

### Oxidation states of nitrogen family

All the elements have 5 electrons in their valence shell. Gain of 3 electrons requires a lot of energy so it takes place only in nitrogen as it is small in size. Nitride ion has -3 oxidation state. The tendency to show -3 oxidation state decreases down the group. All the elements show +3 and +5 oxidation state. On moving down the group the stability of +5 oxidation state decreases while that of +3 oxidation state increases due to inert pair effect.

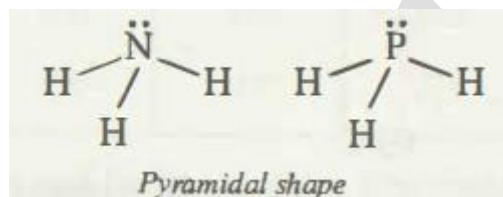
### Maximum covalency of nitrogen family

Since nitrogen does not possess d-orbitals in its valence shell, it can show a maximum covalency of 4. Other elements have empty d-orbitals and can utilize all their valence orbitals to exhibit covalency of 5 or 6.

### Occurance of boron family

Boron occurs in isotopes forms like orthoboric acid, borax, kernite, colemanite. Aluminium is third most abundant element by weight found in earth's crust. Gallium, indium, and thallium are less abundant than aluminium.

### Structure of hydrides of nitrogen family



### Electronic configuration of boron family

The general electronic configuration of elements of boron family is  $ns^2 np^1$ . The valence electrons enter in p-orbital hence they are called as p-block element.

### Atomic and ionic radii of boron family

The atomic and ionic radii of boron family is less than those of group 2 elements. This is because from left to right in a given period, the nuclear charge increases while the new electron enters the same shell.

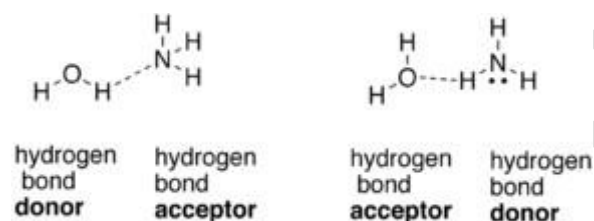
### Order of ionization enthalpy of boron family

The first ionization enthalpies of the elements of boron family are lower than the corresponding elements of group 2, i.e., alkaline earth metals. Ionization enthalpies increases down the group.

### Order of electronegativity of boron family

The elements of boron family are more electronegative than the elements of alkali metals and alkaline earth metals. The electronegativity first decreases from B to Al and then marginally increases down the group.

### Hydrogen bonding in nitrogen family



### Thermal stability of hydride of nitrogen family

All the members form volatile hydrides of the type  $AH_3$ . All hydrides are pyramidal in shape. The bond angle decreases on moving down the group due to decrease in bond pair-bond pair repulsion.

### Electropositive character of boron family

The boron family elements are less electro-positive than alkaline earth metals and on moving down the group this characteristic increases.

### Methods of preparation of oxides of nitrogen family

Oxidation State	Oxides				
	N	P	As	Sb	Bi
+1	N <sub>2</sub> O Nitrous oxide	-	-	-	-
+2	NO Nitric oxide	-	-	-	-
+3	N <sub>2</sub> O <sub>3</sub> Dinitrogen trioxide	P <sub>4</sub> O <sub>6</sub>	As <sub>4</sub> O <sub>6</sub>	Sb <sub>4</sub> O <sub>6</sub>	Bi <sub>2</sub> O <sub>3</sub>
+4	N <sub>2</sub> O <sub>4</sub> Dinitrogen tetroxide	-	-	-	-
+5	N <sub>2</sub> O <sub>5</sub> Dinitrogen pentoxide	P <sub>4</sub> O <sub>10</sub>	As <sub>4</sub> O <sub>10</sub>	Sb <sub>4</sub> O <sub>10</sub>	⊗

Nitrogen has a strong tendency to form  $p\pi-p\pi$  multiple bonds between N and O atoms, whereas other elements of this group do not. Nitrogen forms five oxides with oxidation state from 1 to 5 while others show 3 and 5 only.

### Inert pair effect

The inert pair effect is the tendency of the electrons in the outermost atomic orbital to remain unionized or unshared in compounds of post-transition metals.

### Melting and boiling point trend of boron family

The M.P. and B.P. of boron family do not show regular trend, this is probably due to unusual crystal structures of B to Ga. Actually melting point decreases sharply on moving down the group from B to Ga then increases Ga to Tl.

### Reactivity of boron towards air or dioxygen

All the metals of group 13 react with dioxygen, however the reactivity increases down the group. They form trioxides at high temperature.

### **Reactivity towards acids and bases**

Boron does not react with non-oxidising acids such as hydrochloric acid, all other elements reacts with oxidising and non-oxidising acids.

### **Pentahalides of nitrogen family**

P and Sb form stable pentahalides but nitrogen do not form pentahalides due to absence of d-orbitals in valence shell. Bi do not form pentahalides due to inert pair effect.  $\text{PCl}_5$  is used as a chlorinating agent. Pentahalides are more covalent than the corresponding trihalides. Moreover, the covalent character of halides decreases from nitrogen to bismuth.

### **Reactivity of boron family towards halogens**

Boron family react with halogens at high temperatures forming trihalides.

### **Reactivity of nitrogen towards metals**

All the elements of group 15 form binary compounds with metals in the  $3^{\text{rd}}$  oxidation state.

### **Uses of elements of boron family**

Boron is used as a catalytic agent, as deoxidiser in casting of copper.  
Al is largely used in house hold utensils, as Al foil etc.

### **Physical properties of boron**

1. Boron is an extremely hard solid with high m.p. 2453 K.
2. Elemental boron exists in several different allotropic forms.

### **Anamolous properties of nitrogen**

Exceptionally small atomic size

High electronegativity

High ionisation enthalpy

Absence of d-orbitals in its valence shell

### **$p\pi$ multiple bonds in nitrogen**

Because of its small size and high electronegativity, it forms  $p\pi$ – $p\pi$  multiple bonds. It exists as a diatomic molecule with triple bond. They are held by weak van der Waals forces.

