03 The p-Block Elements

Back Bonding:

- It is a type of π-coordinate bonding.
- In this type of bond one element provide Lone pair to the vacant orbital of other atom in the molecule and that lone pair is delocalised in whole molecule.

Essential condition for back bonding:

- One atom should have Lone pair to donate.
- Other atom should have vacant orbitals to accept Lone pair
- One of the atom must belong to 2^{nd} period. (either it can be a donar or it can be an acceptor)

Effect of back bonding:

(i) Bond length
(ii) Hybridisation of central atom
(iii) Bond angle (may be same or may be increased)
(iv) Acidic and basic nature of molecule
(v) Regular geometry of molecule

Note :

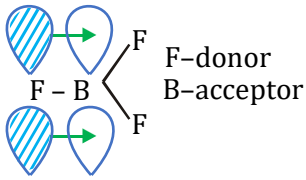
These may or may not change.

Type of back-bonding:

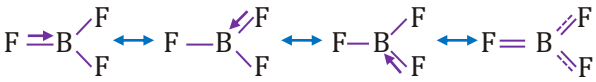
(a) pπ-pπ back-bonding

strength of back bonding

2p – 2p > 2p – 3p > 2p – 4p > 2p – 5p



F–donor
B–acceptor



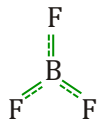
B.O = 1.33

- Due to back bonding partial double bond character is developed i.e. why electron deficiency of B is compensated i.e. why BF_3 do not form dimer.

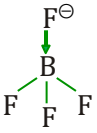
  Lewis acidic strength of boron trihalide

  $BF_3 < BCl_3 < BBr_3 < BI_3$

Ex : Compare B–F Bond length of BF_3 and $BF_4^{\ominus}$



Back Bonding is present
B.O = 1.33

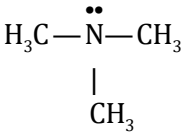


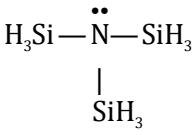
No Back Bonding
B.O = 1.0

Hybridisation state = sp^2	Hybridisation state = sp^3
% s character = 33.33	% s character = 25
Bond order	$BF_3 > BF_4^{\ominus}$
Bond length	$BF_3 < BF_4^{\ominus}$

(b) pπ – dπ Back Bonding (2pπ – 3dπ)

Ex : Why $\ddot{N}(CH_3)_3$ is more basic than $\ddot{N}(SiH_3)_3$





Due to absence of vacant orbital in C.	Due to presence of vacant orbital in Si.
No pπ–pπ Back Bonding	pπ–dπ back bonding
Hybridisation-sp^3	Hybridisation-sp^2
Shape-pyramidal	Shape-trigonal planar
L.P. is available to donate so it is more basic	L.P. is not available on 'N' to donate so it is less Basic

Inert pair effect:

In p-block elements the stability of the lower oxidation state increases on descending the group. Because increased effective nuclear charge holds ns electrons tightly due to poor shielding effect of inner d & f orbitals and thereby, restrict their (ns electrons) participation in bonding only np electrons take part in bond formation. As a result of this, +1 oxidation state of Tl is more stable than it's +3 oxidation state. Pb shows +2 stable oxidation state and Bi shows +3 stable oxidation state.

For example :

Group 13	**Group 14**
B (+3)	C (+4)
Al (+3)	Si (+4)
Ga (+3), (+1)	Ge (+4), (+2)
In (+3), (+1)	Sn (+4), (+2)
Tl (+3), (+1)	Pb (+4), (+2)

Order of stability : $Tl^{1\oplus} > In^{1\oplus} > Ga^{1\oplus}$ (due to inert pair effect)

Order of stability : $Pb^{2\oplus} > Sn^{2\oplus} > Ge^{2\oplus}$ (due to inert pair effect)

Illustration 1:

$PbCl_4$ is stable at room temperature whereas PbI_4 doesn't exist.

Solution:

Due to inert pair effect Pb(+4) is less stable than Pb(+2). Hence it is very good oxidant.

$Pb(IV) + 2e^{\ominus} \longrightarrow Pb(II)$

Reducing abilities of halides follows the sequence

$I^{\ominus} > Br^{\ominus} > Cl^{\ominus}$

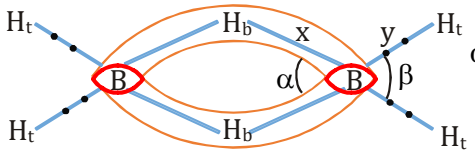
Dimerisation/Polymerisation:

Types of Dimerisation

$3C—2e^{\ominus}$	$3C—4e^{\ominus}$
B_2H_6	$(BeCl_2)_2$
$(BeH_2)_2$	$(BeCl_2)_n$
$(BeH_2)_n$	$(AlCl_3)_2$
$Al_2(CH_3)_6$	
$Ga_2(CH_3)_6$	

(A) By banana Bond or by 3C–2e bond or by $e^{\ominus}$ deficient bond:

(a) B_2H_6



$\alpha < \beta$ = Bond Angle H_t = Terminal hydrogen

x > y = Bond Length H_b = Bridging hydrogen

$2C - 2e^{\ominus}$ bonds = 4 $3C - 2e^{\ominus}$ bonds = 2 $B_2H_6 \rightleftharpoons BH_4^{\ominus} + BH_2^{\oplus}$

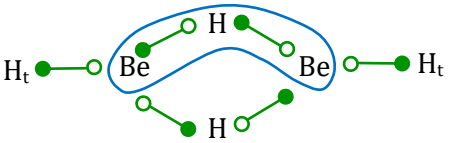
Hybridisation state = sp^3

Electron deficient molecule (act as Lewis acid)

- All four terminal hydrogen are present in same plane both bridging H are present in perpendicular plane.
- If substitution reaction takes place then only 4 terminal H will be substituted.

  $B_2H_6 + 4CH_3–Cl \rightarrow B_2H_2(CH_3)_4 + 4HCl$

(b) $(BeH_2)_2$ (dimer of BeH_2 in vapour state)

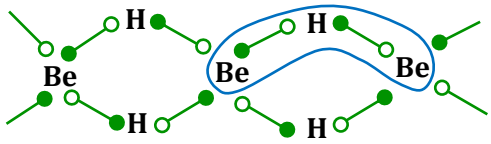


Hybridisation state = sp^2

Planar

electron deficient molecule

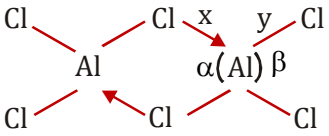
(c) $(BeH_2)_n$ (polymer of BeH_2 in solid state)



Hybridisation state = sp^3
Non-planar
electron deficient molecule

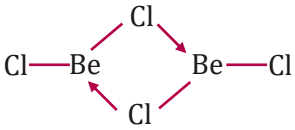
(B) By-coordinate Bond / 3C-4e bond:

(a) Al_2Cl_6 (dimer of $AlCl_3$ in liquid or solid state)



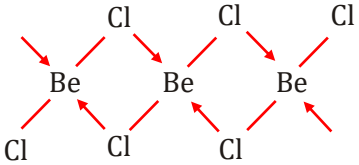
BA = $\alpha < \beta$
BL = $x > y$
Hybridisation state = sp^3
Non-planar
octet complete

(b) $(BeCl_2)_2$ (dimer of $BeCl_2$ in vapour state)



Hybridisation state = sp^2
Planar
electron deficient molecule

(c) $(BeCl_2)_n$ (polymer of $BeCl_2$ in solid state)



Hybridisation state = sp^3
Non-planar
octet complete

Note :

(i) BCl_3, BBr_3 and BI_3 do not form dimer due to smaller size of boron & large size of halogen (due to more steric repulsion)
(ii) BF_3 cannot form dimer due to its back bonding.
(iii) AlF_3 cannot form dimer due to its ionic nature.
(iv) RCOOH forms dimer due to H-bonding.

Boron Family:

Group 13 elements (B, Al, Ga, In, Tl, Nh):

Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron, and gallium, indium and thallium are almost exclusively metallic in character and and nihonium are almost exclusively metallic in character

Occurance:

Boron : Boron is a fairly rare element, mainly occurs as orthoboric acid, (H_3BO_3), Borax, ($Na_2B_4O_7 \cdot 10H_2O$), and Kernite, ($Na_2B_4O_7 \cdot 4H_2O$). There are two isotopic forms of boron ^{10}B (19%) and ^{11}B (81%).

Aluminium : Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%). Bauxite, ($Al_2O_3.2H_2O$) and cryolite, (Na_3AlF_6) are the important minerals of aluminium.

Electronic Configuration:

The outer electronic configuration of these elements is ns^2np^1. A close look at the electronic configuration suggests that while boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 d-electrons, and thallium has noble gas plus 14 f- electrons plus 10 d-electron cores. Thus, the electronic structures of these elements are more complex than for the first two groups of elements discussed in unit 10. This difference in electronic structures affects the other properties and consequently the chemistry of all the elements of this group.

Atomic Radii:

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen.

Atomic radii order	**Ionic Radii order (+3 OS)**
B < Ga < Al < In < Tℓ	B < Al < Ga < In < Tℓ

Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 d-electrons offer only poor screening effect for the outer electrons from the increased nuclear charge in Gallium. Consequently, the atomic radius of Gallium (135 pm) is less than that of Aluminium (143 pm).

Ionization Enthalpy:

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group.

Ionization Enthalpies order

B > Tℓ > Ga > Al > In

The decrease from B to Al is associated with increase in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of d- and f-electrons ,which have low screening effect, to compensate the increase in nuclear charge.

The order of ionisation enthalpies, as expected, is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$. The sum of the first three ionisation enthalpies for each of the elements is very high. Effect of this will be apparent during the study of their chemical properties.

Electronegativity:

Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements.

Physical Properties:

(i) Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point.

(ii) Rest of the members are soft metals with low melting point and high electrical conductivity.

(iii) It is worth while to note that gallium with unusually low melting point (303K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures.

(iv) Density of the elements increases down the group from boron to thallium.

Melting and Boiling points order

M.P. B > Al > Tl > In > Ga

B.P. B > Al > Ga > In > Tl

Electropositive Character:

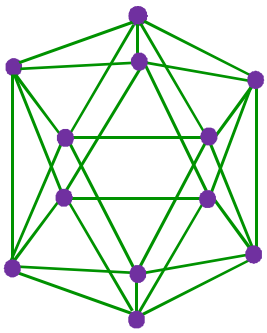
Due to high IE they are less electropositive on moving down the group metallic character increases due to decrease in IE [$\therefore$ B is nonmetals and other elements are metals.]

$$\underbrace{B}_{\text{Non metal}} < \underbrace{Al > Ga > In > Tl}_{\text{Metals}}$$

Note:

Boron exists in many allotropic forms. All the allotropes have basic building B_{12} icosahedral units made up of polyhedron having 20 faces and 12 corners. For example one of the simplest form is :

α - rhombohedral boron.



But Al , In & Tℓ all have close packed metal structure.

Table: Atomic and Physical Properties of Group 13 Elements

Property		Element				
		Boron B	**Aluminium Al**	**Gallium Ga**	**Indium In**	**Thallium Tl**
Atomic number		5	13	31	49	81
Atomic mass/(g mol^{-1})		10.81	26.72	69.72	114.82	204.38
Electronic configuration		$[He]2s^2 2p^1$	$[Ne]3s^2 3p^1$	$[Ar]3d^{10}4s^2 4p^1$	$[Kr]4d^{10}5s^2 5p^1$	$[Xe]4f^{14}5d^{10}6s^2 6p^1$
Atomic radius/pm[a]		(88)	143	135	167	170
Ionic radius M^{3+}/pm[b]		(27)	53.5	62.0	80.0	88.5
Ionic radius M^+/pm		–	–	120	140	150
Ionisation enthalpy (kJ mol^{-1})	$\Delta_i H_1$	801	577	579	558	589
	$\Delta_i H_2$	2427	1816	1979	1820	1971
	$\Delta_i H_3$	3659	2744	2962	2704	2877
Electronegativity[c]		2.0	1.5	1.6	1.7	1.8
Density /g cm^{-3} at 298 K		2.35	2.70	5.90	7.31	11.85
Melting point / K		2453	933	303	430	576
Boiling point / K		3923	2740	2676	2353	1730
$E^{\ominus}$/V for (M^{3+}/M)		–	–1.66	–0.56	–0.34	+1.26
$E^{\ominus}$/V for (M^+/M)		–	+0.55	–0.79(acid) –1.39(alkali)	–0.18	–0.34

[a]Metallic radius, [b]6-coordination, [c]Pauling scale,

Chemical Properties:

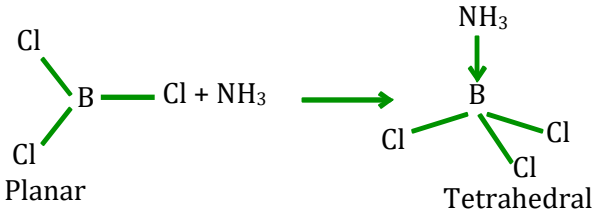
Oxidation state and trends in chemical reactivity:

(i) Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form $Al^{3\oplus}$ ions. In fact, aluminium is a highly electropositive metal.

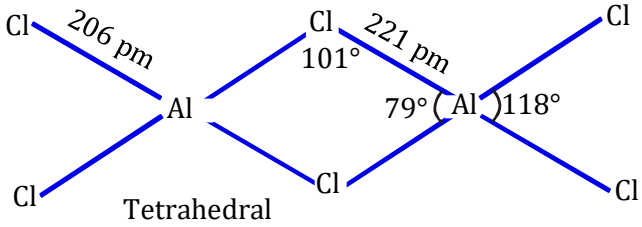
(ii) However, down the group, due to poor shielding effect of intervening d and f orbitals, the increased effective nuclear charge holds ns electrons tightly (responsible for inert pair effect) and thereby, restricting their participation in bonding. As a result of this, only p-orbital electrons may be involved in bonding. In fact in Ga, In and Tℓ, both +1 and +3 oxidation states are observed. The relative stability of +1 oxidation state progressively increases for heavier elements: Al < Ga < In < Tl. In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidising in character.

(iii) The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.

(iv) In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in BF_3) will be only six. Such **electron deficient** molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increase in the size down the group. BCl_3 easily accepts a lone pair of electrons from ammonia to form $BCl_3.NH_3$.



$AlCl_3$ achieves stability by forming a dimer



(v) In trivalent state most of the compounds being covalent are hydrolysed in water. For example, the trichlorides on hyrolysis in water form tetrahedral $[M(OH)_4]^{\ominus}$ species; the hybridisation state of element M is sp^3. Aluminium chloride in acidified aqueous solution forms octahedral $[Al(H_2O)_6]^{3\oplus}$ ion. In this complex ion, the 3d orbitals of Al are involved and the hybridisation state of Al is sp^3d^2

Reactivity towards air:

(i) Boron is unreactive in crystalline form.

(ii) Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack.

(iii) Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.

$2E(s) + 3O_2(g) \xrightarrow{\Delta} 2E_2O_3(s)$

$2E(s) + N_2(g) \xrightarrow{\Delta} 2EN(s)$

(E = element)

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and Gallium oxides are amphoteric and those of Indium and Thallium are basic in their properties.

Reaction with Air at Water:

Al should react air to form a very thin oxide film (10^{-4} to 10^{-6} mm thick) on the surface and protects the metal from further attack

$2\,Al(s) + \frac{3}{2}\,O_2(g) \rightarrow Al_2O_3(s)$ $\Delta H° = -1670$ kJ/mole (Thermal reaction)

Ga and In are attacked neither by cold water nor hot water unless oxygen is present. Tℓ form an oxide on surface

Reactivity towards acids and alkalies:

Boron does not react with acids and alkalies even at moderate temperature; but Aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.

Aluminium dissolves in dilute HCl and liberates dihydrogen.

$2Al(s) + 6HCl(aq) \rightarrow 2Al^{3\oplus}(aq) + 6Cl^{\ominus}(aq) + 3H_2(g)$

However, concentrated nitric acid renders Aluminium passive by forming a protective oxide layer on the surface. Aluminium also reacts with aqueous alkali and liberates dihydrogen.

$$2Al\ (s) + 2NaOH(aq) + 6H_2O(\ell) \rightarrow 2Na^{\oplus}\ [Al(OH)_4]^{\ominus}\ (aq) + 3H_2(g)$$

Sodium tetrahydroxoaluminate(III)

or

$$2NaAlO_2 + 2H_2O$$

Ga, In, Tℓ dissolve in dilute acids liberating H_2 Ga is amphoteric like Al and it dissolves in aq. NaOH liberating H_2 and forming gallates.

Reactivity towards halogens:

These elements react with halogens to form trihalides (except TlI_3).

$2E(s) + 3\ X_2\ (g) \rightarrow 2EX_3\ (s)$ (X = F, Cl, Br, I)

Important Trends And Anomalous Properties Of Boron:

Certain important trends can be observed in the chemical behaviour of group 13 elements. The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[M(OH)_4]^{\ominus}$ and octahedral $[M(H_2O)_6]^{3\oplus}$, except in boron, exist in aqueous medium. The monomeric trihalides, being electron deficient, are strong Lewis acids. Boron trifluoride easily reacts with Lewis bases such as NH_3 to complete octet around boron.

$$F_3B + :NH_3 \rightarrow (F_3B \leftarrow NH_3)$$

It is due to the absence of d orbitals that the maximum covalence of B is 4. Since the d orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4. Most of the other metal halides (e.g., $AlCl_3$) are dimerised through halogen bridging (e.g., Al_2Cl_6). The metal species completes its octet by accepting electrons from halogen in these halogen bridged molecules.

Borax $2B_4O_7.10H_2O$:

Properties :

(i) It is a white crystalline solid of formula $Na_2B_4O_7.10H_2O$. In fact it contains the tetranuclear units $[B_4O_5(OH)_4]^{2\ominus}$ and correct formula; therefore, is $Na_2[B_4O_5(OH)_4].8H_2O$.

(ii) Borax dissolves in water to give an alkaline solution.

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$$

Orthoboric acid

(iii) On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $Co(BO_2)_2$ bead is formed.

Orthoboric acid:

Preparation:

(i) It can be prepared by acidifying an aqueous solution of borax.

$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$

(ii) It is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.)

Property:

(i) Orthoboric acid, H_3BO_3 is a white crystalline solid, with soapy touch.

(ii) It is sparingly soluble in water but highly soluble in hot water.

