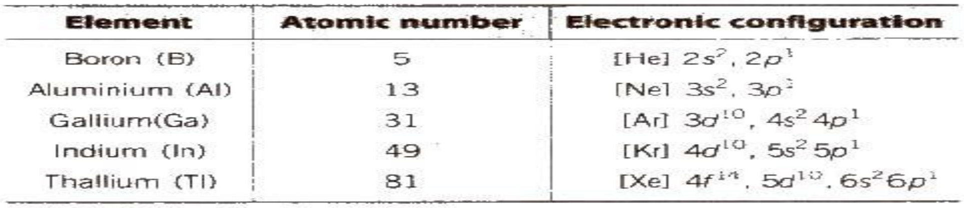
In **p-block elements**, the last electron enters in the outermost p-orbital .. There are six groups of p-block elements in the Periodic Table, numbering from 13 to 18. Their valence shell electronic configuration is ns^2np^{1-6} (except for He).

Group 13

It is also called boron family. It includes B, Al, Ga, In, Tl. AI is the most abundant metal and third most abundant element in the earth's crust.

General Physical Properties of Group 13 Elements

(i) **Electronic configuration** Their valence shell electronic configuration is ns^2np^1



Element	Atomic number	Electronic configuration
Boron (B)	5	[He] $2s^2, 2p^1$
Aluminium (Al)	13	[Ne] $3s^2, 3p^1$
Gallium(Ga)	31	[Ar] $3d^{10}, 4s^2 4p^1$
Indium (In)	49	[Kr] $4d^{10}, 5s^2 5p^1$
Thallium (Tl)	81	[Xe] $4f^{14}, 5d^{10}, 6s^2 6p^1$

(ii) **Atomic radii and ionic radii** Group 13 elements have smaller size than those of alkaline earth metals due to greater effective nuclear charge, Z_{eff}.

Atomic radii increases on going down the group with an anomaly at gallium (Ga). Unexpected decrease in the atomic size of Ga is due to the presence of electrons in d-orbitals which do not screen the attraction of nucleus effectively.

The ionic radii regularly increases from B^{3+} to TI^{3+}.

(iii) **Density** It increases regularly on moving down the group from B to Tl.

(iv) **Melting and boiling points** Melting point and boiling point of group 13 elements are much higher than those of group 2 elements. The melting point decreases from B to Ga and then increases, due to structural changes in the elements.

Boron has a very high melting point because of its three dimensional structure in which B atoms are held together by strong covalent bonds.

Low melting point of Ga is due to the fact that it consists of Ga_2 molecules, and Ga remains liquid upto 2276 K. Hence, it is used in
high temperature thermometer.

(v) **Ionisation enthalpy** (IE) The first ionisation enthalpy values of group 13 elements are lower than the corresponding alkaline earth metals, due to the fact that removal of electron is easy. [ns^2 npl configuration] .

On moving down the group, IE decreases from B to Al, but the next element Ga has slightly higher ionisation enthalpy than A1 due to the poor shielding of intervening d-electrons. It again decreases in In and then increases in the last element Tl

(vi) **Oxidation states** B and Al show an oxidation state of +3 only while Ga, In and TJ exhibit oxidation states of both +1 and +3.

As we move down in the group 13. due to inert pair effect, the tendency to exhibit +3 oxidation state decreases and the tendency to attain +1 oxidation state increases.

Stability of +1 oxidation state follows the order Ga < In < Tl.

Inert pair effect is reluctance of the s-electrons of the valence shell to take part in bonding. It occurs due to poor shielding of the ns^2 – electrons by the intervening d and f – electrons. It increases down the group and thus, the lower elements of the group exhibit lower oxidation states.
(vii) **Electropositive** (metallic) **character** These elements are less electropositive than the alkaline earth metals due to their smaller size and higher ionisation enthalpies.
On moving down the group, the electropositive character first increases from B to Al and then decreases from Ga to TI, due to the presence of d and I-orbitals which causes poor shielding.

(viii) **Reducing character** It decreases down the group from AI to Tl because of the increase in electrode potential value for M^{3+} / M.
Therefore, it follows the order

AI> Ga > In > Tl

(ix) **Complex formation** Due to their smaller size and greater charge, these elements have greater tendency to form complexes than the s-block elements.
(x) **Nature of compounds** The tendency of the formation of ionic compounds increases from B to Tl. Boron forms only covalent compounds whereas AI can form both covalent as well as ionic compounds. Gallium forms mainly ionic compounds, although anhydrous $Ga\ CI_3$ is covalent.

Chemical Properties of 13 Group Elements

(i) **Action of air** Crystalline boron is unreactive whereas amorphous boron is reactive. It reacts with air at 700°C as follows
$4B + 3O_2 \rightarrow 2B_2O_3$
$2B + N_2 \rightarrow 2BN$
AI is stable in air due to the formation of protective oxide film.

$4Al + 3O_2 \rightarrow 2Al_2O_3$
Thallium is more reactive than Ga and In due to the formation of unipositive ion, TI^+.
$4Tl + O_2 \rightarrow 2Tl_20$

(ii) **Reaction with nitrogen**

$$2B + N_2 \xrightarrow{\Delta} \underset{\text{boron nitride}}{2BN}$$

$$2Al + N_2 \xrightarrow{\Delta} \underset{\text{aluminium nitride}}{2AlN}$$

(iii) **Action of water** Both B and AI do: not react with water but amalgamated aluminium react with H_2O evolving H_2.
$2Al(Hg) + 6H_2O\ ) \rightarrow 2AI(OH)_3 + 3H_2 + 2Hg$
Ga and In do not react with pure cold or hot water but Tl forms an oxide layer on the surface.

(iv) **Reaction with alkalies** Boron dissolves in alkalies and gives sodium borates.

$$2B + 6NaOH \xrightarrow{\text{Fusion}} 2Na_3BO_3 + 3H_2$$

Aluminium also reacts with alkali and liberates hydrogen.

$$2Al(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow \underset{\substack{\text{[sodium tetrahydroxo}\\ \text{aluminate (III)]}}}{2Na^+[Al(OH)_4](aq)} + 3H_2(g)$$

(v) **Reaction with carbon**

$$4B + C \xrightarrow{\Delta} \underset{\text{boron carbide}}{B_4C}$$

$$4Al + 3C \longrightarrow \underset{\text{aluminium carbide}}{Al_4C_3}$$

Aluminium carbide is ionic and forms methane with water.

(vi) **Hydrides** Elements of group 13 do not combine directly with H_2 to form hydrides, therefore their hydrides have been prepared by indirect methods, e.g

$$4BF_3 + 3LiAlH_4 \xrightarrow{\text{Dry ether}} \underset{\text{diborane}}{2B_2H_6} + 3LiF + 3AlF_3$$

Boron forms a number of hydrides, they are known as boranes. Boranes catch fire in the presence of oxygen.

$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$; &Delat;$_c$H° = – 1976 kJ mol^{-1}

Boranes are hydrolysed by water.

$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$

Boranes are stable but the stability of hydrides of AI, Ga, In, and Tl decreases on moving down the group because the strength of the M-H bond decreases.

Structure of diborane BH_3 does not exist as such, but exists as a dimer, i.e; B_2H_6(diborane].

In the above structure, B atoms are in Sp^3 – hybrid state. There are six B-H bonds out of which four B-H bonds are normal bonds present in the same plane While rest two B-H bonds behave as bridge bonds, ie; 3c – 2e (three centre-two electrons, also known as banana bond) and present above and below the plane of the molecules which do not I have sufficient number of electrons to form covalent bonds.

Aluminium (AI) forms a polymeric hydride of general formula $(AIH_3)_x$ which decomposes into its elements on heating.

(vii) **Oxides** Except. TI all the elements of group 13 form oxides or general formula M_2O_3 on heating with oxygen.

$$4M + 3O_2 \xrightarrow{\Delta} 2M_2O_3$$

TI forms thallium (l) oxide. Tl_2O which IS more stable than thallium (III) oxide TI_2O_3 due to inert pair effect.

(viii) **Nature of oxides and hydroxides** $B(OH)_3$ or H_3BO_3 is soluble in water, while other hydroxides are insoluble in water.

On moving down the group. there is a change from acidic to amphoteric and then to basic character of oxides and hydroxides or group 13 elements.

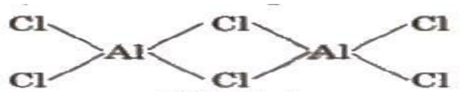
(ix) **Halides** All the elements of boron family (except Tl) form trihalides of type MX_3.

$$2B + 3X_2 \longrightarrow 2BX_3$$

$$B_2O_3 + 3C + 3Cl_2 \xrightarrow{\Delta} 2BCl_3 + 3CO$$

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO$$

All the boron trihalides $[BX_3)$ and aluminium trihalides AlX_3 (except AIF_3 which is ionic) are covalent compounds. AlX_3 exists as dimer while BX_3 is monomer because boron atom is too small to coordinate with four large halide ions. The energy released during the formation of the bridge structure is not sufficient for the cleavage of the typical pπ – pπ bond in BF_3.



$[Al_2Cl_6]$

BF_3 is a colourless gas, BCl_3 and BBr_3 are colourless fuming liquids and BI_3 is a white solid at room temperature. Trihalides of group 13 elements behave as Lewis acids because of their strong tendency to accept a pair of electrons. The relative strength of Lewis acids of boron trihalides is

$BF_3 < BCI_3, < BBr_3, < BI_3$.
This is due to pπ – pπ backbonding in BF_3 which makes it less electron deficient.
The halides of group 13 elements behave as Lewis acids and the acidic character is

$BX_3 > AIX_3 > GaX_3 > InX_3$ (where, X = Cl, Br or 1)
$TICl_3$ decomposes to TICl and $C1_2$ and hence acts as an oxidising agent.

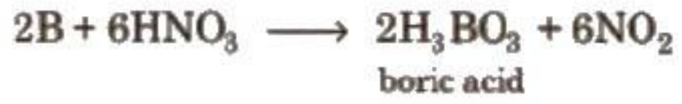
$$TlCl_3 \xrightarrow{\Delta} TlCl + Cl_2$$

Anomalous Behaviour of Boron
Boron shows anomalous behaviour with the other members of the group, due to the following reasons:

(i) Smallest size in the group.
(ii) High ionisation energy.
(iii) Highest electronegativity in the group.
(iv) Absence of vacant d-orbital.

A few points of difference are

1. It is a non-metal while other members of the group are metallic.
2. It shows allotropy while other members do not.
3. It has the highest melting point and boiling point in group 13.
4. It forms only covalent compounds while other members form both ionic and covalent compounds.
5. The halides of boron exist as monomers while AlCI:! exists as a dimer.
6, The oxides and hydroxides of boron are weakly acidic while those of aluminium arc amphoteric and those of other elements are basic.
7. It can be oxidised by concentrated HNO_3 while aluminium becomes passive due to the formation of oxide layer on the surface.



$$2B + 6HNO_3 \longrightarrow \underset{\text{boric acid}}{2H_3BO_3} + 6NO_2$$

Diagonal Relationship between Boron and Silicon
Boron exhibit resemblance with its diagonal element silicon of group 14.

1. Both Band Si are non-metals.
2. Both arc semi-conductors.
3. Both Band Si form covalent hydrides, i.e.. boranes and silanes respectively.
4. Both form covalent, and volatile halides which fume in moist air due to release of HCI gas.

$BCI_3 + 3H_2O \rightarrow H_3 BO_3 + 3HCl$ i
$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$

5. Both form solid oxides which get dissolve in alkalies forming borates and silicates respectively. ..
6. Both react with electropositive metals and give binary compounds, which yield mixture of boranes and silanes on hydrolysis.

