PCl_5

This structure is retained in the solid state for PF_5 but PCl_5 dimerises in the solid state and exists as $[\text{PCl}_4]^+[\text{PCl}_6]^-$

Phosphorous pentachloride is the most important pentahalide and is obtained by treating phosphorous trichloride with chlorine.

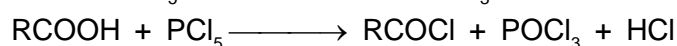
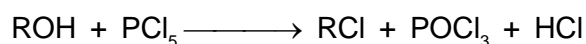


It hydrolyses readily.



Phosphoric acid

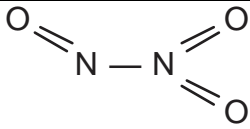
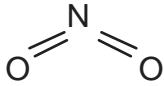
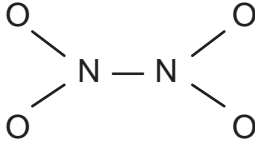
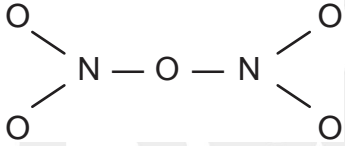
It is widely used in organic synthesis as a halogenating agent.



Nitrogen oxides and oxo acids

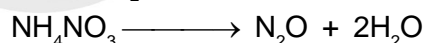
The common oxides and oxoacids of nitrogen are summarized in Table and their structures are also depicted there.

Table: Oxides of Nitrogen

Formula	Name	Structure	Remarks
N ₂ O	Nitrous Oxide	N = N = O	Oxidn. state + 1 (O.S.)
NO	Nitric Oxide	N ≡ O	O. S + 2 Bond order 2.5 Paramagnetic
N ₂ O ₃	Nitrogen Sesquioxide		O.S + 3 Dissociates readily to NO & NO ₂
NO ₂	Nitrogen Dioxide		O.S + 4 Paramagnetic Following equilibrium presents 2NO ₂ = N ₂ O ₄
N ₂ O ₄	Dinitrogen Tetraoxide		O.S + 4 Dissociates to NO ₂
N ₂ O ₅	Dinitrogen Pentoxide		O.S + 5 N-O-N may be bent. Exists as NO ₂ ⁺ NO ₃ ⁻ in solid state

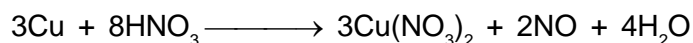
They all exhibit pπ-pπ multiple bonding between nitrogen and oxygen atoms. The other elements of Group 15 cannot form such bonds and consequently nitrogen forms a number of compounds for which P, As, Sb or Bi analogues are not known. Oxides in lower oxidation state are neutral while those in higher oxidation states are acidic.

Nitrous oxide, N₂O, is obtained by the thermal decomposition of ammonium nitrate



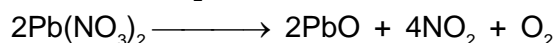
It is used as a mild dental anaesthetic and propellant for aerosols. On atmospheric decomposition it releases nitrogen and oxygen that are environment friendly. However N₂O contributes to green house effect.

Nitric oxide is obtained by the action of dilute nitric acid on copper.

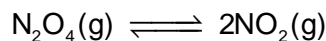


It is released during combustion of fossil fuels and is present in exhausts of automobiles and power plants. It is also obtained by action of lightning on atmosphere nitrogen and oxygen. The NO is slowly oxidized to NO₂, these two gases are collectively referred to as NO_x and contribute to the problem of acid rain and destruction of ozone layer. It is a neutral oxide and is an important intermediate for manufacture of nitric acid by catalytic oxidation of ammonia. It is an odd electron molecule and forms coordination complexes with metal ions. One such complex [Fe(H₂O)₅NO]²⁺ is responsible for the colour in the "brown ring" test for nitrates.

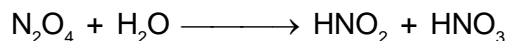
Nitrogen dioxide, NO₂ is a toxic gas obtained by thermal decomposition of lead nitrate.



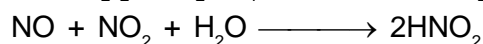
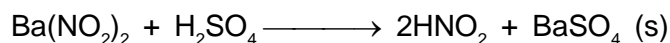
It is an odd electron molecule and dimerizes to give N_2O_4 . At ordinary temperature and pressure, both exist in significant amounts in equilibrium:



Colourless, diamagnetic N_2O_4 has a weak N-N bond that can readily dissociate on warming to give the brown, paramagnetic NO_2 . N_2O_4 is an acidic oxide and dissolves in water to give a mixture of nitrous and nitric acids.



The two important oxo acids of nitrogen are nitrous acid, HNO_2 and nitric acid, HNO_3 . Nitrous acid is a weak acid and is obtained by acidifying a nitrite or by passing an equimolar mixture of NO and NO_2 into water.



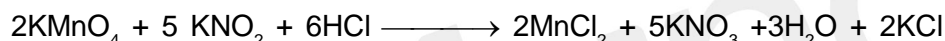
The acid disproportionates on heating



Nitrous acid and nitrites are good oxidizing agents and oxidize iodide to iodine, Fe (II) to Fe (III) and Sn (II) to Sn (IV), e.g.

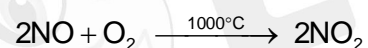


However, strong oxidizing agents like KMnO_4 oxidize nitrites to nitrates.

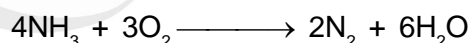


The nitrite ion forms complexes with metals. Coordination to metal ions occurs either through nitrogen or oxygen.

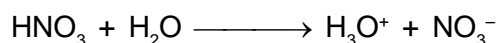
Nitric acid is of immense industrial importance. It is synthesized by the Ostwald (Nobel Prize 1909) process through the following set of reactions.



In the first step, a catalyst specific for NO formation is taken; other wise NH_3 is oxidized to N_2



HNO_3 is a strong acid undergoing complete dissociation in dilute aqueous solution.



It is an excellent oxidizing agent particularly when hot and concentrated. A mixture of concentrated HNO_3 and concentrated HCl in 1:3 ratios is called aqua regia and noble metals like gold and platinum dissolve in it. The reactions of HNO_3 with some metals and non-metals are summarized in table.

Table: Some Reactions of Nitric Acid

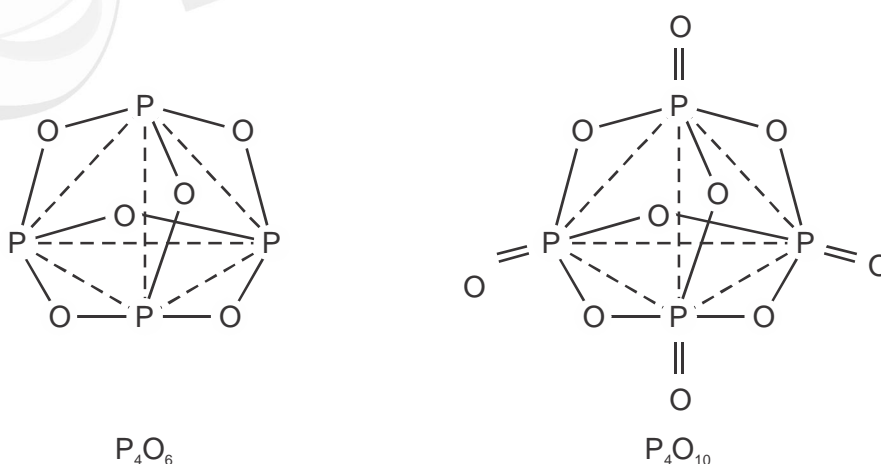
Reactant	Reaction	Remarks
M = Mg, Mn	$M + 2\text{HNO}_3 \rightarrow M(\text{NO}_3)_2 + \text{H}_2$	Very Dilute Acid
M = Zn, Fe, Sn	$4M + 10\text{HNO}_3 \rightarrow 4M(\text{NO}_3)_2 + 5\text{H}_2\text{O} + \text{N}_2\text{O}$ $5M + 12\text{HNO}_3 \rightarrow 5M(\text{NO}_3)_2 + \text{N}_2 + 6\text{H}_2\text{O}$ $4M + 10\text{HNO}_3 \rightarrow 4M(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$	Dilute acid (Oxidizing agent) Very dilute acid
M = Cu, Bi, Hg, Ag	$3M + 8\text{HNO}_3 \rightarrow 3M(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$ $M + 4\text{HNO}_3 \rightarrow M(\text{NO}_3)_2 + 2\text{NO}_2 + \text{H}_2\text{O}$	Dilute acid Conc. Acid
P	$\text{P}_4 + 20\text{HNO}_3 \rightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}$	Conc. Acid
C_6H_6	$\text{C}_6\text{H}_6 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$	Conc. Acid Reaction assisted by adding conc. H_2SO_4

A mixture of concentrated nitric acid and sulphuric acid contains the nitronium ion NO_2^+ and is used to nitrate organic compounds.

The major use of nitric acid (~ 75%) is in the manufacture of ammonium nitrate, most of which is used as a fertilizer. Other uses include manufacture of caprolactam (one of the starting materials for synthesis of Nylon), manufacture of industrially useful organic nitro compounds (nitroglycerine, nitrocellulose etc) and manufacture of nitrates for use in explosives, pyrotechnics etc.

Oxides and Oxo Acids of other elements

Phosphorous, arsenic and antimony form oxides in both +3 and +5 oxidation states, whereas only one oxide of bismuth, Bi_2O_3 is known. Except for Bi_2O_3 all other oxides are dimeric. They are obtained by direct combination. The structures of oxides of phosphorous are shown in fig.


Fig: Oxides of Phosphorus

The four apical bonds in P_4O_{10} have appreciable double bond character due to $p\pi-d\pi$ overlap.

The basic strength of the oxides increases on moving down the group. The oxides of P and As are acidic, those of Sb amphoteric and bismuth oxide is basic. Oxides in higher oxidation states are more acidic.

Oxoacids of Phosphorous, Arsenic & Antimony

The oxoacids of arsenic and antimony are not well – characterized but their salts are known. Phosphorous forms two series of oxo acids – phosphoric acid series containing P (V) and phosphorous acid series containing P (III)

The following generalization can be made:

- b) P is sp^3 hybridized.
- c) Acidic hydrogens are attached to oxygen
- d) The bond between P and non-hydroxylic oxygen has appreciable double bond character.
- e) The P-H bond confers reducing properties.

Some properties of the oxoacids of phosphorous are summarized in table.