(iii) H_3BO_3 is soluble in water and behaves as weak monobasic acid. It does not donate protons like most the acids, but rather it accepts $OH^{\ominus}$. It therefore is Lewis acid ($B(OH)_3$)

$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^{\oplus} + [B(OH)_4]^{\ominus}$

or

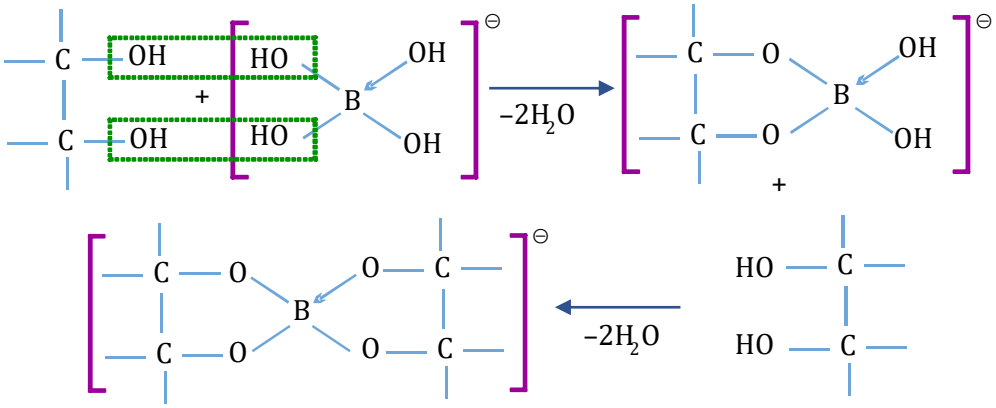
H_3BO_3

Since $B(OH)_3$ only partially reacts with water to form $H_3O^{\oplus}$ and $[B(OH)_4]^{\ominus}$ it behaves as a weak acid. Thus it cannot be titrated satisfactorily with NaOH as a sharp end point is not obtained. If certain polyhydroxy compounds such as glycerol, mannitol or sugar are added to the titration mixture then $B(OH)_3$ behaves as a strong monobasic acid. and hence can now be titrated with NaOH and end point is diluted using phenolphthalein as indicator.

$B(OH)_3 + NaOH \rightleftharpoons Na[B(OH)_4]$

$NaBO_2 + 2H_2O$

The added compound must be a cis diol to enhance the acidic properties in this way the cis-diol forms very stable complexes with $[B(OH)_4]^{\ominus}$ formed in forward direction above, thus effectively removing it from solution. Hence reaction proceeds in forward direction (Le-Chatelier principle.)



On heating, orthoboric acid above 370K forms metabolic acid, HBO_2 which on further heating yields boric oxide, B_2O_3.

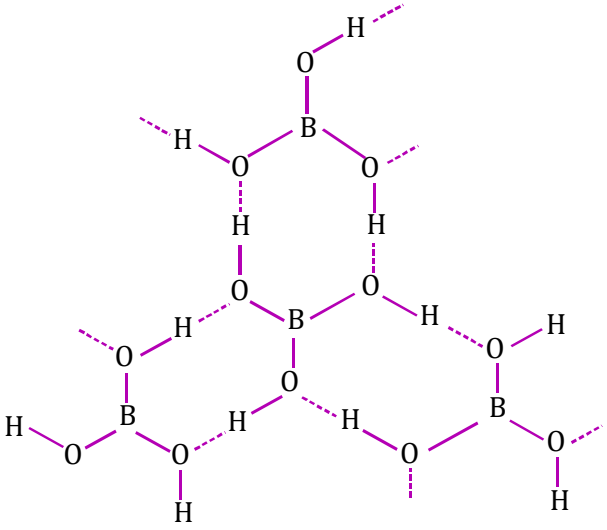
Heating of boric acid:

$H_3BO_3 \xrightarrow{100°C}$ $HBO_2 \xrightarrow{140°C}$ $H_2B_4O_7 \xrightarrow[\text{red hot}]{\Delta}$ B_2O_3

Metaboric acid tetraboric acid Glassy mass

Structure:

It has a layer structure in which planar BO_3 units are joined by hydrogen bonds as shown in figure.



Structure of boric acid; the dotted lines represent hydrogen bonds

Uses of boric acid:

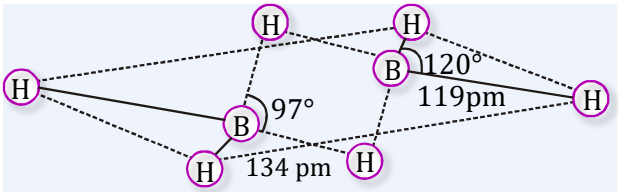
(i) Boric acid is used in manufacturing of optical glasses

(ii) With borax, it is used in the preparation of a buffer solution.

Structure of B_2H_6:

Structure & bonding in diborane:

The structure of diborane is shown in figure. The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. The four terminal B–H bonds are regular two centre-two electron bonds while the two bridge (B–H–B) bonds are different and can be described in terms of three centre–two electron bonds shown in figure.



The structure of diborance, B_2H_6

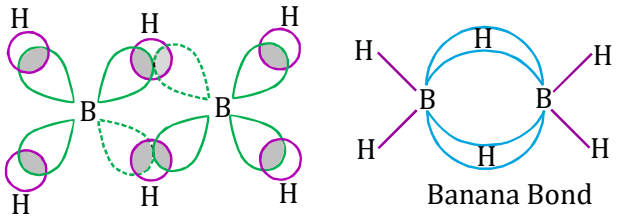


Figure: Bonding in diborane.

Each B atom uses sp^3 hybrid orbitals for bonding. Out of the four sp^3 hybrid orbital on each B atom, one is without an electron shown in broken lines. The terminal B–H bonds are normal 2-centre-2- electron bonds but the two bridge bonds are 3-centre-2-electron bonds. The 3-centre-2-electron bridge bonds are also referred to as banana bonds.

Diborane, B_2H_6:

The simplest boron hydride known, is diborane.

Preparation:

(i) It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.

$3LiAlH_4 + 4BF_3 \longrightarrow 3LiF + 3AlF_3 + 2B_2H_6$

or $LiBH_4$ or $3(BF_3)$

(ii) **Laboratory** method : For the preparation of diborane involves the oxidation of sodium borohydride with iodine.

$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$

(iii) **Industrial scale** : By the reaction of BF_3 with sodium hydride.

$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$

Other reaction of preparation of B_2H_6:

$Mg_3B_2 + HCl \longrightarrow B_2H_6 + B_4H_{10} + B_5H_9$ etc.
(10%)

$B_4H_{10} \xrightarrow[100°C]{\Delta} B_2H_6 + H_2 +$ higher borane

BCl_3 (or $B Br_3$) $+ 6H_2 \xrightarrow[\text{discharge at low pressure}]{\text{Electric}} B_2H_6 + 6HCl$

Properties:

(i) Diborane is a colourless, highly toxic gas with a b.p. of 180 K.

(ii) Diborane catches fire spontaneously upon exposure to air.

(iii) It burns in oxygen releasing an enormous amount of energy.

$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$; $\Delta_cH° = -1976$ kJ mol^{-1}

Most of the higher boranes are also spontaneously flammable in air.

(iv) Boranes are readily hydrolysed by water to give boric acid.

$B_2H_6(g) + 6H_2O(\ell)$ (Cold is enough) $\rightarrow 2B(OH)_3(aq) + 6H_2(g)$

$B_2H_6 + HCl$ (dry) $\xrightarrow[AlCl_3]{\text{anh.}} B_2H_5Cl + H_2$

(v) Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts, $BH_3.L$

$B_2H_6 + 2NMe_3 \rightarrow 2BH_3.NMe_3$

$B_2H_6 + 2CO \rightarrow 2BH_3.CO$

Reaction of ammonia with diborane gives initially $B_2H_6.2NH_3$ which is formulated as $[BH_2(NH_3)_2]^{\oplus}$ $[BH_4]^{\ominus}$; further heating gives borazine, $B_3N_3H_6$ known as "inorganic benzene" in view of its ring structure with alternate BH and NH groups.

$3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^{\oplus}[BH_4]^{\ominus} \xrightarrow{T > 200°C} 2B_3N_3H_6 + 12H_2$

$B_3N_3H_6 \xrightarrow{T > 200°C} (BN)_x$

(vi) Reaction with MeOH

$B_2H_6 + 6MeOH \longrightarrow 2B(OMe)_3 + 6H_2$

Some Important Compounds of Boron:

Some useful compounds of boron are borax, orthoboric acid and diborane. We will briefly study their chemistry.

Preparation of Borax:

Borax

$$2CaO \cdot 3B_2O_3 + 2Na_2CO_3 \longrightarrow 2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$$

↓ Filtered – $CaCO_3$ (as residue)

Colemanite

$NaBO_2$ in filtrate + $Na_2B_4O_7 \cdot 10H_2O$ as residue ← Concentrated and allowed to crystallise out and filtered ← $Na_2B_4O_7 + NaBO_2$ (in solution)

↓ CO_2 passed and crystallise out again

$[4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3]$

$Na_2B_4O_7 \cdot 10H_2O \downarrow$

* $H_3BO_3 + H_2O_2 \longrightarrow (H_2O) + (HO)_2B{-}O{-}O{-}H \xrightarrow{NaOH} Na_2 \cdot \left[(HO)_2{-}B\begin{matrix}O{-}O\\ O{-}O\end{matrix}B{-}(OH)_2\right] .6H_2O$

Sodium peroxy borate used in washing powder as brightner

Alums : M_2SO_4, $M'_2(SO_4)_3 \cdot 24\ H_2O$

Properties: Swelling characteristics

where M = $Na^{\oplus}$, $K^{\oplus}$, $Rb^{\oplus}$, $Cs^{\oplus}$, $Ag^{\oplus}$, $Tl^{\oplus}$, $NH_4^{\oplus}$ (except $Li^{\oplus}$)

M' = $Al^{3\oplus}$, $Cr^{3\oplus}$, $Fe^{3\oplus}$, $Mn^{3\oplus}$, $Co^{3\oplus}$

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Potash alum
$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	Ammonium alum
$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$	Chrome alum
$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$	Ferric alum

Preparation: $Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$

$Al_2(SO_4)_3 + K_2SO_4 + \text{aq. sol}^n \longrightarrow$ crystallise

Uses: (i) Act as coagulant

(ii) Purification of water

(iii) Tanning of leather

(iv) Mordant in dying

(v) Antiseptic

Carbon Family:

Group 14 elements (C,Si,Ge,Sn,Pb,Fl):

Carbon, silicon, germanium, tin, lead and flerovium are the members of group 14

Covalent Radius:

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completely filled d and f orbitals in heavier members.
Covalent radii : C < Si < Ge < Sn < Pb

Ionization Enthalpy:

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electrons is visible here also. In general the ionisation enthalpy decreases down the group. Small decrease in Δ_iH from Si to Ge, Ge to Sn and slight increase in Δ_iH from Sn to Pb is the consequence of poor shielding effect of intervening d and f orbitals and increase in size of the atom.
C > Si > Ge > Pb > Sn (IE_1 values)

Melting and Boiling Points:

M.P. : C > Si > Ge > Pb > Sn
B.P. : Si > Ge > Sn > Pb

Electronegativity:

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity values for elements from Si to Pb are almost the same.

Physical Properties:

All group 14 members are solids. Carbon and Silicon are non-metals, Germanium is a metalloid, whereas Tin and Lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

Table: Atomic and Physical Properties of Group 14 Elements

Property		Element				
		Carbon C	Silicon Si	Germanium Ge	Tin Sn	Lead Pb
Atomic number		6	14	32	50	82
Atomic mass/(g mol^{-1})		12.01	28.09	72.60	118.71	207.2
Electronic configuration		$[He]2s^2 2p^2$	$[Ne]3s^2 3p^2$	$[Ar]3d^{10}4s^2 4p^2$	$[Kr]4d^{10}5s^2 5p^2$	$[Xe]4f^{14}5d^{10}6s^2 6p^2$
Covalent radius/pm[a]		77	118	122	140	146
Ionic radius M^{4+}/pm[b]		–	40	53	69	78
Ionic radius M^{2+}/pm[b]		–	–	73	118	119
Ionisation enthalpy kJ mol^{-1}	Δ_iH_1	1086	786	761	708	715
	Δ_iH_2	2352	1577	1537	1411	1450
	Δ_iH_3	4620	3228	3300	2942	3081
	Δ_iH_4	6220	4354	4409	3929	4082
Electronegativity[c]		2.5	1.8	1.8	1.8	1.9
Density[d] /g cm^{-3}		3.51[e]	2.34	5.32	7.26[f]	11.34
Melting point / K		4373	1693	1218	505	600
Boiling point / K		–	3550	3123	2896	2024
Electrical resistivity/ohm cm (293 K)		$10^{14} - 10^{16}$	50	50	10^{-5}	2×10^{-5}

[a]for M^{IV} oxidation state; [b]6–coordination; [c] Pauling scale; [d]293 K; [e] for diamond; for graphite, density is 2.22; [f]β-form (stable at room temperature)

Chemical Properties:

Oxidation states and trends in chemical reactivity:

(i) The group 14 elements have four electrons in outermost shell.

(ii) The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states. Since the sum of the first four ionization enthalpies is very high, compounds in +4 oxidation state are generally covalent in nature.

(iii) In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb. It is due to the inability of ns^2 electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group.

(iv) Carbon and Silicon mostly show +4 oxidation state.

(v) Germanium forms stable compounds in +4 state and only few compounds in +2 state.

(vi) Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent).

(vii) Lead compounds in +2 state are stable and in +4 state are strong oxidising agents.

(viii) In tetravalent state the number of electrons around the central atom in a molecule (e.g., carbon in CCl_4) is eight. Being electron precise molecules, they are normally not expected to act as electron acceptor or electron donor species. Although carbon cannot exceed its covalence more than 4, other elements of the group can do so. It is because of the presence of d orbital in them. Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like, $SiF_6^{2\ominus}$, $[GeCl_6]^{2\ominus}$, $[Sn(OH)_6]^{2\ominus}$ exist where the hybridisation of the central atom is sp^3d^2.

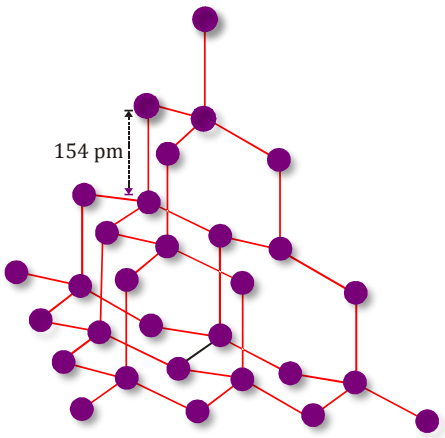
Allotropes of Carbon Family:

Diamond (kinetically most stable allotrope of carbon, meta stable phase of carbon):

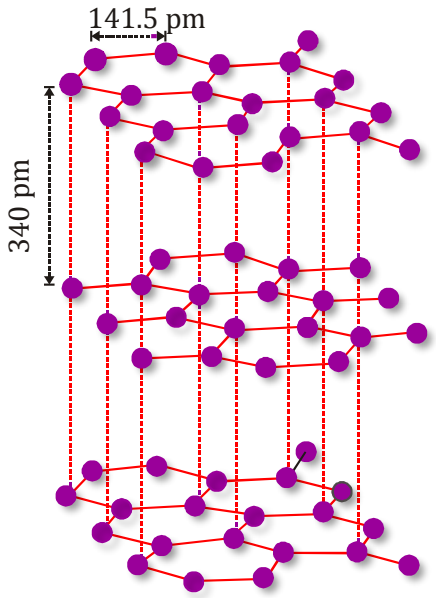
- It has a **crystalline lattice**. A rigid three dimensional network of carbon atoms.
- Each carbon atom undergoes **sp^3 hybridisation** and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion.
- **C–C bond length is 154 pm**.
- It is very difficult to break **extended covalent bonding** and, therefore, diamond is a **very hard** substance.

Uses :-

- Used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.
- Diamond is a precious stone and used in jewellery. It is measured in **carats** (1 carat = 200 mg).



The structure of diamond



The structure of graphite

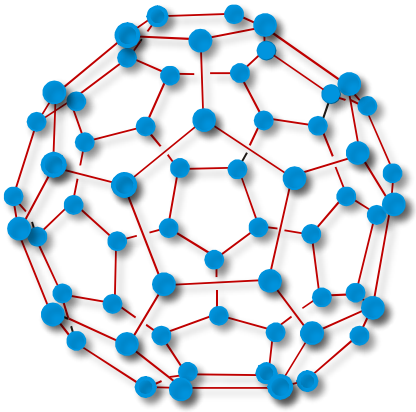
Graphite (Thermodynamically most stable allotrope of carbon):

- Layered structure. **Layers are held by van der Waals forces** and distance between two **layers is 340 pm.**
- Each layer is composed of **planar hexagonal rings of** carbon atoms. C—C bond length within the **layer is 141.5 pm.**
- Each carbon atom in hexagonal ring **undergoes sp^2 hybridisation** and makes three sigma bonds with three neighbouring carbon atoms. **Fourth electron forms a π bond**. The electrons are delocalised over the whole sheet. Thus, graphite is lusturous.
- Electrons are mobile and, therefore, graphite conducts electricity along the sheet.
- Graphite cleaves easily between the layers and, therefore, it is very soft and slippery.
- **Uses :-** Due to slippery nature graphite is used as **a dry lubricant** in machines running at high temperature, where oil cannot be used as a lubricant.
- **Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis.**

Fullerenes:

- Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as Helium or Argon.
- The sooty material formed by condensation of vapourised C_n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above.
- **Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules.**
- **Fullerene C_{60} :-** molecule has **a shape like soccer ball** and **called Buckminsterfullerene**. **It contains 20, six- membered rings and 12, five membered rings.**
- This ball shaped molecule has **60 vertices** and each one is occupied by one carbon atom and it also **contains both single and double bonds** with C–C distances of 143.5 pm and 138.3 pm respectively. **Spherical fullerenes are also called bucky balls in short.**
- A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings.

- All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms.
- The remaining electron at each carbon is delocalised in molecular orbitals, which in turn give aromatic character to molecule. However, because of non-planar nature of fullerenes, their aromatic character gets diminished and reactivity increases.



[The structure of C_{60}, Buckminsterfullerene : Note that molecule has the shape of a soccer ball (football)]

Important Points for Carbon:

- **Thermodynamic stability order :** Graphite > Diamond > Fullerene C_{60}
- **It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, ΔH_f of graphite is taken as zero. ΔH_f values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol^{-1}, respectively**.
- Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes.
  - ⇒ **Carbon black** is obtained by burning hydrocarbons in a limited supply of air.
  - ⇒ **Charcoal and coke** are obtained by heating wood or coal respectively at high temperatures in the absence of air.