Boron and Its Compounds

Occurrence

It does not occur in free state. Its important minerals are

(i) Borax (or Tineal), $Na_2B_4O_7$ * 1OH_2O
(ii) Kernite, $Na_2B_4O_7$ * 4H_2O
(iii) Orthoboric acid, H_3BO_3

Isolation

Elemental boron is obtained by following methods :

(i) By reduction of boric oxide with highly electropositive metals like K, Mg, AI, Na etc, in the absence of air.

$$B_2O_3 + 6K \xrightarrow{\Delta} 2B + 3K_2O$$

(ii) By the reaction of boron halides with hydrogen,

$$2BCl_3 + 3H_2 \xrightarrow{1270K} 2B + 6HCl$$

Uses of Boron

(i) As a semi-conductor.
(ii) Boron steel rods are used to control the nuclear reactions.

${}_5B^{10} + {}_0n^1 \rightarrow {}_5B^{11}$
1. Borax or Sodium Tetraborate Decahydrate [$Na_2B_4O_7$ * 1OH_2O]

Preparation

It occurs naturally as tineal in dried up lakes. It is obtained by boiling of mineral colemanite with a solution of Na_2Co_3.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 + 2NaBO_2 + \underset{\text{borax}}{Na_2B_4O_7}$$

$NaBO_2$ can be removed by passing CO_2 through it.
$4NaBO_2 + CO_2 \rightarrow Na_2CO_3 + Na_2B_{<4}O_7$

Properties

1. Its aqueous solution is basic in nature.

$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$
2. On heating with ethyl alcohol and cone.H_2SO_4it gives volatile vapours of triethyl borate which burn with a green flame.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$
$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{triethylborate}}{B(OC_2H_5)_3} + 3H_2O$$

3. Action of heat

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow[-10H_2O]{\text{Heat, swells}}$$

$$Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{\underset{\text{sodium metaborate}}{2NaBO_2} + \underset{\text{boric anhydride}}{B_2O_3}}_{\text{glassy bead}}$$

Borax bead is used for the detection of coloured basic radicals under the name borax bead test e.g.,

$$CoSO_4 \xrightarrow{\Delta} CoO + SO_3 ;$$

$$CoO + B_2O_3 \longrightarrow \underset{\text{cobalt metaborate (blue)}}{Co(BO_2)_2}$$

Basic radical or salt	Fe	Cr	Ni
Colours of borax bead	Green	Green	Brown

2. **Boric Acid or Orthoboric Acid** [H_3BO_3 or $B(OH)_3$]

Preparation

By treating borax with dil. HCl or dil. H_2SO_4.

$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCI + 4H_3BO_3$

Properties

1. It is a weak monobasic acid (Lewis acid).

$H_3BO_3 + 2H_2O \rightarrow [B(OH)_4]^- + H_3O^+$

2. With C_2H_5OH and cone H_2SO_4, it gives triethyl borate.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} B(OC_2H_5)_3 + 3H_2O$$

3. Heating effect

$$\underset{\substack{\text{orthoboric}\\\text{acid}}}{H_3BO_3} \xrightarrow{273\text{ K}} \underset{\substack{\text{metaboric}\\\text{acid}}}{HBO_2} \xrightarrow{473\text{ K}} \underset{\substack{\text{tetraboric}\\\text{acid}}}{H_2B_4O_7} \xrightarrow[\text{hot}]{\text{Red}} \underset{\substack{\text{boron}\\\text{trioxide}\\\text{(Boric anhydride)}}}{B_2O_3}$$

Uses

It is used as an antiseptic and eye lotion under the name ‘boric lotion’, and as a food preservative.

3. **Borazine or Borazole**, [$B_3N_3H_6$]

It is a colourless liquid having a six membered ring of alternating B and N atoms. It is also called ‘inorganic benzene’. It is prepared by B_2H_6 as follows

$$3B_2H_6 + 6NH_3 \xrightarrow{\Delta} 2B_3N_3H_6 + 12H_2$$

$$1 \quad : \quad 2$$

The π electrons in borazine are only partially delocalised. It is more reactive than benzene

Compounds of Aluminium

1.**Anhydrous Aluminium Chloride** [$AICI_3$ or $A1_2C1_6$]

Preparation

It can not be prepared by heating $AICI_3$. $6H_2O$.

$$2AlCl_3 \cdot 6H_2O \xrightarrow{\Delta} 2Al(OH)_3 + 6HCl$$

$$2Al(OH)_3 \xrightarrow{\text{Heat}} Al_2O_3 + 3H_2O$$

It can be prepared

(i) By passing dry chlorine or HCl gas over heated Al.

$$2Al + 3Cl_2 \xrightarrow{\text{Heat}} 2AlCl_3$$
$$2Al + 6HCl \xrightarrow{\text{Heat}} 2AlCl_3 + 3H_2$$

(ii) By heating a mixture of alumina and carbon in a current of dry chlorine.

$$Al_2O_3 + 3C + 3Cl_2 \xrightarrow{\Delta} 2AlCl_3 + 3CO$$

Properties

1. $AlC1_3$ fumes in moist air due to hydrolysis.
$AlC1_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCI$
2. It behaves as Lewis acid.

Uses

It is used as a catalyst in Friedel-Craft reaction and as a mordant dye.

2.**Aluminium Oxide or Alumina** [AI_2O_3]

It is the most stable compound of aluminium and occurs in nature as colourless corundum and several coloured oxides, (it present in combination with different metal oxides) like ruby (red), topaz (yellow), sapphire (blue), and emerald (green), which are used as precious stones (gems).

Alum

The term alum is given to double sulphates of the type X_2SO_4 * $Y_2(SO_4)_3$ * $24H_2O$ where, X represents a monovalent cation such as Na^+, K^+ and NH^+_4, while Y is a trivalent cation such a Al^3,Cr^{3+}, Fe^{3+} and Co^{3+}(Li^+ does not form alum).
Some important alums are

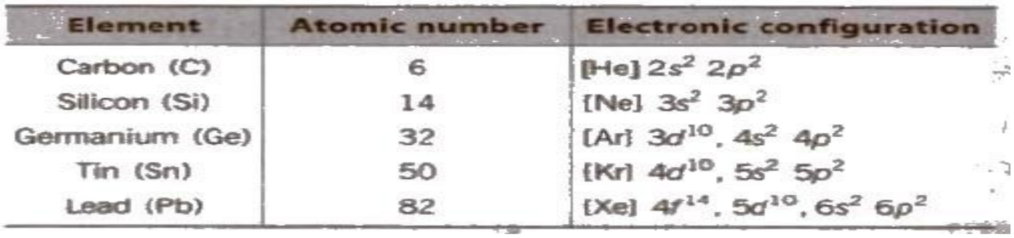
(i) Potash alum K_2SO_4 * $Al_2(SO_4)_3$ * $24H_2O$
(ii) Sodium alum Na_2SO_4 * $A1_2(SO_4)_3$. $24H_2O$
(iii) Ammonium alum $(NH_4)_2SO_4$ * $AI_2(SO_4)_3$ $24H_2O$
(iv) Ferric alum $(NH_4)_2SO_4$ * $Fe_2(SO_4)_3$ $24H_2O$
Potash alum is prepared in the laboratory by mixing hot equimolar quantities of K_2SO_4 and $Al_2(SO_4)_3$. The resulting solution on concentration and crystallisation gives potash alum.
Note 1. A mixture of Al powder NH_4NO_3 is called ammonal and is lUed in bombs.
2. Al is the chief constituent of silver paints.

3. $A1_2(SO_4)_3$ 1.8 used for making fire proof clothes.

Group 14

General Physical Properties of Group 14 Elements

(i) Electronic configuration Their valence shell electronic configuration is ns^2 np^2



Element	Atomic number	Electronic configuration
Carbon (C)	6	[He] $2s^2$ $2p^2$
Silicon (Si)	14	[Ne] $3s^2$ $3p^2$
Germanium (Ge)	32	[Ar] $3d^{10}$, $4s^2$ $4p^2$
Tin (Sn)	50	[Kr] $4d^{10}$, $5s^2$ $5p^2$
Lead (Pb)	82	[Xe] $4f^{14}$, $5d^{10}$, $6s^2$ $6p^2$

(ii) **Metallic character** C and Si are non-metals, Ge is a metalloid and Sn and Pb are metals.
(iii) **Appearance** C is black. Si is light-brown, Ge is greyish, Sn and Pb are silvery white.

(iv) **Density** Density increases with increase m atomic number due to increase in mass per unit volume down the group.
(v) **Melting points and boiling points** The melting points and boiling points decrease from carbon to lead but carbon and silicon have very high melting and boiling points due to their giant structure.
(vi) **Oxidation state** They exhibit +2 and +4 oxidation state. The compounds of Pb in +4 oxidation state are powerful oxidising agents since, +2 oxidation state of Pb is more stable due to inert pair effect.
The compounds in +2 oxidation state are ionic in nature and in + 4 oxidation state are covalent in nature (According to Fajan's rule).

(vii) **Ionisation enthalpy** It decreases from C to So. For Pb. it ie slightly higher than Sn.
(viii) **Electronegativity values** The value decreases from C to Pb but not in a regular manner probably due to filling of d-orbitals III and Sn and f- orbitals In Pb.
(ix) **Catenation** The greater the strength of element-element bond. the greater is the strength of catenation.
C >> Si > Ge = Sn > Pb (catenation).

(x) **Allotropy** All the elements of this group except Pb exhibit allotropy.
In cold countries white tin changes to grey tin and results in decrease in density. This is called tin disease or tin plague.

(xi) **Valency** All elements exhibit tetra valency. In case of carbon, 406 kJ mol^{-1} of energy is required for promotion of 2s – electron to 2p.
Formation of two extra bonds provide this energy.

(xii) **Atomic and ionic radii** Both increase from C to Pb.
(xiii) Multiple bonding Carbon forms pπ – pπ bonds with itself and with S, N and O. Other clements show negligible tendency of this
type due to their large size. Others form dπ – pπ multiple bonds.

Chemical Properties of Group 14 Elements
(a) **Hydrides** All members of the group form covalent hydrides. Their number and ease of formation decreases down the group.
Hydrides of carbon are called hydrocarbons (alkanes, alkenes or alkynes).

Hydrides of Si and Ge are known as silanes and germanes.

The only hydrides of Sn and Pb are SnH4 (stannane) and PbH_4 (plumbane),
Their thermal stability decrease down the group.

Their reducing character increases down the group.

(ii) Halides All the elements give tetrahedral and covalent halides of the type MX_4 except $PbBr_4$, and PbI_4.
Thermal stability

$CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$
Order of thermal stability with common metals

$MF_4 > MCl_4 > MBr_4 > MI_4$
Except CX_4 other tetrahalides can hydrolysed due to the presence of vacant d-orbitals.
$SiX_4 + 2H_2O \rightarrow SiO_2 + 4Hx$.
ease of hydrolysis: $SiX_4 > GeX_4 > SnX_4 > PbX_4$

Except C, other elements form dihalides of the type MX_2 which are nlOre ionic and have higher melting points and boiling points, e.g., $SnC1_2$ is a solid whereas $SnC1_4$ is a liquid at room temperature.
$SnCl_2 . 5H_2O$ is called bitter of tin and is used as a mordant in dyeing.
(iii) **Oxides** They form two types of oxides. mono-oxides of the type MO. e.g.,
CO (neutral) and SiO, GeO. SnO. PbO(all basic) and dioxides of the type MO_2

$$\underbrace{CO_2, SiO_2}_{\text{acidic}} \quad \underbrace{GeO_2, SnO_2 \text{ and } PbO_2}_{\text{amphoteric}}$$

CO_2 is linear gas at ordinary temperature. Solid CO_2 is known as **dry ice** or **drikold**.
SiO_2 is a solid with three dimensional network in which Si is bonded to four oxygen atoms tetrahedrally and covalently. A mass of hydrated silica (SiO_2) formed from skeletons of minute plants, known as diatoms, is called kieselguhr. It is a highly parous material and is used in the manufacture of dynamite.