### **methods of extraction of boron**

Boron is extracted from boric acid and colemanite minerals.

### **Chemical properties of boron**

1. Boron reacts with dioxygen to form trioxide.
2. Boron does not react with non-oxidizing acids such as hydrochloric acid, however, reacts at high temperature with sulphuric and nitric acid.
3. Boron resists the action of alkalis up to 773 K but above this temperature, it reacts forming borates and liberating dihydrogen gas.

### **Catenation property of group 15**

The elements of group 15 also show property of catenation, but, to a less extent than carbon. Phosphorous has the maximum tendency for catenation. Nitrogen has least tendency due to weak bond of N–N. Nitrogen can form chains up to three N-atoms.

### **Diagonal relationship of boron and silicon**

Boron shows some anomalous properties in the respective group to which it belongs, in these anomalous properties they resemble the second elements of the succeeding group. Thus boron

and silicon shows similarities in their properties this develops diagonal relationship between them.

### **Reactivity of nitrogen and phosphorous**

Due to triple bond in nitrogen, the bond length is small and bond energy is large. It is unreactive and inert.

P-P bond is much weaker so it is more reactive than nitrogen. The reactivity decreases down the group from As to Bi.

### **Anomalous behaviour of boron**

1. Boron is a nonmetal while other member are metals.
2. Boron shows allotropy while other member do not.
3. Amongst the elements of group 13, boron has highest melting and boiling point.
4. Boron hydride is quite stable.

### **Structure composition of borax**



1. Borax is most important compound of boron family, which contains tetra nuclear units, in which boron is bonded to oxygen atom and hydroxy group.

### **Methods of preparation of borax**

1. From tincal: Naturally occurring borax is called tincal or suhaga. Tincal obtained from dried up lakes contains about 50% borax.
2. It is boiled with water and filtered to remove insoluble impurities of clay, sand etc.
3. The filtrate is concentrated when crystals of borax separate out.

### Physical properties of dinitrogen

It is colourless, tasteless and non-toxic gas.

It is very slightly soluble in water.

It has low freezing point.

### Properties of borax

1. It is white crystalline solid, less soluble in cold water but more soluble in hot water.
2. The aqueous solution of borax is alkaline due to hydrolysis.

### borax bead test

On heating, borax lose its water of crystallization and swells up to form puffy mass. On further heating, it melts into a clear liquid which solidifies to a transparent glass like, bead which consists of sodium metaborate and boric anhydride.

### Uses of borax

Borax is used in manufacture of enamels and glazes for earthen wares, as a flux in soldering, in the preparation of medicinal soaps due to antiseptic properties etc.

### Methods of preparation of orthoboric acid

**1.From borax.** Boric acid is obtained by treating a hot concentrated solution of borax with hydrochloric acid or sulphuric acid. The resulting solution on concentration gives crystals of boric acid.

**2.By hydrolysis of boron compounds.** Boric acid can also be prepared by the hydrolysis of boron compounds such as halides, hydrides and nitrides.

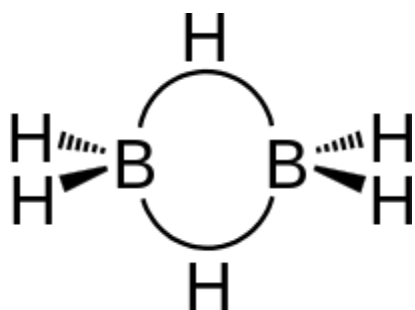
### Properties of orthoboric acid

It is white crystalline solid with a soft soapy touch having a low density of  $1.48 \text{ gm}^3$ . It is sparingly soluble in cold water but fairly soluble in hot water. Boric acid behaves as a very weak acid.

### Uses of orthoboric acid

Boric acid is used in the manufacture of heat resistant boron silicate glasses. It is used as a preservatives for milk and food stuffs and also used in the manufacture of enamels and glazes in pottery.

### Structure of diborane



1. In diborane, each boron atom has three valence electrons for sharing. X-diffraction studies shows that, there are two types hydrogen atoms in boron structure, called as terminal hydrogen.
2. Bonding diagram of diborane (B<sub>2</sub>H<sub>6</sub>) showing with curved lines a pair of three-center two-electron bonds, each of which consists of a pair of electrons bonding three atoms, two boron atoms and a hydrogen atom in the middle.
3. Diborane adopts a D<sub>2h</sub> structure containing four terminal and two bridging hydrogen atoms.

### Uses of boron hydride

Sodium borohydride is used to reduce aldehydes and ketones in the production of pharmaceuticals including vitamin A as well as many flavorings and aromas.

### Properties and uses of aluminium chloride

Aluminium chloride (AlCl<sub>3</sub>) is white, but samples are often contaminated with iron trichloride, giving it a yellow colour. The solid has a low melting and boiling point. It is mainly produced and consumed in the production of aluminium metal, but large amounts are also used in other areas of chemical industry. The compound is often cited as a lewis acid. Its best application in chemical industry is being a catalyst.



### **Method of preparation of alum**

In order to obtain alum from alunite, it is calcined and then exposed to the action of air for a considerable time. During this exposure it is kept continually moistened with water, so that it ultimately falls to a very fine powder. This powder is then lixiviated with hot water, the liquor decanted, and the alum allowed to crystallize.

### **Properties and uses of alum**

Alums are useful for a range of industrial processes. They are soluble in water, and crystallize in regular octahedra. When heated they liquefy, and if the heating is continued, the water of crystallization is driven off, the salt froths and swells and at last an amorphous powder remains. They are astringent and acidic.

### **Preparation of potash alum**

1. Potash alum is prepared by leaching of alumina from bauxite.
2. Which is then reacted with potassium sulphate to prepare potash alum.

### **Properties and uses of potash alum**

1. Uses : Aluminum potassium sulfate or potash alum, is used as an astringent and antiseptic in various food preparation processes such as pickling and fermentation and as a flocculant for water purification.
2. Properties : It is soluble in water. When it is heated it gives nearly porous mass which is known as burnt-alum.