Uses of Carbon:

- **Graphite fibres** embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes.
- **Crucibles** made from graphite are inert to dilute acids and alkalies.
- Being **highly porous, activated charcoal** is used in adsorbing poisonous gases; also used in water filters to remove organic contaminators and in airconditioning system to control odour.
- **Carbon black** is used as black pigment in black ink and as filler in automobile tyres.
- **Coke** is used as a fuel and largely as a reducing agent in metallurgy.

Carbon Monoxide:

Prepration:

(i) Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.

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

(ii) On small scale pure CO is prepared by dehydration of formic acid with concentrated H_2SO_4 at 373 K

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

(iii) On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H_2 thus produced is known as **water gas** or **synthesis gas**.

$C(s) + H_2O(g) \xrightarrow{473-1273K} CO(g) + H_2(g)$

When air is used instead of steam, a mixture of CO and N_2 is produced, which is called **producer gas**.

$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273K} 2CO(g) + 4N_2(g)$ Producer gas

Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

(iv) By heating potassium ferrocyanide with conc. H_2SO_4 : When potassium ferrocyanide in powdered state is heated with concentrated H_2SO_4, CO is evolved. Dilute H_2SO_4 should never be used because it shall evolve highly poisonous gas HCN.

$K_4[Fe(CN)_6] + 3H_2SO_4 \longrightarrow 2K_2SO_4 + FeSO_4 + 6HCN$

$6HCN + 12H_2O \longrightarrow \underset{\text{Formic acid}}{6HCOOH} + 6NH_3$

$6NH_3 + 3H_2SO_4 \longrightarrow 3(NH_4)_2SO_4$

$6HCOOH \xrightarrow{H_2SO_4} 6CO + 6H_2O$

$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 6CO + 3(NH_4)_2SO_4$

Properties:

(i) Carbon monoxide is a colourless, odourless and almost water insoluble gas.

(ii) It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals. This property of CO is used in the extraction of many metals from their oxides ores.

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

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

Detection:

(a) burns with blue flame

(b) CO is passed through $PdCl_2$ solution giving rise to black ppt.

$CO + PdCl_2 + H_2O \longrightarrow CO_2\uparrow + \underset{\text{Black metallic deposition}}{Pd\downarrow} + 2HCl$

Estimation:

$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$

$I_2 + S_2O_3^{2\ominus} \longrightarrow 2I^{\ominus} + S_2O_6^{2\ominus}$

Absorbers:

(a) Cu_2Cl_2 : $Cu_2Cl_2 + 2CO + 4H_2O \longrightarrow [CuCl(CO)(H_2O)_2]$

Bonding in CO molecule:

In CO molecule, there are one sigma and two π bonds between carbon and oxygen. Because of the presence of a lone pair on Carbon, CO molecule acts as a donor and reacts with certain metals when heated to form **metal carbonyls**.

Poisonous nature of CO:

The highly poisonous nature of CO arises because of its ability to form a **complex with haemoglobin**, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

Carbon Dioxide:

Prepration:

(i) It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.

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

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

(ii) **Laboratory** by the action of dilute HCl on calcium carbonate.

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

(iii) **Commercial scale** by heating limestone.

Properties:

(i) It is a colourless and odourless gas.

(ii) Its low solubility in water makes it of immense biochemical and geo-chemical importance.

(iii) With water, it forms carbonic acid, H_2CO_3 which is a weak dibasic acid and dissociates in two steps:

$H_2CO_3(aq) + H_2O(\ell) \rightleftharpoons HCO_3^{\ominus}(aq) + H_3O^{\oplus}(aq)$

$HCO_3^{\ominus}(aq) + H_2O(\ell) \rightleftharpoons CO_3^{2\ominus}(aq) + H_3O^{\oplus}(aq)$

H_2CO_3/ $HCO_3^{\ominus}$ buffer system helps to maintain pH of blood between 7.26 to 7.42. Being acidic in nature, it combines with alkalies to form metal carbonates.

Use of CO_2

Carbon dioxide, which is normally present to the extent of ~ 0.03 % by volume in the atmosphere, is removed from it by the process known as **photosynthesis**. It is the process by which green plants convert atmospheric CO_2 into carbohydrates such as glucose. The overall chemical change can be expressed as:

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

By this process plants make food for themselves as well as for animals and human beings.

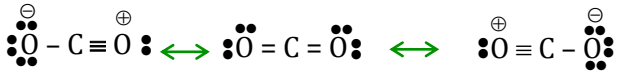
Harmful effect of CO_2:

Unlike CO, it is not poisonous. But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO_2 content of the atmosphere. This may lead to increase in **green house effect** and thus, raise the temperature of the atmosphere which might have serious consequences.

(i) Carbon dioxide can be obtained as a solid in the form of **dry ice** by allowing the liquified CO_2 to expand rapidly and dry ice is used as a refrigerant for ice-cream and frozen food.

(ii) Gaseous CO_2 is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher.

(iii) A substantial amount of CO_2 is used to manufacture urea. In CO_2 molecule carbon atom undergoes sp hybridisation. Two sp hybridised orbitals of carbon atom overlap with two p orbitals of oxygen atoms to make two sigma bonds while other two electrons of carbon atom are involved in p_π–p_π bonding with oxygen atom. This results in its linear shape [with both C–O bonds of equal length (115 pm)] with no dipole moment. The resonance structures are shown below:



Resonating structures of carbon dioxide

Note:

Carbongene has 95% O_2 and 5% CO_2 and is used as an antidote for poisoning of CO.

Silicon (Si):

Occurrence:

Silicon is the second most abundant (27.2%) element after oxygen (45.5%) in the earth's crust. It does not occur free in nature but in the combined state, it occurs widely in form of silica and silicates. All mineral rocks, clays and soils are built of silicates of magnesium, aluminium, potassium or iron. Aluminium silicate is however the most common constituent of rocks and clays.

Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

(i) Feldspar – $K_2O.\ Al_2O_3.\ 6SiO_2$

(ii) Kaolinite – $Al_2O_3.\ 2SiO_2.\ 2H_2O$

(iii) Asbestos – $CaO.\ 3MgO.\ 4SiO_2$

Preparation:

(i) From silica (sand): Elemental silicon is obtained by the reduction of silica (SiO_2) with high purity coke in an electric furnace.

$$SiO_2(s) + 2C(s) \xrightarrow{\text{high temp.}} Si(s) + 2CO(g)$$

(ii) From silicon tetrachloride ($SiCl_4$) or silicon chloroform ($SiHCl_3$) : Silicon of very high purity required for making semiconductors is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen followed by purification by zone refining.

$$SiCl_4(l) + 2H_2(g) \longrightarrow Si(s) + 4HCl(g)$$

$$SiHCl_3(s) + H_2(g) \longrightarrow Si(s) + 3HCl\ (g)$$

Physical Properties:

(i) Elemental silicon is very hard having diamond like structure.

(ii) It has shining luster with a melting point of 1793 K and boiling point of about 3550 K.

(iii) Silicon exists in three isotopes, i.e., $^{28}_{14}Si$, $^{29}_{14}Si$ and $^{30}_{14}Si$, but $^{28}_{14}Si$ is the most common isotope.

Chemical Properties:

Silicon is particularly unreactive at room temperature towards most of the elements except fluorine. Some important chemical reactions of silicon are discussed below.

(i) Action of air : Silicon reacts with oxygen of air at 1173 K to form silicon dioxide and with nitrogen of air at 1673 K to form silicon nitride,.

$Si(s) + O_2(g) \xrightarrow{1173K} SiO_2(s)$

Silicon dioxide

$3Si(s) + 2N_2(g) \xrightarrow{1673K} Si_3N_4(s)$

Silicon nitride

(ii) Action of steam : It is slowly attacked by steam when heated to redness liberating dihydrogen gas.

$Si(s) + 2H_2O(g) \xrightarrow{\text{redness}} SiO_2(s) + 2H_2(g)$

(iii) Reaction with halogens: It burns spontaneously in fluorine gas at room temperature to form silicon tetrafluoride (SiF_4).

$Si(s) + 2F_2(g) \xrightarrow{\text{Room temp.}} SiF_4(l)$

However, with other halogens, it combines at high temperatures forming tetrahalides.

(iv) Reaction with carbon : Silicon combines with carbon at 2500°C forming silicon carbide (SiC) known as carborundum.

$Si(s) + C(s) \xrightarrow{2500°C} SiC(s)$

Carborundum is an extremely hard substance next only to diamond. It is mainly used as an abrasive and as a refractory material.

Uses :

(i) Silicon is added to steel as such or more usually in form of ferrosilicon (an alloy of Fe and Si) to make it acid-resistant.

(ii) High purity silicon is used as semiconductors in electronic devices such as transistors.

(iii) It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

Compounds of Silicon:

Silane:

$Si_nH_{2n+2} \longrightarrow SiH_4 \;\&\; Si_2H_6$

Only these two are found

Higher molecules are not formed. Because Si can't show catenation property

Hot Mg + Si–vap $\longrightarrow Mg_2Si \xrightarrow{\text{dil. } H_2SO_4} MgSO_4 + SiH_4 + Si_2H_6 + ...$

Silicones:

It is an organosilicon polymer

Types of silicones:

(i) Linear silicones

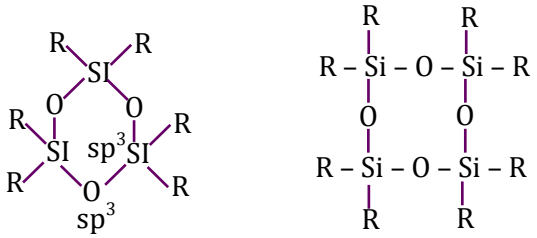
$$R_2SiCl_2 + H_2O \xrightarrow[-2HCl]{} R_2Si(OH)_2 \xrightarrow[H_2O]{\Delta} \underset{\text{Linear silicone}}{-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-}$$

$$R\text{-}Cl \xrightarrow[\text{Silicon}]{\text{Cu powder}} R_2SiCl_2 \xrightarrow{H_2O} R_2Si(OH)_2 \xrightarrow{\text{Condensation}} \text{Linear silicone}$$

$$R_2CCl_2 + H_2O \xrightarrow[\substack{-2HCl \\ \text{looses } H_2O \text{ redily}}]{} R_2C(OH)_2 \xrightarrow{-H_2O} R-\overset{O}{\overset{\|}{C}}-R$$

(ii) Cyclic silicones

Silicones may have the cyclic structure also having 3, 4, 5 and 6 nos. of silicon atoms within the ring. Alcohol analogue of silicon is known as silanol

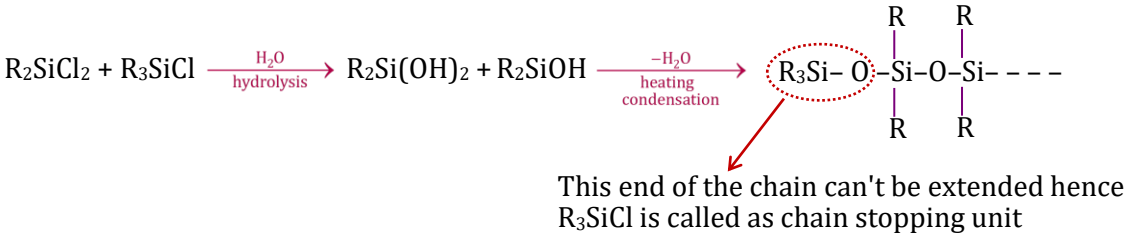


cyclic silicone not planar

(iii) Dimer silicones

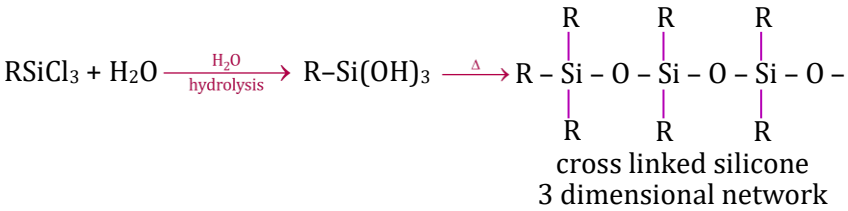
$$R_3SiCl \xrightarrow{H_2O} \underset{\text{Silanol}}{R_3SIOH} \xrightarrow[\Delta]{-H_2O} R_3SI-O-SiR_3$$

Note:



* Using R_3SiCl in a certain proportion we can control the chain length of the polymer

(iv) Crossed linked silicones



It provides the crosslinking among the chain making the polymer more hard and hence controling the proportion of $RSiCl_3$ we can control the hardness of polymer.

Uses

(1) It can be used as electrical insulator (due to inertness of Si–O–Si bonds)

(2) It is used as water repellant ($\because$ surface is covered) eg. car polish, shoe polish, masonary works in buildings

(3) It is used as antifoaming agent in sewage disposal, beer making and in cooking oil used to prepare potato chips.

(4) As a lubricant in the gear boxes and light weight machinery

Silica (SiO_2):

Occurrence:

Silica or silicon dioxide occurs in nature in the free state as sand, quartz and flint and in the combined state as silicates like, Feldspar : $K_2O.Al_2O_3.6SiO_2$, Kaolinite : $Al_2O_3.2SiO_2.2H_2O$ etc.

Properties :

(i) Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.

(ii) Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.

$$SiO_2(s) + 4HF(l) \longrightarrow SiF_4(l) + 2H_2O(l)$$

(iii) It also combines with metallic oxides at high temperature giving silicates e.g.

$$SiO_2(s) + CaO(s) \xrightarrow{\Delta} CaSiO_3(s)$$

(iv) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.

$$SiO_2(s) + Na_2CO_3(s) \xrightarrow{\text{high temp.}} Na_2SiO_3(s) + CO_2(g)$$

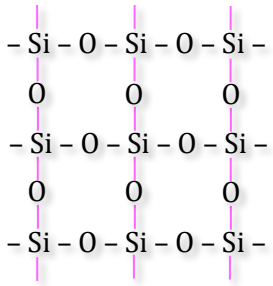
$$SiO_2(s) + Na_2SO_4(s) \xrightarrow{\text{high temp.}} Na_2SiO_3(s) + SO_3(g)$$

$$3SiO_2(s) + Ca_3(PO_4)_2(s) \xrightarrow{\text{high temp.}} 3CaSiO_3(s) + P_2O_5(g)$$

The first two examples quoted here are important in glass making.

Structures of Silica:

Silica has a three-dimensional network structure. In silica, silicon is sp^3-hybridized and is thus linked to four oxygen atoms and each oxygen atom is linked to two silicon atoms forming a three-dimensional giant molecule as shown in figure. This three-dimensional network structure imparts stability to SiO_2 crystal and hence a large amount of energy is required to break the crystal resulting in high melting point.



Uses:

(i) Sand is used in large quantities to make mortar and cement.

(ii) Being transparent to ultraviolet light, large crystal of quartz are used for making lenses for optical instruments and for controlling the frequency of radio-transmitters.

(iii) Powdered quartz is used for making silica bricks.

(iv) Silica gel ($SiO_2.xH_2O$) is used as a desiccant (for absorbing moisture) and as an adsorbent in chromatography.

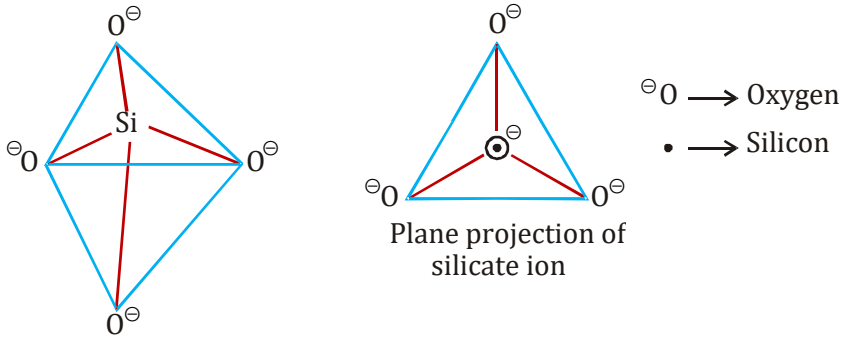
Quartz

Quartz is extensively used as a piezoelectric material; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts. Kieselghur, an amorphous form of silica is used in filtration plants.

Silicates:

Silicates are metal derivatives of silicic acid, H_4SiO_4 or $Si(OH)_4$. Silicates are formed by heating metal oxide or metal carbonates with sand, e.g.,

$Na_2CO_3 \xrightarrow[SiO_2]{\text{Fused with sand}} Na_4SiO_4, Na_2(SiO_3)_n$, etc.



Silicates have basic unit of $SiO_4^{4\ominus}$, each silicon atom is bonded with four oxide ions tetrahedrally.

There are following types of silicates

Silicates	Sharing of O-atom / Basic Tetrahedral unit	Contribution of O-atom/Basic Tetrahedral unit	General formula
Ortho	0	4	$SiO_4^{4\ominus}$
Pyro	1	3.5	$Si_2O_7^{6\ominus}$
Cyclic	2	3	$(SiO_3)_n^{2n\ominus}$
Simple chain (pyroxene)	2	3	$(SiO_3)_n^{2n\ominus}$
Double chain (Amphibole)	(3, 2) av = 2.5	$\frac{11}{4}=\left(\frac{5.5}{2}\right)$	$(Si_4O_{11})_n^{6n\ominus}$
2D or (Sheet)	3	2.5	$(Si_2O_5)_n^{2n\ominus}$
3D	4	2	$(SiO_2)_n$

- Silicates are metal derivatives of silicic acid, H_4SiO_4 or $Si(OH)_4$,
- Silicates are formed by heating metal oxide or metal carbonates with sand.

  $Na_2CO_2 \xrightarrow[SiO_2]{\text{Fused with sand}} Na_4SiO_4, Na_2(SiO_3)_n$, etc.
- Silicates are the product (s) of hetro catenation of Si – O bond.
- A large number of silicates minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos.
- Two important man – made silicates are glass and cement.

Illustration 2:

Why Si – O bond shows tendency of hetro catenation.

Consider the following π bond formation 3p – 2p overlaps.

Si – O P – O S – O Cl – O

Solution:

Si – O < P – O < S – O < Cl –O (p bond formation tendency)

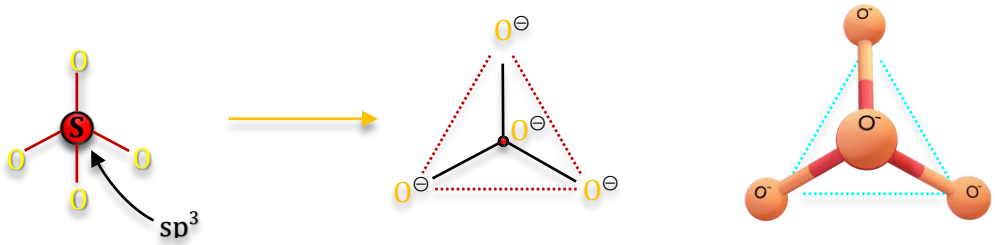
Si – O > P – O > S – O > Cl – O (Polymerisation/ Hetro–catenation tendency)

Si – O show tendency of hetro – catenation because π – bond is relatively ineffective / weak.