Table: Oxoacids of Phosphorous

Formula	Name of Acid	Preparation	Remarks
H_3PO_2	Hypophosphorous	White P_4 + alkali	Monobasic Reducing $pK_a = 1.244$
H_3PO_3	Orthophosphorous	P_4O_6 or $PCl_3 + H_2O$	Dibasic, Reducing $pK_1 = 1.26$ $pK_2 = 6.70$
$(HPO_2)_n$	Metaphosphorous	$PH_3 + O_2$ (low pressure)	Polymerizes Structure not known
$H_4P_2O_6$	Hypophosphoric	Red P + alkali	Tetrabasic $pK_1 = 2.2$ $pK_2 = 2.8$ $pK_3 = 7.3$ $pK_4 = 10.0$
H_3PO_4	Orthophosphoric	$P_4O_{10} + H_2O$	Tribasic $pK_1 = 2.15$ $pK_2 = 7.20$ $pK_3 = 12.37$
$H_4P_2O_7$	Pyrophosphoric	Heat Phosphates or H_3PO_4	Tetrabasic $pK_1 = 1.0$ $pK_2 = 1.8$ $pK_3 = 6.6$ $pK_4 = 9.6$
$(HPO_3)_n$	Metaphosphoric	Heat H_3PO_4 to $350^\circ C$	Ring Structure

Some condensed phosphoric acids are known. The PO_4 tetrahedra are linked to form chains and structures of some of these are shown in Fig.

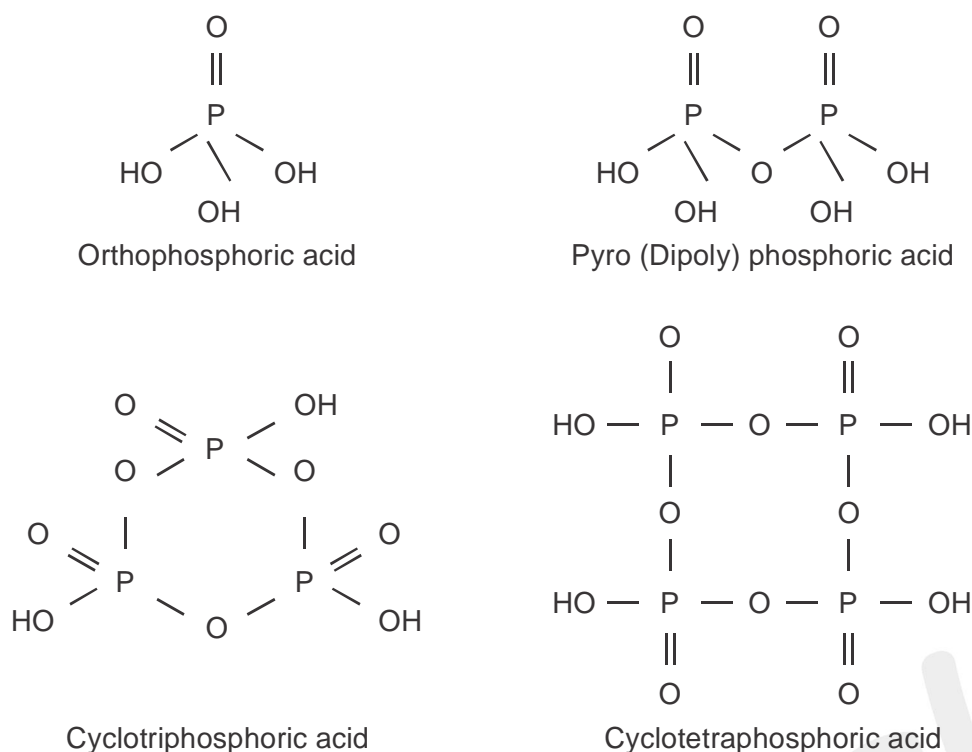


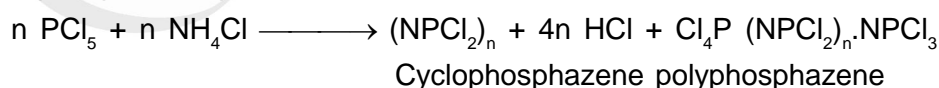
Fig: Some oxoacids of Phosphorus

The P – O – P linkage is very important in the biological system, as it is the prime store of energy. The energy of the bond (29 KJ mol^{-1}) is released by the hydrolysis of adenosine triphosphate.

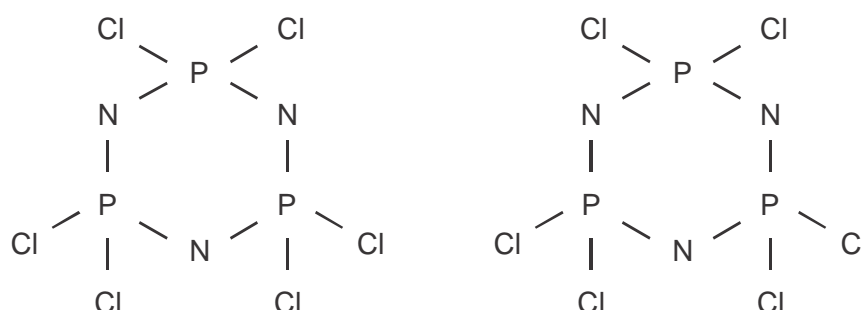
The world production of phosphates is about 50,000,000 tons. Phosphates find various uses in the food industry, in water softening, in fertilizers, toothpastes and detergents.

Phosphazenes

Nitrogen and phosphorous show little tendency to catenate by themselves. However they bond together to form cyclic and long chain polymers called phosphazenes (earlier referred to as phosphnitric polymers) containing alternate phosphorous and nitrogen atoms. In these compounds phosphorous and nitrogen are present in +5 and +3 oxidation states respectively. They may be prepared by the reaction between phosphorous pentachloride and ammonium chloride in dichloromethane at 120 to 150 C.

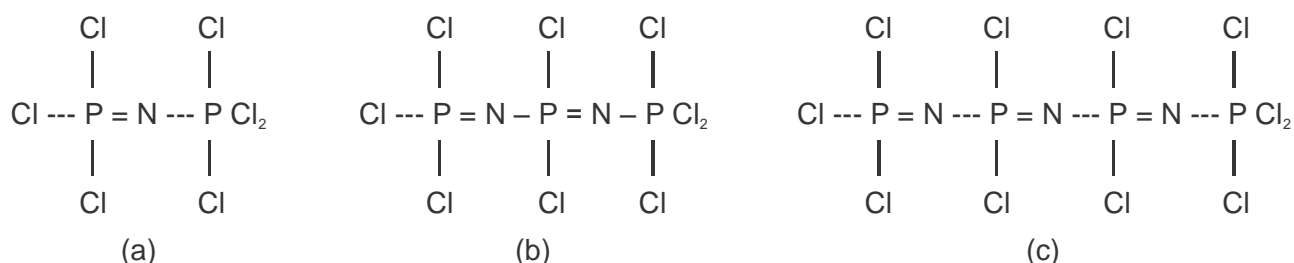


The reaction produces a mixture of ring compounds and short linear chains. Among the ring compounds the trimer and tetramer have been well characterized. The former exists as planar six membered rings with equal P—N distance ($\sim 158 \text{ pm}$), considerably shorter than the P – N single bond ($\sim 177 \text{ pm}$). This indicates a structure similar to benzene. The compound displays aromaticity though less than benzene. The compound can be expressed as a resonance hybrid, the N atoms are sp^2 hybridized and the P atoms are sp^3 hybridized.



The tetramer has a puckered structure.

A few chain polymers are:



Other atoms or groups can replace the Cl atoms. The amino, alkoxy, phenoxy and fluoro derivatives are stable and attracting interest as rigid plastics, plastic films, foams, fibres and elastomers. Such molecules (molar mass > 500,000) are water repellent, flame resistant, flame resistant have good dielectric strength and are flexible at low temperatures. Due to these unique properties they have many potential uses but their cost is prohibitive. After silicones they are the most important inorganic polymers.

Group 16

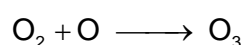
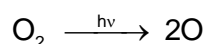
The first two elements of this group, sometimes referred to as the “chalcogen” group, are familiar as oxygen, the colourless gas, vital for life and comprising about 21% of the earth’s atmosphere and sulphur, a yellow non-metallic solid. The third element, selenium is not as well known, but is important in xerography processes. Tellurium is of less commercial importance, used in small amounts in metal alloys, tinting of glass and as catalysts in rubber industry. All isotopes of polonium (discovered by Marie Curie) are radioactive. Non-metallic character is maximum in oxygen and sulphur, weaker in selenium and tellurium whereas polonium is metallic. Some selected physical properties are shown in Table.

Table: Physical properties of Group 16 elements

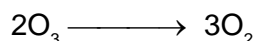
Property	O	S	Se	Te	Po
Atomic Number	8	16	34	52	84
Electronic Configuration	[He]2s ² 2p ⁴	[Ne]3s ² 3p ⁴	[Ar]3d ¹⁰ 4s ² 4p ⁴	[Kr]4d ¹⁰ 5s ² 5p ⁴	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴
Covalent radius (pm)	66	104	117	137	146
Ionization Energy (I st) (KJmol ⁻¹)	1314	1000	941	869	812
Electron Affinity (KJmol ⁻¹)	141	200	195	190	180
Electronegativity	3.61	2.58	2.42	2.15	2.10
Melting Point (°C)	-218.8	112.8	217.0	452.0	250.0
Boiling Point (°C)	183.0	444.7	685.0	990.0	962.0

Allotropic forms

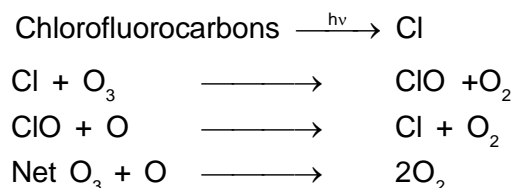
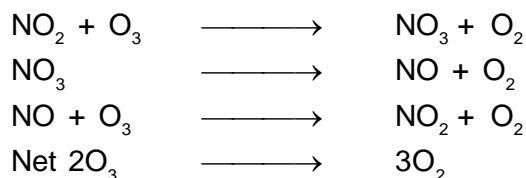
Oxygen exists primarily as the diatomic O₂ that is paramagnetic, but traces of triatomic O₃ (ozone) are found in the upper atmosphere and in the vicinity of electrical discharges. Ozone is diamagnetic and is formed when oxygen absorbs ultraviolet radiation from the sun.



Ozone also absorbs ultraviolet radiation and decomposes back to oxygen

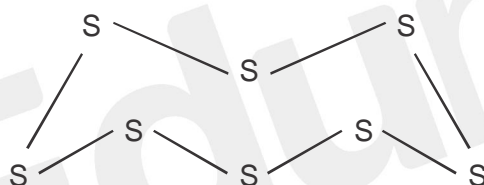


In the upper atmosphere a steady- state concentration of ozone is achieved which protects the earth's surface from ultraviolet radiation. Recently there has been a serious concern about the depletion of the ozone layer. Oxides of nitrogen (from high- flying aircraft) and chlorine atoms (from decomposition of chlorofluorocarbons used as aerosols, refrigerants etc.) catalyze the decomposition of ozone.