### **Uses of boron and their compounds**

1. Boron is an extremely hard refractory solid with high melting point.
2. Boron fibers have enormous tensile strength and hence are used to make bullet-proof vests and light composite materials for aircraft.
3. It is used in steel industry for increasing hardness etc.

### **Uses of aluminium and its compounds**

Being light and good conductor of electricity it is used for making transmission cables and for winding the moving coils of dynamo or motors. Its foils are used in wrapping fine particles etc.

### **Occurance of carbon family**

In carbon family, carbon occur in the native state in form of coal, graphite, and diamond. Silicon, is the second most abundant element by weight in the earth's crust. Tin occur in form of tinnestone or cassiterite. The principal ore of lead is galena. Germanium occurs in traces.

### **Physical properties of ammonia**

1. Ammonia is a colorless gas with pungent odour.
2. Its freezing and boiling points are 198.4K and 239.7K.
3. It is highly soluble in water.

### **Order of covalent radii of carbon family**

Atomic radii of these elements regularly increase as we move down the group primarily due to the addition of new energy shell at each succeeding elements.

### **Chemical properties of ammonia**

Thermal Stability: Ammonia is highly stable.

Combustible: Ammonia is combustible in air.

Basic Character: Ammonia molecule has a strong tendency to donate its lone pair of electrons of nitrogen to other molecules.

### **Uses of ammonia**

In the manufacture of fertilizers such as urea, ammonium phosphate, ammonium nitrate, ammonium sulphate etc.

In the manufacture of rayon.

In the manufacture of nitric acid by Ostwald's process.

Used as a reagent in laboratory.

Used as a refrigeration fluid.

### **Ionization enthalpy of carbon family**

The ionization enthalpy of carbon family is higher than corresponding elements of boron family due to increased nuclear charge.

### **Tests of ammonia**

The ammoniacal smell of ammonia is easily detectable having a characteristic pungent smell. Ammonia turns moist red litmus blue, and moist turmeric paper brown. When added to a solution of copper sulphate, ammonia turns the solution deep blue.

### **Physical properties of carbon family**

All the carbon family member are solids. Carbon and silicon are non metals, germanium is metalloid, whereas tin and lead are soft metals with low melting points. The M.P. and B.P. of carbon family are higher than those of corresponding elements of boron family.

### **Oxidation of carbon family**

The carbon family elements have four electrons in outer most shell. All the elements show an oxidation state of +4. However, as we move down the group from C to Pb, the stability of +4 oxidation state decreases while that of +2 oxidation state increases due to inert pair effect.

### **Discovery of ammonia**

Ammonia was discovered by the two German chemists Fritz Haber and Karl Bosch. Industrially ammonia is made by the Haber-Bosch process which converts nitrogen gas into the air into ammonia.

### **Occurrence of Ammonia**

Ammonia is found in trace quantities in the nature, being produced from the nitrogenous animal and vegetable matter. It occurs in nature in the form of salt deposits.

### **Trend of covalent to ionic character down the group of carbon family**

In carbon family covalent character decreases from top to bottom and ionic character increases, because non-metallic property of C and Si decreases and metallic property of tin and lead increases.

### **Trend in oxidising and reducing properties of carbon family**

1. Sn in +2 oxidation state is reducing agent.
2. Lead compounds are stable in +2 state. Lead in +4 oxidation state acts as oxidizing agent, so the oxidizing and reducing nature from top to bottom become specific.
3. Carbon always present in +2 to +4 oxidation states.

### **Tendency of formation of p(pi) - p(pi) bonds in carbon family**

1. In carbon family Carbon have tendency to form  $p\pi-p\pi$  multiple bonds with itself and with other atoms of small size and high electronegativity, because its size is small, but other element with heavier nucleus do not form this type of bond due to large and diffused atomic orbitals.

### **Tendency to form d(pi) - p(pi) bonds in carbon family**

1. Carbon does not have d-orbitals and hence it does not form  $d\pi-p\pi$  bonds.
2. However, silicon and other heavier elements of this group because of presence of vacant d-orbitals in them tend to form  $d\pi-p\pi$  bond.

### **Maximum covalency and tendency to form complexes in carbon family**

Carbon because of the absence of d-orbitals, cannot expand its valency and hence, its maximum covalency or coordination number is four. But other member show coordination greater than 4 forming penta-coordinated and hexa-coordinated complexes.

### **Reactivity of carbon towards oxygen and their properties**

All the element of group 14 when heated in oxygen form oxides. These are mainly of two types, i.e., monoxides of the formula MO and dioxides of the formula MO<sub>2</sub>. These oxides shows the properties like acid-base character, reducing-oxidizing nature etc.

### **Reactivity of carbon family towards water and their properties**

Carbon, silicon and germanium do not decompose water at all. Tin decomposes steam to form tin oxide and dihydrogen gas.

### **Reactivity of carbon family towards halogens and their properties**

Except C all members of carbon series form halides of formula  $MX_4$ , which are covalent in nature.

### **Properties of compound of lead**

In a vast majority of compounds lead forms, it occurs in oxidation states +2 and +4. One principal difference between lead(II) and lead(IV) compounds is that the former are normally ionic and the latter are often covalent. Even the strongest oxidizing elements (oxygen, fluorine) oxidize lead to only lead(II) initially.

### **Extraction of Lead**

Lead is mainly extracted from galena. The extraction involves following steps:

Concentration

Reduction

Purification

### **Purification of lead**

Lead can be purified by following processes:

Softening process

Desilverisation

Electrolytic refining

### **Physical properties of lead**

It is bluish gray metal

malleable but not ductile

Poor conductor of electricity

### **Chemical properties of lead**

lead is not attacked by dry air. When heated with air or oxygen it forms monoxide. Lead dissolved in hot con. HCl and NaOH.

### **Uses of Lead**

Lead is used : for making pipes for ing water, for making bullets and lead accumulators, and alloys.