Basic unit:

- Basic structural unit is $SiO_4^{4\ominus}$ (Silicate, i.e. derived from silicic acid).

  $H_4SiO_4 \longrightarrow SiO_4^{4\ominus}$



- In all silicates, oxidation state of 'Si' is +4 and 'O' is –2
- All silicates are sp^3 hybridised and non-planar

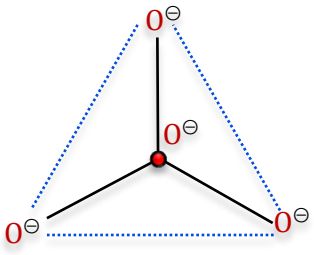
Type of Silicates:

1. Ortho Silicate (Neso Silicate)
2. Pyro Silicate (Sore Silicate or Di-Silicate)
3. Cyclic Silicate (Ring Silicate)
4. Single chain Silicate (Pyroxene Silicate)
5. Double chain Silicate (Amphibole Silicate)
6. 2-D Sheet Silicate (Sheet Silicate or Phylo Silicate)
7. 3-D Silicate (Tacto Silicate)

Type of Silicates:

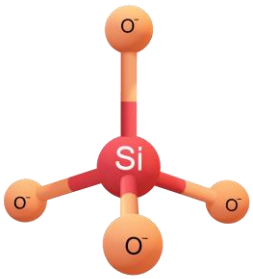
1. Ortho Silicate:

- Only single unit.
- Number of oxygen atom(s) shared per basic tetrahedral unit = 0
- Contribution of oxygen atom(s) per basic tetrahedral unit = 4
- General Formula : $SiO_4^{4\ominus}$



Example

Zircon ($ZrSiO_4$)



2. Pyro Silicate:

- Two basic unit.
- Number of oxygen atom(s) shared per basic tetrahedral unit = 1
- Contribution of oxygen atom(s) per basic tetrahedral unit = 3.5
- General Formula : $Si_2O_7^{6\ominus}$

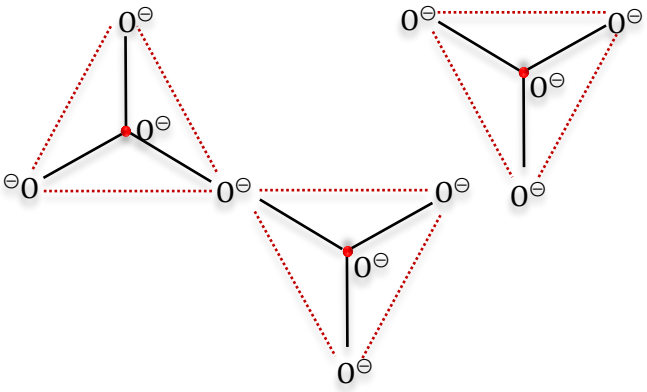


Illustration 3:

Hemimorphite $Zn_3Si_2O_7 \cdot Zn(OH)_2 \cdot 2H_2O$

Find out the value of :

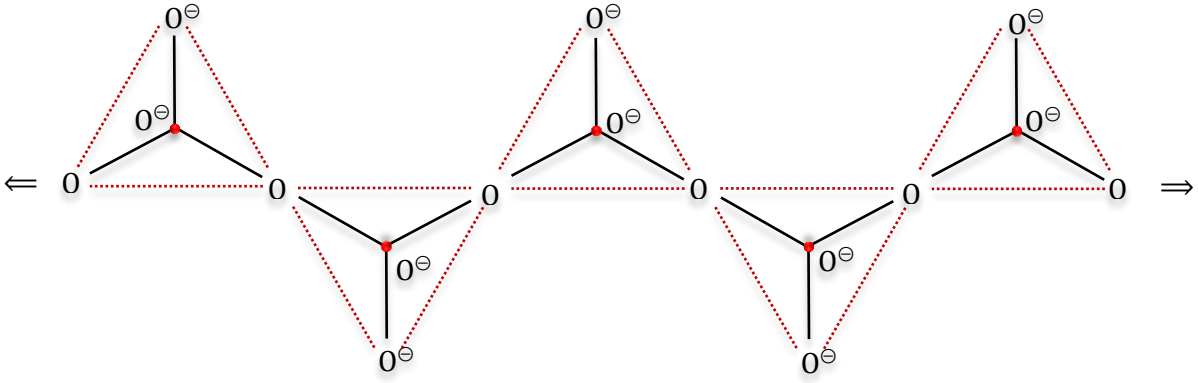
$MgxSi_2O_7$

Solution:

$2x + 4 \times 2 - 7 \times 2 = 0$

$x = 3$

3. Single chain Silicate (Pyroxene Silicate)



- n number of unit.
- Number of oxygen atom(s) shared per basic tetrahedral unit = 2
- Contribution of oxygen atom(s) per basic tetrahedral unit = 3
- General Formula : $(SiO_3^{2\ominus})_n$

  Example : Kinoite $Ca_2Cu_2Si_3O_{10}$

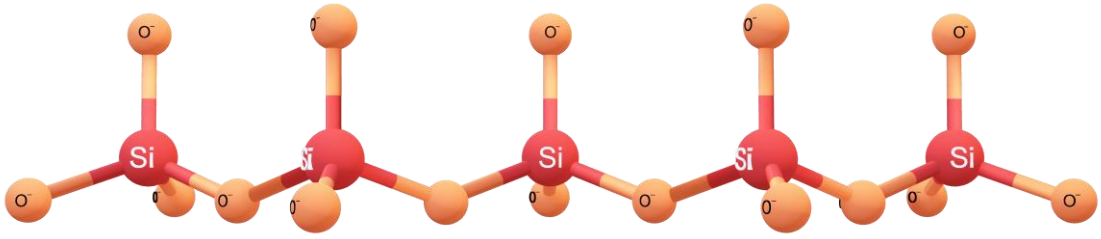
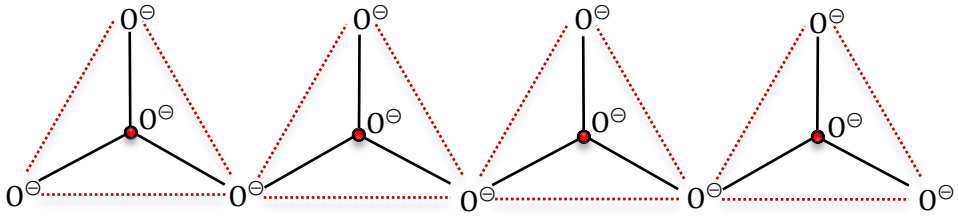


Illustration 4:

Find the molecule formula of 4 membered pyroxene silicate

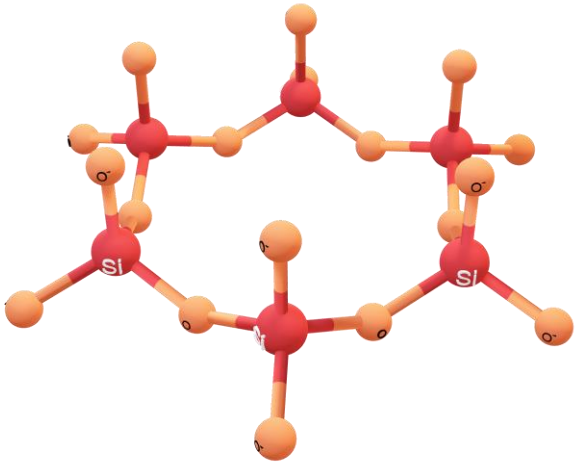
Solution:

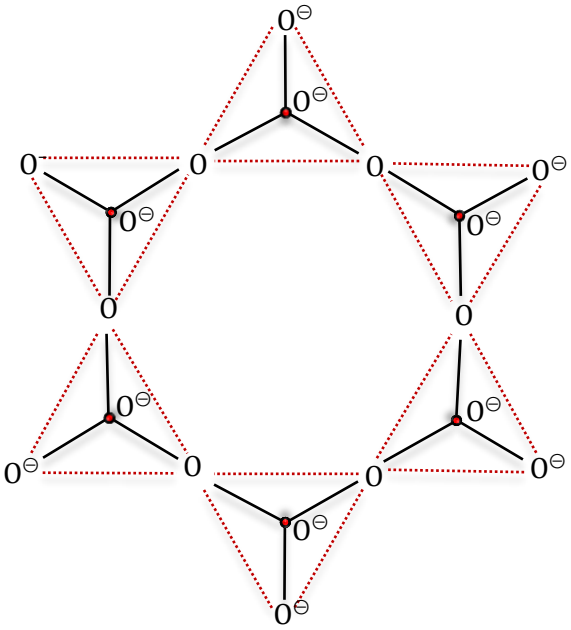


$= (SiO_3^{2\ominus})4 + 02^{\ominus}$

$= Si4O_{13}^{10\ominus}$

4. Cyclic Silicate:

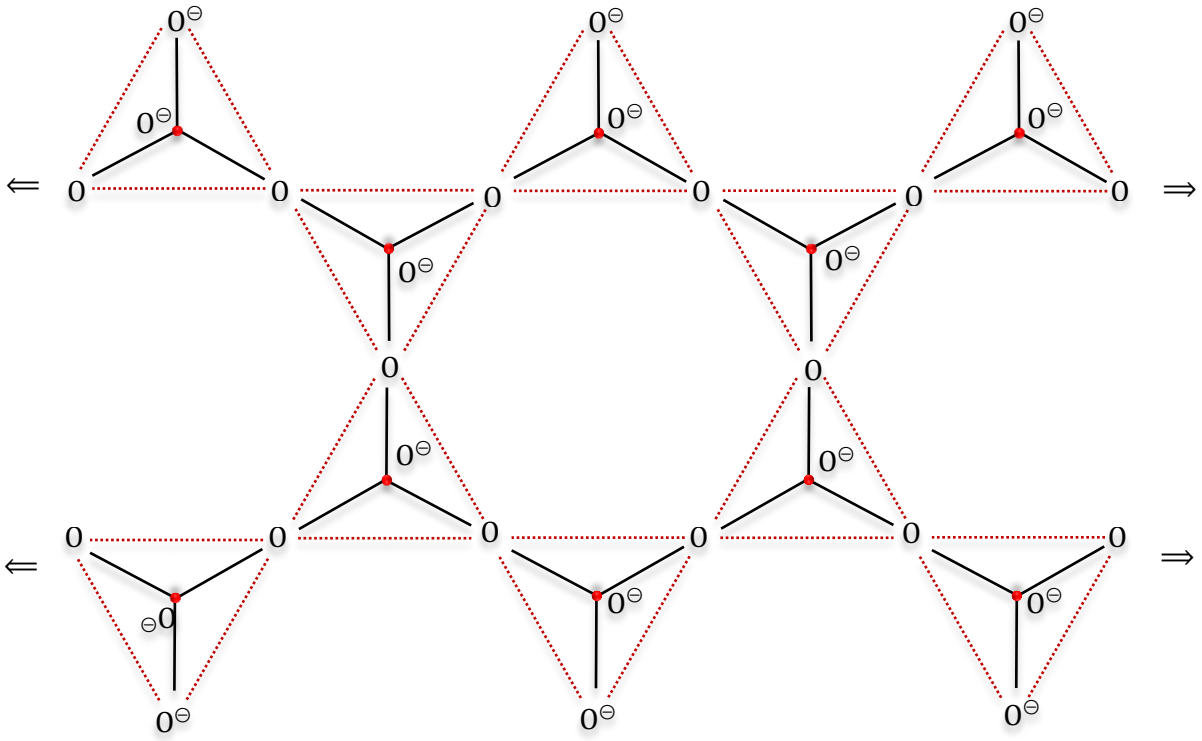




- n number of unit.
- Two oxygen is shared for centre unit.
- General Formula : $(SiO_3^{2\ominus})_n$

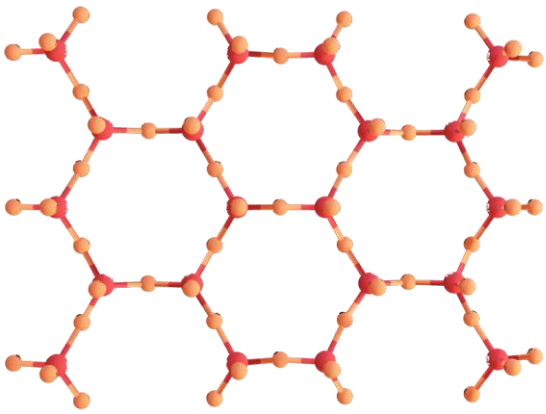
  Example : Beryl $Be_3Al_2Si_6O_{18}$

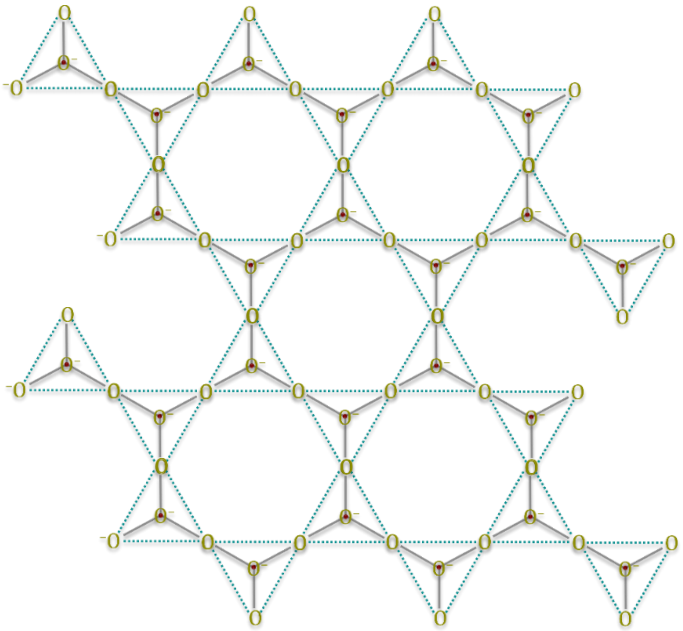
5. Double chain Silicat (Amphibole Silicate):



- n number of unit.
- shared oxygen is 2 & 3 and average is 2.5
- General Formula : $(Si_4O_{11})_n^{6n\ominus}$
  Example : Tremolite $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$

6. Sheet Silicate:

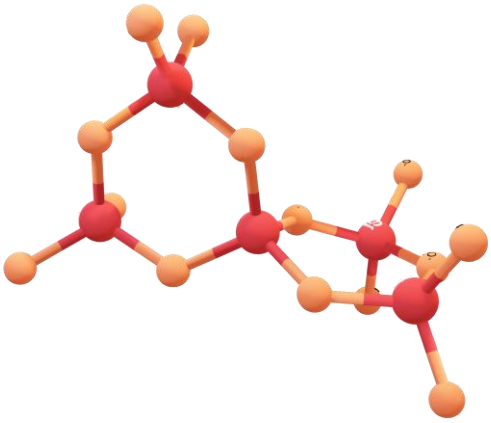


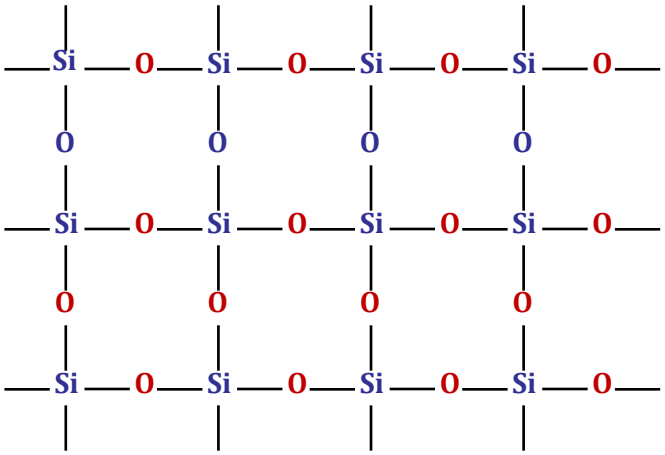


- n number of unit.
- Three oxygen is shared for centre unit.
- General Formula : $(Si_2O_5^{2\ominus})_n$

Example : Talc $(Mg_3(OH)_2(Si_2O_5)_2)$

7. 3-D Silicate:





- n number of unit.
- Number of oxygen atom(s) shared per basic tetrahedral unit = 4
- Contribution of oxygen atom(s) per basic tetrahedral unit = 2
- General Formula : $(SiO_2)_n$
- Example : Silica $(SiO_2)_n$

Illustration 5:

Name the type of the structure of silicate in which one oxygen atom of $[SiO_4]^{4\ominus}$ is shared ?

A. Linear chain silicate
B. Sheet silicate
C. Pyro silicate
D. Three dimensional

Solution:

(C)

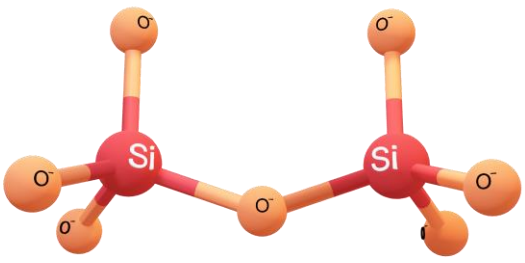


Illustration 6:

Which one of the following anions is present in the chain structure of silicates :

A. $SiO_4^{4\ominus}$

B. $Si_2O_7^{6\ominus}$

C. $(Si_2O_5^{2\ominus})_n$

D. $(SiO_3^{2\ominus})_n$

Ans.(D)

Solution:

Sodium Zeolite [$Na_2Al_2Si_2O_8.xH_2O$] :

Uses :

a) To make hard water soft

b) For cracking of hydrocarbons

ZSM-5:

Use : To convert Ethyl Alcohol into petrol.

- Glass and cement are man made silicates.

Zeolites If aluminium atoms replace few silicon atoms in three-dimensional network of silicon dioxide, overall structure known as aluminosilicate, acquires a negative charge. Cations such as Na+ , K+ or Ca2+ balance the negative charge. Examples are feldspar and zeolites. Zeolites are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation, e.g., ZSM-5 (A type of zeolite) used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of "hard" water.