Carbon

Free states (diamond. graphite, coal etc.) and combined states (oxides, carbonates, hydrocarbons etc.)

Allotropic Forms of Carbon

The crystalline forms include

(i) **Diamond** It is the hardest and has three dimensional polymeric structure in which hybridisation of C is sp^3. It is covalent solid. melting point 3650°C. density 3.51 g/cm^3 and bad conductor of heat and electricity.
(ii) Graphite It is dark grey. having hexagonal plates, hybridisation of each C is sp^2. It is good conductor of heat and electricity due to the presence of free electrons. It was also known as black lead. It is a very good lubricant.
Aqua dag Suspensions of graphite in water.
Oil dag Suspension of graphite in oil lubricants.
(iii) **Fullerenes** These are the only pure form of carbon. C_{60} molecule contains 12 five membered rings and 20 six membered rings. The five membered rings are connected to six membered rings while six membered rings are connected to both five and six membered rings. These are used in microscopic ball bearings, light weight batteries, in synthesis of new plastics and new drugs.
Amorphous forms of carbon are

(i) Coal The different forms of coal are peat (60 % C), lignite (70 % C), Bituminous (78 % C), Semi Bituminous (83 % C) and anthracite (90 % C). Bituminous is most common variety of coal.

(ii) Coke It is obtained by destructive distillation of coal

$$\text{Coal} \xrightarrow{DD} \text{coke } (80° - 90\% \text{ C})$$

(iii) **Charcoal or wood charcoal** It is obtained by heating wood strongly in absence of air. When heated with steam, it becomes more activated. It is used to remove colouring matters and odoriferous gases.
(iv) **Bone black or animal charcoal** It is obtained by destructive distillation of bones in iron retort. By products are bone oil or pyridine. It is used as adsorbent. On burning, it gives bone ash which is calcium phosphate and used in the manufacture of phosphorous and phosphoric acid.
(v) **Lamp-black** It is obtained by burning vegetable oils in limited supply of air. It is used in the manufacture of printing ink, black paint, varnish and carbon paper.
(vi) **Carbon-black** It is obtained by burning natural gas in limited supply of air. It is added to rubber mixture for making automobile tyres.

Coal Gas

Preparation By destructive distillation of coal.

Composition
H_2 = 45 – 55 % N_2 = 2 – 12 %
CH_4 = 25 – 35 % CO_2 = 0 – 3 %
CO = 4 – 11 % O_2 = 1 – 1.5 %
Ethylene, acetylene, benzene, etc. = 3 – 5 %

Uses It is used as illuminant, as fuel and to provide inert atmosphere in the metallurgical processes.

Natural Gas

It is found along with petroleum below the surface of earth.

Composition CH_4 = 60 – 80 %
Higher hydrocarbons = 2 – 12%

C_2H_6 = 5 – 10 %, C_3H_8 = 3 – 18 %

Uses It is used as a fuel.Its partial combustion yields carbon black (reinforcing agent for rubber).

Oil Gas

Preparation

$$\text{Kerosene} \xrightarrow[\text{absence of air}]{\text{Heated in}} \text{Mixture of simple hydrocarbons}$$

Uses It is used as fuel in laboratories in Bunsen burners.

Wood Gas

Preparation Destructive distillation of wood gives wood gas (CH_4, C_2H_6 H_2)

Uses It is used as fuel.

Liquified Petroleum Gas (LPG)

Composition n-butane + Iso-butane

Uses It is used as domestic fuel.

Carbon Monoxide (CO)

Preparation

(i) $2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$

(ii) $HCOOH \xrightarrow[\text{Conc. } H_2SO_4]{373\text{ K}} H_2O + CO$

(iii) It is manufactured in the form of water gas and producer gas

$$C(g) + H_2O(g) \xrightarrow[473\text{ K} - 1273\text{ K}]{} \underbrace{CO(g) + H_2(g)}_{\text{water gas}}$$

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273\text{ K}} \underbrace{2CO(g) + 4N_2(g)}_{\text{producer gas}}$$

Properties

It is colourless, odourless and almost water insoluble gas. It is a powerful reducing agent. CO is used in the extraction of many metals from their oxide ores.

$$Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$$

$$ZnO(s) + CO(g) \xrightarrow{\Delta} Zn(s) + CO_2(g)$$

Carbon Dioxide (CO_2)

Preparation

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$$

$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$$

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

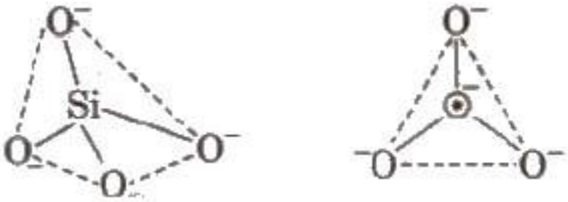
Properties It is a colourless and odourless gas. With water, it forms carbonic acid. $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$

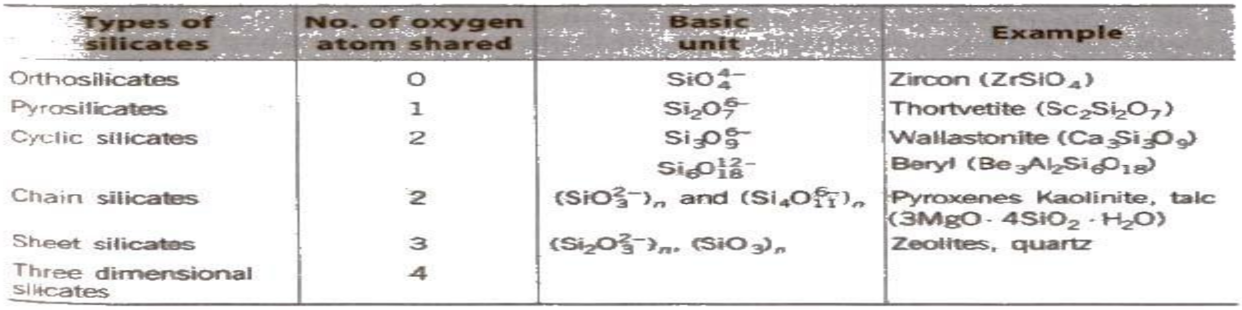
Photosynthesis $6CO_2 + H_2O \xrightarrow[\text{Chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$

Compounds of Silicon

Silicates

Silicates are metal derivatives of silicic acid, H_2SiO_3 and can be obtained by fusing metal oxides or metal carbonates with sand. The basic structural unit of silicates is SiO^{-4}_4.





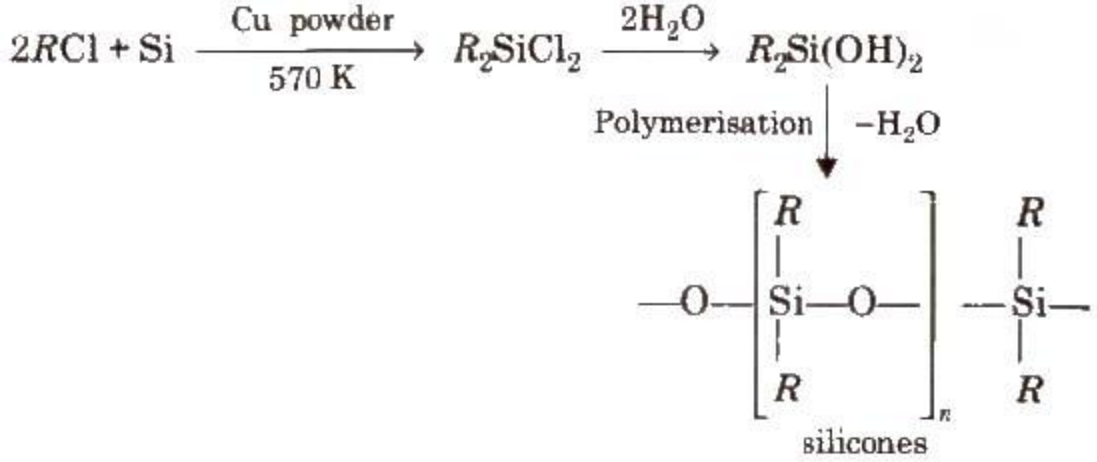
Types of silicates	No. of oxygen atom shared	Basic unit	Example
Orthosilicates	0	SiO_4^{4-}	Zircon ($ZrSiO_4$)
Pyrosilicates	1	$Si_2O_7^{6-}$	Thortvetite ($Sc_2Si_2O_7$)
Cyclic silicates	2	$Si_3O_9^{6-}$ $Si_6O_{18}^{12-}$	Wallastonite ($Ca_3Si_3O_9$) Beryl ($Be_3Al_2Si_6O_{18}$)
Chain silicates	2	$(SiO_3^{2-})_n$ and $(Si_4O_{11}^{6-})_n$	Pyroxenes Kaolinite, talc ($3MgO \cdot 4SiO_2 \cdot H_2O$)
Sheet silicates	3	$(Si_2O_3^{2-})_n$, $(SiO_3)_n$	Zeolites, quartz
Three dimensional silicates	4		

Talc consists of planar sheets which can slip over one another due to weak forces of attraction, and is a constituent of talcum powder. That's
Why talcum powder has a slippery touch.

Mica (abrak) is naturally occurring aluminium silicate $[KH_2AI_3(SiO_4)]_3$ or $KAI_3Si_3O_{10}(OH)_2$.

Silicones

The linear, cyclic or cross linked polymeric compounds containing (R_2SiO) as a repeating units, are known as silicones. They are manufactured from alkyl substituted chlorosilanes.



Silicones are chemically inert, water repellent, heat resistant, good electrical insulators. These are used as lubricants (vaseline), insulators etc.

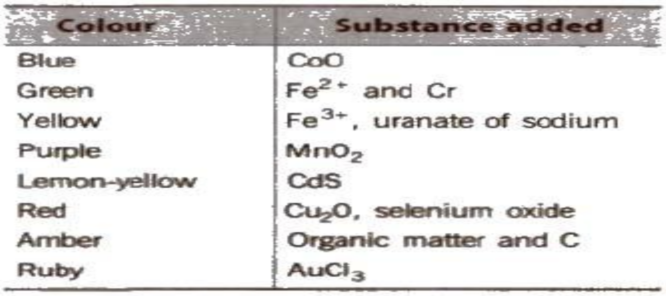
Carborundum

It is second hardest material known and has formula SiC (silicon carbide), It is used as high temperature semiconductor, in transistor diode rectifiers.

Glass

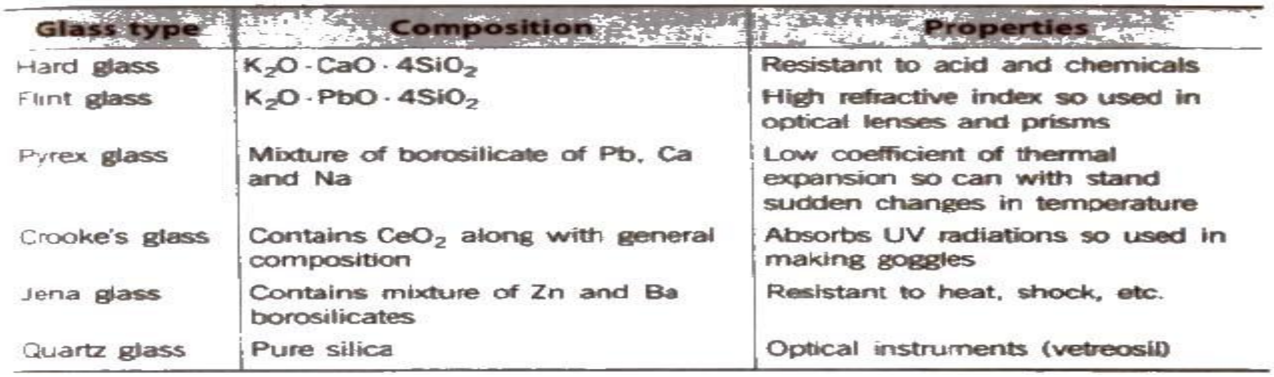
it is a transparent or translucent amorphous substance obtained by fusion of sodium carbonate (or sodium SUlphate), calcium carbonate and sand (silica). It is not a true solid, so its melting point is not sharp.