### **Anomalous behaviour of carbon**

Carbon is the 1st element in the p-block family, hence its atomic number is very small i.e. 6, because of small atomic number, the size of carbon atom is very small as compared to other element in the group. So the physical and chemical properties of carbon is different than other member in the series.

### **Allotropes of carbon and examples**

Carbon shows allotropic forms like Diamond, graphite and Buckminsterfullerene.

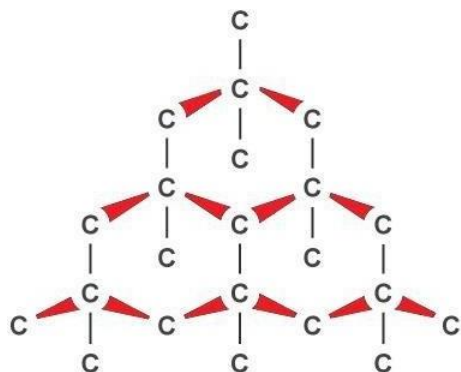
### **Solubility of carbon**

Carbon forms covalent compounds is preferably soluble in non-polar solvents.

### **Action of carbon with oxygen**

Carbon reacts with oxygen to form carbon monoxide and carbon dioxide.

### Structure of Diamond



1. Diamond has three dimensional structure.
2. Each carbon atom is bonded to four other carbon atoms, which occupy four corners of a tetrahedron and each of these carbon four carbon atoms are bonded to four more carbon atoms.
3. Such a pattern is repeated in the entire crystal atoms.

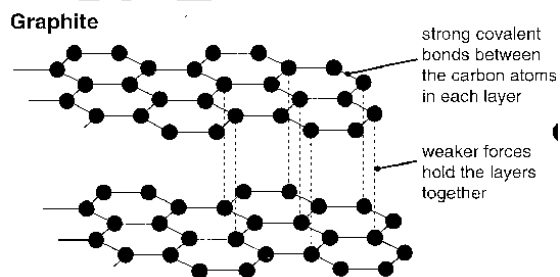
### Discovery of Nitric acid

A Dutch Chemist named Johann Rudolf Glauber made a new discovery, he was the first to make the compound Nitric Acid, with the distillation of salt peter and sulfuric acid. The compound that he created, was later named "Glaubers Salt", after the man who discovered it.

### Properties and uses of diamond

Diamond has high density of  $3.51 \text{ gcm}^{-3}$  due to three dimensional giant structure. It is a non-conductor of electricity. Diamond is the hardest substance on the earth. It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

### Structure of graphite



1. Graphite has a two dimensional sheet like structure and the sheets may be considered as fused system of planar hexagonal rings.
2. In the planar hexagonal rings, each carbon atom is bonded to three other carbon atom.

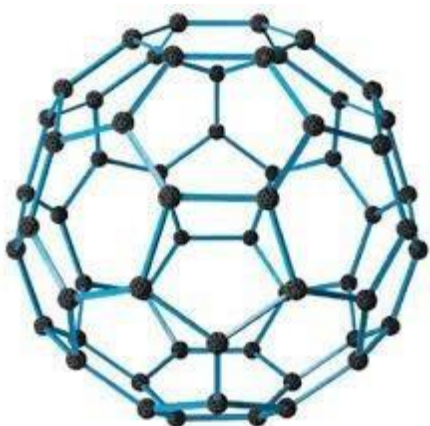
### Occurrence of Nitric acid

Nitric acid is not a naturally occurring substance, it is created in a laboratory. The most common way that it is made is by taking nitrogen dioxide and mixing it with water, but, this must be done in the presence of air.

### Properties and uses of graphite

Graphite contain carbon atom which shows  $sp^2$  hybridization, hence, it become good conductor of heat and electricity. It is very soft and slippery and for this reason, graphite is used as lubricant in machine running at high temperature, where oil cannot be used as lubricant.

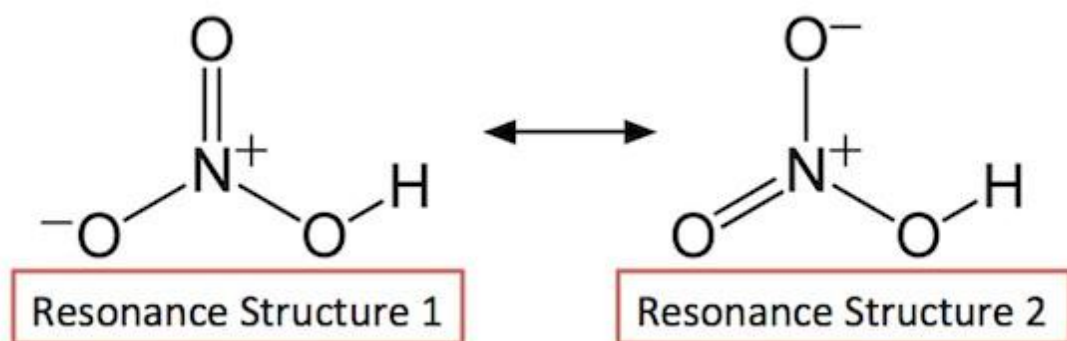
### Fullerenes



1. Fullerene is a newly discovered allotrope of carbon which contain soccer ball shaped cluster of carbon atoms  $C_{60}$ .



### Structure of nitric acid



### Method of preparation and separation of fullerenes

Fullerenes are made by heating of graphite in an electric arc in the presence of inert gases such as helium or argon. In this process, the sooty materials formed by condensation of vaporized C<sub>n</sub> small molecules consists of mainly C<sub>60</sub> with smaller quantity C<sub>70</sub> and traces of fullerenes consisting of even number of carbon atoms up to 350 or above.

### Physical Properties of nitric acid

Nitric acid is a transparent, colorless or yellowish, corrosive liquid with an acrid odor.

### Chemical Properties of nitric acid

**Stability-** Pure nitric acid is not very stable. Even at ordinary temperature, in presence of sunlight it undergoes slight decomposition.