Hydride:

CH_4 SiH_4 GeH_4 SnH_4 PbH_4 →

Bond strength : Decreases ↓

Thermal stability : Decreases ↓

Reducing strength : Increases ↑

Acidic strength : Increases ↑

Glass:

- Transparent, Supercooled Liquid or amorphous Solid.
- It has no sharp melting point.
- Glass has no definite chemical Formula but can be represented by formula.
  $xM_2O.\ yM'O.\ 6SiO_2$
  M : Monovalent Metals
  M': Bivalent Metal

Some Important Compounds of Carbon and Silicon:

Types of Carbide:

(i) Ionic and salt like:

Classification on basis of no. of carbon atoms present in hydrocarbon found on their hydrolysis
- (a) C_1 unit
- (b) C_2 unit
- (c) C_3 unit

C_1 unit: Al_4C_3, Be_2C

$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$

$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

C_2 unit: CaC_2, BaC_2

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + CH \equiv CH$

C_3 unit: Mg_2C_3

$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3{-}C \equiv CH$: Propyne

(ii) Covalent carbide : SiC & B_4C

(iii) Interstitial carbide :

(Transition element or inner transitional elements forms this kind of carbide)

Interstitial carbide formation doesn't affect the metallic lusture and electrical conductivity. ($\because$ no chemical bond is present, no change in property)

SiC (Carborundum):

Preparation

$SiO_2 + 2C(coke) \xrightarrow{2000\text{ to }2500^\circ C} Si + 2CO\uparrow$

$Si + C \xrightarrow{2000\text{ to }2500^\circ C} SiC$

Note:

(i) SiC has diamond like or wurtzite structure

(ii) SiC is often dark purple, black or dark green due to traces of Fe and other impurities but pure sample are pale yellow to colourless.

Properties

(i) It is very hard and is used in cutting tools and abrasive powder (polishing material)

(ii) It is very much inert

(iii) It is not being affected by any acid except H_3PO_4

Tin & its compound:

(i) $Sn \xrightarrow[+O_2]{1500^\circ C} SnO_2$ [Burns with a bright flame]

$Sn \xrightarrow{Cl_2,\ \Delta} SnCl_4$

$Sn \xrightarrow{S,\ \Delta} SnS_2$

(ii) $Sn + 2H_2O$ → (room temp.) No reaction; (At high. temp.) $SnO_2 + 2H_2$

(iii) Reaction with acid.

{Due to nonoxidizing nature}

Sn →
- dil. HCl → Reaction is very slow
- hot conc. HCl → $Sn + 2HCl \longrightarrow SnCl_2 + H_2\uparrow$
- dil. H_2SO_4 → Dissolve Sn Slowly forming $SnSO_4 + H_2\uparrow$
- hot conc. H_2SO_4 → $Sn + 4H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2SO_2 + 4H_2O$
- cold dil. HNO_3 → $4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$
- hot conc. HNO_3 → $5Sn + 20HNO_3 \longrightarrow \underset{\text{Metastannic Acid}}{H_2Sn_5O_{11}.4H_2O} + 20NO_2 + 5H_2O$

(iv) $Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2\uparrow$.

or

KOH [In absence of air K_2SnO_2 forms and in contact with air it readily converts into K_2SnO_3]

Oxides: SnO_2(White) $\xleftarrow[\text{heated}]{1500°C\ \text{strongly}}$ $Sn + O_2$; $+\frac{1}{2}O_2$; Δ

SnO (grey) $SnC_2O_4 \xrightarrow[\text{out of contact of air}]{\Delta} SnO\ (grey) + CO + CO_2$; $H_2Sn_5O_{11}.4H_2O$

& SnO_2 (white) Δ (in absence of air)

$SnCl_2 \xrightarrow{KOH} Sn(OH)_2$

Both are amphoteric in nature :

$SnO + H_2SO_4 \longrightarrow SnSO_4 + H_2O$

$SnO + 2HCl \longrightarrow SnCl_2 + H_2O$

$SnO + 2NaOH \text{ or } KOH \xrightarrow{\text{cold}} Na_2SnO_2 \text{ or } K_2SnO_2 + H_2O$

But conc. hot alkali behaves differently.

$2SnO + 2KOH \text{ or } NaOH \longrightarrow K_2SnO_3 \text{ or } Na_2SnO_3 + Sn + H_2O$

* $Bi(OH)_3 + \underset{\text{(black)}}{[Sn(OH)_4]^{2\ominus}} \longrightarrow Bi\downarrow + [Sn(OH)_6]^{2\ominus}$

$SnO_2 + 2H_2SO_4 \xrightarrow{\Delta} Sn(SO_4)_2 + 2H_2O$

(**Soluble only** in hot conc. H_2SO_4)

$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$

$SnCl_2$ & $SnCl_4$:

(1) $Sn + 2HCl\ (\text{hot conc.}) \longrightarrow SnCl_2 + H_2\uparrow$

$SnCl_2.2H_2O \xrightarrow{\Delta} Sn(OH)Cl + HCl\uparrow + H_2O\uparrow \Rightarrow$ Hence anh. $SnCl_2$ cannot be obtained.

$\downarrow$

$SnO + HCl\uparrow$

$\{SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCl\uparrow$ fumes comes out$\}$

(2) A piece of Sn is always added to preserve a solution of $SnCl_2$.

$6SnCl_2 + 2H_2O + O_2 \longrightarrow 2SnCl_4 + 4Sn(OH)Cl\downarrow$ (white ppt)

$SnCl_4 + Sn \longrightarrow 2SnCl_2$

$SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4\downarrow$ (white ppt.) + 4HCl

(3) $SnCl_2 + HCl \longrightarrow HSnCl_3 \xrightarrow{HCl} H_2SnCl_4$

$SnCl_4 + 2HCl \longrightarrow H_2SnCl_6$ (Hexachloro stannic (IV) acid)

$SnCl_4 + 2NH_4Cl \longrightarrow (NH_4)_2SnCl_6$ (colourless crystalline compound known as "pink's salt")

(4) Reducing Properties of $SnCl_2$:

$Sn^{2\oplus} + 2Fe^{3\oplus} \longrightarrow 2Fe^{2\oplus} + Sn^{4\oplus}$

$2Cu^{2\oplus} + Sn^{2\oplus} \longrightarrow 2Cu^{\oplus} + Sn^{4\oplus}$

$Hg^{2\oplus} + Sn^{2\oplus} \longrightarrow Hg\downarrow + Sn^{4\oplus}$

$PhNO_2 + SnCl_2 / HCl \longrightarrow PhNH_2 + Sn^{4\oplus}$

$K_2Cr_2O_7 + SnCl_2 + HCl \longrightarrow Cr^{3\oplus} + Sn^{4\oplus} + KCl + H_2O$

(5) Readily combines with $I_2 \Rightarrow SnCl_2I_2 \Rightarrow$ This reaction is used to estimate tin.

Formation of $SnCl_4$:

(i) Sn (molten) + Cl_2 (Excess) (dry) $\longrightarrow SnCl_4$

(ii) $2HgCl_2 + SnCl_2 \longrightarrow 2Hg\downarrow + SnCl_4$

(iii) Sn + Aq. regia $\longrightarrow SnCl_4 + NO + H_2O$

* $SnCl_4.5H_2O$ is known as butter of tin $\Rightarrow$ used as mordant.

$(NH_4)_2SnCl_6$ is known as 'pink's salt' $\Rightarrow$ used in calico printing.

Mosaic gold : SnS_2 yellow crystalline substance :

$Sn + 4NH_4Cl \longrightarrow (NH_4)_2SnCl_4 + 2NH_3 + H_2$

$2(NH_4)_2SnCl_4 + 2S \longrightarrow SnS_2 + 2NH_4Cl + (NH_4)_2SnCl_6$

Note :

Mosaic gold used for filling purpose (in joining gold pieces)

* **Distinction of $Sn^{2\oplus}$ / $Sn^{4\oplus}$:**

(i) H_2S (ii) $Hg^{2\oplus}$ (iii) $Fe^{3\oplus} + K_3[Fe(CN)_6] \xrightarrow{Sn^{2\oplus}}$ Blue ppt.

Compounds of lead:

Oxides of lead:

(i) PbO (ii) Pb_3O_4 (Red)

(iii) Pb_2O_3(reddish yellow) (Sesquioxide) (iv) PbO_2 (dark brown)

(1) PbO → Yellow (Massicot) $\xrightarrow[\text{and powdered}]{\text{fused, cooled}}$ Litharge

→ Reddish yellow (litharge)

Laboratory Prep^{n}. :

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

$PbO_2 \xrightarrow{\text{above } 600^\circ C}$

$Pb_3O_4 \longrightarrow$

$Pb_2O_3 \longrightarrow$

PbO, hotoxide easily reducedto Pb by H_2 or C.

$\xrightarrow{H_2} Pb + H_2O$

$\xrightarrow{C} Pb + CO$

Preparation of Pb_2O_3 :

$2PbO + NaOCl \longrightarrow Pb_2O_3 + NaCl$

$Pb_2O_3 + 2HNO_3 \longrightarrow PbO_2\downarrow + Pb(NO_3)_2 + H_2O$

This reaction suggests that Pb_2O_3 contains PbO_2.

(2) Pb_3O_4: $6PbO + O_2 \underset{500^\circ C}{\overset{350^\circ C}{\rightleftharpoons}} 2Pb_3O_4$ {In the same way, prove that its formula is $2PbO.PbO_2$}

$Pb_3O_4 + 4HNO_3$ (cold conc.) or (hot dil.) $\longrightarrow 2Pb(NO_3)_2 + PbO_2\downarrow + 2H_2O$

But $2Pb_3O_4 + 6H_2SO_4 \xrightarrow{\Delta} 6PbSO_4 + 6H_2O + O_2$

$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2$

(3) PbO_2: Insoluble in water :

HNO_3, But reacts with HCl and H_2SO_4 (hot conc.) but does not react with HNO_3 and soluble in hot NaOH / KOH.

(i) $Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

(ii) $Pb(OAc)_2 + Ca(OCl)Cl + H_2O \longrightarrow PbO_2$[Brown(dark)] $+ CaCl_2 + 2CH_3CO_2H$

↓

Excess bleaching powder is being removed by stirring with HNO_3

Reaction : $PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$

$2PbO_2 + 2H_2SO_4 \xrightarrow{\Delta} 2PbSO_4 + 2H_2O + O_2$

$PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O$

PbO_2 : Powerful oxidising agent :

(i) $PbO_2 + SO_2 \longrightarrow PbSO_4$ [spontaneously]

(ii) $PbO_2 + 2HNO_3 + (COOH)_2 \longrightarrow Pb(NO_3)_2 + 2CO_2 + 2H_2O$

(iii) $2Mn(NO_3)_2 + 5PbO_2 + 2H_2SO_4 \longrightarrow 3Pb(NO_3)_2 + 2PbSO_4\downarrow + 2HMnO_4 + 2H_2O$

$PbCl_4$: Exists as $H_2[PbCl_6]$

$PbO_2 + 4HCl \longrightarrow PbCl_4 + 2H_2O$

{ice cold conc. saturated with Cl_2}

$PbCl_4 + 2HCl \longrightarrow H_2PbCl_6$

TetraEthyl lead:

$4Na–Pb$ (alloy 10%–Na.) $+ 4C_2H_5Cl$ (vap.) $\longrightarrow 3Pb + Pb(Et)_4 + 4NaCl$

It is antiknocking agent.

Nitrogen family: (Pnicogens)

Group-15 Elements (N, P, As, Sb, Bi, Mc):

This is some times known as group of pnicogens.

(i) As we go down the group, there is a shift from non-metallic to metallic through metalloidic character.

(ii) Nitrogen and phosphorus are **non-metals**, Arsenic and Antimony **metalloids** and Bismuth and moscovium are **typical metals**.

Occurrence :

Nitrogen : Molecular nitrogen comprises 78% by volume of the atmosphere. It is 33rd most abundant element in the earth's crust. In the earth's crust, it occurs as sodium nitrate, $NaNO_3$ (called Chile saltpetre) and potassium nitrate KNO_3(Indian saltpetre). It is found in the form of proteins and nucleic acid in plants and animals.

Phosphorus :

(i) It is eleventh most abundant element in earth's crust occurs in minerals of the apatite family, $Ca_9(PO_4)_6$. CaX_2 (X = F, Cl or OH) (e.g., fluorapatite $Ca_9(PO_4)_6.CaF_2$) chlorapatite $Ca_9(PO_4)_6.CaCl_2$) and also found as hydroxylapatite.

(ii) It is also present in nucleic acid (in DNA and RNA) which are the main components of phosphate rocks.

Other Elements:

(iii) Arsenic , Antimony and Bismuth are found mainly as sulphide minerals.

(iv) Moscovium is a synthetic radioactive element. Its symbol is Mc, atomic number 115, atomic mass 289 and electronic configuration [Rn] $5f^{14}6d^{10}7s^2\ 7p^3$. Due to very short half life and availability in very little amount, its chemistry is yet to be established.

Electronic Configuration :

The valence shell electronic configuration of these elements is ns^2np^3.

Atomic and Ionic Radii :

Covalent radius : N < P < As < Sb < Bi

Explanation :

Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d and/or f orbitals in heavier members.

Ionisation Enthalpy :

N > P > As > Sb > Bi (IE_1 values)

Explanation :

Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half-filled p orbitals electronic configuration and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$.

Electronegativity :

$$\underset{(1.9)}{N} > \underset{(1.9)}{P} > As > Sb = Bi$$

Explanation :

The electronegativity value, in general, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced.

Metallic Character

N < P	As < Sb	Bi < Mc
Non metal	Metalloid	Metal

Physical Properties :

(i) All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids.

(ii) Metallic character increases down the group.

(iii) Nitrogen and Phosphorus are non-metals, Arsenic and Antimony metalloids and Bismuth and moscovium are metals. This is due to decrease in ionisation enthalpy and increase in atomic size.

(iv) The boiling points, in general, increase from top to bottom in the group but the melting point increases upto Arsenic and then decreases upto Bismuth.

(v) Except Nitrogen all the elements show allotropy.

P $\rightarrow$ exists in three allotropic form as white, red and black

As, Sb $\rightarrow$ exist as yellow and grey

Bi $\rightarrow$ exists as α, β, γ, δ allotropic form

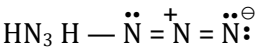
Table: Atomic and Physical Properties of Group 15 Elements

Property	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Atomic mass/g mol^{-1}	14.01	30.97	74.92	121.75	208.98
Electronic configuration	$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10} 4s^2 4p^3$	$[Kr]4d^{10} 5s^2 5p^3$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$
Ionisation enthalpy I	1402	1012	947	834	703
(Δ_iH/kJ mol^{-1}) II	2856	1903	1798	1595	1610
III	4577	2910	2736	2443	2466
Electronegativity	3.0	2.1	2.0	1.9	1.9
Covalent radius/pm[a]	70	110	121	141	148
Ionic radius /pm	171[b]	212[b]	222[b]	76[c]	103[c]
Melting point/K	63*	317[d]	1089[e]	904	544
Boiling point /K	77.2*	554[d]	888[f]	1860	1837
Density/[g cm^{-3} (298 K)]	0.879[g]	1.823	5.778[h]	6.697	9.808

[a] E^{III} single bond (E = element); [b] E^{3-}; [c] E^{3+}; [d] White phosphorus; [e] Grey α-form at 38.6 atm; [f] Sublimation temperature; [g] At 63 K; [h] Grey α-form; * Molecular N_2.

Catenation

* The group 15 elements also show catenation property but to much smaller extent than Carbon. For example hydrazine (H_2NNH_2) has two N atoms bonded together HN_3 has three N atoms.



* Among group 15 elements P has the maximum tendency for catenation forming cyclic as well as open chain compounds consisting of many Phosphorous atoms.
  P_2H_4 has two P atoms bonded together the lesser tendency of elements of group 15 to show catenation in compression to Carbon is their low dissociation enthalpies.

C – C	353.3 kJ /mole
N – N	160.8 kJ / mole
P – P	201.6 kJ / mole
As – As	147.4 kJ / mole

Chemical Properties:

Oxidation states and trends in chemical reactivity:

(i) The common oxidation states of these elements are –3, +3 and +5.

(ii) The tendency to exhibit –3 oxidation state decreases down the group due to increase in size and metallic character. Bismuth hardly forms any compound in –3 oxidation state.

(iii) The stability of +5 oxidation state decreases down the group. The only well characterised Bi (V) compound is BiF_5.

(iv) The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group.

(v) Nitrogen exhibits + 1, + 2, + 4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxoacids.

(vi) In the case of Nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,

(i) $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

(vii) Similarly, in case of Phosphorus nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid.

(ii) $4H_3PO_3 \xrightarrow{\text{Heat}} 3H_3PO_4 + PH_3$

(viii) +3 oxidation state in case of Arsenic, Antimony and Bismuth becomes increasingly stable with respect to disproportionation.

(ix) Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding.

(x) The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence, expand their covalency as in $PF_6^{\ominus}$.

Anomalous properties of nitrogen

(i) Nitrogen has unique ability to form p_π - p_π multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O).

(ii) Heavier elements of this group do not form p_π-p_π bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.

(iii) Nitrogen exists as a diatomic molecule with a triple bond (one σ and two π) between the two atoms. N_2 bond enthalpy (941.4 kJ $mol^{\ominus 1}$) is very high.

(iv) Phosphorus, Arsenic and Antimony form single bonds as P–P, As–As and Sb–Sb while bismuth forms metallic bonds in elemental state.

(v) The single N–N bond is weaker than the single P–P bond because of high interelectronic repulsion of the non-bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen.

(vi) Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form d_π–p_π bond as the heavier elements can e.g., $R_3P{=}O$ or $R_3P{=}CH_2$ (R=alkyl group).

(vii) Phosphorus and arsenic can form d_π–d_π bond also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

(i) Reactivity towards hydrogen:

All the elements of Group 15 form hydrides of the type EH_3 where E = N, P, As, Sb or Bi. Some of the properties of these hydrides are shown in Table. The hydrides show regular gradation in their properties. The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$.

Table : Properties of Hydrides of Group 15 Elements

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point/K	195.2	139.5	156.7	185	—
Boiling point/K	238.5	185.5	210.6	254.6	290
(E–H) distance/pm	101.7	141.9	151.9	170.7	—
HEH angle (°)	107.8	93.6	91.8	91.3	—
$\Delta_f H^\ominus$/kJ $mol^{\ominus 1}$	– 46.1	13.4	66.4	145.1	278
$\Delta_{diss}H^\ominus$ (E – H)/kJ $mol^\ominus$	389	322	297	255	—

(ii) Reactivity towards oxygen: All these elements form two types of oxides: E_2O_3 and E_2O_5. The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type E_2O_3 of Nitrogen and Phosphorus are purely acidic, that of Arsenic and Antimony amphoteric and those of Bismuth predominantly basic.