Ozone is a more powerful oxidizing agent than oxygen. Some diatomic and triatomic ions of oxygen are known e.g. O_2^- (Superoxide), O_2^{2-} (Peroxide), O_3^- (Ozonide)

More allotropes are known for sulphur than for any other element. The most stable form at room temperature is orthorhombic or α -sulphur. This consists of S_8 molecules, arranged in a puckered ring



At 96°C , orthorhombic sulphur is converted to monoclinic or β -sulphur in which the S_8 rings are arranged to give a different structure. Heating sulphur results in interesting changes in viscosity. At 119°C , a yellow liquid is obtained whose viscosity decreases up to 155° because of increased thermal motion. The viscosity increases sharply above 159°C till about 200°C , when it again decreases with the liquid acquiring a reddish tinge at high temperature. This variation in viscosity involves the tendency of S-S bonds to break and reform at high temperature. Above 159°C , the S_8 rings open giving chains, these react among themselves to give S_{16} chains, S_{24} chains and so on. At about 180°C , when the liquid has maximum viscosity, chains exceeding 200,000 sulphur atoms are known. The longer the chain, the greater is the viscosity. At higher temperatures, these chains break and the viscosity decreases. When molten sulphur is poured into cold water, a rubbery solid, plastic sulphur or γ -sulphur is obtained.

General group Trends

The size of the Group 16 elements increases down the group as extra shells of electrons are added. The ionization enthalpy decreases as the size of the atom increases. The ionization enthalpies of the Group 16 elements are strikingly less than these of the corresponding Group 15 elements. This is attributed to the fact that Group 15 elements have $ns^2 np^3$ configuration, the p orbitals are half filled conferring extra stability and consequently removal of an electron is difficult. The electronegativities decrease with increasing atomic number. Thus in view of the fall in electronegativity, metallic character within the group increases with increase in atomic size.

The large difference in melting and boiling points between oxygen and sulphur can be explained on the basis of their structure. Oxygen exists as diatomic molecules and the bond energy of $\text{O}=\text{O}$ is very high (498 kJ mol^{-1}). The molecules are held by weak van der Waal's forces. Sulphur exists as S_8 , the

S-S bond energy (264 KJ mol^{-1}) is greater than O-O bond energy (142 KJ mol^{-1}). Thus sulphur has greater catenation power than oxygen and higher melting and boiling points.

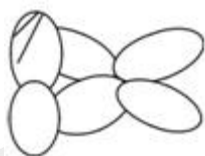
Oxidation states and Bond type

The elements have outermost electronic configuration of $ns^2 np^4$ and can achieve noble gas configuration by gaining two electrons forming M^{2-} ion or by acquiring a share in two electrons by forming two covalent bonds. The M^{2-} ion is known for oxygen (which is highly electronegative) and to a lesser extent for sulphur. Sulphur, selenium and tellurium show +2, +4 and +6 oxidation states. The +4 and +6 oxidation states are realized by utilizing vacant d orbitals. Oxygen always displays -2 oxidation state in metallic and non-metallic oxides except in OF_2 where it shows +2 oxidation state. This is because fluorine is more electronegative than oxygen.

Oxygen, and to a lesser extent, sulphur differ from other members in their ability to catenate and form peroxides H-O-O-H and polysulphides, H_2S_n ($n=2$ to 8) respectively.

The tendency to form multiple bonds decreases down the group. Carbon dioxide ($O=C=O$) is very stable, carbon disulphide is moderately stable, the corresponding selenium compound is less stable whereas the tellurium compound is not known.

The bond between sulphur and oxygen are shorter than a single bond. In addition to the σ - bond between the elements, a π -bond is formed by overlap of filled 2p orbitals of oxygen with a vacant 3d-orbital of sulphur. This is called a $p\pi$ - $d\pi$ bond. The sizes and energies of the 2p orbital of oxygen and 3d orbital of sulphur are comparable allowing effective overlap.



2p of O (Filled)
3d of S (Vacant)

Compounds Hydrides

Binary hydrides of general formula H_2X are known for all elements. They are angular in shape (sp^3 hybridization with two lone pairs) (Fig). The bond angles decrease down the group (Table).

Table: Some Properties of Group 16 Hydrides

Boiling Point ($^{\circ}\text{C}$)		Enthalpy of formation (KJmol^{-1})	Bond angle (H-M-H)
H_2O	100	-242	104.5°
H_2S	-60	-20	92°
H_2Se	-42	+81	91°
H_2Te	-2.3	+154	90°

The bond angle is lower than the tetrahedral bond angle (109.5°) due to greater repulsion between the lone pairs. On moving down the group, the electro negativity of the Group 16 element decreases, the bond pair moves away from the central atom, the lone pair is more tightly held causing greater distortion. For lower hydrides, the bond angle approaches 90° suggesting that almost pure p-orbitals are used in bond formation. The thermal stability and bond enthalpy of the hydrides decreases down the group and the acidic nature increases. The abnormally high boiling point of water is due to intermolecular hydrogen bonding.

Oxygen forms another hydride, H_2O_2 (Fig)

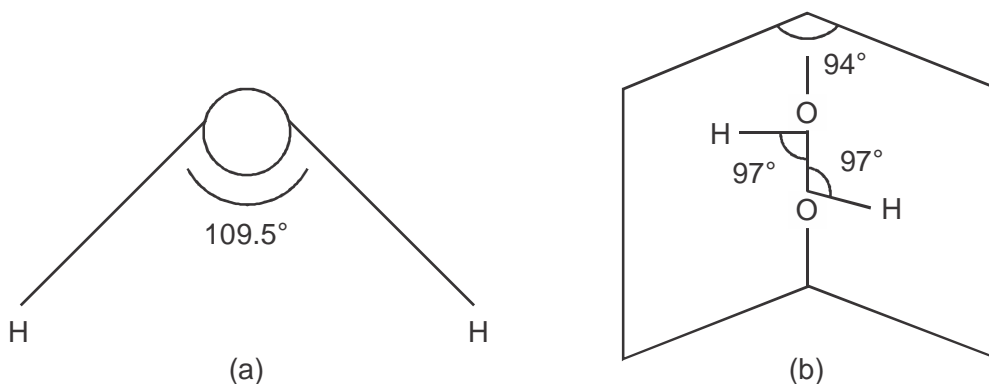
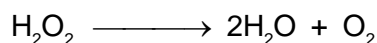


Fig: The Structures of (a) H_2O (b) H_2O_2

It decomposes readily and is a strong oxidizing agent



Halides

The elements form a number of compounds with halogens (Table)

Table: Binary Halides of Group 16 Elements

	Fluorides	Chlorides *	Bromides *	Iodides *
O	$\text{OF}_2, \text{O}_2\text{F}_2$	$\text{Cl}_2\text{O}, \text{ClO}_2$	$\text{Br}_2\text{O}, \text{BrO}_2$	$\text{I}_2\text{O}_4, \text{I}_2\text{O}_5$
		$\text{Cl}_2\text{O}_6, \text{Cl}_2\text{O}_7$	BrO_3	I_4O_9
S	$\text{S}_2\text{F}_2, \text{SF}_2, \text{SF}_4, \text{SF}_6,$ S_2F_{10}	$\text{S}_2\text{Cl}_2, \text{SCl}_2$ SCl_4	S_2Br_2	-
Se	$\text{Se}_2\text{F}_2, \text{SeF}_4$ SeF_6	$\text{Se}_2\text{Cl}_2, \text{SeCl}_2$ SeCl_4	$\text{Se}_2\text{Br}_2, \text{SeBr}_2$ SeBr_4	-
Te	$\text{TeF}_4, \text{TeF}_6$	$\text{TeCl}_2, \text{TeCl}_4$	$\text{TeBr}_2, \text{TeBr}_4$	$\text{TeI}_2, \text{TeI}_4$
Po	-	$\text{PoCl}_2, \text{PoCl}_4$	$\text{PoBr}_2, \text{PoBr}_4$	PoI_4

* in case of oxygen, oxides

The binary compounds of oxygen with halogens are covalent. The structures of some halides are shown in Fig.

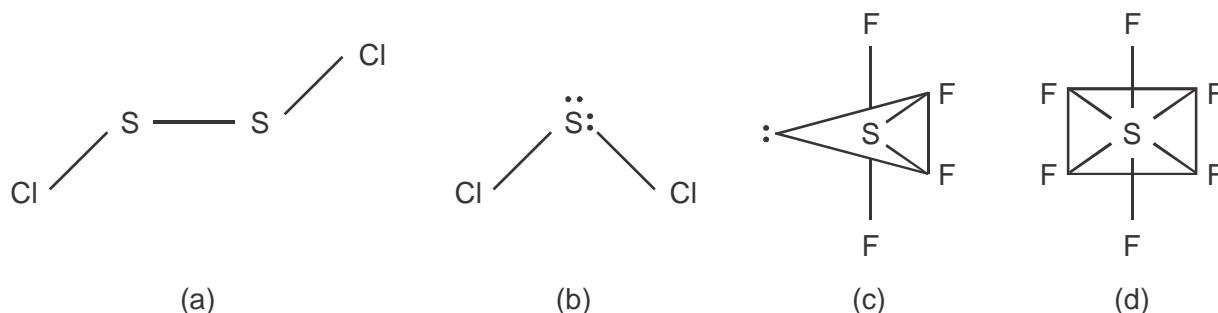


Fig: The structures of some sulphur halides

The highest oxidation state of +6 is realized only with fluorine, SF_6 is inert due to a sterically hindered sulphur atom in an octahedral structure (sp^3d^2 hybridization). It is unaffected by water as the protected sulphur atom does not allow hydrolysis, a thermodynamically favoured reaction. On the other hand SeF_6 and TeF_6 are more reactive and TeF_6 is hydrolyzed due to large size of Te. This allows the formation of an intermediate with higher coordination number.

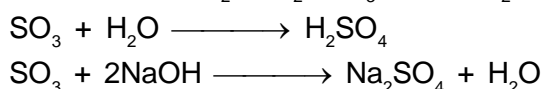
Oxides

Oxygen reacts with practically all elements in the periodic table, except lighter noble gases, to form oxides. Oxides may be classified as:

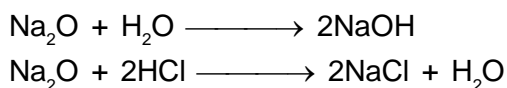
- iii) Normal oxides - Here oxygen shows oxidation state of -2 . They may be ionic or covalent eg. CaO , CO_2 ,
- iv) Peroxides - These contain O-O linkage eg. H_2O_2 , Na_2O_2
- v) Suboxides - They involve bonds between atoms of the element, in addition to bonds between element and oxygen e.g. C_3O_2 ($\text{O}=\text{C}=\text{C}=\text{C}=\text{O}$)
- vi) Superoxides - They contain O_2^- ion and are formed by some alkali metals eg. KO_2

Oxides may also be classified as acidic, basic, neutral or amphoteric depending on their reaction with water.