**Acidic nature-** Nitric acid is a strong monobasic acid.

**Oxidizing property-** Nitric acid and nitrites are good oxidizing agent and convert iodides to iodine, sulphites to sulphates, ferric salts to ferric and stannous to stannic.

### Carbon nano tubes and its properties

Carbon nanotubes (CNTs) are an allotrope of carbon. They take the form of cylindrical carbon molecules and have novel properties that make them potentially useful in a wide variety of applications in nanotechnology, electronics, optics and other fields of science.

### **Amorphous allotropic form of carbon**

Those allotropic form of carbon which are not present in crystalline form are called as Amorphous allotropic form of carbon. Charcoal and lampblack is the example of this forms.

### **Uses of Nitric acid**

1. Nitric acid plays a significant role in the manufacture of various products such as

Fertilizers such as calcium nitrate, ammonium nitrate etc.

Nitrate salts such as calcium nitrate, silver nitrate, ammonium nitrate.

Dyes, perfumes, drugs etc. from coal tar products.

2. It is used in the purification of silver, gold, platinum etc.

3. Nitric acid is used in etching designs on copper, brass, bronze ware etc.

### **Atomic and physical properties of carbon**

Carbon with atomic number 6 undergoes in hybridization and shows  $sp^3$  hybridization, because of that, it is tetrahedral in nature and show property called catenation. Carbon is present in several micro crystalline forms which were regarded as amorphous. These are coal, coke, charcoal, lamp black etc.

### **Chemical properties of carbon**

Carbon when heated in oxygen forms carbon monoxide and carbon dioxide. CO is neutral but CO<sub>2</sub> is acidic in nature. Carbon is not affected by water and combines with halogens to form both simple and mixed halides.

### **Uses of carbon**

Graphite mainly used in plastic material form, such as fishing nets, tennis rackets, air crafts etc.

Coke is used as fuel. Carbon black is used as black pigment in black ink and filler in automobile.

### Methods of preparation of carbon monoxide

1. Direct combination of carbon in limited supply of oxygen or air gives carbon monoxide.
2. On small scale pure carbon monoxide is prepared by dehydration of formic acid with concentrated sulphuric acid at 373 K .

### Properties and uses of carbon monoxide

It is a colorless and odorless gas and almost soluble in water. It is powerful reducing agent and reduces almost all the metals oxides other than those of alkali and alkaline earth metals, aluminum and few transition metals. CO is used in extraction of many metals from their oxides.

### Method of preparation of Carbon dioxide

1. It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.
2. It is prepared in the laboratory by the action of dilute HCl on calcium carbonate.

### Chemical properties of carbon dioxide

Carbon dioxide is an acidic oxide and reacts with water to give carbonic acid. Carbon dioxide reacts with alkalis to give carbonates and bicarbonates.

### Uses of carbon dioxide

1. Large quantities of solid carbon dioxide (i.e. in the form of dry ice) are used in processes requiring large scale refrigeration.
2. Carbon dioxide is also used in fire extinguishers as a desirable alternative to water for most fires.
3. It is a constituent of medical gases as it promotes exhalation. It is also used in carbonated drinks.

### Methods of preparation of dry ice

1. Gases with a high concentration of carbon dioxide are produced.
2. Such gases can be a byproduct of another process, such as producing ammonia from nitrogen and natural gas, or large-scale fermentation. Second, the carbon dioxide-rich gas is pressurized and refrigerated until it liquefies.

3. Next, the pressure is reduced. When this occurs some liquid carbon dioxide vaporizes, causing a rapid lowering of temperature of the remaining liquid.
4. As a result, the extreme cold causes the liquid to solidify into a snow-like consistency.
5. Finally, the snow-like solid carbon dioxide is compressed into either small pellets or larger blocks of dry ice.

#### **Properties and uses of dry ice**

1. Dry ice is comprising two oxygen atoms bonded to a single carbon atom.
2. It is colorless, with a sour zesty odor, non-flammable, and slightly acidic.
3. At pressures below 5.13 atm and temperatures below 56.4 C (69.5 F) CO<sub>2</sub> changes from a solid to a gas with no intervening liquid form, through a process called sublimation.
4. The opposite process is called deposition, where CO<sub>2</sub> changes from the gas.

#### **Allotropes of phosphorous**

The allotropes of phosphorous are red, black and white phosphorous.

#### **Properties of white phosphorous**

##### **Properties:**

It is white-to-transparent and soft waxy solid.

It is soluble in CS<sub>2</sub> but insoluble in water.

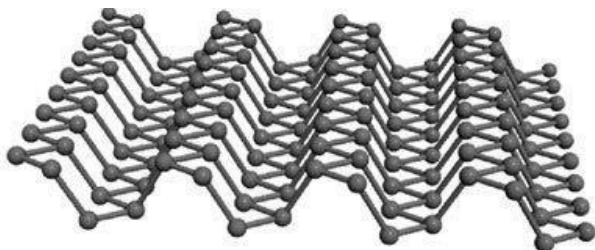
It glows in dark due to slow oxidation producing yellowish-green light.

#### **Red phosphorous**

When white phosphorus is heated in the atmosphere of CO<sub>2</sub> or coal gas at 300°C, red phosphorous is produced.

It has more atoms linked together in a network than white phosphorus does, which makes it much more stable. It is not quite as flammable, but given enough energy it still reacts with air. For this reason, we now use red phosphorus in matches.

## Black phosphorous



**BP (Black phosphorus)**

The most stable form of phosphorous is black phosphorous. It has two forms:  $\alpha$ -phosphorous and  $\beta$ -phosphorous.

### Properties of black phosphorous

It has two forms:  $\alpha$  black phosphorous and  $\beta$  black phosphorous. It can be sublimed in the air and has opaque monoclinic or rhombohedral crystals. It is very stable allotrope of phosphorous. It does not conduct electricity. It is highly polymerised form of phosphorous and has black metallic lustre.