(iii) Reactivity towards halogens: These elements react to form two series of halides: EX_3 and EX_5. Nitrogen does not form pentahalide due to non-availability of the d orbitals in its valence shell. Pentahalides are more covalent than trihalides. All the trihalides of these elements except those of Nitrogen are stable. In case of Nitrogen, only NF_3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.

(iv) Reactivity towards metals: All these elements react with metals to form their binary compounds exhibiting –3 oxidation state, such as, Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

Dinitrogen:

Preparation :

(a) Commercial preparation :

Dinitrogen is produced **commercially** by the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.p. 90 K).

(b) Laboratory preparation :

(i) Dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(\ell) + NaCl\ (aq)$$

Small amounts of NO and HNO_3 are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate.

(ii) Dinitrogen can also be obtained by the thermal decomposition of ammonium dichromate.

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

Note :

Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

$$Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$$

$$2NaN_3 \xrightarrow{300^\circ C} 2Na + 3N_2$$

(c) Other preparation

$2NH_3 + 3NaOCl \longrightarrow N_2 + 3NaCl + 3H_2O$

$2NH_3 + 3Ca(OCl)_2 \longrightarrow 2N_2 + 3CaCl_2 + 6H_2O$

$8NH_3 + 3Br_2 \longrightarrow N_2 + 6NH_4Br$

$\underset{(\text{red,overheated})}{2NO} + 2Cu \longrightarrow \underset{(\text{Black})}{2CuO} + N_2$

Cl_2 passed into liquid NH_3

$3Cl_2 + 2NH_3(\ell) \longrightarrow N_2 + 6HCl$

$6NH_3 + 6HCl \longrightarrow 6NH_4Cl$

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

In this method conc. of NH_3 should not be lowered down beyond a particular limit.

$$3Cl_2 + NH_3 \longrightarrow \underset{\downarrow}{NCl_3} + 3HCl$$

(Tremendously explosive)

Physical properties :

(i) Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.

(ii) Nitrogen atom has two stable isotopes: ^{14}N and ^{15}N.

(iii) It has a very low solubility in water (23.2 cm^3 per litre of water at 273 K and 1 bar pressure)

(iv) Dinitrogen has low freezing and boiling points.

Chemical Properties:

Reaction with metal : At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:

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

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

Reaction with metal: It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia:

$$N_2(g)+3H_2(g)\underset{}{\overset{773k}{\rightleftharpoons}}2NH_3(g)\,; \qquad \Delta_fH^{\ominus} = -46.1\ kJ/mol.$$

Dinitrogen combines with dioxygen only at very high temperature (at about 2000 K) to form nitric oxide, NO.

$$N_2+O_2(g)\underset{}{\overset{Heat}{\rightleftharpoons}}2NO(g)$$

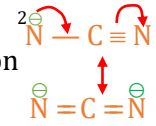
Absorption on calcium carbride

N_2 can be absorbed by calcium carbide at the temperature around 1000°C.

$$CaC_2 + N_2 \xrightarrow{1100°C} \underbrace{CaNCN + C}_{\text{nitrolim}}$$

It is a very good fertiliser.

Cyanamide ion



$$(Ca(NCN) + C) + 3H_2O \rightarrow CaCO_3 + 2NH_3 + C$$

Slowly decomposes

$NH_2 — CO — NH_2$

(Intermidiate formed)

Illustration 7:

Why dinitrogen is inert at room temperature ?

Solution:

Dinitrogen is inert at room temperature because of the high bond enthalpy of N ≡ N triple bond. Reactivity, however, increases rapidly with rise in temperature.

Types of Nitride :

Salt like or ionic : Li_3N, Na_3N, K_3N, Ca_3N_2, Mg_3N_2, Be_3N_2

Covalent : $A\ell N$, BN, Si_3N_4, Ge_3N_4, Sn_3N_4

Interstitial : MN $\underbrace{(M = Sc, Ti, Zr, Hf, La)}_{HCP\,or\,FCC}$

Number of metal atom per unit cell is equal to number of octahedral voids per unit cell.

All the octahedral voids are occupied by nitrogen atoms. Hence the formula is MN.

HCP : Hexagonal closed packing

FCC : Face centred cubic

Uses :

(i) The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen, (e.g., calcium cyanamide).

(ii) It also finds use where an inert atmosphere is required (e.g., in iron and steel industry, inert diluent for reactive chemicals).

(iii) Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

Ammonia:

Preparation:

(i) Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous organic matter e.g., urea.

$$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

(ii) Small scale preparation

By the decomposition of ammonium salts when treated with caustic soda or calcium hydroxide.

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

$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$

(iii) Large scale manufacturing (Haber's Process)

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \; ; \; \Delta_fH^{\ominus} = -46.1 \text{ kJ mol}^{\ominus 1}$$

* According to Le Chatelier's principle, high pressure and low temperature would favour the formation of ammonia.
* The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200 atm), with a temperature of ~ 700 K.
* Use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.
* The flow chart for the production of ammonia is shown in figure. Earlier, iron was used as a catalyst with Molybdenum as a promoter.

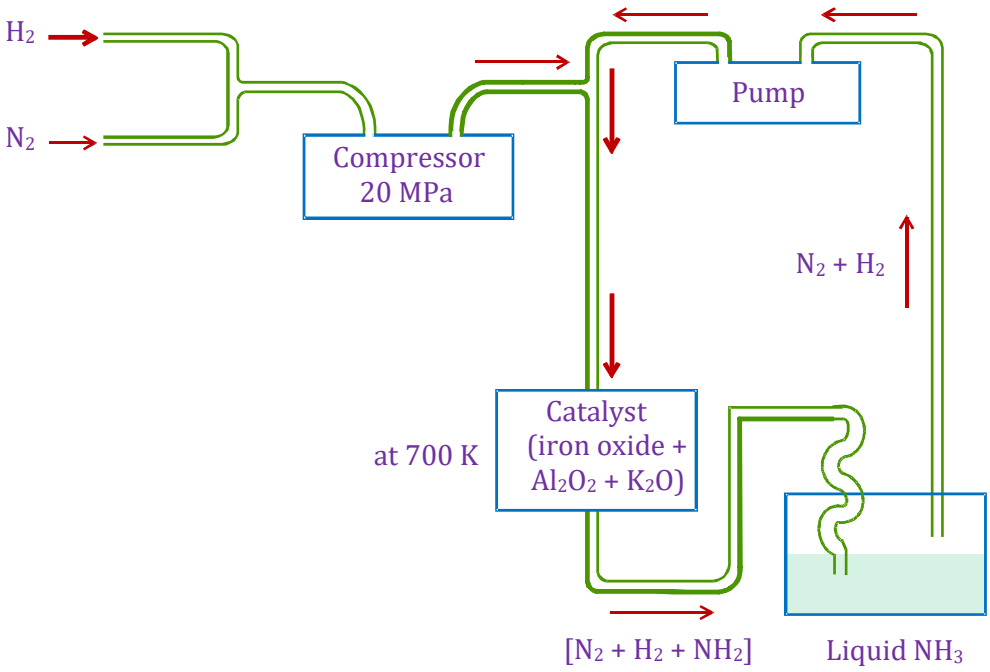


Fig. Flow chart for the manufacture of ammonia

Other preparation :

(i) Nitrate or nitrite reduction : $NO_3^{\ominus}$ / $NO_2^{\ominus}$ + Zn or Al + NaOH $\longrightarrow$ NH_3 + $[Zn(OH)_4]^{2\ominus}$ or $[Al(OH)_4]^{\ominus}$

(ii) Metal nitride hydrolysis : $N^{3\ominus} + 3H_2O \longrightarrow NH_3\uparrow + 3\,OH^{\ominus}$

Properties:

(i) Ammonia is a colourless gas with a pungent odour.

(ii) Its freezing and boiling points are 198.4 and 239.7 K respectively.

(iii) In the solid and liquid states, it is associated through hydrogen bonds as in the case of water and that accounts for its higher melting and boiling points than expected on the basis of its molecular mass.

(iv) Ammonia gas is highly soluble in water.

(v) **Basic character :**

Its aqueous solution is weakly basic due to the formation of $OH^{\ominus}$ ions.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^{\oplus}(aq) + OH^{\ominus}(aq)$$

It forms ammonium salts with acids, e.g., NH_4Cl, $(NH_4)_2SO_4$, etc.

As a weak base, it precipitates the hydroxides (hydrated oxides in case of some metals) of many metals from their salt solutions.

For example,

$$ZnSO_4(aq) + 2NH_4OH(aq) \longrightarrow \underset{\text{(White ppt)}}{Zn(OH)_4(s)} + (NH_4)_2SO_4(aq)$$

$$FeCl_3(aq) + NH_4OH(aq) \longrightarrow \underset{\text{(brown ppt)}}{Fe_2O_3.xH_2O(s)} + NH_4Cl(aq)$$

In ammonia molecule the presence of a lone pair of electrons on the nitrogen atom makes it a Lewis base. It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of metal ions such as $Cu^{2\oplus}$, $Ag^{\oplus}$:

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

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

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

Other reactions:

CH_3COOH is strong acid in liq. NH_3 while in water is weak acid.

$AcOH \rightleftharpoons \overset{\ominus}{AcO} + H^{\oplus}$

$NH_3 + H^{\oplus} \longrightarrow NH_4^{\oplus}$

$H_2O + H^{\oplus} \longrightarrow H_3O^{\oplus}$

Basicity order: $\Rightarrow NH_3 > H_2O$

more solvation of $H^{\oplus}$ in NH_3.

Hydrolysis and Ammonolysis occurs in a same way.

$SiCl_4 + 4H_2O \longrightarrow 4HCl + Si(OH)_4 \xrightarrow{\Delta} SiO_2 + 2H_2O$

$SiCl_4 + 8NH_3 \longrightarrow 4NH_4Cl + Si(NH_2)_4 \xrightarrow{\Delta} Si_3N_4 + NH_3\uparrow$

Rate of hydrolysis and Ammonolysis will be affected by the presence of HCl vapour & NH_4Cl vapour respectively.

Uses :

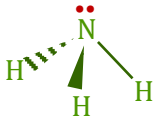
(i) Ammonia is used to produce various nitrogenous fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate).

(ii) In the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid.

(iii) Liquid ammonia is also used as a refrigerant.

Bonding in ammonia :

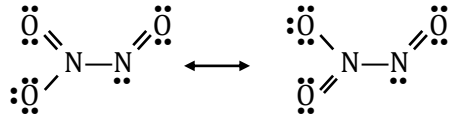
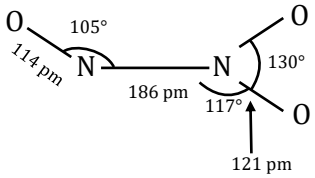
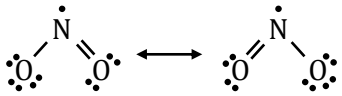
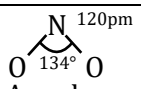
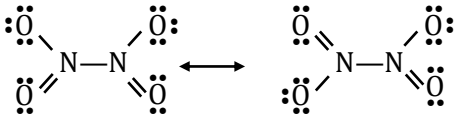
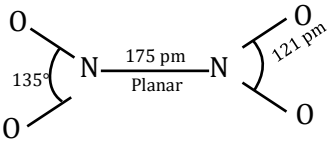
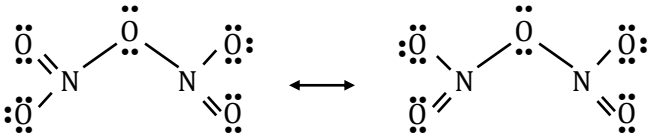
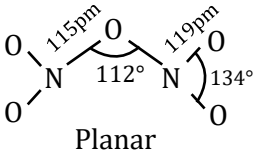
The ammonia molecule is trigonal pyramidal with the nitrogen atom at the apex. It has three bond pairs and one lone pair of electrons.

Structure of NH_3 

Oxides of Nitrogen:

Nitrogen forms a number of oxides in different oxidation states. The names, formulas, preparation and physical appearance of these oxides are given in Table.

Oxides of Nitrogen				
Name	**Formula**	**Oxidation state of nitrogen**	**Common methods of preparation**	**Physical appearance and chemical nature**
Dinitrogen oxide [Nitrogen (I) oxide]	N_2O	+1	$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide]	NO	+2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen (III) oxide]	N_2O_3	+3	$2NO + N_2O_4 \xrightarrow{-30°C} 2N_2O_3$	Pale Blue solid (MP = –100.1°C), acidic, Intense blue liquid (–30° C)
Nitrogen dioxide [Nitrogen (IV) oxide]	NO_2	+4	$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO + O_2$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen (IV) oxide]	N_2O_4	+4	$2NO_2 \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4$	Colourless solid/ liquid, acidic
Dinitrogen pentaoxide [Nitrogen(V) oxide]	N_2O_5	+5	$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$	colourless solid, acidic

Structure of Oxides of Nitrogen		
Formula	**Resonance structures**	**Bond Parameters**
N_2O	$\ddot{N} = N = \ddot{O} \leftrightarrow :N \equiv N - \ddot{O}:$	N—N—O 113 pm 119 pm Linear
NO	$:\dot{N} = \ddot{O} \leftrightarrow :N = \dot{O}:$	N—O 115 pm
N_2O_3		
NO_2		 Angular
N_2O_4		
N_2O_5		 Planar

Preparation:

1. N_2O

(i) $NH_4NO_3 \longrightarrow N_2O + H_2O$

(ii) $(NH_4)_2SO_4 + NaNO_3 \longrightarrow NH_4NO_3 + Na_2SO_4$

$\downarrow$

$N_2O + 2H_2O$

(iii) $Zn + HNO_3 \underset{(\text{dil.\& cold})}{\longrightarrow} Zn(NO_3)_2 + N_2O + H_2O$

2. NO

(i) $Cu + HNO_3\ (1:1) \underset{(\text{hot \& conc})}{\longrightarrow} Cu(NO_3)_2 + NO + H_2O$

(ii) $KNO_3 + FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + K_2SO_4 + NO + H_2O$

$FeSO_4 + NO \longrightarrow FeSO_4 . NO \xrightarrow{\Delta} FeSO_4 + NO\uparrow$

(iii) Ostwald's process–Restricted oxidation of NH_3.

Industrial process.

$4NH_3 + 5O_2 \xrightarrow[750°C,\ Pt\text{-}Cat]{6\ atm} 4NO + 6H_2O$

3. N_2O_3

(i) $HNO_3 + As_2O_3 \longrightarrow H_3AsO_4 + N_2O_3$

(ii) $Cu + HNO_3(6M) \longrightarrow Cu(NO_3)_2 + \underbrace{(NO + NO_2)}_{\text{cool}(-30^\circ C)\downarrow}$

Blue liq (N_2O_3)

4. NO_2

(i) $M(NO_3)_2 \xrightarrow{\Delta} MO + 2NO_2 + \frac{1}{2}O_2$

M = Pb, Cu, Ba, Ca

(ii) $(Cu, Pb, Ag) + \underset{(\text{hot \& conc.})}{HNO_3} \longrightarrow \text{M-nitrate} + NO_2 + H_2O$

5. N_2O_5

(i) $2HNO_3 + P_2O_5 \longrightarrow 2HPO_3 + N_2O_5$

(ii) $4AgNO_3 + 2Cl_2(\text{dry gas}) \longrightarrow 4AgCl + 2N_2O_5 + O_2$

Properties:

(I) Decoposition Behaviour

(i) $N_2O \xrightarrow{500^\circ C - 900^\circ C} 2N_2 + O_2$

(ii) $2NO \xrightarrow{800^\circ C} N_2 + O_2$

(iii) $N_2O_3 \xrightarrow[(\text{Blue liq.}) \text{ at } (-30^\circ C)]{\text{Room temp.}} NO_2 + NO$

(iv) $2NO_2 \xrightarrow{620^\circ C} 2NO + O_2$

$\underset{\substack{(\text{white solid})\\ \text{at}(-11^\circ C)}}{N_2O_4} \xrightarrow{-11^\circ C} \underset{\text{Brown gas}}{2NO_2}$

(v) $\underset{\substack{\text{colourless}\\ \text{solid}}}{N_2O_5} \xrightarrow{30^\circ C} \underset{\text{yellow liq.}}{N_2O_5} \xrightarrow{40^\circ C} 2NO_2 + \frac{1}{2}O_2$

(II) Reaction with H_2O & NaOH

	H_2O	**NaOH**
(i) N_2O :	Fairly soluble in water and produces neutral solution	-------
(ii) NO :	Sparingly soluble in water and produces neutral sol^n.	-------
(iii) N_2O_3:	$2HNO_2$ Hence it is known as anhydride of HNO_2	$NaNO_2$
(iv) NO_2:	$HNO_2 + HNO_3$ called as mixed anhydride	$NaNO_2 + NaNO_3$
(v) N_2O_5:	$2HNO_3$ called as anhydride of HNO_3	$NaNO_3$

Other properties:

$N_2O : 2N_2O \longrightarrow 2N_2 + O_2$ { mixture contains $33\%\ O_2$ compared to 20% in air

Hence, it is a better supporter for combustion.

$S + 2N_2O \longrightarrow SO_2 + 2N_2$
$2P + 5N_2O \longrightarrow P_2O_5 + 5N_2$
$Mg + N_2O \longrightarrow MgO + N_2$
$2Na + N_2O \longrightarrow Na_2O + N_2$
$Cu + N_2O \longrightarrow CuO + N_2$
$H_2 + N_2O \longrightarrow H_2O + N_2$

NO :

(i) It burns : $NO + \frac{1}{2} O_2 \longrightarrow NO_2$

(ii) It supports combustion also for molten sulphur and hot phosphorous.
$S + 2NO \longrightarrow SO_2 + N_2$
$2P + 5NO \longrightarrow P_2O_5 + \frac{5}{2} N_2$

(iii) It is being absorbed by $FeSO_4$ solution.

(iv) It is having reducing property.
$HOCl + NO + H_2O \longrightarrow HNO_3 + HCl$

(v) NO shows oxidising property also.
$SO_2 + 2NO + H_2O \longrightarrow H_2SO_4 + N_2O$
$H_2S + 2NO \longrightarrow H_2O + S\downarrow + N_2O$
$3SnCl_2 + 2NO + 6HCl \longrightarrow 3SnCl_4 + 2NH_2OH$ (Used for NH_2OH preparation)

(vi) NO combines with X_2 (X_2= Cl_2,Br_2,I_2) to produce NOX
$2NO + X_2 \longrightarrow 2NOX$

N_2O_3 : No more properties.