General formula of glass is $Na_2O * CaO * 6SiO_2$.
Coloured glasses are obtained by adding certain substance to the molten mass.



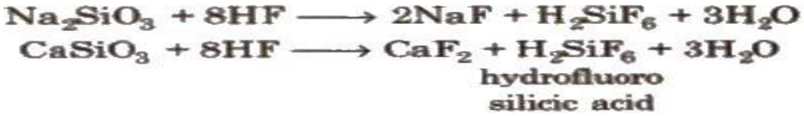
Colour	Substance added
Blue	CoO
Green	Fe^{2+} and Cr
Yellow	Fe^{3+}, uranate of sodium
Purple	MnO_2
Lemon-yellow	CdS
Red	Cu_2O, selenium oxide
Amber	Organic matter and C
Ruby	$AuCl_3$

Different Varieties of Glass



Glass type	Composition	Properties
Hard glass	$K_2O \cdot CaO \cdot 4SiO_2$	Resistant to acid and chemicals
Flint glass	$K_2O \cdot PbO \cdot 4SiO_2$	High refractive index so used in optical lenses and prisms
Pyrex glass	Mixture of borosilicate of Pb, Ca and Na	Low coefficient of thermal expansion so can with stand sudden changes in temperature
Crooke's glass	Contains CeO_2 along with general composition	Absorbs UV radiations so used in making goggles
Jena glass	Contains mixture of Zn and Ba borosilicates	Resistant to heat, shock, etc.
Quartz glass	Pure silica	Optical instruments (vetreosil)

Glass is attacked by HF. This property is used in the etching of glass



$$Na_2SiO_3 + 8HF \longrightarrow 2NaF + H_2SiF_6 + 3H_2O$$
$$CaSiO_3 + 8HF \longrightarrow CaF_2 + \underbrace{H_2SiF_6}_{\text{hydrofluoro silicic acid}} + 3H_2O$$

Compounds of Lead

Chrome yellow ($PbCrO_4$)

It is prepared by adding potassium chromate to lead chromate and is used as a yellow pigment under the name chrome yellow. On treating with alkali. it gives basic lead chromate or chrome red, $PbCrO_4 * PbO$.

Basic lead carbonate, $Pb(OH)_2 . 2PbCO_3$

It is also known as white lead and is prepared by adding sodium carbonate solution to any lead salt.

$3Pb(NO_3)_2 + 3Na_2CO_3 + H_2O \rightarrow Pb(OH)_2 * 2PbCO_3 + 6NaNO_3 + CO_2$

It is used as white paint. The disadvantage of using white lead in paints is that it turns black by the action of H_2S of the atmosphere.

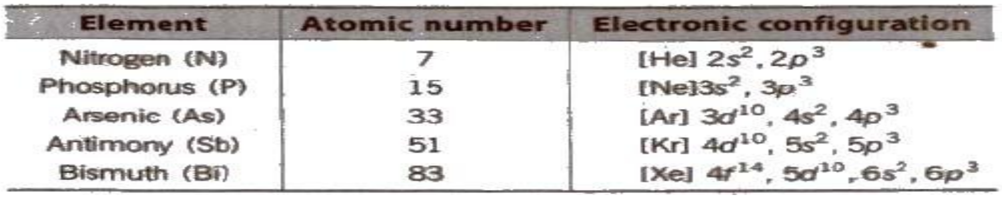
lead poisoning is called plumbosolvency which increases in the excess of nitrates, organic acids and ammonium salts.

Group 15

The 15 group of the Periodic Table consists of nitrogen. phosphorus. arsenic, antimony and bismuth. These elements are known as pnicogens and their compounds as **pniconides**.

Physical Properties of Group 15 Elements

(i) **Electronic configuration** Their valence shell electronic configuration is $ns^2 np^3$



Element	Atomic number	Electronic configuration
Nitrogen (N)	7	[He] $2s^2, 2p^3$
Phosphorus (P)	15	[Ne]$3s^2, 3p^3$
Arsenic (As)	33	[Ar] $3d^{10}, 4s^2, 4p^3$
Antimony (Sb)	51	[Kr] $4d^{10}, 5s^2, 5p^3$
Bismuth (Bi)	83	[Xe] $4f^{14}, 5d^{10}, 6s^2, 6p^3$

(ii) **Metallic character** N and P are non-metals, As and Sb are metalloids and Bi is metal.
(iii) **Physical state** Nitrogen is the first element after hydrogen which is diatomic gas in native form. All other elements in the group are solids.
(iv) **Atomicity** N2 is diatomic while others are triatomic E_4.
(V) **Melting and boiling points** The melting point increases from nitrogen to arsenic. The boiling points increase regularly on moving down the group.
(Vi) **Density** It increases down the group.
(Vii) **Atomic radii** It increases with increase in atomic number as we go down the group.
(viii) **Allotropy** All the elements (except Bi) exhibit allotropy. Nitrogens – α nitrogen, β – nitrogen.
Phosphorus – White, red, black
Arsenic – Grey, yellow, black
Antimony – Metallic yellow (explosive)

(ix) **Oxidation state**

N	P	As	Sb	Bi
−3 to +5	−3, +3, +4, + 5	+3, + 5	+3, + 5	+3, + 5

Nitrogen has a wide range of oxidation states.

The stability of +3 oxidation state increases and stability of +5 oxidation state decreases on moving down the group due to inert pair effect.

(x) **Ionisation enthalpy** Ionisation energy of nitrogen is very high due to its small size and half-filled highly stable configuration. The ionisation energy decreases down the group.
(xi) **Electronegativity** It decreases from nitrogen to bismuth.
(xii) **Catenation** 'They exhibit the property of catenation but to lesser extent due to weak E – E bond than 14 group elements.
(xiii) **Reactivity** Elemental nitrogen is highly unreactive because of its strong triple bond. (almost as inert as noble gases).
White phosphorus is extremely reactive and kept in water. It is inflammable and can be ignited at 45°C.

Chemical Properties of Group 15 Elements
(i) **Hydrides** All the elements of this group form hydrides of the type EH_3, which are covalent and pyramidal in shape. Some properties follows the order as mentioned

NH_3	>	PH_3	>	AsH_3	>	SbH_3	>	BiH_3
ammonia		phosphine		arsine		stibine		bismuthine

[These properties are

1. Thermal stability,
2. Basic strength,
3. Solubility in water,
4. Bond angle NH_3 (107.4°); PH_3 (92°),AsH_3 (91°), SbH_3(90°),
5. Strength of M – H bond

Some properties follow the order

$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
[These properties are

1. Reducing character
2. Covalent character
3. Rate of combustion

(ii) **Halides** All the elements of this group form trihalides, MX_3 and except nitrogen all form pentahalides, MX_5, e.g., NCi_3, NI_3, PCI_3, $BiCI_3$, $AsCI_3$, PCl_5 etc. Trihalides (except of N) behaves as Lewis acid and the order of their strength is $PCl_3 > AsCl_3 > SbCl_3$ Trihalides of N behave as Lewis base and has the following order of strength

$NF_3 < NCl_3 < NBr_3 < NI_3$

NCl_3 is an explosive compound

(iii) **Oxides** All the elements of this group form oxides of the type M_2O_3 and M_2O_5.

Oxides of N $\underset{\text{Strongly acidic}}{N_2O_5,\ N_2O_4,}\ N_2O_3$ $\underbrace{NO\quad N_2O}_{\text{neutral}}$

Oxides of P $\underset{\text{strongly acidic}}{P_4O_{10}}$ P_2O_3

As_4O_6 is called white arsenic and is a poison.

The acidic strength of pentoxide and trioxides decrease on moving down the group, i.e.,

$N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5$

BiOCI is called pearl white.

Nitrogen and its Compounds

1. **Dinitrogen** (N2)

Preparation

$$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

$$Ba(N_3)_2 \longrightarrow Ba + 3N_2 \qquad \text{(pure nitrogen)}$$

Properties

1. Nitrogen does not react with alkali metals except Li but reacts with alkaline earth metals to give metal nitride.

$$6Li + N_2 \xrightarrow{\text{Heat}} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{\text{Heat}} Mg_3N_2$$

2. Reaction with oxygen

$$N_2(g) + O_2(g) \overset{\text{2000 K}}{\rightleftharpoons} 2NO(g)$$

3. Reaction with non-metals

$$2B + N_2 \xrightarrow{\text{Heat}} 2BN$$

4. Reaction with CaC_2

$$CaC_2 + N_2 \xrightarrow{\text{1273 K}} \underbrace{CaCN_2 + C}_{\text{nitrolim}}$$

Uses Liquid N_2 is used as refrigerant. Nz is used in the manufacture of HNO_2, NH_2, $CaCN_2$(calcium cyanamide) and other nitrogenous compounds. It is used for filling electric bulbs.

2. **Ammonia** (NH3)

Preparation

(i) **Lab method**

$2NH_4Cl + Ca(OH)_2 \rightarrow CaCI_2 + 2NH_3 + 2H_2O$

(ii) **Haber’s process**

$$N_2 + 3H_2 \xrightarrow[\text{Low temperature, high pressure}]{\text{Fe/Mo}} 2NH_3$$

(iii) $AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$

(iv) $NH_2CONH_2 \xrightarrow[2H_2O]{} 2NH_3 + H_2O + CO_2$

Properties

1. It is a colourless gas with characteristic pungent odour. It is extremely soluble in water due to H – bonding.

2. It is a strong Lewis base and used in the metal ion detection as

$$\underset{\text{[blue]}}{Cu^{2+}(aq)} + 4NH_3(aq) \longrightarrow \underset{\text{[deep blue]}}{[Cu(NH_3)_4]^{2+}}$$

$$Ag^+(aq) + Cl^-(aq) \longrightarrow \underset{\text{(white ppt)}}{AgCl(s)}$$

$$AgCl(s) + 2NH_3(aq) \longrightarrow \underset{\text{soluble}}{[Ag(NH_3)_2]Cl(aq)}$$

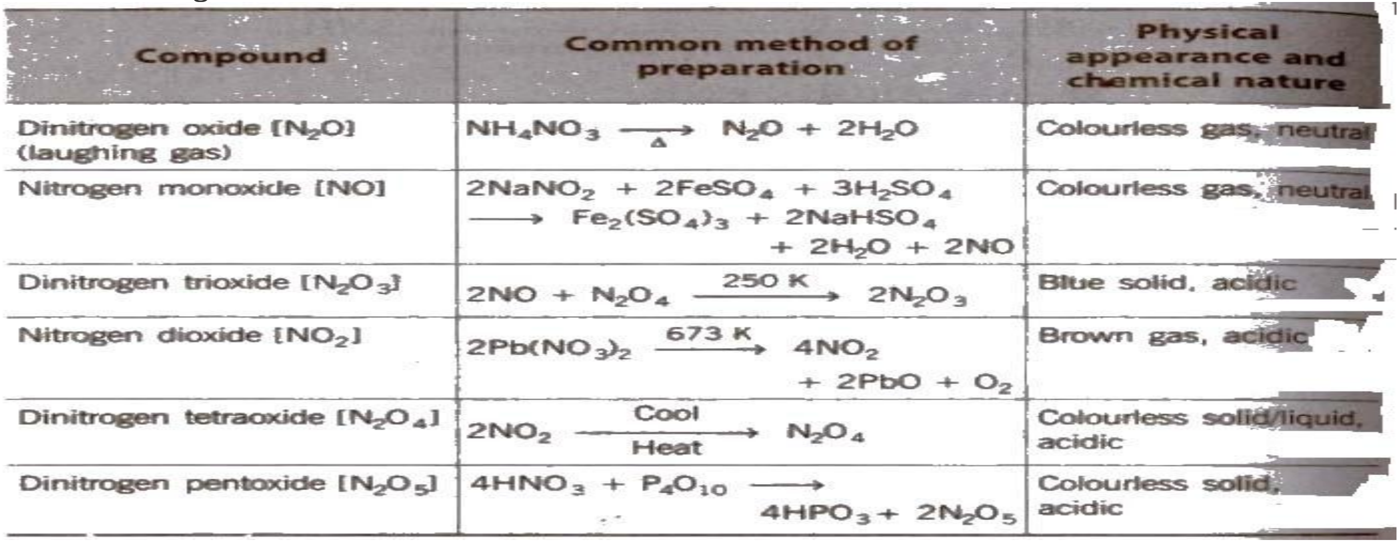
3. Reaction with chlorine

When NH_3 is in excess, N_2 is the main product.
$8NH_3 + 3C1_2 \rightarrow 6NH_4CI + N_3$
When $C1_2$ is in excess, NCl_3 is the main product.
$NH_3 + 3C1_2 \rightarrow NCl_3 + 3HCl$
4. Reaction with Nesseler's reagent

$$NH_3 + \underbrace{2K_2HgI_4 + 3KOH}_{\text{Nessler's reagent}} \longrightarrow \underset{\substack{\text{iodide of Millon's base}\\ \text{(brown ppt)}}}{H_2N{-}HgO{-}HgI} + 7KI + 2H_2O$$

Uses It is used as a refrigerant and to produce various nitrogenous fertilizers.