### Reactivity of allotropes of phosphorus

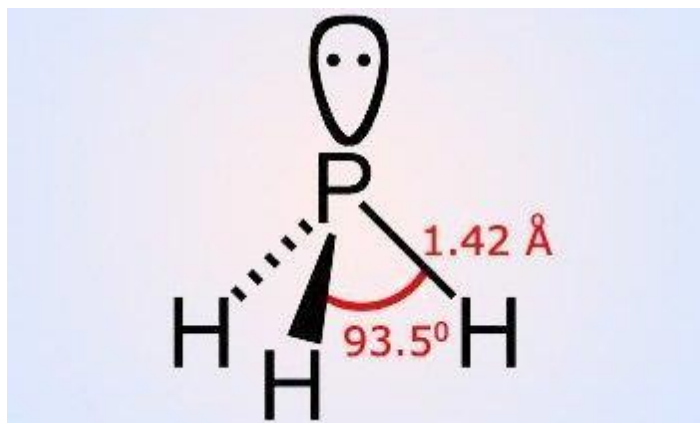
White phosphorus is the most reactive while black phosphorus is the least reactive. Therefore, white phosphorus is stored under water to protect it from air while red and black are stable in air.

### Different types of glasses and preparation

Glass is a non-crystalline amorphous solid that is often transparent. Following are the different types of glasses :

- 1) Network Glass : The glass which do not contain silica as measure constituent is called as network glass. It includes fluoride glasses, borate glasses etc.
- 2) Soda glass : It is prepared by sodium carbonate and silica.
- 3) Colored glass : Small amounts of metallic oxides are mixed with the hot molten mixture of sand, sodium carbonate and limestone. The desired colour determines the choice of the metallic oxide to be added, as different metallic oxides give different colors to the glass.
- 4) Plate Glass : Plate glass is thicker than ordinary glass. It has a very smooth surface. It is made by floating a layer of molten glass over a layer of molten tin. It is used in shop windows and doors.

### Structure of phosphine



It is  $sp^3$  hybridised. Three of the four  $sp^3$  orbitals with  $1s$ -orbitals of hydrogen atoms to form three P–H  $\sigma$ -bonds while the fourth one contains the lone pair of electrons.

### Physical properties of phosphine

It is a colourless gas having rotten fish smell.

It is highly poisonous gas.

### Uses of phosphine

In semiconductor industries it is used in small amounts as a dopant

$PH_3$  is used in Holmes signal due to its property of spontaneous combustion

For the production of smoke screens

### Properties of silanes

Silane is the silicon analogue of methane. Because of the greater electronegativity of hydrogen in comparison to silicon, this SiH bond polarity is the opposite of that in the CH bonds of methane. One consequence of this reversed polarity is the greater tendency of silane to form complexes with transition metal.

Silanes are used as coupling agents to adhere fibers such as carbon fibres to certain polymer matrices, stabilizing the composite material.

### Methods of preparation of silicon tetrachloride

It is prepared by heating either by heating silicon or silicon carbide with chlorine.

### Properties and uses of silicon tetrachloride

1. Physical state: It is volatile liquid b.p. 330.57 K.
2. Hydrolysis: It undergoes partial dehydration to give silica gel.
3. Reduction: Reduction of  $\text{SiCl}_4$  with dihydrogen gives silicon.

**Uses:** It is used to prepare silica gel which is amorphous and very porous.

### Properties of silicon dioxide

Since Si-O bonds are very strong, silica is relatively inert and has a very high melting point. It does not react with halogens, dihydrogen and most of the acids and metals even at high temperatures. It is used as a catalyst in petroleum industry and as an adsorbent in column chromatography.

### Properties of silicon carbide

Pure SiC is colorless. The brown to black color of industrial product results from iron impurities. The rainbow-like luster of the crystals is of silicon dioxide that forms on the surface. It is a semiconductor of electricity. It is used for its hardness in processes such as grinding, honing, water-jet cutting. Particles of silicon carbide are laminated to paper to create sandpapers.

### Method of preparation of silicones

When methyl chloride reacts with silicon in the presence of copper as a catalyst at 570 K, various types dichlorodimethylsilane is formed which on polymerization and elimination of HCl molecules gives silicones.

### Properties and uses of silicones

1. Silicones made up of short chain molecules are oily liquids, silicones with medium chains behave as viscous oily, jellies and greases, those with very long chains behave as rubbery elastomers and resins.
2. Being biocompatible, they are used in surgical and cosmetic implants.

## Silicates

Silicates are the compounds in which the anions present are either discrete  $\text{SiO}_4$  tetrahedra or a number of such units joined together through corner.

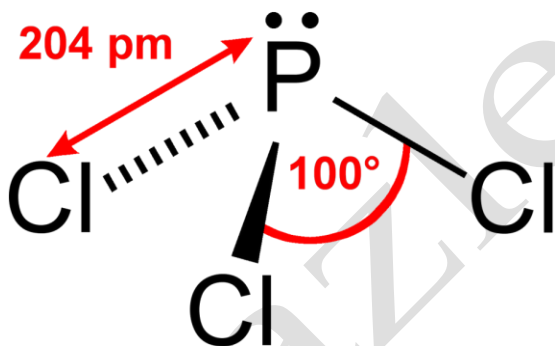
### Structure of silicates

Silicates show tetrahedral structure in which small open circles represent oxygen atoms and the small closed circle inside represent the silicon atom.

## Zeolites

If some of the silicon atoms in a three dimensional network silicate are replaced by  $\text{Al}^{+3}$  ions, the overall structure thus obtained carries a negative charge and is called as aluminosilicate. Such three-dimensional structure is called as feldspar and zeolites.

### Structure of phosphorus trichloride



$\text{PCl}_3$  is  $\text{sp}^3$  hybridised. Three of its  $\text{sp}^3$  orbitals overlap with p-orbitals of three chlorine atoms to form three  $\text{P}-\text{Cl}$ ,  $\sigma$ -bonds while the fourth contains lone pair of electrons.

### Physical properties of Phosphorus trichloride

It is colourless pungent smelling liquid which boils at 347 K and solidifies at 161 K.