NO_2 :

(1) It is having oxidising property.
$S + NO_2 \longrightarrow SO_2 + NO$
$2P + 5NO_2 \longrightarrow P_2O_5 + 5NO$
$C + 2NO_2 \longrightarrow CO_2 + 2NO$
$SO_2 + NO_2 + H_2O \longrightarrow H_2SO_4 + NO$
$H_2S + NO_2 \longrightarrow H_2O + S\downarrow + NO$
$CO + NO_2 \longrightarrow CO_2 + NO$
NO not formed : $2KI + 2NO_2 \longrightarrow I_2 + 2KNO_2$

(2) Reducing property of NO_2.
$2KMnO_4 + 10NO_2 + 3H_2SO_4 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 10HNO_3$
$O_3 + 2NO_2 \rightarrow \underbrace{O_2} + N_2O_5$
not the reduction product of O_3

N_2O_5 :

$I_2 + 5N_2O_5 \longrightarrow I_2O_5 + 10NO_2$
I_2O_5 is used for the estimation of CO
$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$
$I_2 + 2S_2O_3^{2\ominus} \longrightarrow 2I^{\ominus} + S_4O_6^{2\ominus}$
$N_2O_5 + NaCl \longrightarrow NaNO_3 + NO_2Cl$
This proves that N_2O_5 is consisting of ion pair of $NO_3^{\ominus}$ & $NO_2^{\oplus}$

Nitric acid:

It was named aqua fortis (means strong water) by alchemists.

Preparation :

Laboratory Method : By heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

$$KNO_3 / NaNO_3 + H_2SO_4 \rightarrow KHSO_4/NaHSO_4 + HNO_3$$

Large scale preparation (Ostwald's process) :

(i) This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.

$$4NH_3(g) + \underset{\text{(From air)}}{5O_2(g)} \xrightarrow[500K, 9bar]{Pt/Rh\text{-gauge catalyst}} 4NO(g) + 6H_2O(g)$$

(ii) Nitric oxide thus formed combines with oxygen giving NO_2.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

(iii) Nitrogen dioxide so formed, dissolves in water to give HNO_3.

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass.

Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4.

Birkeland Eyde Process or arc process

step 1 $N_2 + O_2 \xrightarrow[\text{Electric Arc}]{3000^0\,C} 2NO - \text{heat}$

step 2 $NO + \frac{1}{2} O_2 \longrightarrow NO_2$

step 3 $2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

step 4 $HNO_2 \longrightarrow HNO_3 + NO + H_2O$

Properties:

Physical properties:

It has extremely corrosive action on the skin and causes painful sores.

(i) It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K).

(ii) Laboratory grade nitric acid contains ~ 68% of the HNO_3 by mass and has a specific gravity of 1.504.

(iii) Nitric acid usually acquires yellow or brown colour due to its decomposition by sunlight into NO_2.

$$4HNO_3 \xrightarrow{\text{Sunlight}} 4NO_2 + 2H_2O + O_2$$

The yellow or brown colour of the acid can be removed by warming it to (60°-80°)C and bubbling dry air through it.

Chemical properties:

Acidic character in aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^{\oplus}(aq) + NO_3^{\ominus}(aq)$$

Oxidising nature: Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

or $2HNO_3 \longrightarrow H_2O + 2NO + 3O$

(i) Oxidation of non-metals : The nascent oxygen oxidises various non-metals to their corresponding oxyacids of highest oxidation state.

(1) Sulphur is oxidised to sulphuric acid

$$S + 6HNO_3 \xrightarrow[(conc.\ and\ hot)]{} H_2SO_4 + 6NO_2 + 2H_2O$$

(2) Carbon is oxidised to carbonic acid

$$C + 4HNO_3 \xrightarrow[(conc.\ and\ hot)]{} H_2CO_3 + 4NO_2 + 2H_2O$$

(3) Phosphorus is oxidised to orthophosphoric acid.

$$2P + 10HNO_3 \xrightarrow[(conc.\ and\ hot)]{} 2H_3PO_4 + 10NO_2 + 2H_2O$$

(4) Iodine is oxidised to iodic acid

$$I_2 + 10HNO_3 \xrightarrow[(conc.\ and\ hot)]{} 2HIO_3 + 10NO_2 + 4H_2O$$

(ii) Oxidation of metalloids

Metalloids like non-metals also form oxyacids of highest oxidation state.

(1) Arsenic is oxidised to arsenic acid

$2As + 10HNO_3 \rightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O$

or $As + 5HNO_3 \xrightarrow[(conc.\ and\ hot)]{} H_3AsO_4 + 5NO_2 + H_2O$

(2) Antimony is oxidised to antimonic acid

$$Sb + 5HNO_3 \xrightarrow[(conc.\ and\ hot)]{} H_3SbO_4 + 5NO_2 + H_2O$$

(3) Tin is oxidised to meta-stannic acid.

$$Sn + 2HNO_3 \xrightarrow[(conc.\ and\ hot)]{} H_2SnO_3 + 4NO_2 + H_2O$$

(iii) Oxidation of Compounds:

(1) Sulphur dioxide is oxidised to sulphuric acid

$SO_2 + 2HNO_3 \rightarrow H_2SO_4 + 2NO_2$

(2) Hydrogen sulphide is oxidised to sulphur

$H_2S + 2HNO_3 \rightarrow 2NO_2 + 2H_2O + S$

(3) Ferrous sulphate is oxidised to ferric sulphate in presence of H_2SO_4

$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

(4) Iodine is liberated from KI.

$6KI + 8HNO_3 \rightarrow 6KNO_3 + 2NO + 3I_2 + 4H_2O$

(5) HBr, HI are oxidised to Br_2 and I_2, respectively.

$2HBr + 2HNO_3 \rightarrow Br_2 + 2NO_2 + 2H_2O$

Similarly, $2HI + 2HNO_3 \rightarrow I_2 + 2NO_2 + 2H_2O$

(6) Ferrous sulphide is oxidised to ferric sulphate

$FeS + HNO_3 \rightarrow Fe_2(SO_4)_3 + 8NO_2 + 4H_2O$

(7) Stannous chloride is oxidised to stannic chloride is presence of HCl.

$2HNO_3 + 14H \xrightarrow[\text{Hydroxylamine}]{} NH_2OH + NH_3 + 5H_2O$

$NH_3 + HNO_3 \longrightarrow NH_4NO_3$

$7SnCl_2 + 14HCl + 3HNO_3 \rightarrow 7SnCl_4 + NH_2OH + NH_4NO_3 + 5H_2O$

(8) Oxidiation of organic compounds .

Sawdust catches fire when nitric acid is poured on it.

Turpentine oil bursts into flames when treated with fuming nitric acid.

Toluene is oxidised to benzoic acid with dil. HNO_3.

Cane sugar is oxidised to oxalic acid.

$C_{12}H_{22}O_{11} + 36HNO_3 \longrightarrow 6(COOH)_2 + 36NO_2 + 23H_2O$

Reaction with metal concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as Gold and Platinum. Au & Pt dissolve in aqua regia a mixture of 25% conc. HNO_3 & 75% conc. HCl. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

Ex. $3Cu + 8\ HNO_3(\text{dilute}) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

$Cu + 4HNO_3(\text{conc.}) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

$4Zn + 10HNO_3(\text{dilute}) \longrightarrow 4\ Zn(NO_3)_2 + 5H_2O + N_2O$

$Zn + 4HNO_3(\text{conc.}) \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$

Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Armstrong postulated that primary action of nitric acid is to produce hydrogen in the nascent form. Before this hydrogen is allowed to escape, it reduces the nitric acid into number of products like NO_2, NO, N_2O, N_2 or NH_3 according to the following reactions:

$\text{Metal} + HNO_3 \longrightarrow \text{Nitrate} + H$

$2HNO_3 + 2H \longrightarrow 2NO + 2H_2O$

$2HNO_3 + 6H \longrightarrow 2NO + 4H_2O$

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

$2HNO_3 + 16\ H \longrightarrow 2NH_3 + 6H_2O$

The progress of the reaction is controlled by a number of factors :

(a) the nature of the metal,

(b) the concentration of the acid,

(c) the temperature of the reaction,

(d) the presence of other impurities.

Action on Proteins:

Nitric acid attacks proteins forming a yellow nitro compound called xanthoprotein. It, therefore, stains skin and renders wool yellow. This property is utilized for the test of proteins.

Uses :

(i) The major use of nitric acid is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics.

(ii) It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds.

(iii) Major uses are in the **pickling of stainless steel**.

(iv) Etching of metals.

(v) Use as an oxidiser in rocket fuels.

Note :

Pickling is a metal surface treatment used to remove impurities, such as stains, inorganic contaminants, rust or scale from ferrous metals, copper, precious metals and aluminium alloys. A solution called pickle liquor, which contains strong acids, is used to remove surface impurities.

Oxoacids of nitrogen:

$H_2N_2O_2$ (hyponitrous acid), HNO_2 (nitrous acid) and HNO_3 (nitric acid). Amongst them HNO_3 is the most important.

Nitrous acid (HNO_2):

Preparation

(a) M-nitrite $\xrightarrow[HCl \text{ or } H_2SO_4]{\text{dil.acid}} HNO_2$

(b) $N_2O_3 + H_2O \longrightarrow 2HNO_2$

Properties:

(a) **Oxidising property** : Because of its easy oxidation to liberate nascent oxygen, it acts as a strong oxidant

$2HNO_2 \longrightarrow H_2O + 2NO + [O]$

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

$SnCl_2 + 2HNO_2 + 2HCl \longrightarrow SnCl_4 + 2NO + 2H_2O$

$SO_2 + 2HNO_2 \longrightarrow H_2SO_4 + 2NO$

$H_2S + 2HNO_2 \longrightarrow 2H_2O + S\downarrow + 2NO$

$2FeSO_4 + 2HNO_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NO + 2H_2O$

$Na_3AsO_3 + 2HNO_2 \longrightarrow Na_3AsO_4 + 2NO + H_2O$

(b) **Reducing property** : Nitrous acid also acts as a reducing agent as it can be oxidised into nitric acid.

$HNO_2 + [O] \longrightarrow HNO_3$

$2KMnO_4 + 5HNO_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$

$K_2Cr_2O_7 + 3HNO_2 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3HNO_3 + 4H_2O$

$H_2O_2 + HNO_2 \longrightarrow H_2O + HNO_3$

(c) Reaction with NH_3 / $-NH_2$ compounds :

$2HNO_2 + \underset{\text{Urea}}{NH_2CONH_2} \longrightarrow 2N_2 + CO_2 + 3H_2O$

$HNO_2 + NH_3 \longrightarrow NH_4NO_2 \longrightarrow N_2 + 2H_2O$

$HNO_2 + C_2H_5NH_2 \longrightarrow C_2H_5OH + N_2 + H_2O$

$HNO_2 + C_6H_5 - NH_2 \cdot HCl \xrightarrow{<5^\circ C} C_6H_5N = NCl + 2H_2O$

Benzene diazonium chloride

$HNO_2 + \text{thiourea} \longrightarrow N_2\uparrow + H^{\oplus} + SCN^{\ominus} + 2H_2O$

$HNO_2 + \text{sulphamic acid} \longrightarrow N_2\uparrow + 2H^{\oplus} + SO_4^{2\ominus} + H_2O$

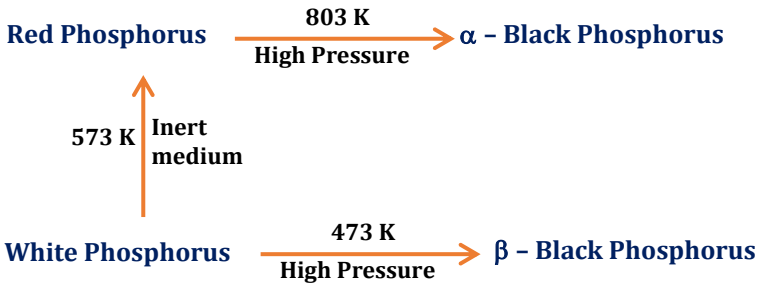
Allotropic Forms of Phosphorus:

Property	White phosphorus	Red phosphorus
1. Physical state	Soft waxy solid.	Brittle powder.
2. Colour	White when pure. Attains yellow colour on standing.	Red.
3. Odour	Garlic	Odourless.
4. Solubility in water	Insoluble.	insoluble
5. Solubility in CS_2	Soluble.	Insoluble.
6. Physiological action	Poisonous.	Non-poisonous.
7. Chemical activity	Very active.	Less active.
8. Stability	Unstable.	Stable.
9. Phosphorescence	Glows in dark	Does not glow in dark.
10. Molecular formula	P_4	Complex polymer.

Black phosphorus

α-black and β-black are two forms of black phosphorus. When red phosphorus is heated in a sealed tube at 803K, an α-black form is formed. It can be sublimed in the air and has either rhombohedral crystals or opaque monoclinic. It does not oxidize in the air. When white form is heated under high pressure at 473 K β-Black is formed. It does not burn in the air up to 673K.

Order of stability or MP or density: White < Red < Black



Prepration of white Phosphorus:

(i) Boneash or Apatite rock (both have same formula) $\left\{\right.$ $Ca_3(PO_4)_2 + 3SiO_2 \xrightarrow{1200^\circ C} 3CaSiO_3 + P_2O_5$

$2P_2O_5 + 10C \xrightarrow[\text{(Coke)}]{1500^\circ C} \underset{\text{white 'P'}}{P_4} + 10CO\uparrow$

(ii) $Ca_3(PO_4)_2 + 3H_2SO_4\,(conc.) \longrightarrow 3CaSO_4 + 2H_3PO_4$

$$H_3PO_4 \xrightarrow[-H_2O]{320^\circ C} \underset{\text{meta phosphoric acid}}{HPO_3}$$

$$\underset{\text{Coke}}{12C} + 4HPO_3 \xrightarrow{1000^\circ C} 2H_2\uparrow + 12CO\uparrow + \underset{\text{white 'P'}}{P_4}$$

Reactions of 'P':

* $P + H_2SO_4\,(hot\ \&\ conc.) \longrightarrow H_3PO_4 + SO_2 + H_2O$

  $P + KIO_3 + H_2SO_4 \longrightarrow H_3PO_4 + I_2 + K_2SO_4$

* Reaction with hot metal —

  $3Na + P \longrightarrow Na_3P$

  $3Mg + 2P \longrightarrow Mg_3P_2$

  $3Ca + 2P \longrightarrow Ca_3P_2$

  $2Cu + 2P \longrightarrow Cu_3P_2$

  $Al + P \longrightarrow AlP$

Phosphine:

Preparation:

(i) Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.

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

$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$

(ii) Laboratory prepration it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + \underset{\text{(sodium hypophosphite)}}{3NaH_2PO_2}$$

Pure PH_3 is non inflammable but becomes inflammable owingto the presence of P_2H_4 or P_4 vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.

Other preparation:

$PH_4I + KOH \longrightarrow KI + PH_3 + H_2O$ } Purest PH_3
(PH_3+HI)

$2AlP + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + PH_3\uparrow$

$4H_3PO_3 \xrightarrow{\Delta} PH_3 + 3H_3PO_4$

Phyiscal Properties :

(i) It is a colourless gas with rotten fish smell and is highly poisonous.

(ii) It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.

(iii) It is slightly soluble in water but soluble in CS_2 . The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2.

Chemical Properties :

(i) It absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$$

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

Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g.,

$$PH_3 + HBr \rightarrow PH_4Br$$

(ii) $PH_3 + O_2 \xrightarrow{150^\circ} P_2O_5 + H_2O$

(iii) $PH_3 + 3Cl_2 \longrightarrow PCl_3 + 3HCl$

(iv) $PH_3 + 4N_2O \xrightarrow[\text{sparking}]{\text{electrical}} H_3PO_4 + 4N_2$

(v) $PH_3 + 6AgNO_3 \longrightarrow \underset{\text{yellow ppt.}}{[Ag_3P \bullet 3AgNO_3 \downarrow]} + 3HNO_3$

$$Ag_3P \bullet 3AgNO_3 + 3H_2O \xrightarrow{\text{on standing}} \underset{\text{Black ppt.}}{6Ag \downarrow} + 3HNO_3 + H_3PO_3$$

(vi) $PH_3 + 4HCHO + HCl \longrightarrow [P(CH_2OH)_4]^{\oplus}Cl^{\ominus}$

white/colourless solid which is used for making fire-proof cotton fabrics

Note :

Like NH_3, PH_3 also can form addition product.

$\Downarrow$ ⇘

$CaCl_2 \bullet 8NH_3$, $Cu_2Cl_2 \bullet 2PH_3$, $AlCl_3 \bullet 2PH_3$, $SnCl_4 \bullet 2PH_3$

PH_3 can be absorbed by Ca(OCl)Cl.

$PH_3 + 3Ca(OCl)Cl + 3H_2O \longrightarrow PCl_3 + 3HCl + 3Ca(OH)_2$

$2NH_3 + 3Ca(OCl)Cl \longrightarrow N_2 + 3CaCl_2 + 3H_2O$

Uses :

(i) The spontaneous combustion of phosphine is technically used in Holme's signals. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.

(ii) It is also used in smoke screens.

PHOSPHORUS HALIDES:

Phosphorus forms two types of halides, PX_3 (X = F, Cl, Br, I) and PX_5 (X = F, Cl, Br).

Phosphorus Trichloride:

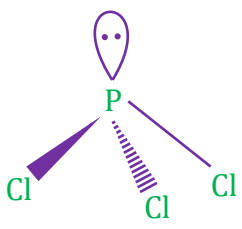
Preparation

(i) By passing dry chlorine over heated white phosphorus.

$P_4 + 6Cl_2 \longrightarrow 4PCl_3$

(ii) By the action of thionyl chloride with white phosphorus.

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



Properties

(i) It is a colourless oily liquid

(ii) Hydrolyses in the presence of moisture.

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

(iii) It reacts with organic compounds containing –OH group such as CH_3COOH, C_2H_5OH.

$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$

$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$

Phosphorus Pentachloride:

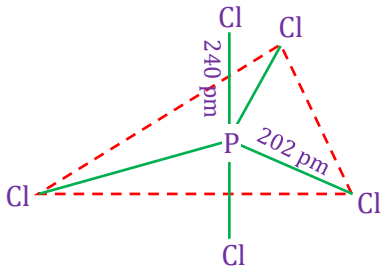
Preparation:

(i) By the reaction of white phosphorus with excess of dry chlorine.

$P_4 + 10Cl_2 \rightarrow 4PCl_5$

(ii) By the action of SO_2Cl_2 on phosphorus.

$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$



Properties :

(i) PCl_5 is a yellowish white powder

(ii) It hydrolysis in moist air to $POCl_3$ and finally gets converted to phosphoric acid.

$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$

(iii) When heated, it sublimes but decomposes on stronger heating.

$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$

(iv) It reacts with organic compounds containing –OH group converting them to chloro derivatives.