Oxides of Nitrogen



Compound	Common method of preparation	Physical appearance and chemical nature
Dinitrogen oxide [N_2O] (laughing gas)	$NH_4NO_3 \xrightarrow[\Delta]{} N_2O + 2H_2O$	Colourless gas, neutral
Nitrogen monoxide [NO]	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	Colourless gas, neutral
Dinitrogen trioxide [N_2O_3]	$2NO + N_2O_4 \xrightarrow{250\ K} 2N_2O_3$	Blue solid, acidic
Nitrogen dioxide [NO_2]	$2Pb(NO_3)_2 \xrightarrow{673\ K} 4NO_2 + 2PbO + O_2$	Brown gas, acidic
Dinitrogen tetraoxide [N_2O_4]	$2NO_2 \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4$	Colourless solid/liquid, acidic
Dinitrogen pentoxide [N_2O_5]	$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$	Colourless solid, acidic

NO_2 contains odd number of valence electrons. On dimerisation. it is converted to stable N_2O_4 molecule with even number of electrons .

3.**Nitric acid** (HNO_3)

It is a stronger acid than H_3PO_4.

Preparations

(i) Lab method

$NaNO_3 + H_2SO_4$ (cone.) → $NaHSO_4 + HNO_3$

(ii) Ostwald's process

$$4NH_3 + 5O_2 \xrightarrow[500\text{ K, 9 bar}]{\text{Pt/Rh gauge}} 4NO + 6H_2O$$

$$2NO + O_2 \rightleftharpoons 2NO_2$$

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

Physical properties It is a syrupy, colourless, pungent liquid usually available as 68 % and 15.7 M aqueous solution is often yellow due to small concentrations of NO_2.

Chemical reactions

1. **Action of nitric acid on zinc under different conditions**

Cold and dil HNO_3

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

Cold and concentrated HNO_3

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

2. **Action of nitric acid on copper under different conditions**

Cold and dil. HNO_3

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

Cold and concentrated HNO_3

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

3. **Reaction with non-metals**

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2$$

$$S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

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

4. **Brown ring test of nitrate**

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{[brown]}}{[Fe(H_2O)_5NO]^{2+}} + H_2O$$

5. Metals like Fe. Cr. Ni, AI or Co becomes inactive or passive due to stable oxide layers.

Structure of nitric acid

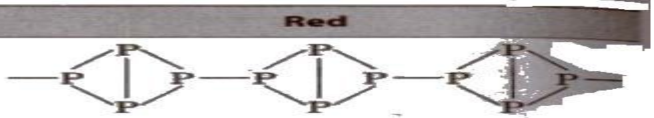
Uses It is used

1. in the manufacturing of fertilizers.
2. for purification of silver and gold.
3. in the manufacturing of explosives and as oxidising agent.
4. as nitrating reagent

Phosphorus and its Compounds Allotropic Forms of Phosphorus

(i) White phosphorus
(ii) Red phosphorus
(iii) Black phosphorus

Some Points of Distinction Between White and Red Phosphorus

S.No.	Property	White	Red
1.	Structure		
2.	Odour	Garlic smell	Odourless
3.	Conductivity	Bad conductor	Semi-conductor
4.	Physiological action	Poisonous translucent solid	Non-poisonous
5.	Hardness	Soft	Brittle
6.	Action of KOH	PH_3	No action
7.	Action of Cl_2	PCl_3 or PCl_5	On heating PCl_3 or PCl_5
8.	In dark	Shines	Does not shine

Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K. It does not oxidise in air.

Match box side contains red P or P_2S_3 + glue and on tip of match stick. red P, $KelO_3$ chalk and glue is deposited.

Chemical properties

1. With non-metals

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$
$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$
$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$

2. With compounds

$$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{sodium hypophosphite}}{3NaH_2PO_2} + PH_3$$
$$P_4 + 20HNO_3 \longrightarrow \underset{\text{orthophosphoric acid}}{4H_3PO_4} + 4H_2O + 20NO_2$$

Uses It is used in match boxes, explosives, as rat poison, in fertilizers and alloys

1. **Phosphine** (PH_3)

Preparation It is prepared by following methods

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$
$$Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$$
$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$$
$$PH_4I + KOH \longrightarrow KI + H_2O + PH_3$$

Properties

1. It is a colourless gas with rotten fish like smell and is highly poisonous. It explodes in contact. with traces of oxidising agents like HNO_3,$C1_2$ and Br_2 vapours.

$3CuSO_4 + 2PH_3 \rightarrow CU_3P_2 + 3H_2SO_4$

$3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCI$

2. Phosphine is weakly basic.

$PH_3 + HBr \rightarrow PH^+_4Br^-$

Uses It is used to prepare smoke screens in warfare. A mixture of CaC_2 and Ca_3P_2 is used in Holme’s signals.

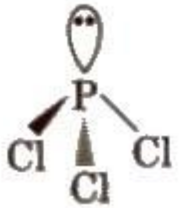
2. **Phosphorus Trichloride** (PCl_5)

Preparation

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$
$$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

Properties It is a colourless oily liquid. having pyramidal shape [sp^3 – hybridised]

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$
$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$
$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$



Structure of PCl_3

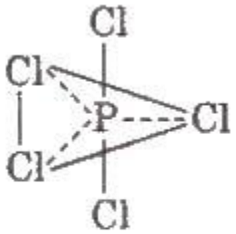
3.**Phosphorus Pentachloride** (PCI5)

Preparation

$P_4 + 10\ Cl_2 \rightarrow 4\ PCl_5$

$P_4 + 10\ SO_2CI_2 \rightarrow 4PCl_5 + 10\ SO_2$

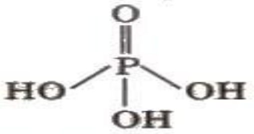
Structure PCl_5 in gaseous and liquid phases has sp^3d – hybridization and its shape is trigonal bipyramidal. The three equatorial P – CI bonds are equivalent while the two axial bonds are longer equatorial bonds.



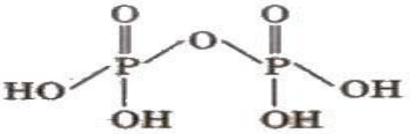
Properties In solid state, PCI_5 exists as an ionic solid, $[PCI_4]^+ [PCl_6]^-$ in which, the cation, $[PCI_4]^+$ is tetrahedral and the anion $[PCl_6]^-$ is octahedral.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$
$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$
$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$
$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$
$$2Ag + PCl_5 \longrightarrow 2AgCl + PCl_3$$
$$Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3$$

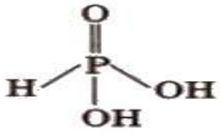
Oxoacids of Phosphorus



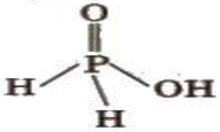
orthophosphoric acid (H_3PO_4)



pyrophosphoric acid ($H_4P_2O_7$)



orthophosphorous acid (H_3PO_3)



hypophosphorous acid (H_3PO_2)

In toothpaste, $CaHPO_4 * 2H_2O$ is added as mild abrasive and polish agent.

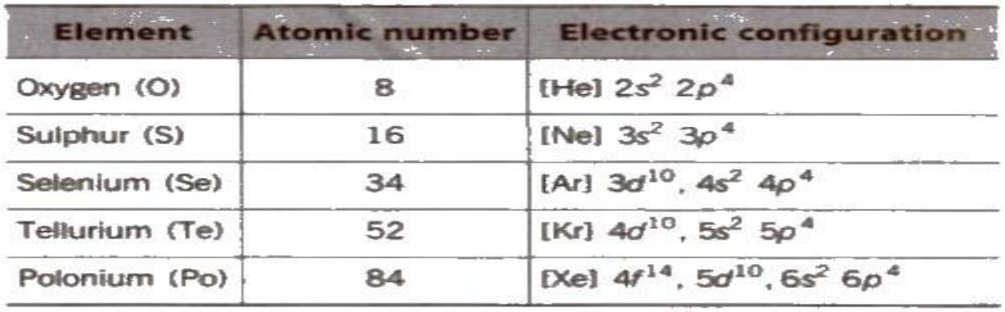
Group 16

The elements oxygen (0), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po) belong to group 16 of the Periodic Table. These elements are known as chalco gens, i.e., ore forming elements.

The name sulphur has been derived from sanskrit word ‘Sulvezi’ meaning ‘killer of copper’.

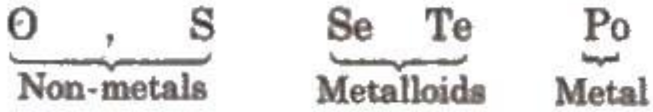
General Physical Properties of Group 16 Elements

(i) **Electronic configuration** Their valence shell electronic configuration is ns^2, np^4.



Element	Atomic number	Electronic configuration
Oxygen (O)	8	$[He]\ 2s^2\ 2p^4$
Sulphur (S)	16	$[Ne]\ 3s^2\ 3p^4$
Selenium (Se)	34	$[Ar]\ 3d^{10}, 4s^2\ 4p^4$
Tellurium (Te)	52	$[Kr]\ 4d^{10}, 5s^2\ 5p^4$
Polonium (Po)	84	$[Xe]\ 4f^{14}, 5d^{10}, 6s^2\ 6p^4$

(ii) **Metallic and non-metallic character**



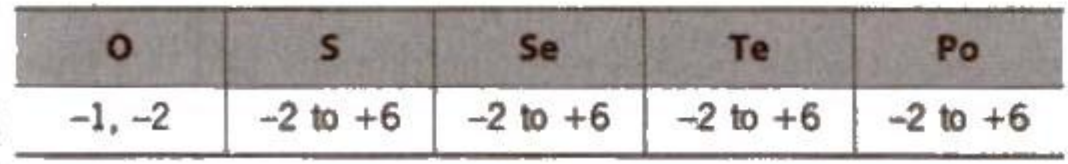
$$\underbrace{O\ ,\ S}_{\text{Non-metals}} \qquad \underbrace{Se\ \ Te}_{\text{Metalloids}} \qquad \underbrace{Po}_{\text{Metal}}$$

(iii) **Abundance** O > S > Se > Te > Po

(iv) **Density** It increases down the group regularly,

(v) **Melting point and boiling point** Both show a regular increase down the group due to increase in molecular weight and van der Waals’ forces of attraction.

(vi) **Oxidation state**



O	S	Se	Te	Po
–1, –2	–2 to +6	–2 to +6	–2 to +6	–2 to +6

In OF_2, the oxidation state of oxygen is +2.