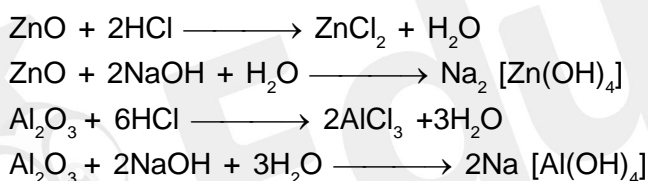
Acidic oxides (oxides of non-metals) dissolve in water giving acidic solution and react with bases forming salt and water eg CO_2 , SO_2 , SO_3 , and NO_2 etc.



Basic oxides (oxides of metals) may dissolve in water to give alkaline solutions. They all dissolve in acids to give salt and water eg. Na_2O , MgO etc.



Amphoteric oxides dissolve in both acids and bases eg. Al_2O_3 , ZnO etc.



Neutral oxides have neither acidic nor basic properties eg. CO , N_2O .

The elements of Group 16 form several oxides, which are listed in table, whilst the structures of some important ones are shown in Fig.

Table: Oxides of Group 16 Elements

Element	MO_2	MO_3	Other Oxides
S	SO_2	SO_3	$\text{S}_n \text{O}$ ($n=2, 6$ to 10)
Se	SeO_2	SeO_3	
Te	TeO_2	TeO_3	Te O
Po	PoO_2		Po O

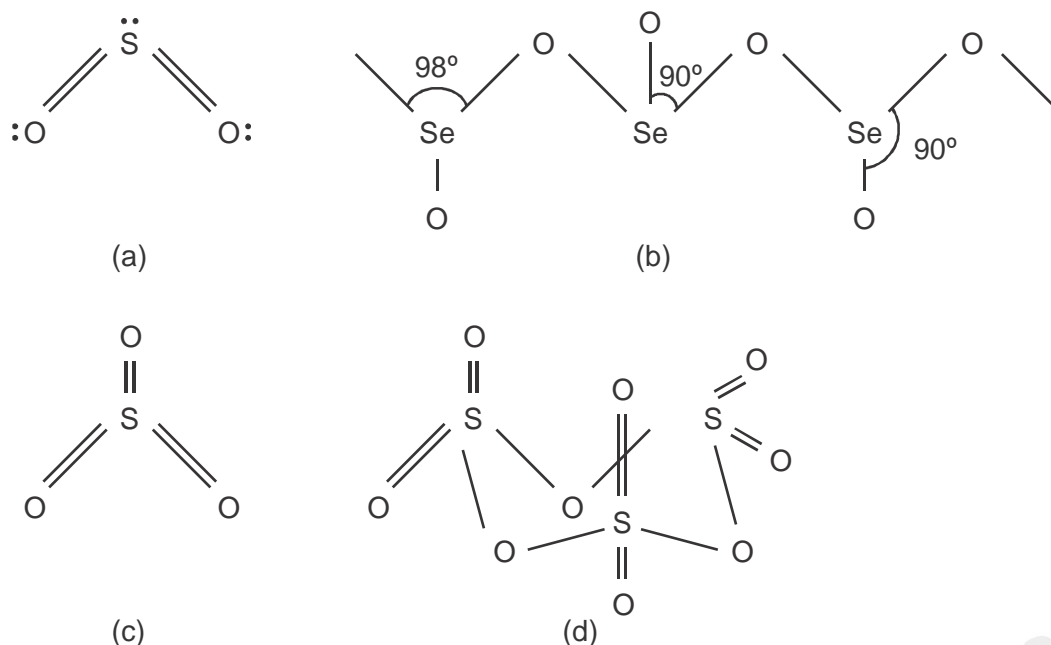


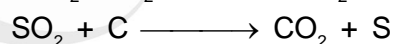
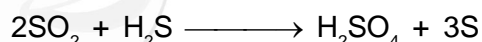
Fig: The Structures of (a) SO_2 (gaseous) (b) SeO_2 (solid) (c) SO_3 (gaseous) (d) Trimer of SO_3 (solid)

The dioxides and trioxides of S and Se have been well characterized. Sulphur dioxide and selenium dioxide are acidic in nature whereas tellurium dioxide is amphoteric. This illustrates increase in basic character on descending a group. SO_2 contains sulphur in +4 oxidation state and may act as both reducing and oxidizing agent depending on the other reactant. The following reactions illustrate this.

a) As reducing agent:



b) As oxidizing agent:

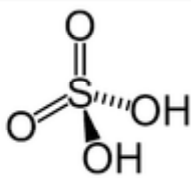
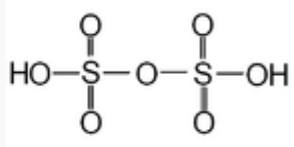
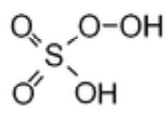
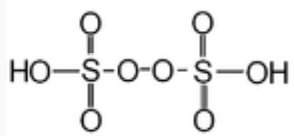
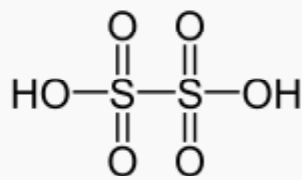
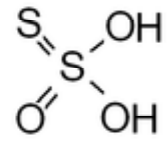
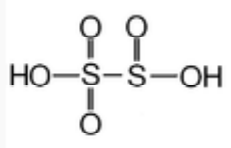
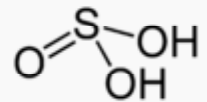


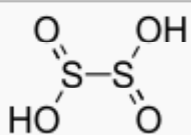
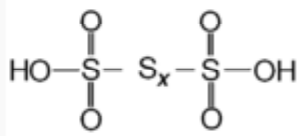
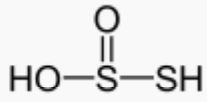
The most important trioxide is SO_3 , which is used in the manufacture of H_2SO_4 . It is an acidic oxide and a powerful oxidizing agent and can oxidize HBr to Br_2 and P to P_4O_{10} .

Oxoacids of Sulphur

Sulphur forms a large number of oxoacids which are listed in Table. Many do not exist in the free state but are known as anions of salts. The oxidation state of sulphur may vary from -2 to +6.

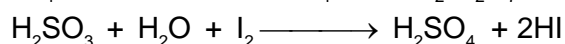
Table: Oxoacids of Sulphur

Acid	Formula	Oxidation state(s)	Structure
Sulfuric acid	H_2SO_4	VI	
Polysulfuric acids including disulfuric acid or pyrosulfuric acid	$H_2SO_4 \cdot nSO_3$	VI	
Peroxymonosulfuric acid	H_2SO_5	VI	
Peroxydisulfuric acid	$H_2S_2O_8$	VI	
Dithionic acid	$H_2S_2O_6$	V	
Thiosulfuric acid	$H_2S_2O_3$	-II (for the terminal sulfur) , VI (for the central atom)	
Disulfurous acid or pyrosulfurous acid	$H_2S_2O_5$	V (of the sulfur atom bonded to 3 oxygen atoms), III (of other sulfur atom)	
Sulfurous acid	H_2SO_3	IV	

Dithionous acid	$H_2S_2O_4$	III	
Polythionic acids	$H_2S_xO_6$	0 (for the bridging S atoms), V (for the terminal central S atoms)	
Thiosulfurous acid	$H_2S_2O_2$	-I (for the exterior sulfur atom), III (for the central atom)	

Sulphurous Acid (H_2SO_3)

Though SO_2 is highly soluble in water, most of it is present as $SO_2 \cdot H_2O$ (hydrate) and H_2SO_3 exists in minutes amounts. However its salts, sulphites (SO_3^{2-}) and hydrogen sulphites (HSO_3^-) are well known. Sulphurous acid possesses both oxidizing and reducing properties. It reduces iodine to HI, $KMnO_4$ to $MnSO_4$ (decolorizes $KMnO_4$) and $K_2Cr_2O_7$ to $Cr_2(SO_4)_3$ (turns $K_2Cr_2O_7$ green).

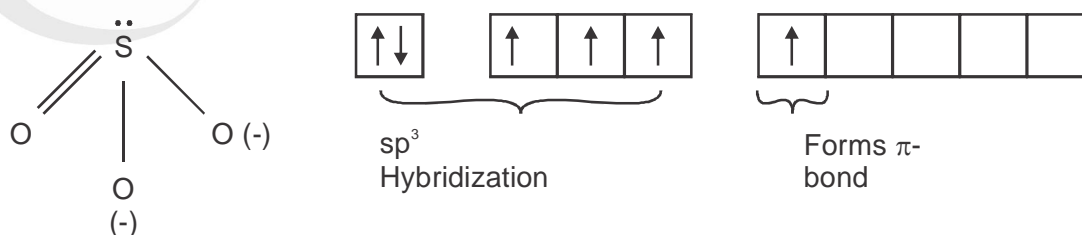


In the presence of strong reducing agents it behaves as an oxidizing agent.



The sulphite ion has a pyramidal structure that is tetrahedral with one position occupied by a lone pair. The bond angle O-S-O is slightly distorted (106°) due to lone pair. The bond length (151 pm) indicates double bond character.

Electronic structure of sulphur atom excited state

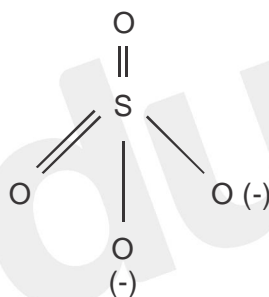


Sulphuric acid is a very important industrial chemical. It is a colourless, viscous liquid, a strong acid oxidizing agent and a powerful dehydrating agent. Some reactions of H_2SO_4 are shown in Table.