### Occurrence of oxygen family

Oxygen is the most abundant of all the elements. It occurs in the free state as  $O_2$  and makes 20.46% by volume. It also occurs in the form of ozone. It makes up 46.6% by weight of the earth's crust. Sulphur occurs less abundantly. Selenium and tellurium are less abundant than sulphur and occur as selenides and tellurides in sulphide ores.

### Electronic configuration

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Oxygen	8	[He] $2s^2 2p^4$	16	2
Sulphur	16	[Ne] $3s^2 3p^4$	16	3
Selenium	34	[Ar] $3d^{10} 4s^2 4p^4$	16	4
Tellurium	52	[Kr] $4d^{10} 5s^2 5p^4$	16	5
Polonium	84	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$	16	6

### Atomic and ionic radii

The atomic radii of group 16 are smaller than those of group 15 elements. The atomic radii of the elements of oxygen family increase down the group.

### Ionization enthalpy of oxygen family

The first I.E of group 16 are unexpectedly lower while their second I.E are higher than those of the corresponding elements of group 15.

### Electron gain enthalpy

The elements of group 16 have two electrons less than nearest noble gas configuration. They have high tendency to accept electrons and have large negative electron gain enthalpies. The value for oxygen is least negative in this group.

### **Electronegativity of oxygen family**

The elements of group 16 have higher E.N values than the group 15 elements. Oxygen is the second most electronegative element. Electronegativity decreases down the group.

### **Metallic and non-metallic character**

Because of high I.E, the elements of group 16 are less metallic. As we move down the group, the I.E decreases and hence the metallic character increases.

### **Melting point of oxygen family**

The melting point increase regularly as we go down the group up to tellurium. The melting points of polonium are lower than those of tellurium.

### **Boiling point of oxygen family**

The boiling point increase regularly as we go down the group up to tellurium. The boiling points of polonium are lower than those of tellurium.

### **Atomicity of oxygen family**

Oxygen exists as diatomic gas at room temperature because of the absence of d-orbitals in oxygen molecule, while other exist as octa-atomic solids, .

### **Trend in density of oxygen family**

Metallic character increases down the group, with tellurium classified as a metalloid and polonium as a metal. Melting point, boiling point, density, atomic radius, and ionic radius all increase down the group.

### Catennation property of oxygen family

Because of stronger S-S bonds as compared to O-O bonds sulphur has more tendency to form catenation than oxygen.

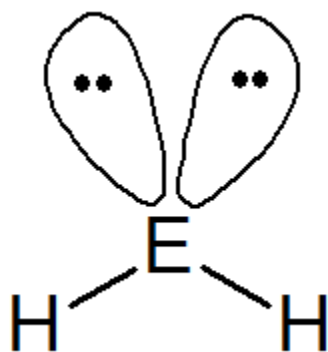
### Allotropes of oxygen family

Oxygen exists in two metallic forms O<sub>2</sub>, O<sub>3</sub>. Sulphur exist as **yellow rhombic** ( $\alpha$ -sulphur) and **monoclinic** ( $\beta$ -sulphur) forms, are the most important forms.

### Oxidation state of oxygen family

Oxygen family contain -2 as common oxidation state, other than that 1,2,4 and 6 are also some oxidation states.

### Structure of hydrides of oxygen family



All the hydrides have angular shape involving sp<sup>3</sup> hybridisation of the central atom. The bond angles decrease from H<sub>2</sub>O to H<sub>2</sub>Te.

### Dihalides of oxygen family

All elements except selenium form dihalides. They are sp<sup>3</sup> hybridised. They have bent structure due to the presence of lone pairs.

## Discovery of oxygen

Joseph Priestly is usually given credit for the discovery of oxygen, however it has been said that Carl Wilhelm Scheele had also independently discovered the element. Both chemists were able to produce oxygen by heating mercuric oxide ( $\text{HgO}$ ).

## Anomalous behaviour of oxygen

The reasons are:

- Small size
- Higher electronegativity
- Non-availability of d-orbitals

Oxygen is a gas while others are solids at room temperature. Oxygen is a non-metal. Sulphur is non-metallic while others exhibit metallic character. Due to small size and high E.N, oxygen form  $p\pi-p\pi$  multiple bonds with elements having similar size. Oxygen is paramagnetic while others are diamagnetic.

## Chemical properties of oxygen

Oxygen is a highly reactive element, highly paramagnetic, and is easily capable of combining with other elements. One of oxygen's most important chemical properties is that it supports combustion. Oxygen also combines with elements at room temperature, for example, the formation of rust. Decaying is an example of oxygen reacting with compounds. Carbon dioxide and water are the main products of decay.

## Oxides

The binary compounds of metals and non-metals with oxygen are called oxides. The oxidation state of oxygen is always -2. The nature of bonding is may be ionic or covalent. e.g  $\text{Al}_2\text{O}_3, \text{MgO}$ .

## Preparation of oxygen from hydrogen peroxide

Oxygen can be made from **hydrogen peroxide**, which decomposes slowly to form **water and oxygen**. The rate of reaction can be increased by using a catalyst, manganese(IV) oxide. When manganese(IV) oxide is added to hydrogen peroxide, bubbles of oxygen are given off.

### **Preparation of oxygen from fractional distillation of liquid air**

The liquefied air is passed into the bottom of a fractionating column. Just as in the columns used to separate oil fractions, the column is warmer at the bottom than it is at the top. The liquid nitrogen boils at the bottom of the column. Gaseous nitrogen rises to the top, where it is piped off and stored. Liquid oxygen collects at the bottom of the column. The boiling point of argon - the noble gas that forms 0.9% of the air - is close to the boiling point of oxygen, so a second fractionating column is often used to separate the argon from the oxygen.

### **Oxidation of iron in the presence of moisture**

Iron (or steel) corrodes more quickly than most other transition metals and readily does so only in the presence of both oxygen (in air) and water to form an iron oxide.

### **Conditions for rusting**

Air and water vapour are the essential conditions for rusting.

### **Tests for oxygen**

Oxygen supports combustion. So, a good method of testing for oxygen is to take a glowing splint and place it in a sample of gas, if it re-ignites, the gas is oxygen.