(vii) **Ionisation energy** They possess a large amount of ionisation energy which decreases gradually from 0 to Po due to increase in size of atoms and increase in screening effect.

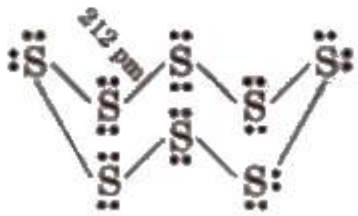
(viii) **Electron affinity** They have high electron affinity which decrease from O to Po. As the size of the atom increases. the extra added electron feels lesser attraction by nucleus and hence, electron affinity decreases.

(ix) **Electronegativity** It decreases down the group due to decrease in effective nuclear charge down the group.

(x) **Catenation** 16 group elements follow the order as shown below

S-S > Se-Se > O-O > Te-Te

(xi) **Atomicity** Oxygen is diatomic, sulphur and selenium are octaatomic with puckered ring structure.



(xii) **Allotropy**

Oxygen – Dioxygen (O_2) and ozone (O_3)

Sulphur – Rhombic (01′ a) sulphur. Ss

Monoclinic (or β) sulphur, S_8(most stable), plastic sulphur

(xiii) **Atomic radii and ionic radii** They increase regularly from O to Po.

Chemical Properties of 16 Group Elements

(i) **Hydrides** All these elements form stable hydrides of the type H_2E. (Where. E = 0, S, Se, Te and Po).

$2H_2 + O_2 \Leftrightarrow 2H_2O$

$FeS + H_2SO_4 \rightarrow H_2S + FeSO_4$

H_2O is a liquid due to hydrogen bonding. While others are colourless gases with unpleasant smell.

[Down the group acidic character increases from H_2O to H_2Se. All the hydrides except water possess reducing property and this character increases from H_2 S to H_2 Te.

(ii) **Halides** The stability of the halides decreases in the order

$F^- > Cl^- > Br^- > 1^-$

Amongst hexahalides, hexafluorides are the only stable halides. AD hexafluorides are gaseous in nature. SF_6 is exceptionally stable for steric reasons.

SF_4 is a gas, SeF_4 is a liquid and TeF_4 is a solid. These fluoride have sp_3 d-hybridisation and see-saw geometry. They behave Lewis acid as well as Lewis base e.g.,

$SF_4 + BF_3 \rightarrow SF_4 \rightarrow BF_3$

$SeF_4 + 2F^- \rightarrow [SeF_6]^{2-}$

The well known mono halides are dimeric in nature. Example are S_2F_2, S_2C1_2, S_2Br_2, Se_2C1_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given below

$2\ SeCI_2 \rightarrow SeCI_4 + Se$

(ill) **Oxides** They form AO_2 and AO_3 type oxides. Their acidic nature follow the order

$SO_2 > SeO_2 > TeO_2 > PoO_2$ and $SO_3 > SeO_3 > TeO_3$

Ozone is considered as oxides of oxygen.

SO_2 is a gas having sps -hybridisation and V-shape.

SO_3 is a gas which is sp2-hybridised and planar in nature.

SeO_2 is a volatile solid consists of non-planar infinite chains.

SeO_3 has tetrameric cyclic structure in solid state. SO_2 and SO_3 are the anhydrides of sulphurous (H_2SO_3) and sulphuric acid (H_2SO_4) respectively.

Note In photocopying (xerox) machines Se acts as photoconductor.

Oxygen and its Compounds

1. Dioxygen

Priestley and **Scheele** prepared oxygen by heating suitable oxygen compounds.

Preparation By action of heat on oxygen rich compounds

(i) **From oxides**

$$2HgO \xrightarrow{\Delta} 2Hg + O_2 \uparrow$$

$$2Ag_2O \longrightarrow 4Ag + O_2 \uparrow$$

$$2PbO_2 \longrightarrow 2PbO + O_2 \uparrow$$

(ii) **From peroxides and other oxides**

$$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O_2$$

(iii) **From certain compounds**

$$2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$$

$$2CaOCl_2 \longrightarrow 2CaCl_2 + O_2$$

Physical properties It is colourless, odourless, tasteless, slightly heavier than air and sparingly soluble in water.
Chemical properties On heating it combines directly with metals and non-metals, e.g.,

$$C + O_2 \longrightarrow CO_2$$
$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$
$$S + O_2 \longrightarrow SO_2$$
$$N_2 + O_2 \xrightarrow{3000°C} 2NO$$

$2Mg + O_2 \rightarrow 2MgO$
$4Na + O_2 \rightarrow 2\ Na_2O \rightarrow Na_2O_2$
Combination with O_2 is accelerated by using catalyst. Platinum is particularly an active catalyst.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$$

Uses It is used in welding and cutting oxy-hydrogen or oxy-acetylene torch and in iron and steel industry to increase the content of blast in the Bessemer and open hearth process. It is also used for life support systems e.g., in hospitals, for divers, miners and mountaineers.
Tests
1. With NO it gives reddish brown fumes of NO_2.
2. It is adsorbed by alkaline pyrogallol.

2. **Ozone** (O_3)
Preparation By passing silent electric discharge through cold, dry oxygen in ozoniser. (Lab method) –
$3O_2 \Leftrightarrow 2O_3$; + 284.3 kJ
Physical properties It is pale blue gas with characteristic strong smell. It is slightly soluble in water.
Chemical reactions
1.**Decomposition**

$$2O_3 \xrightarrow{573\,K} 3O_2;\ \Delta H = 284\ kJ/mol$$

2. **Oxidising action**

$$O_3 \longrightarrow O_2 + [O]$$
$$PbS + 4[O] \longrightarrow PbSO_4$$
$$H_2S + [O] \longrightarrow H_2O + S$$
$$2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O$$

3. It acts as a powerful oxidising agent. It liberates iodine from neutral KI solution and the liberated L,turns starch paper blue.

$2KI + H_2 + O_3 \rightarrow 2KOH + I_2 + O_2$
I_2 + Starch → Blue colour
Uses It is used

1. as a germicide and disinfectant for sterilizing water.
2. ail a bleaching agent for oils, ivory wax and delicate fibres.
3. for detecting ‘the position of double bond in unsaturated compounds.
4. in destroying odours coming from cold storage room, slaughter houses and kitchen of hotels.

compounds of Sulphur

1.**Sulphur Dioxide** (SO_2)

Method of preparation

(i) By heating sulphur in air

(i) **By heating sulphur in air**

$$S + O_2 \xrightarrow{\Delta} SO_2$$

(ii) **Roasting iron pyrites in excess of air**

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

(iii) **Lab method**

$$SO_3^{2-}(aq) + 2H^+(aq) \longrightarrow H_2O(l) + SO_2(g)$$

Physical properties SO_2 is a colourless gas with pungent smell and is highly soluble in water.

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3$$

Chemical reactions It turns lime water milky due to the formation of calcium bisulphite. However, in excess of SO_2 milkiness disappears due to the formation of calcium bisulphite.

$$Ca(OH)_2 + SO_2 \longrightarrow \underset{\text{milkiness}}{CaSO_3} + H_2O$$

$$CaSO_3 + SO_2 + H_2O \longrightarrow \underset{\text{soluble}}{Ca(HSO_3)_2}$$

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$$

$$SO_2(g) + Cl_2(g) \longrightarrow SO_2Cl_2(l)$$

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

Reducing agent

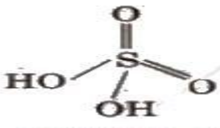
$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

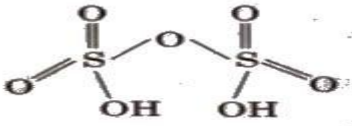
$$5SO_2 + 2MnO_4^- + 2H_2O \longrightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

when H_2S gas is passed through a saturated solution of SO_2 till its smell disappears, it turns in a milky solution the Wacken roder’s liquid. When H_2S is passed through H_2SO_4 the reaction is called Wacken roder’s reaction.

Oxoacids of Sulphur

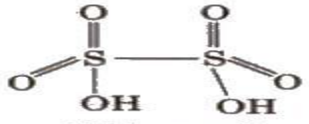

sulphurous acid
(H_2SO_3)

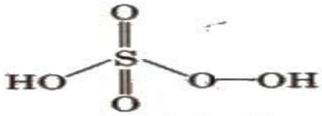

sulphuric acid
(H_2SO_4)

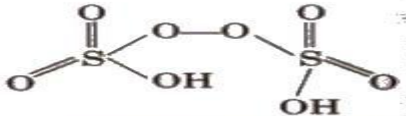

oleum (pyrosulphuric acid)
($H_2S_2O_7$)


thiosulphurous acid
($H_2S_2O_2$)


dithionous acid
($H_2S_2O_4$)


dithionc acid
($H_2S_2O_6$)


peroxomonsulphuric acid
or Caro’s acid
(H_2SO_5)


peroxodisulphuric acid
($H_2S_2O_8$)

2. **Sulphuric Acid** (H_2SO_4)

Sulphuric acid is one of the most important industrial chemicals world wide. It is called the king of chemicals. It is manufactured by lead chamber process or contact process. Contact process involves three steps:

(i) Burning of sulphur or sulphur ores ill air to generate SO_2.
(ii) Conversion of $_2$ to $_2$ by the reaction with oxygen in the presence of a catalyst (V_2O_5).
(iii) Absorption of SO_3 in H_2SO_4 to give oleum ($H_2S_2O_7$) which upon
hydrolysis gives H_2SO_4.

Properties

1. Sulphuric acid is a colourless, dense, oily liquid.

$MX + H_2SO_4 \rightarrow 2HX + M_2SO_4$

2. Concentrated sulphuric acid is a strong dehydrating agent.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$$

The burning sensation of concentrated H_2SO_4 on skin.

3. Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric acid and nitric acid.

$$S + 2H_2SO_4\,(\text{conc.}) \longrightarrow 3SO_2(g) + 2H_2O$$
$$C + 2H_2SO_4(\text{conc.}) \longrightarrow CO_2 + 2SO_2 + 2H_2O$$
$$Cu + 2H_2SO_4(\text{conc.}) \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

Uses It is used in petroleum refining, in pigments paints and in detergents manufacturing.

3. **Hypo**

It is chemically sodium thiosulphate pentahydrate, $Na_2S_2O_3 * 5H_2O$.

Preparation 1. It is prepared by boiling sodium sulphite solution with flowers of sulphur and stirring till the alkaline reaction has disappeared.

$Na_2SO_3 + S \rightarrow Na_2S_2O_3$

2. It is also prepared by **spring's reaction.**

$Na_2S + Na_2SO_3 + I_2 \rightarrow Na_2S_2O_3 + 2NaI$

Properties 1. It is a colourless, crystalline and efflorescent substance.

2. It gives white ppt with a dilute solution of $AgNO_3$. Which quickly changes into black due to the formation of Ag_2S.

$$S_2O_3^{2-} + 2Ag^+ \longrightarrow \underset{\text{white ppt}}{Ag_2S_2O_3}$$
$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$$

Uses

1. Due to its property of dissolving silver halide, it is used in photography for fixing under the name hypo.

$2\,Na_2S_2O_3 + AgBr \rightarrow Na_3\,[\,Ag(S_2O_3)_2] + NaBr$

2. During bleaching, it is used as antichlor,

$Na_2S_2O_3 + CI_2 + H_2O \rightarrow Na_2SO_4 + S + 2HCI$

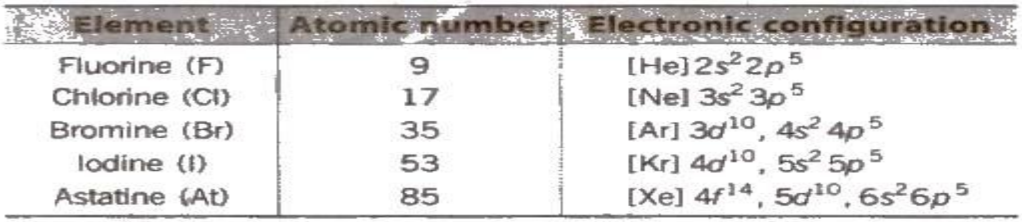
3. It is used to remove iodine stain, for volumetric estimation of iodine and in medicines.