Table: Some Reactions of Sulphuric Acid

Reactant	Reaction	Remarks
Zn	$\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$	Dilute Acid
Cu	$\text{Cu} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2$	Concentrated acid
C	$\text{C} + \text{H}_2\text{SO}_4 \rightarrow \text{CO} + \text{SO}_2 + \text{H}_2\text{O}$	Concentrated Acid (oxidizing agent)
NaBr	$2\text{NaBr} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{NaHSO}_4 + \text{Br}_2$	Concentrated Acid (oxidizing agent)
NaI	Similar reaction	
Sugar	$\text{C}_{12}\text{H}_{22}\text{O}_{11} \rightarrow 12\text{C} + 11\text{H}_2\text{O}$	Concentrated Acid (dehydrating agent)

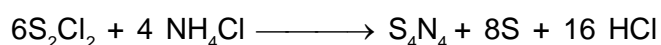
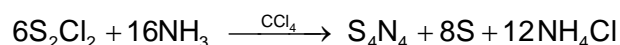
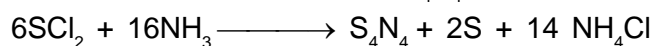
H_2SO_4 is a dibasic acid forming two series of salts, hydrogen sulphate (HSO_4^-) and sulphate (SO_4^{2-}). The SO_4^{2-} ion has a tetrahedral structure



The worldwide production of sulphuric acid is ~ 180 million tons. It is used in fertilizer production, in the manufacture of chemicals, polymers, soaps and detergents, paints pigments dye intermediates and in petroleum refining.

Compounds of Sulphur and Nitrogen

Compounds containing sulphur –nitrogen rings are an area of considerable interest. N and S are diagonally related in the periodic table and have comparable charge densities and electronegativities. The compounds formed have unusual structures, which cannot be explained by the usual bonding theories. The best known is tetrasulphur tetranitride, S_4N_4 that is obtained as follows:



S_4N_4 is a thermo chromic solid i.e. changes colour with temperature – colourless at liquid nitrogen temperature, orange at room temperature and red at 100°C . It is stable in air, but may detonate with shock or friction, it exists as a cradle –shaped ring (Fig). The average S-N bond length (162 pm) indicates delocalized double bond character. The S --- S distances at top and bottom of cradle are ~258 pm indicating weak S-S bonding. S_4N_4 is thus a cage structure.

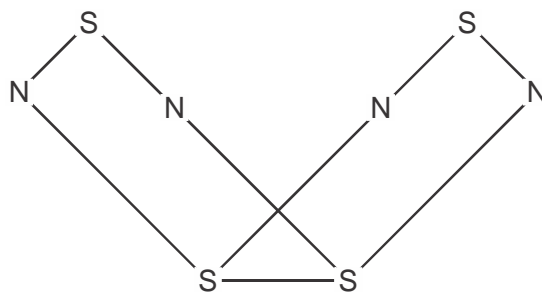
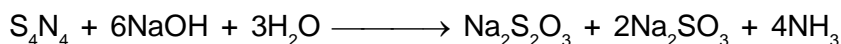


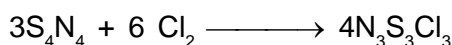
Fig: The Structure of S₄ N₄

S₄N₄ is slowly hydrolyzed by water, but reacts rapidly with warm NaOH when the cage breaks.

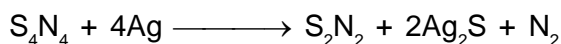


Reduction of S₄N₄ with tin (II) chloride gives tetrasulphur tetraimide, S₄(NH)₄ isoelectronic with S₈ and existing in a crown configuration.

S₄N₄ on oxidation with chlorine produces trithiazyl trichloride.



If S₄N₄ is vaporized under reduced pressure and passed through silver wool, disulphur dinitrogen, S₂N₂ is obtained



It is a crystalline solid having a cyclic structure

Anomalous Behaviour of Oxygen

Oxygen differs in certain aspects from the other members of the group. This is mainly due to its small size, high electronegativity and non-availability of d orbitals. The main differences are

- Oxygen is a diatomic gas, others are polyatomic solids
- Oxygen always shows negative oxidation state (-2) except in compounds with fluorine, where it shows positive oxidation state (eg. In OF₂, oxidation state is +2)
- Oxygen has a tendency towards extensive hydrogen bond formation.

Group 17

The elements in this group are non-metallic in nature. The group comprises of fluorine, chlorine, bromine, iodine and astatine. The last element is radioactive. They are collectively known as halogens (Greek, halos + gen, salt former). The most common compound containing a halogen is sodium chloride (common salt), known since antiquity. Due to high reactivity, halogens do not occur free in nature but in form of salts (halides).

The elements have seven electrons in their outermost shell (ns² np⁵). They acquire noble gas configuration by either gaining an electron to form halide ion, or acquiring a share in one electron by forming a covalent bond. All natural halogens are diatomic. Some physical properties of halogens are summarized in Table.

Table: Physical properties of Group 17 elements

Property	F	Cl	Br	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 5s ² 5p ⁵
Covalent radius (pm)	64	99	114	133
Ionization Energy (I st) (KJ mol ⁻¹)	1681	1251	1140	1008
Electron Affinity (KJ mol ⁻¹)	333	349	325	295
Electronegativity	4.19	2.87	2.68	2.36
Melting Point (°C)	-218.6	-101	-7.25	113.6 *
Boiling Point (°C)	-188.1	-34	59.5	185.2
ΔH dissociation (KJ mol ⁻¹)	158.6	242.6	192.8	151.1

General group Trends

The halogens are all coloured. Fluorine and chlorine are pale –yellow and yellowish –green gases respectively; bromine is a dark-red liquid and iodine a black, lustrous solid that readily sublimates giving a purple vapour.

The halogens are the smallest atoms in the respective periods of the periodic table and the size increases with increase in atomic number. The halogens have very high electronegativity values, which decrease with increase in size. Fluorine is the most electronegative element in the periodic table.

Halogens need one electron to complete the octet, thus the electron affinity values are high. The electron affinity decreases from chlorine to iodine. The electron affinity of fluorine is less than that of chlorine; this is because of the small size of the fluorine atom, which makes the incoming electron encounter a lot of electron – electron repulsion.

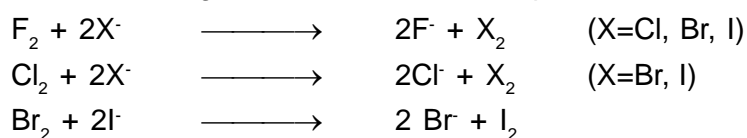
The X-X bond dissociation enthalpy decreases from Cl₂ to I₂. The value for F₂ is abnormally low and it is likely that the weakness of the F-F bond is largely a consequence of repulsions between the nonbonding electron pairs. The low bond enthalpy is responsible for the high reactivity of fluorine.

Oxidation States

Fluorine is the most electronegative element and always shows an oxidation state of -1. This oxidation state is the most common and stable state for all halogens. The other members display positive oxidation states (+1) with oxygen or fluorine. They can also display oxidation states of +3, +5 and +7 by utilizing vacant d orbitals. Positive oxidation states are displayed in halogen oxides and interhalogens. Oxidation states of +4 and +6 are less common and displayed in ClO₂, BrO₂, I₂O₄, Cl₂O₆ and BrO₃.

Oxidizing Power

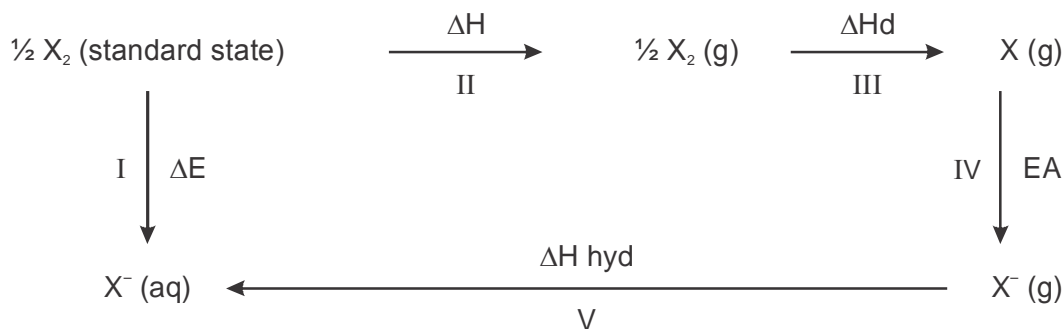
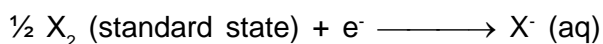
The halogens are good oxidizing agents. Generally speaking, a higher member displaces a lower from the halide. The following reactions illustrate this point.



The oxidizing power decreases down the group, which is reflected in their decreasing reduction potential values.

Element	F ₂	Cl ₂	Br ₂	I ₂
E ⁰ (V)	2.87	1.40	1.09	0.62
$\frac{1}{2} X_2 \longrightarrow 2X^- (aq)$				

The strength of an oxidizing agent depends on several energy terms. The reaction represents the oxidizing action of a halogen and is best represented in the form of a Born - Haber Cycle



If the standard state of the halogen is solid i.e. for I₂, ΔH is the sum of enthalpy of fusion and enthalpy of vaporization. For a liquid halogen, i.e. Br₂, ΔH is enthalpy of vaporization. Energy is absorbed in steps II and III and released in IV and V. From Hess's law ΔE is given by:

$$\Delta E = \Delta H + \Delta Hd + EA + \Delta H \text{ hyd}$$

Where ΔHd = enthalpy of dissociation

EA = electron affinity

ΔHhyd = enthalpy of hydration

For F₂ and Cl₂ which exist as gases, ΔH is omitted. The enthalpy changes associated with the reaction (I) decrease from fluorine to iodine (Table). The high oxidizing power of fluorine is attributed to low enthalpy of dissociation and high enthalpy of hydration.

Table: Enthalpy Values for $\frac{1}{2} X_2 \rightarrow X^- (aq)$

Molecule	$\frac{1}{2}\Delta H_{\text{vap}}$ (KJmol ⁻¹)	$\frac{1}{2}\Delta H_{\text{dissoc}}$ (KJmol ⁻¹)	Electron affinity (KJmol ⁻¹)	$\frac{1}{2}\Delta H_{\text{hyd}}$ (KJmol ⁻¹)	Total ΔH (KJmol ⁻¹)
F ₂	-	+79.4	-333	-460	-713.6
Cl ₂	-	+121.3	-349	-348	-575.7
Br ₂	+15	+96.4	-325	-318	-531.6
I ₂	+30	+75	-295	-305	-4950

Some important reactions of halogens are listed in Table.