### **Ozone gas**

Ozone is a colourless, odourless reactive gas comprised of three oxygen atoms. It is found naturally in the earth's stratosphere, where it absorbs the ultraviolet component of incoming solar radiation that could be harmful to life on earth.

### **preparation of ozone**

In preparation of ozone the reaction is initiated by a sparkless or silent electric discharge, to produce less heat, as **ozone** is prone to decomposing back into oxygen with a rise in temperature

## Ozone layer

The ozone layer is a deep layer in the stratosphere, encircling the Earth, that has large amounts of ozone in it. The layer shields the entire Earth from much of the harmful ultraviolet radiation that comes from the sun.

### Location of ozone layer

The Ozone layer is actually located in the stratosphere in a region that is 10 to 50 km above the Earth.

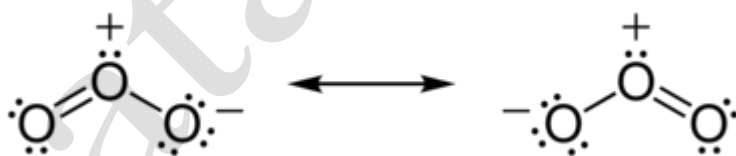
### Discovery of ozone layer

The ozone layer was discovered in 1913 by the french physicists Charles Fabry and Henri Buisson. Its properties were explored in detail by the british meteorologist G. M. B. Dobson, who developed a simple spectrophotometer (the Dobsonmeter) that could be used to measure stratospheric ozone from the ground.

### Ozone depletion

Ozone depletion is the term commonly used to describe the thinning of the ozone layer in the stratosphere. Ozone depletion occurs when the natural balance between the production and destruction of ozone in the stratosphere is tipped in favour of destruction.

### Structure of ozone



The symbols + and - show, that ozone molecules are short of electrons on the locations where these signs occur. This means that ozone is a dipolar molecule. This causes ozone to have characteristic properties. Ozone reacts very selectively and is electrophilic.

### **Catenation of sulphur**

The most important allotrope is plastic sulphur or x-sulphur. It is obtained by pouring molten sulphur into cold water when a soft rubber like mass called plastic sulphur is obtained. It is an amorphous form of sulphur. It is soft and elastic like rubber in the beginning but hardens on standing and cooling and gradually changes into rhombic sulphur. It does not have a sharp melting point. It has a zig-zag chains and contains  $S_8$  sometimes.

### **Electronic configuration of p-block family and oxidation states**

The general electronic configuration of elements is  $ns^2np^1$  to  $ns^2np^6$ . The maximum oxidation state shown by a p-block element is equal to the total number of valence electrons. The number of possible oxidation states increases towards right of the periodic table.

### **Elements of nitrogen family**

Nitrogen, phosphorous, arsenic, antimony, bismuth

### **General chemical behaviour of p-block elements**

The p-block is the only block which contain metal, non-metal, metalloids. The compounds formed by highly reactive metal with non-metals are generally ionic because of large difference in electro negativity. On other hand, the compounds formed by non-metals themselves are highly covalent in nature due to less electronegative difference.

### **Occurrence of nitrogen family**

Nitrogen makes about 78% by volume of the atmosphere. Phosphorous do not occur in free state and is very reactive. The elements arsenic, antimony and bismuth are not very abundant.

### Electronic configuration of Nitrogen family

Element	Atomic Number	Electronic Configuration	Group Number	Period Number
Nitrogen	7	[He] $2s^2 2p^3$	15	2
Phosphorus	15	[Ne] $3s^2 3p^3$	15	3
Arsenic	33	[Ar] $3d^{10} 4s^2 4p^3$	15	4
Antimony	51	[Kr] $4d^{10} 5s^2 5p^3$	15	5
Bismuth	83	[Xe] $4f^{14} 5d^{10} 6s^2 6p^3$	15	6

Chemical behavior of first element of each group as compared to the subsequent members of the same group of p-block elements

It is interesting to note that first members of each group of p-block elements differs from its succeeding members of their respective group. The two main reasons for this difference are:

Size and other properties which depend upon size.

Absence of d-orbitals in the valence shell.

### Atomic radii trends of nitrogen family

Atomic radii increase in size down the group.

	Nitrogen	Phosphorous	Arsenic	Antimony	Bismuth
Atomic radius(pm)	65	100	115	145	160

### Ionic radii of nitrogen family

On moving down the group atomic and ionic radii increase with increase in atomic number.

### Ionization enthalpy

The ionization enthalpies of the elements of group 15 are much higher than those of the corresponding elements of group 14. Down the group it decrease regularly.



### Electronegativity of nitrogen family

Group 15 elements are more electronegative than group 14 elements. It shows a gradual decrease on moving down the group from N to Bi.

### Atomic volume in nitrogen family

#### Periodic Trends

Element/Symbol	Atomic Number	Covalent Radius (pm)
Nitrogen (N)	7	75
Phosphorus (P)	15	110
Arsenic (As)	33	121
Antimony (Sb)	51	140

### Metallic character of nitrogen family

Metallic character increases down the group, i.e.,  $N < P < As < Sb < Bi$

### Melting point of nitrogen family

Melting point (amount of energy required to break bonds to change a solid phase substance to a liquid phase substance) increases down the group.

### Boiling point of nitrogen family

Boiling point (amount of energy required to break bonds to change a liquid phase substance to a gas) increases down the group.

### Density of nitrogen family

Density of nitrogen family increases down the group from N to Bi.

### **Allotropes of nitrogen family**

Except nitrogen and bismuth, all the elements of this group show allotropy. Phosphorous exists in three allotropic forms i.e red, black and red.

Arsenic and antimony exist in two allotropic forms i.e., yellow and grey.

### **Chemical properties of nitrogen family**

The top two elements, nitrogen and phosphorus, are non-metals, forming -3 charged anions. Nitrogen is a diatomic gas and phosphorus is a solid. The elements arsenic, antimony, and bismuth all have some characteristics of semi-metals such as brittleness as a free element. They have 5 electrons in their valence shell.