Group 17

The 17 group of Periodic Table contains five elements fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (As) combinedly known as halogens (salt forming elements). Astatine is artificially prepared radioactive element.

General Physical Properties of Group 17 Elements

(i) **Electronic configuration** Their valence shell electronic configuration is ns^2, np^5



Element	Atomic number	Electronic configuration
Fluorine (F)	9	$[He] 2s^2 2p^5$
Chlorine (Cl)	17	$[Ne] 3s^2 3p^5$
Bromine (Br)	35	$[Ar] 3d^{10}, 4s^2 4p^5$
Iodine (I)	53	$[Kr] 4d^{10}, 5s^2 5p^5$
Astatine (At)	85	$[Xe] 4f^{14}, 5d^{10}, 6s^2 6p^5$

(ii) Physical state Intermolecular forces in halogens are weak and increase down the group. Thus, F_2 and Cl_2 are gases, Br_2 is volatile liquid and I_2 is solid.

(iii) Atomicity All are diatomic in nature.

(iv) Abundance Being very reactive in nature, they are not found free in nature. Their presence in earth's crust follows the order.

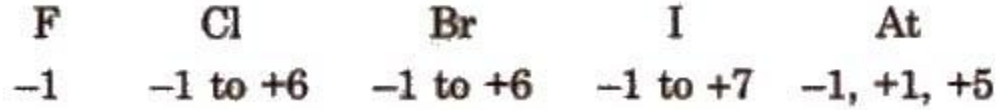
$F_2 > Cl_2 > Br_2 > I_2$

(v) **Colour** They absorb light in the visible range forming excited states and are thus, coloured in nature.

F_2	Cl_2	Br_2	I_2
pale yellow	yellowish green	reddish brown	deep violet

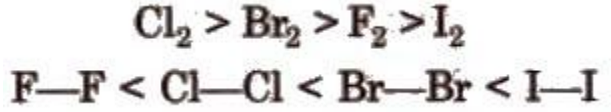
(vi) **Metallic character** All the elements are non-metals and metallic character increases down the group. Thus, 1 forms 1+.

(vii) **Oxidation state**



F	Cl	Br	I	At
–1	–1 to +6	–1 to +6	–1 to +7	–1, +1, +5

(viii) **Bond energy and bond length** The bond length increases from fluorine to iodine and in the same order bond energy decreases However, the bond dissociation energy of F2 is lesser due to its smaller size. The order of bond energy is



$$Cl_2 > Br_2 > F_2 > I_2$$

$$F—F < Cl—Cl < Br—Br < I—I$$

(he) **Density** It increases down the group in a regular fashion and follows the order F > Cl > Br > 1.

(x) **Ionisation enthalpy** The ionisation enthalpy of halogens is very high and decreases down the group. The iodine also forms I^+ and I^{3+} and forms compounds like leI, lCN, IPO_4. In molten state, the compounds conduct electricity showing ionic character.

(xi) Electron affinity The halogens have the high values for electron affinity. The order of electron affinity is

$C1_2 > F_2 > Br_2 > I_2$

Due to small size of fluorine (hence, high electron density), the extra electron to be added feels more electron-electron repulsion. Therefore. fluorine has less value for electron affinity than chlorine.

(xii) **Reduction potentials and oxidising nature** $E°_{red}$ of halogens are positive and decrease from F to I. Therefore, halogens act as strong oxidising agents and their oxidising power decreases from fluorine to iodine. Fluorine is the strongest oxidising agent and is most reactive. That's why it is prepared by the electrolysis of a mixture of KHF_2 and anhydrous HF using Monel metal as a catalyst.

(xii) **Solubility** Halogens are soluble in water which follows the order

$F_2 > C1_2 > Br_2 > I_2$

The solubility of iodine in water is enhanced in the presence of KI.

$KI + I_2 \Leftrightarrow KI_3 \Leftrightarrow K^+ + I^-_2$

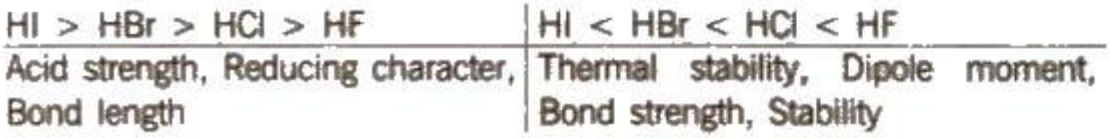
I_2 forms blue colour complex with starch.

Chemical Properties of Group 17 Elements

(i) **Hydrides** HF is a low boiling liquid due to intermolecular hydrogen bonding, while HCI, HBr, HI are gases. The boiling point follows the trend

HF > Hi > HBr > HCl

Some other properties show the following trend :



HI > HBr > HCl > HF	HI < HBr < HCl < HF
Acid strength, Reducing character, Bond length	Thermal stability, Dipole moment, Bond strength, Stability

(ii) **Oxides** Fluorine forms two oxides, OF_2 and O_2F_2, but only OF_2 is thermally stable at 2.98K O_2F_2 oxidises plutonium to PuF_6 and the reaction is used for removing plutonium as PuF_6 from spent nuclear fuel.

Chlorine forms a number of oxides such as, CI_2O, CI_2O_3, Cl_2O_5 , Cl_2O_7 , CIO_2 and CIO_2 is used as a bleaching agent for paper pulp, textiles and in water treatment.

Br_2O BrO_2 BrO_3 are the least stable bromine oxides and exist only at low temperatures. They are very powerful oxidising agents.

The iodine oxides, i:e., I_2O_4, I_2O_5,I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

(iii) **Reaction with alkali**

$$2F_2 + \underset{\text{(cold dilute)}}{2NaOH} \longrightarrow 2NaF + OF_2 + H_2O$$

$$2F_2 + \underset{\text{(hot conc.)}}{4NaOH} \longrightarrow 4NaF + O_2 + 2H_2O$$

Other halogens form hypohalite with dilute NaOH and halate with cone. $NaOH_4$.

$$X_2(g) + \underset{\text{(cold dilute)}}{2OH^-} \xrightarrow{150°C} X^- + \underset{\text{(hypohalite ion)}}{OX^-} + H_2O$$

$$X_2(g) + \underset{\text{(hot conc.)}}{6OH^-} \xrightarrow{70°C} 5X^- + \underset{\text{(halate ion)}}{XO_3^-} + 3H_2O$$

(iv) **Oxoacids of halogens** Higher oxoacids of fluorine such as HFO_2, HFO_3 do not exist because fluorine. is most electronegative

and has absence of d-orbitals.

+3 oxidation state of bromine and iodine are unstable due to inert pair effect. therefore, $HBrO_2$ and HIO_2. do not exist.

Acidic character of oxoacids decreases as the electronegativity of halogen atom decreases. Thus, the order of acidic strength.

$$\underset{\text{(hypofluorous > acid)}}{HOF} > \underset{\text{(hypochlorous acid)}}{HOCl} > \underset{\text{(hypobromous acid)}}{HOBr} \xrightarrow{\text{Acidic nature decreases}} \underset{\text{(hypoiodous acid)}}{HOI}$$

For the oxoacids of same halogens. acidic strength and thermal stability increase as the number of O atoms increases

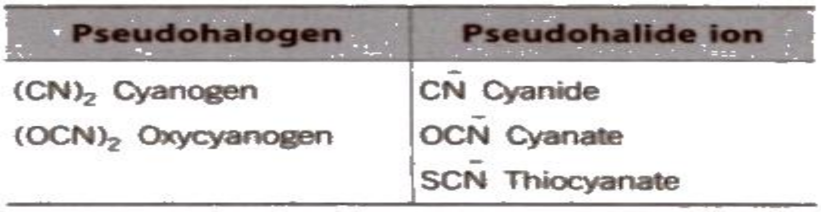
Interhalogen Compounds

When two different halogens react with each other, interhalogen compounds are formed. These compounds are covalent and diamagnetic in nature. They are volatile solids or liquids except elf which is a gas at 298 K. Interhalogen compounds are more reactive than halogens (except fluorine).

The XY_3 type compounds have bent 'T' shape, XY_5 type compounds have square pyramidal shape and IF_7 has pentagonal bipyramidal structure.
BrF_3 has "T" shaped structure due to 3 bp and 2 lp.
ICI is more reactive than I_2 due to weak bond. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.
$U(s) + 3ClF_3(l) \rightarrow UF_6(g) + 3ClF(g)$

Pseudohalogens and Pseudohalides

The substances behaving like halogens are known as pseudohalides. Some examples are



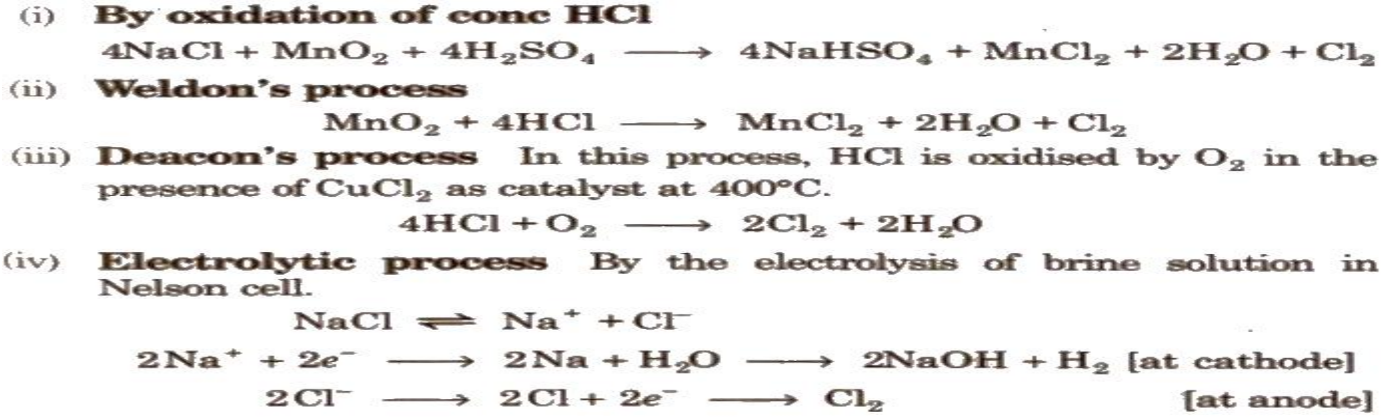
Pseudohalogen	Pseudohalide ion
$(CN)_2$ Cyanogen	$C\bar{N}$ Cyanide
$(OCN)_2$ Oxycyanogen	$OC\bar{N}$ Cyanate
	$SC\bar{N}$ Thiocyanate

Chlorine and its Compounds

Occurrence

Common salt, NaCI is most important. Chlorine is also present in sea water and as rock salt.

Preparation of Chlorine



(i) **By oxidation of conc HCl**

$$4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow 4NaHSO_4 + MnCl_2 + 2H_2O + Cl_2$$

(ii) **Weldon's process**

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

(iii) **Deacon's process** In this process, HCl is oxidised by O_2 in the presence of $CuCl_2$ as catalyst at 400°C.

$$4HCl + O_2 \longrightarrow 2Cl_2 + 2H_2O$$

(iv) **Electrolytic process** By the electrolysis of brine solution in Nelson cell.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$2Na^+ + 2e^- \longrightarrow 2Na + H_2O \longrightarrow 2NaOH + H_2 \text{ [at cathode]}$$

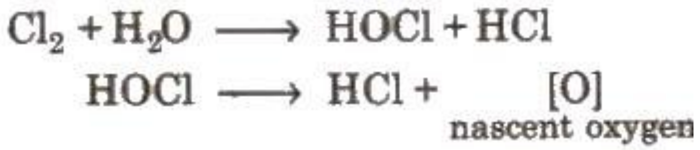
$$2Cl^- \longrightarrow 2Cl + 2e^- \longrightarrow Cl_2 \text{ [at anode]}$$

Properties

It is yellowish green gas, collected by upward displacement of air poisonous in nature, soluble in water. It's aqueous solution is known as chlorine water.