Table: Some Reactions of Halogens

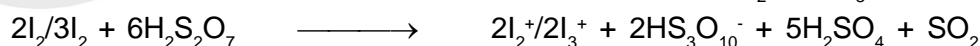
Reaction	Remarks
$X_2 + H_2 \rightarrow 2HX$	All halogens
$nX_2 + 2M \rightarrow 2MX_n$	Most metals form halides, reaction with F_2 vigorous
$3X_2 + 2P \rightarrow 2PX_3$	All halogens, similar reaction with As, Sb, Bi
$5X_2 + 2P \rightarrow 2PX_5$	F_2 , Cl_2 and Br_2
$X_2 + 2S \rightarrow S_2X_2$	Cl_2 and Br_2
$2Cl_2 + S \rightarrow SCl_4$	
$3F_2 + S \rightarrow SF_6$	
$X_2 + H_2O \rightarrow H^+ + X^- + HOX$	Cl_2 and Br_2
$F_2 + 2H_2O \rightarrow 4H^+ + 4F^- + O_2$	
$X_2 + SO_2 \rightarrow SO_2 X_2$	F_2 and Cl_2
$X_2 + CO \rightarrow CoX_2$	Cl_2 and Br_2
$X_2 + H_2S \rightarrow 2HX + S$	All halogens
$3X_2 + 8NH_3 \rightarrow N_2 + 6NH_4X$	F_2 , Cl_2 , Br_2

Basic Properties of Halogens

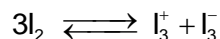
Metallic character increases down the group and decreases across a period. It has been seen in Groups 14, 15 and 16 that the last member (Pb, Bi, Po) has metallic character. This is not very apparent in halogens as very little is known about the last element, astatine. However, there are certain evidences to show existence of halogen cations.

Fluorine is the most electronegative element; it has no tendency to display positive oxidation state. ClF ionizes to form Cl^+ and F^- . Br^+ exist in complexes like $[Br(\text{Pyridine})]^+ NO_3^-$. ICl on electrolysis liberates iodine at anode, indicating formation of I^+ . Many pyridine complexes of I^+ are known eg. $[I(\text{py})]^+ NO_3^-$, $[I(\text{py})_2]^+ ClO_4^-$ and $[I(\text{py})]^+ CH_3COO^-$, (py = pyridine).

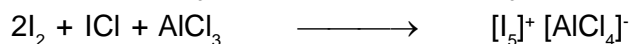
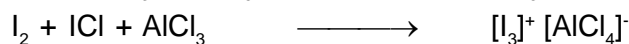
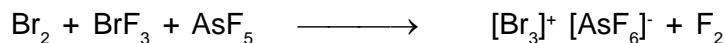
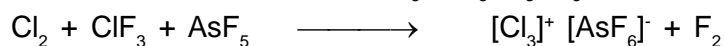
Iodine dissolves in oleum to give a blue solution that contains I_2^+ and I_3^+



Molten iodine conducts electricity and it has been shown that I_3^+ and I_3^- are present

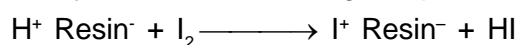


Many other compounds containing Cl_3^+ , Br_3^+ , I_3^+ , I_5^+ have been prepared.



ICl is an electrophilic iodinating agent, believed to contain I^+

When a solution of iodine in an inert solvent is passed through a cation-exchange resin, some iodine is retained by the resin, indicating the presence of I^+



The structures of the triatomic and penta-atomic cations are shown in Fig.

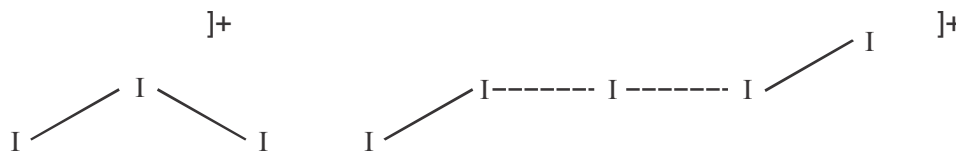


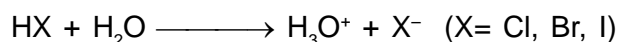
Fig: The structures of I_3^+ and I_5^+

Compounds

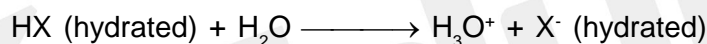
Hydrogen Halides

Binary compounds of hydrogen and halogen are formulated as HX and in the anhydrous state are referred to as hydrogen halides. Their aqueous solutions are called hydrohalic acids. The halogens react with hydrogen forming HX. The reaction with fluorine is violent and explosive while that with iodine is slow illustrating decrease in reactivity on moving down the group. At room temperature HF is a liquid due to strong intermolecular hydrogen bonding, while others are gases. The melting and boiling points shows a gradual increase in the order $HCl < HBr < HI$.

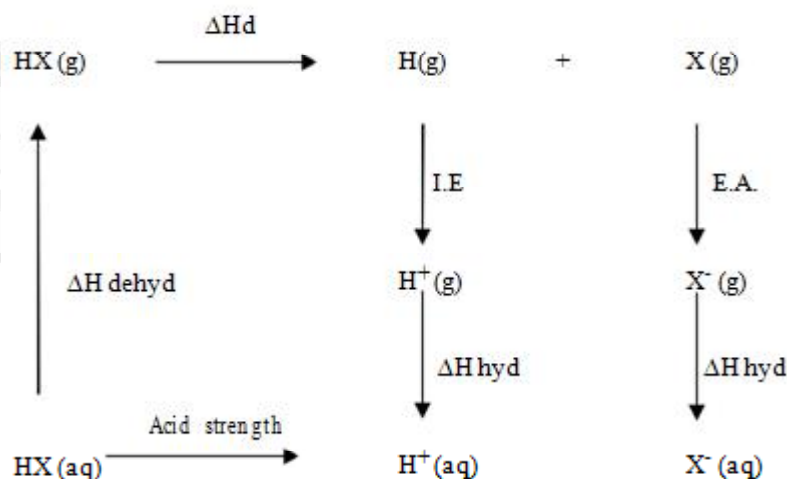
The hydrogen halides are covalent in the gaseous state, but in aqueous solution they ionize and behave as strong acids (except HF, which is a weak acid, $pK_a = 3.2$ at $25^\circ C$). The ionization may be represented as



As fluorine is the most electronegative element, the H-F bond has maximum ionic character and HF should be the strongest acid, however the reverse is true. The paradox arises due to the fact that acid strength which is given by the following reaction



It involves various enthalpy parameters as shown:



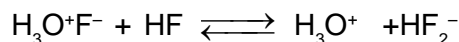
Thus acid strength = $\Delta H \text{dehyd} + \Delta H_d + I.E. + E.A. + \Delta H_{\text{hyd}}$ of H^+ and X^-

Where

ΔH_{dehyd}	=	enthalpy of dehydration
ΔH_d	=	enthalpy of dissociation
I.E.	=	ionization enthalpy
E.A.	=	electron affinity
ΔH_{hyd}	=	enthalpy of hydration

For HF, the enthalpy of dehydration and enthalpy of dissociation are very high. The high enthalpy of hydration of F^- cannot compensate for the same and the total enthalpy change for HF is least negative.

Due to strong hydrogen bonding between F^- and H_3O^+ ($F^- \cdots H^+ - OH_2$), ion pairs of the type $H_3O^+F^-$ are formed, lowering the concentration of H_3O^+ and decreasing acidity. As the concentration of HF increases, the tendency to form H_3O^+ increases:



Halogen Oxides

A large number of halogen oxides are known (Table), some of which are unstable.

Table: Compounds of Halogens with Oxygen

Fluorides		Oxides					
Compound	Oxidation State	Chlorine Compound	Oxidn State	Bromine Compound	Oxidn State	Iodine Compound	Oxidation State
OF_2	-1	Cl_2O	+1	Br_2O	+1	I_2O_5	+5
O_2F_2	-1	ClO_2	+4	BrO_2	+4		
		Cl_2O_6	+6	BrO_3	+6		
		Cl_2O_7	+7				

The binary compounds of fluorine and oxygen are referred to as fluorides. The most stable oxide is I_2O_5 . The oxides of chlorine and bromine decompose readily. The bonds are largely covalent due to small electronegativity difference, however some ionic character is noted in iodine oxides. ClO_2 and Cl_2O find some practical importance as bleaching agents and germicides, while I_2O_5 is used in estimation of carbon monoxide



The reaction is quantitative and the liberated iodine may be estimated by titration with sodium thiosulphate



The structures of some halogen oxides are shown in Fig.

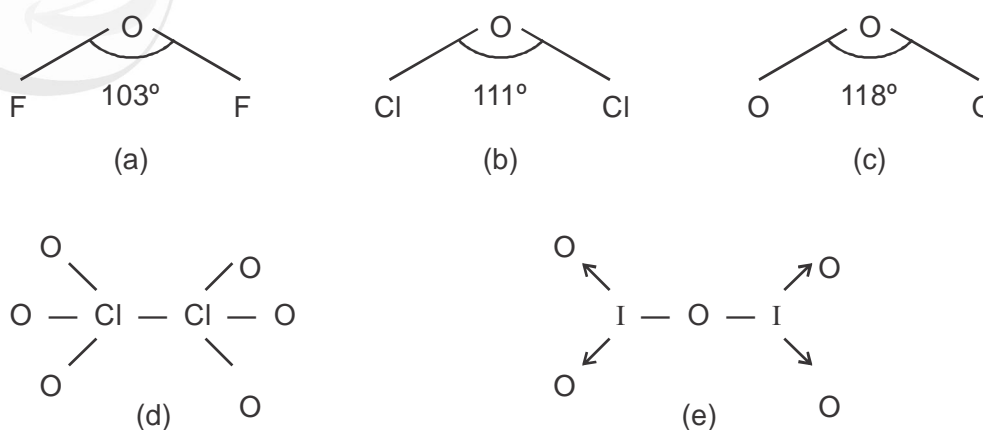


Fig: The structures of (a) OF_2 (b) Cl_2O (c) ClO_2 (d) Cl_2O_6 (e) I_2O_5

The structure of OF_2 , Cl_2O and Br_2O are all related to a tetrahedron with two positions occupied by lone pair of electrons (like H_2O). Repulsion between the lone pairs reduces the bond angle in F_2O from the tetrahedral angle of $109^\circ 28'$ to 105° . In Cl_2O and Br_2O , the bond angles increase due to steric crowding of the large halogen atoms.

Oxoacids of Halogens

Four series of oxoacids of halogens are known (Table).

Table: Oxo acids of Halogens

	HOX	HXO ₂	HXO ₃	HXO ₄
Oxidation State of Halogen	+1	+3	+5	+7
	HOF			
	HOCl	HClO ₂	HClO ₃	HClO ₄
	HOBr	HBrO ₂	HBrO ₃	HBrO ₄
	HOI		HIO ₃	HIO ₄

The structures of the ions formed are shown in fig.