Chemical Reactions

(i) **Action of water**

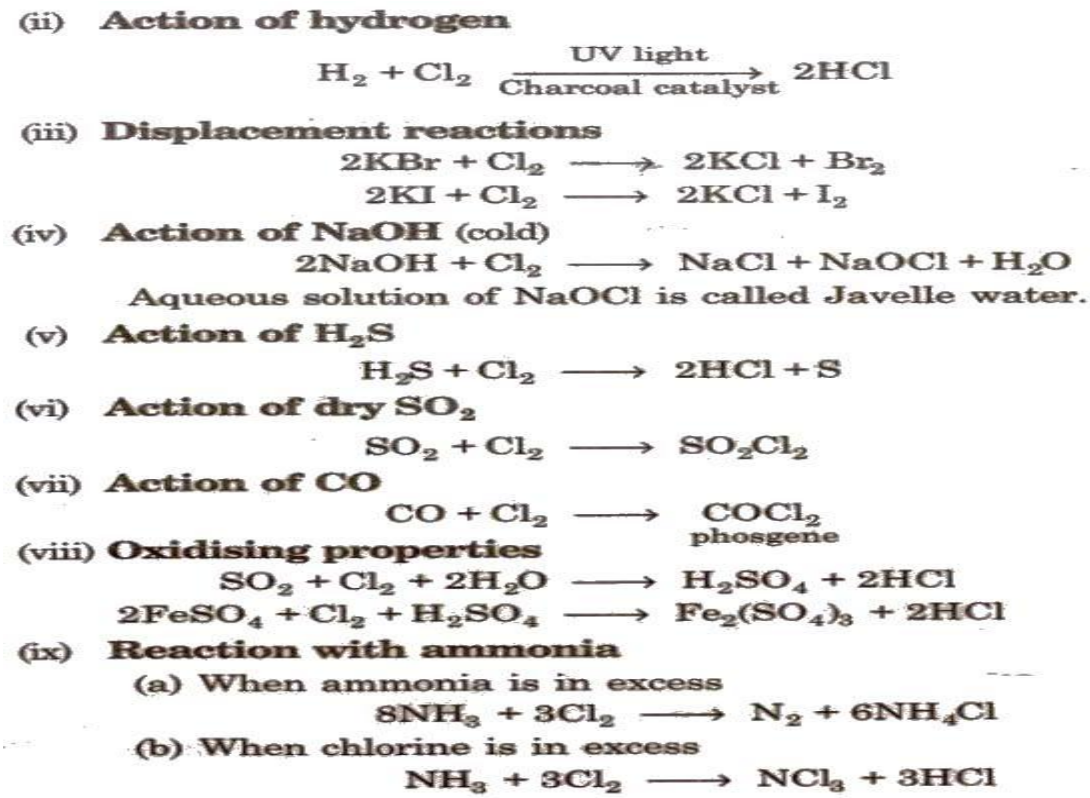


$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

$$HOCl \longrightarrow HCl + \underset{\text{nascent oxygen}}{[O]}$$

Coloured matter + [0] → colourless matter.

The bleaching action of chlorine is due to oxidation and is permanent.



(ii) Action of hydrogen

$$H_2 + Cl_2 \xrightarrow[\text{Charcoal catalyst}]{\text{UV light}} 2HCl$$

(iii) Displacement reactions

$$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$$

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

(iv) Action of NaOH (cold)

$$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

Aqueous solution of NaOCl is called Javelle water.

(v) Action of H_2S

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

(vi) Action of dry SO_2

$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2$$

(vii) Action of CO

$$CO + Cl_2 \longrightarrow \underset{\text{phosgene}}{COCl_2}$$

(viii) Oxidising properties

$$SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$

$$2FeSO_4 + Cl_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$

(ix) Reaction with ammonia

(a) When ammonia is in excess

$$8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$$

(b) When chlorine is in excess

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

(x) **Chromyl chloride test** When a mixture of chloride and solid $K_2Cr_2O_7$ is heated with concentrated H_2SO_4 in a dry test tube, deep red vapours of chromyl chloride are evolved.

$$Cl^- + K_2Cr_2O_7 + H_2SO_4 \longrightarrow \underset{\text{red vapours}}{CrO_2Cl_2} + KHSO_4 + HSO_4^- + H_2O$$

When these vapours are passed through NaOH solution, the solution becomes yellow due to the formation of sodium chromate

$$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{yellow}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

The yellow solution is neutralised with acetic acid and on addition of lead acetate gives a yellow precipitate of lead chromate.

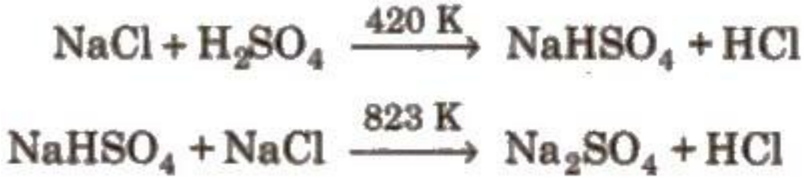
$$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow \underset{\text{yellow ppt.}}{PbCrO_4} + 2CH_3COONa$$

Uses

It is used as a bleaching agent, disinfectant and in the manufacture of $CHCl_3$,CCl_4, DDT, anti-knocking compounds and bleaching powder.

Hydrochloric Acid (Hel)

Preparation

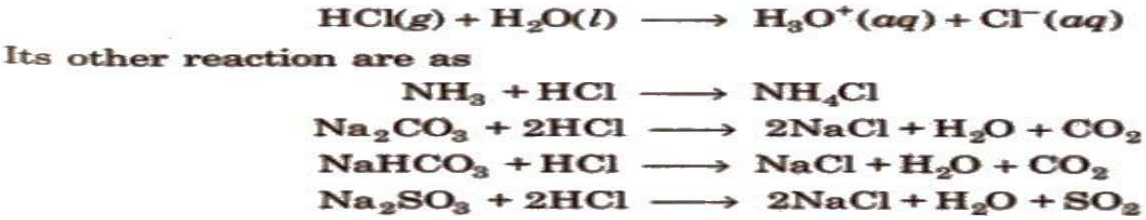


$$NaCl + H_2SO_4 \xrightarrow{420\ K} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{823\ K} Na_2SO_4 + HCl$$

Properties

It is a colourless and pungent smelling gas. It is extremely soluble in water and ionises as below



$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

Its other reaction are as

$$NH_3 + HCl \longrightarrow NH_4Cl$$

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$$

Noble metals like gold, platinum can dissolve in aqua-regia [three part cone HCl and one part of cone HNO_3].

Uses

It is used in the manufacture of chlorides. chlorine, in textile and dyeing industries, in medicine and in extraction of glue from animal tissues and bones.

Iodine (I_2)

It's major SOurce is deep sea weeds of laminaria variety. Their ashes which is called kelp contain 0.5% iodine as iodides.

Another source of 12 is caliche or crude chile saltpetre ($NaNO_3$) which contains 0.2%, $NaIO_3$

Iodine is purified by sublimation.

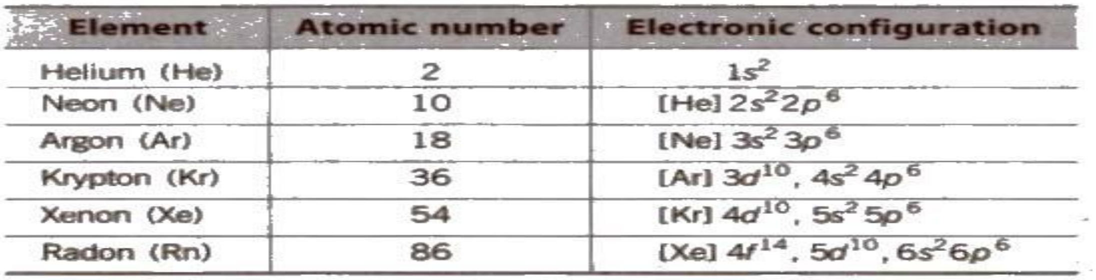
It shows no reaction with water. Tincture of iodine is a mixture of I_2 and Kl dissolved in rectified spirit.

18 Group

The 18 group of the Periodic Table consists of colourless, odourless gases at room temperature, isolated by William Ramsay in 1898 from air

General/Physical Characteristics of Group 18 Elements

(i) **Electronic configuration** Their valence shell electronic configuration is ns^2, np^2 except He.



Element	Atomic number	Electronic configuration
Helium (He)	2	$1s^2$
Neon (Ne)	10	$[He]\ 2s^2 2p^6$
Argon (Ar)	18	$[Ne]\ 3s^2 3p^6$
Krypton (Kr)	36	$[Ar]\ 3d^{10}, 4s^2 4p^6$
Xenon (Xe)	54	$[Kr]\ 4d^{10}, 5s^2 5p^6$
Radon (Rn)	86	$[Xe]\ 4f^{14}, 5d^{10}, 6s^2 6p^6$

(ii) **Physical state** They are all gases under ordinary conditions of temperature and pressure.

(iii) **Abundance** In 1.O% air, the abundance follows the order

Ax > Ne > He > Kr > Xe

(iv) **Atomicity** The Cp / Cv = 1.67 shows their monoatomic nature.

However under high energy conditions, several molecular ions such as He^+_2, HeH^+, $HeH^{2+}$and Ar^+_2 are formed in discharge tubes. They only survive momentarily and are detected spectroscopically.

(v) **Melting and boiling points** Due to the increase in magnitude of van der Waals' forces, the melting point and boiling point increases from He to Rn.

(vi) **Atomic radii** The atomic radii increases from He to Rn. It corresponds to the van der Waals' radii. So it has greatest atomic size in respective period.
(vii) **Density** The density of noble gases increases down the group.
(viii) **Heat of vaporisation** They have very low values of heal of vaporisation due to weak van der Waals' forces of attraction. The value increases down the group.
(ix) **Solubility in water** They are slightly soluble in water and solubility increases from He to Rn.
(x) **Liqnefication** It is extremely difficult to liquify inert gases due to weak van der Waals' forces of attraction among their molecules. Hence, they posses low value of critical temperature also.
(xi) **Ionisation energy** All noble gases possess very stable (ns^2 and ns^2 np6) electronic configuration. Therefore. ionisation energy of noble gases is very high and decreases down the group.
(xii) **Electron affinity** Due to the presence of stable electronic configuration, they have no tendency to accept additional electron. Therefore, electron affinity is almost zero.

Chemical Properties of Group 18 Elements

The noble gases are inert in nature because of their completely filled subshells. In 1962, the first compound of noble gases was prepared. It is hexafluoroplatinate (prepared by Bartlett).

$Xe + PtF_6 \rightarrow Xe[PtF_6]$
Now, many compounds of Xe and Kr are known with fluorine and oxygen.

Preparation of Compounds of Xenon

(i) $\underset{\text{(Xe in excess)}}{Xe(g)} + F_2(g) \xrightarrow{673\text{ K, 1 bar}} XeF_2(s)$

(ii) $\underset{\text{(1 : 5 ratio)}}{Xe(g)} + 2F_2(g) \xrightarrow{873\text{ K, 7 bar}} XeF_4(s)$

(iii) $\underset{\text{(1: 20 ratio)}}{Xe(g)} + 3F_2(g) \xrightarrow{573\text{ K, 60-70 bar}} XeF_6(s)$

(iv) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

Chemical Reactions of Xenon Compounds

$$XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$$
$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$$
$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

Thank You

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