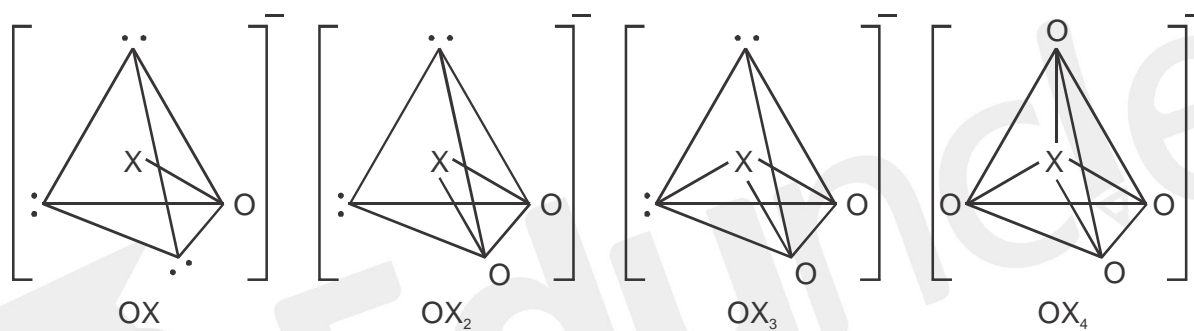
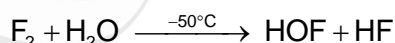
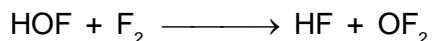
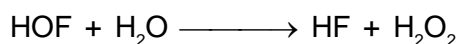


Fig: The Structures of Oxo anions

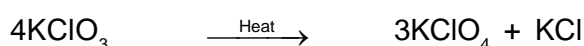
The halogen atom is sp^3 hybridized, there is significant $p\pi - d\pi$ -bonding involving filled 2p orbital of oxygen and vacant d orbitals on halogens. Many of the oxoacids are known in solution, or in form of salts. Fluorine being more electronegative than oxygen does not form any oxoacid except the unstable HOF, which is obtained by passing F_2 over ice



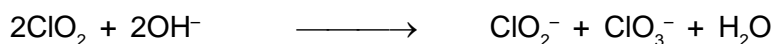
It is difficult to prepare and isolate because of its reactivity towards H_2O and F_2



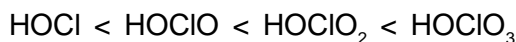
The oxoacids of chlorine are well known and arise from disproportionation of chlorine and related reactions:



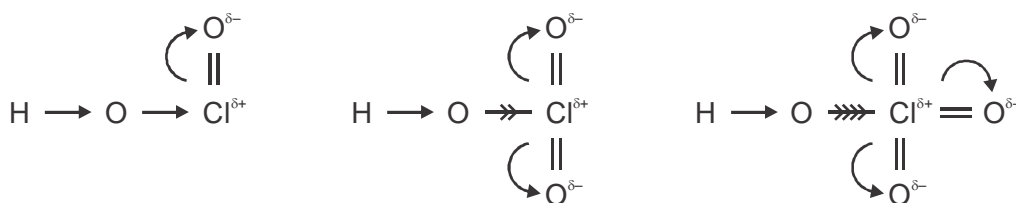
In basic solution chlorine dioxide disproportionate to form chlorate and chlorite and the latter is used to form the free acid.



The acid strength of oxoacids increases with increase in oxidation number of the order of acid strength is



As the oxidation state of the halogen increases, the number of oxygen atoms attached to the halogen increases. As oxygen is more electronegative, the halogen – oxygen bond is polarized leaving a small positive charge on the halogen. This now attracts the electrons of O-H bond towards itself, facilitating loss of hydrogen as proton. Greater the number of oxygen atoms, more is the acidity



Acid strength of oxoacids with halogen in the same oxidation state, decreases with decrease in electro-negativity of the halogen.



Sodium hypochlorite (NaOCl) is used in bleaching cotton fabrics, wood pulp and is a disinfectant. Anhydrous perchloric acid (HClO_4) is a very powerful oxidizing agent. Periodic acid (HIO_4) is used to oxidize alkenes to glycols.

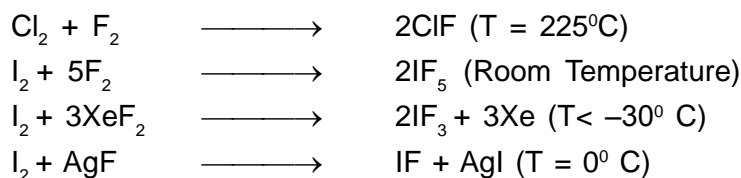
Interhalogens

Halogens react with each other to form interhalogens. These are subdivided into four types. AX , AX_3 , AX_5 , AX_7 (Table)

Table: Some interhalogen compounds

AX	AX_3	AX_5	AX_7
ClF	ClF_3	ClF_5	IF_7
BrF	BrF_3	BrF_5	
BrCl	IF_3	IF_5	
ICl	I_2Cl_6		
IBr			
IF (unstable)			

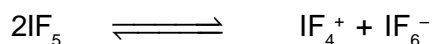
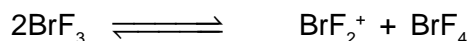
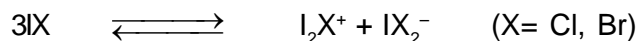
The total number of halogen atoms is even as this gives rise to diamagnetic species. They are generally more reactive than the parent halogens (except fluorine) as A-X bond is weaker than X-X bond. The interhalogens can be prepared in a variety of ways, including direct reaction of the elements (the favoured product often depends on ratio of halogens used) and reaction of metal halides or other halogenating agents. Examples include



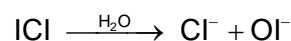
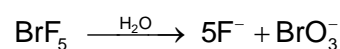
Some interhalogens may serve as intermediates in synthesis of other interhalogens



Several interhalogens undergo auto ionization in the liquid state and are used as non-aqueous solvents



The interhalogens are hydrolyzed to give halide and oxohalide; the larger halogen forms the oxohalide



The shapes of some interhalogens are given in table.

Table: Shapes of interhalogens on basis of VSEPR Theory

Molecules	No. of electron pairs around A	No. of Bond Pairs	No. of lone pairs	Shape
AX	4	1	3	Linear
AX ₃	5	3	2	T – Shaped
SX ₅	6	5	1	Square Pyramid
AX ₇	7	7	0	Pentagonal bipyramidal

The structure can be derived by VSEPR theory. As expected interhalogens of the types AX are linear. Interhalogens of the type AX₃ (ClF₃) are T-shaped, where the central halogens 'A' (Cl) is sp^{3d} hybridized with two lone pairs of electrons (Fig). ICl₃ exists as a dimer, (ICl₃)₂, in the solid state in which two T-shaped ICl₃ units are joined together.

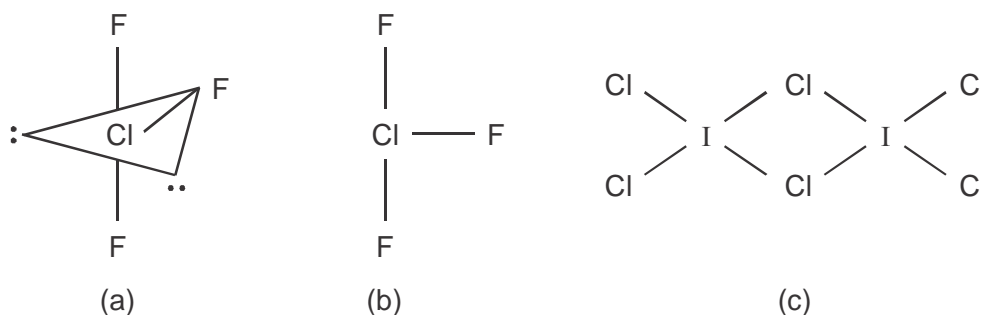


Fig : The structures of Cl F₃ and (ICl₃)₂

Interhalogens of the type AX_5 and AX_7 have square pyramidal and pentagonal bipyramidal structures respectively (Fig)

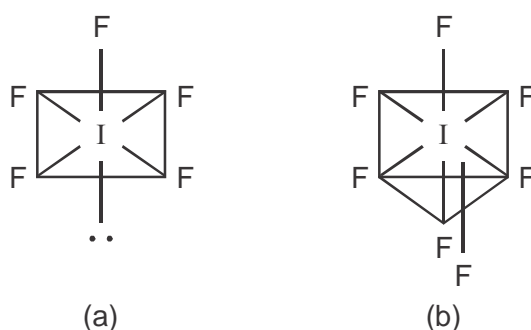


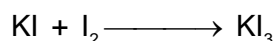
Fig: The structures of (a) IF_5 and (b) IF_7

In AX_5 the central halogen is sp^3d^2 hybridized and there is one lone pair of electrons whereas in AX_7 the central halogen has sp^3d^3 hybridization.

Ternary interhalogens have recently been reported e.g. $IFCl_2$, $IFCl$.

Polyhalides and polyhalonium ions

Halide ions associate with molecules of halogens or interhalogens to form polyhalides. The solubility of iodine is enhanced in potassium iodide due to formation of triiodide ion, I_3^- .



More complex ions like I_5^- , I_7^- are known. Polyhalides containing two or three different halogens are known eg $[ICl_2]^-$, $[BrF_4]^-$, $[BrICl]^-$ etc. polyhalonium cations eg. $[ICl_2]^+$, $[BrF_2]^+$ are obtained as a result of auto ionization of ICl_3 and BrF_3 . Other cations e.g. Br_3^+ , I_3^+ $[ClF_6]^+$ etc. are also known.

Pseudohalogens

Parallels have been observed between the chemistry of the halogens and other dimeric species. Such molecules are called pseudohalogens eg. Cyanogens $(CN)_2$, thiocyanogen $(SCN)_2$ and selenocyanogen $(SeCN)_2$. A pseudohalogen is a univalent chemical aggregate, comprising of two or more electronegative atoms, which in the free state show properties similar to halogens. They combine with hydrogen to form an acid and with silver, a salt insoluble in water. The anions of pseudohalogens are called pseudohalides. The most important pseudohalide is CN^- and its similarity with Cl^- is shown in Table.

Table: Comparison of a Pseudohalogen with a Halogen

Characteristics	Examples	
	Halogen	Pseudohalogen
Neutral diatomic species	Cl_2	$(CN)_2$
Anion	Cl^-	CN^-
Acid with hydrogen	HCl	HCN
Insoluble Salts	AgCl	AgCN
Interhalogen compound	ICl, BrCl	ClCN, BrCN, ICN
Anionic Complexes	$[CoCl_6]^{3-}$	$[Co(CN)_6]^{3-}$
	$[CuCl_4]^{2-}$	$[Cu(CN)_4]^{2-}$

Group 18

The elements in Group 18, long designated as the “inert” or “rare” gases, no longer satisfy these labels. They are known to form chemical compounds and are rather abundant. They are better referred to as “noble” gases due to their reluctance to react under normal conditions. This group comprises of helium, neon, argon, krypton, xenon and radon. Apart from radon, which is radioactive, the others are present in the atmosphere.

Helium has two electrons, which forms a complete shell $1s^2$. The others have a complete octet of electrons and the configuration is $ns^2 np^6$. This configuration is very stable and is related to their un-reactivity. These elements have an electrons affinity of nearly zero and very high ionization energy. Under normal conditions these elements have very little tendency to gain or lose electrons.

Important properties of noble gases are summarized in Table.

Table: Physical properties of the Noble Gases

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic Number	2	10	18	36	54	86
Electronic Configuration	$1s^2$	$[\text{He}]2s^2 2p^6$	$[\text{Ne}]3s^2 3p^6$	$[\text{Ar}]3d^{10} 4s^2 4p^6$	$[\text{Kr}]4d^{10} 5s^2 5p^6$	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^6$
Vander Waal's radius (pm)	-	131	174	189	210	215
Ionization Energy (KJmol^{-1})	2372	2081	1521	1351	1170	1037
Melting Point ($^{\circ}\text{C}$)	-	-248.6	-189.4	-157.2	-111.8	-71.0
Boiling Point ($^{\circ}\text{C}$)	-269	-246.1	-185.9	-153.4	-108.1	18.1

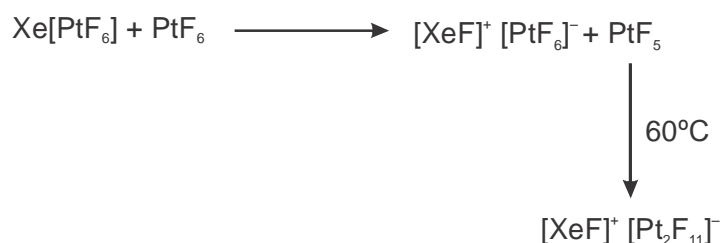
Physical Properties

The elements exist as colourless, monoatomic gases. Individual atoms are held by weak vander waals forces, hence melting points and boiling points are very low. In fact the boiling point of helium is the lowest of any element.

Chemistry

The first chemical compounds containing noble gases were known as clathrates or cage compounds where noble gas atoms were trapped in the crystal lattice of other compounds. When water or solutions containing quinol (p- dihydroxybenzene) were crystallized under high pressures of certain gases, the molecules of the gas were trapped in the cavities in the hydrogen-bonded lattice. Clathrates of argon, krypton and xenon have been prepared. No clathrates are known for helium and neon, which are too small to be trapped.

Even though clathrates of three noble gases were known, no real compounds containing covalently bonded noble gas atoms were synthesized till 1962. Neil Bartlett (1962) observed that PtF_6 changed colour on exposure to air. He attributed this to the formation of $\text{O}_2^+ [\text{PtF}_6]^-$. He noted the similarity in ionization energies of xenon (1170 KJ mol^{-1}) and oxygen molecule (1175 KJ mol^{-1}) and repeated the experiment, reacting Xe with PtF_6 . He obtained a yellow solid and formulated it as $\text{Xe}^+ [\text{PtF}_6]^-$. The reaction was found to be more complicated.



This opened the field for the study of chemistry of noble gases. In a matter of months XeF_2 and XeF_4 were characterized.

The known noble gas compounds of xenon are the most diverse followed by some compounds of krypton. The study of radon chemistry is hampered by its radioactivity. The first stable compound of argon, ArF has been reported recently (2000). The ionization energies of the lighter noble gases are too high to allow formation of compounds. Most compounds of noble gases are restricted to the highly electronegative elements, fluorine and oxygen.

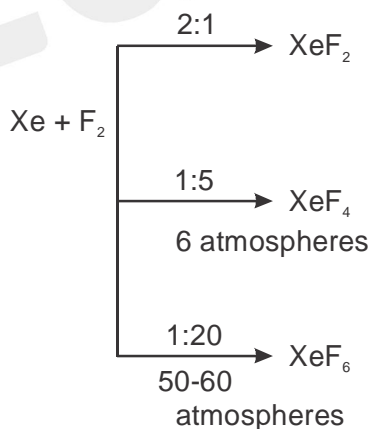
Compounds of Xenon

Some compounds of xenon are shown in Table.

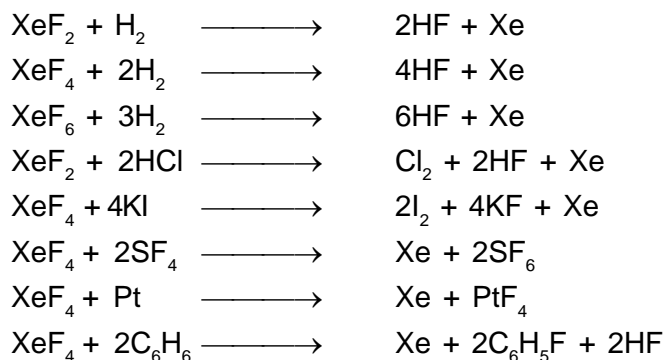
Table: Some Compounds of Xenon

Compounds	Oxidation state	Number of electron pairs around Xe			Structure
		Bond Pairs	Lone Pairs	Total	
XeF_2	+2	2	3	5	Linear
XeF_4	+4	4	2	6	Square planar
XeF_6	+6	6	1	7	Distorted octahedral
XeO_3	+6	6	1	7	Pyramidal (3Xe=O bonds)
SeO_2F_2	+6	6	1	7	See – saw (2Xe=O bond)
XeOF_4	+6	6	1	7	Square pyramid (one Xe=O bond)
XeO_4	+8	8	0	8	Tetrahedral (4Xe = O bonds)

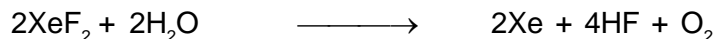
Xenon and fluorine combine on heating in a sealed nickel vessel at 400°C , the product depends on the F_2/Xe ratio



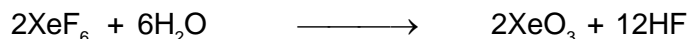
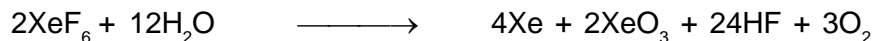
The fluorides are strong oxidizing and fluorinating agents as indicated by the following reactions



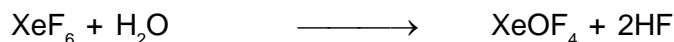
The fluorides differ in their reactivity with water. XeF_2 undergoes slow hydrolysis in neutral or acidic medium, but rapid hydrolysis in alkaline medium.



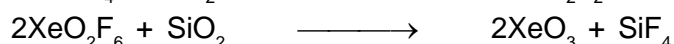
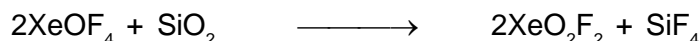
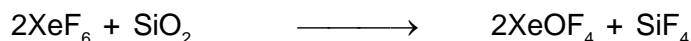
The reactions of XeF_4 and XeF_6 are violent and the explosive XeO_3 is formed.



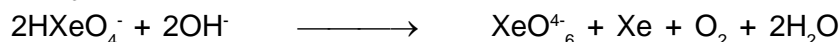
With small amounts of water, partial hydrolysis occurs to give XeOF_4



XeF_6 is highly reactive and combines with silica



XeO_3 undergoes alkaline hydrolysis to give the xenate ion, HXeO_4^- which disproportionate to give perxenate (XeO_6^{4-}) and Xe



Perxenates are powerful oxidizing agents XeF_2 acts as a fluoride ion donor and reacts with covalent pentafluorides forming species of the type $[\text{XeF}]^+ [\text{MF}_6]^-$, $[\text{XeF}]^+ [\text{M}_2\text{F}_{11}]^-$ and $[\text{Xe}_2\text{F}_3]^+ [\text{MF}_6]^-$, (M= P, As, Sb, Nb, Ta, Ru, Rh, Ir, Pt). XeF_4 reacts less readily with PF_5 ,

AsF_5 and SbF_5 . XeF_6 reacts both as fluoride ion donor and acceptor forming species like $[\text{XeF}_5]^+ [\text{MF}_6]^-$ (M = As, Pt) and $\text{M}^+[\text{XeF}_7]^-$ (M= Rb, Cs)

The structures of some xenon compounds are shown in Figure. XeF_2 and XeF_4 have structures entirely in accordance with VSEPR description. XeF_2 is linear (Xe is sp^3d hybridized and there are three lone pairs on Xe). XeF_4 is planar (sp^3d^2 hybridized Xe with two lone pairs).

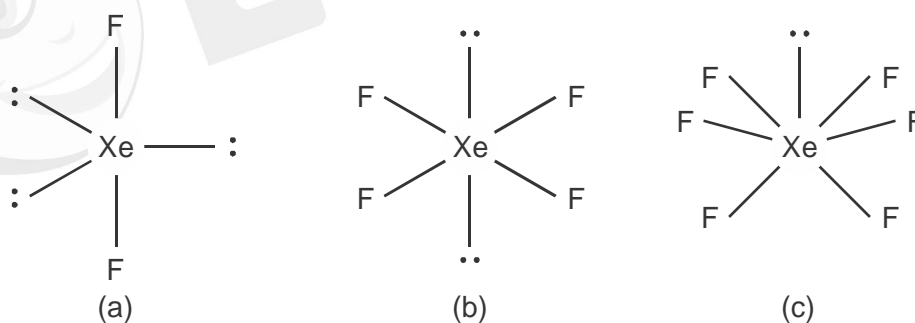
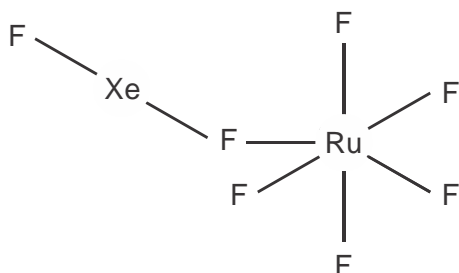


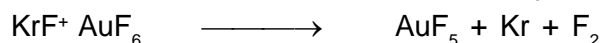
Fig: The structures of xenon fluorides

The structure of XeF_6 cannot be interpreted by VSEPR theory, which predicts sp^3d^3 hybridization with one lone pair occupying a definite position on xenon. However no definite location of the lone pair is noted. The structure seems to be distorted octahedral with the lone pair apparently emerging from the centre of one of the faces.

Positive ions containing xenon are also known. The compound $[\text{XeF}]^+ [\text{RuF}_6]^-$ has the linear XeF^+ ion attached to the fluorine of the anion. The anion comprises of Ru, octahedrally surrounded by six F atoms.



The chemistry of krypton is much more limited. The only known neutral fluoride is KrF_2 , which is useful as a fluorinating agent. It can raise metals to unusual oxidation states.



The first compound containing the Kr-O bond was $[\text{Kr}(\text{OTeF}_5)_3]$ which is unstable.

The radioactivity of radon has made the study of its chemistry difficult. RnF_2 and a few other compounds have been observed through tracer studies.