$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$

$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

(v) Finely divided metals on heating with PCl_5 give corresponding chlorides.

$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$

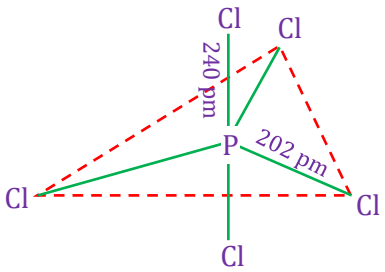
$Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$

Uses :

It is used in the synthesis of some organic compounds, e.g., C_2H_5Cl, CH_3COCl.

Note :

In gaseous and liquid phases, it has a trigonal bipyramidal structure as shown. The three equitorial P–Cl bonds are equivalent, while the two axial bonds are longer than equitorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equitorial bond pairs.



In the solid state it exists as an ionic solid, $[PCl_4]^{\oplus}[PCl_6]^{\ominus}$ in which the cation, $[PCl_4]^{\oplus}$ is tetrahedral and the anion, $[PCl_6]^{\ominus}$ is octahedral.

Oxides of phosphorus:

It forms two important oxides which exist in dimeric forms.-

Phosphorus (III) Oxides (P_4O_6):

Preparation

Phosphorus trioxides is formed when phosphorus is burnt in a limited supply of air and inert atmosphere.

$$P_4 + 3O_2 \text{ (limited)} \longrightarrow P_4O_6$$

Properties

(a) **Heating in air :** On heating in air, it forms phosphorus pentoxide.

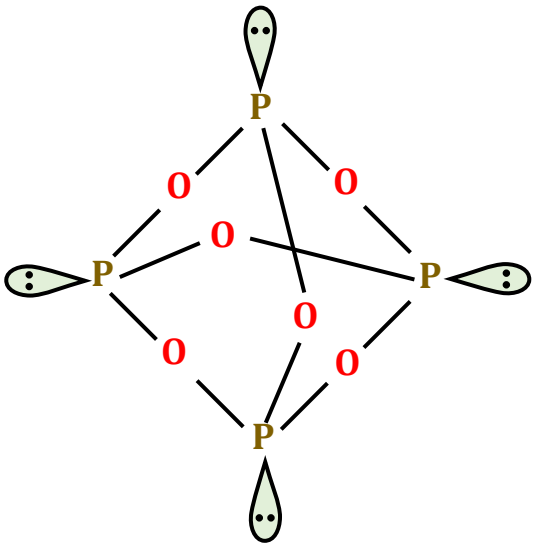
$$P_4O_6 + 2O_2 \longrightarrow \underset{\text{Phosphorus (V) oxide}}{P_4O_{10}}$$

(b) **Action of water :** It dissolves in cold water to give phosphorus acid.

$$P_4O_6 + 6H_2O\ (\text{cold}) \longrightarrow \underset{\text{Phosphorus acid}}{4H_3PO_3}$$

It is, therefore, considered as anhydride of phosphorus acid.

(c) **Structure of P_4O_6:**



Note:

With hot water, it gives phosphoric acid and inflammable phosphine.

Structure

(a) Each atom of phosphorus in P_4O_6 is present at the corner of a tetrahedron

(b) Each phosphorus atom is covalently bonded to three oxygen atoms and each oxygen atom is bonded to two phosphorus atoms.

(c) It is clear from the structure that the six oxygen atoms lie along the edges of the tetrahedron of P atoms.

Phosphorus (V) oxide (P_4O_{10}):

Preparation : It is prepared by heating white phosphorus in excess of air.

$$P_4 + 5O_2 \text{ (excess)} \xrightarrow{\Delta} P_4O_{10}$$

Properties:

(a) It is snowy white solid.

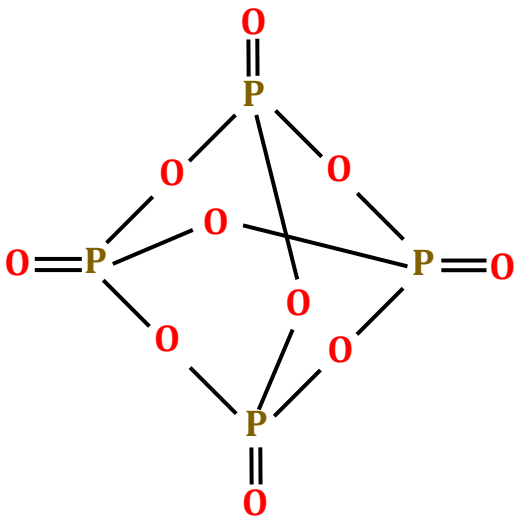
(b) Action with water : It readily dissolves in cold water forming metaphosphoric acid.

$$P_4O_{10} + 2H_2O\ (\text{Cold}) \longrightarrow \underset{\text{Metaphosphoric acid.}}{4HPO_3}$$

With hot water it gives phosphoric acid.

$$P_4O_{10} + 6H_2O\ (\text{Hot}) \longrightarrow \underset{\text{Phosphoric acid}}{4H_3PO_4}$$

(c) Structure of P_4O_{10}:



(d) Dehydrating nature : Phosphorus pentoxide has strong affinity for water and, therefore, acts as a powerful dehydrating agent. It extracts water from many inorganic and organic compounds.

(e) P_4O_{10} is a very strong dehydrating agent and extracts water from many compounds including sulphuric acid and nitric acid.

$$2HClO_4 \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Chlorine (VII) oxide}}{Cl_2O_7}$$

$$\underset{\text{Acetamide}}{2CH_3CONH_2} \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Methyl cyanide}}{CH_3CN}$$

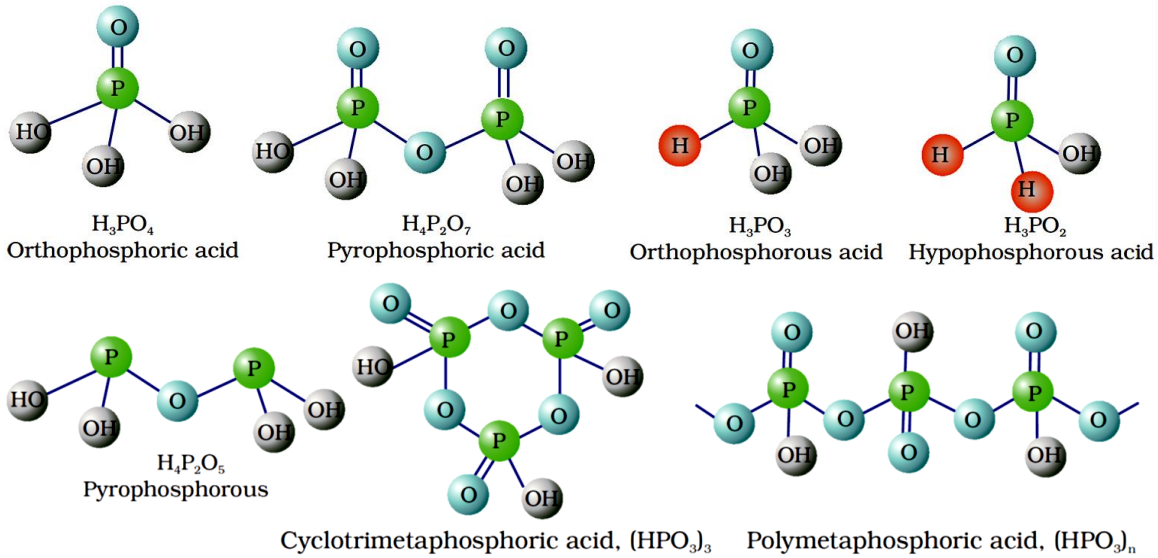
Oxoacids of Phosphorus:

The important oxoacids of phosphorus with their formulas, methods of preparation and the presence of some characteristic bonds in their structures are given in a table.

Oxoacids of Phosphorus				
Name	**Formula**	**Oxidation state of Phosphorus**	**Characteristic bonds and their number**	**Preparation**
Hypophosphorus (Phosphinic)	H_3PO_2	+ 1	One P — OH Two P — H One P = O	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+ 3	Two P — OH One P — H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+ 3	Two P — OH Two P — H Two P = O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+ 4	Four P — OH Two P = O One P — P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+ 5	Three P — OH One P = O	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+ 5	Four P — OH Two P = O One P — O — P	heat phosphoric acid
Metaphosphoric*	$(HPO_3)_n$	+ 5	Three P — OH Three P = O Three P — O — P	phosphorous acid + Br_2, heat in a sealed tube

Structure of oxoacid :

In oxoacids phosphorus is tetrahedrally surrounded by other atoms. All these acids contain at least one P = O bond and one P – OH bond. The oxoacids in which phosphorus has lower oxidation state (less than +5) contain, in addition to P = O and P–OH bonds, either P–P (e.g., in $H_4P_2O_6$) or P–H (e.g., in H_3PO_2) bonds but not both. H_3PO_3 and H_3PO_2 are diabasic and monobasic respectively.



Structures of some important oxoacids of phosphorus

Note:-

(i) These acids in +3 oxidation state of phosphorus tend to disproportionate to higher and lower oxidation states. For example, phophorous acid on heating disproportionates to give orthophosphoric acid (or phosphoric acid) and phosphine.

$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

(ii) The acids which contain P–H bond have strong reducing properties. Thus, hypophosphorous acid is a good reducing agent as it contains two P–H bonds and reduces, $AgNO_3$ to metallic silver.

$4AgNO_3 + 2H_2O + H_3PO_2 \rightarrow 4Ag + 4HNO_3 + H_3PO_4$

Heating Effect :

$H_3PO_2 \xrightarrow{140°C} PH_3 + H_3PO_4$

$\underset{\text{orthophosphoric acid}}{H_3PO_4} \xrightarrow[220°C]{\text{gentle heat}} \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} \xrightarrow[320°C]{\text{strong heat}} \underset{\text{metaphosphoric acid}}{(HPO_3)_n}$

Graham salt:

Graham's salt is the best known of these long chain polyphosphates, and is formed by quenching molten $NaPO_3$. Graham's salt is soluble in water. These solutions give precipitates with metal ions such as $Pb^{2\oplus}$ and $Ag^{\oplus}$ but not with $Ca^{2\oplus}$ and $Mg^{2\oplus}$. Graham's salt is sold commercially under the trade name Calgon. In industry it is incorrectly called sodium hexametaphosphate crystallizing. It is widely used for softening water.

$$NaH_2PO_4 \xrightarrow{>240°C} \underset{\text{Sodium trimetaphosphate}}{(NaPO_3)_3} \xrightarrow{625°C} NaPO_3(\text{liquid melt}) \xrightarrow[\text{cooling}]{\text{rapid}} \underset{\text{(Graham's salt) (glass)}}{(NaPO_3)_n}$$

Oxygen family (Chalcogens):

Group 16 Elements (O, S, Se, Te, Po, Lv):

This is sometimes known as group of chalcogens.

Occurrence:

Oxygen is the most abundant of all the elements on earth crust. Oxygen forms about 46.6% by mass of earth's crust. Dry air contains 20.946% oxygen by volume. However, the abundance of sulphur in the earth's crust is only 0.03-0.1%. Combined sulphur exists primarily as sulphates such as gypsum $CaSO_4.2H_2O$, epsom salt $MgSO_4.7H_2O$, baryte $BaSO_4$ and sulphides such as galena PbS, zinc blende ZnS, copper pyrites $CuFeS_2$. Traces of sulphur occur as hydrogen sulphide in volcanoes. Organic materials such as eggs, proteins, garlic, onion, mustard, hair and wool contain sulphur.

Selenium and tellurium are also found as metal selenides and tellurides in sulphide ores. Polonium occurs in nature as a decay product of thorium and uranium minerals.

Livermorium is a synthetic radioactive element. Its symbol is Lv, atomic number 116, atomic mass 292 and electronic configuration [Rn] $5f^{14}6d^{10}7s^2\ 7p^4$. It has been produced only in a very small amount and has very short half-life (only a small fraction of one second). This limits the study of properties of Lv.

Electronic Configuration:

The valence shell electronic configuration of these elements is ns^2np^4.

Atomic and Ionic Radii	:	O < S < Se < Te < Po
Ionisation Enthalpy	:	O > S > Se > Te > Po (IE_1 values)
Most Negative Electron Gain Enthalpy	:	S > Se > Te > Po > O
Electronegativity	:	O > S > Se > Te > Po
Metallic Character	:	O < S < Se < Te < Po

Melting and Boiling points:

M.P. : O < S < Se < Po < Te

B.P. : O < S < Se < Po < Te

Elemental State:

Oxygen exist as diatomic molecular gas in this case there is pπ – pπ overlap thus two O atoms form double bond O = O. The intermolecular forces in O_2 are weak VB forces. So O_2 exist as gas . On the other hand, other elements of family do not form stable pπ – pπ bonds and do not exist as M_2 molecules. Other atoms are linked by single bonds and form poly atomic complex molecules for

Eg. S – S_8, Se – Se_8

Allotropy:

All element exhibit allotropy for e.g.

Oxygen – O_2 and O_3

Liquid O_2 - pale blue

Solid O_2 - blue

Physical Properties:

(i) Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium and Livermorium are metals.

(ii) Polonium is radioactive and is short lived (Half-life 13.8 days).

(iii) All these elements exhibit allotropy.

(iv) The melting and boiling points increase with an increase in atomic number down the group. The large difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exists as diatomic molecule (O_2) whereas sulphur exists as polyatomic molecule (S_8).

Table: Some Physical Properties of Group 16 Elements

Property	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic mass/g mol^{-1}	16.00	32.06	78.96	127.60	210.00
Electronic configuration	$[He]2s^2 2p^4$	$[Ne]3s^2 3p^4$	$[Ar]3d^{10} 4s^2 4p^4$	$[Kr]4d^{10} 5s^2 5p^4$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$
Covalent radius/(pm[a])	66	104	117	137	146
Ionic radius E^{2-}/pm	140	184	198	221	230[b]
Electron gain enthalpy, /$\Delta_{eg}H$ kJ mol^{-1}	–141	–200	–195	–190	–174
Ionisation enthalpy ($\Delta_i H_1$)/kJ mol^{-1}	1314	1000	941	869	813
Electronegativity	3.50	2.58	2.55	2.01	1.76
Density/g cm^{-3} (298 K)	1.32[c]	2.06[d]	4.19[e]	6.25	–
Melting point/K	55	393[f]	490	725	520
Boiling point /K	90	718	958	1260	1235
Oxidation states*	–2,–1,1,2	–2,2,4,6	–2,2,4,6	–2,2,4,6	2,4

[a]Single bond; [b]Approximate value; [c]At the melting point; [d]Rhombic sulphur; [e]Hexagonal grey; [f]Monoclinic form, 673 K.

* Oxygen shows oxidation states of +2 and +1 in oxygen fluorides OF_2 and O_2F_2 respectively.

Chemical Properties:

Oxidation states and trends in chemical reactivity:

(i) The stability of -2 oxidation state decreases down the group. Polonium hardly shows –2 oxidation state.

(ii) Electronegativity of oxygen is very high, it shows negative oxidation state as –2 except Oxygen shows oxidation states of +2 and +1 in oxygen fluorides OF_2 and O_2F_2 respectively.

(iii) Elements of the group exhibit+ 2, + 4, + 6 oxidation states but + 4 and + 6 are more common.

(iv) Sulphur, selenium and tellurium usually show + 4 oxidation state in their compounds with oxygen and +6 with fluorine.

Anomalous behaviour of oxygen:

The anomalous behaviour of oxygen, like other members of p-block present in second period is due to its small size and high electronegativity. One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in H_2O which is not found in H_2S. The absence of d orbitals in oxygen limits its covalency to four and in practice, rarely exceeds two. On the other hand, in case of other elements of the group, the valence shells can be expanded and covalency exceeds four.

(I) Reactivity with hydrogen:

(i) All the elements of Group 16 form hydrides of the type H_2E (E = O, S, Se, Te, Po).

(ii) Their acidic character increases from H_2O to H_2Te. The increase in acidic character can be explained in terms of decrease in bond enthalpy for the dissociation of H–E bond down the group. Owing to the decrease in enthalpy for the dissociation of H–E bond down the group, the thermal stability of hydrides also decreases from H_2O to H_2Po.

(iii) All the hydrides except water possess reducing property and this character increases from H_2S to H_2Te.

Properties of Hydrides of Group 16 Elements

Property	H_2O	H_2S	H_2Se	H_2Te
m.p./K	273	188	208	222
b.p./K	373	213	232	269
H—E distance /pm	96	134	146	169
HEH angle (°)	104	92	91	90
$\Delta_f H$/kJ $mol^{\ominus 1}$	– 286	– 20	73	100
Δ_{diss} H (H – E)kJ $mol^{\ominus 1}$	463	347	276	238
Dissociation constant[a]	$1.8 \times 10^{\ominus 16}$	$1.3 \times 10^{\ominus 7}$	$1.3 \times 10^{\ominus 4}$	$2.3 \times 10^{\ominus 3}$

[a]Aqueous solution, 298k

(II) Reactivity with oxygen:

(i) All these elements form oxides of the EO_2 and EO_3 types where E = S, Se, Te or Po.

(ii) Ozone (O_3) and sulphur dioxide (SO_2) are gases while selenium dioxide (SeO_2) is solid.

(iii) Reducing property of dioxide decreases from SO_2 to TeO_2; SO_2 is reducing while TeO_2 is an oxidising agent.

(iv) Besides EO_2 type, sulphur, selenium and tellurium also form EO_3 type oxides (SO_3, SeO_3, TeO_3). Both types of oxides are acidic in nature.

(III) Reactivity towards the halogens :

(i) Elements of Group 16 form a large number of halides of the type, EX_6, EX_4 and EX_2 where E is an element of the group and X is a halogen.

(ii) The stability of the halides decreases in the order $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$.

(iii) Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride, SF_6 is exceptionally stable for steric reasons.

Amongst tetrafluorides, SF_4 is a gas, SeF_4 a liquid and TeF_4 a solid. These fluorides have sp^3d hybridisation and thus, have trigonal bipyramidal structures in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as see-saw geometry. All elements except oxygen form dichlorides and dibromides (because they form oxides). These dihalides are formed by sp^3 hybridisation and thus, have tetrahedral structure. The well known monohalides are dimeric in nature. Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given below:

$2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$

Dioxygen:

(a) Laboratory method

(i) By heating oxygen containing salts such as chlorates, nitrates and permanganates.

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

(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.

$2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g)$

$2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$

$2HgO(s) \rightarrow 2Hg(\ell) + O_2(g)$

$2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$

(iii) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.

$$2H_2O_2(aq) \rightarrow 2H_2O(\ell) + O_2(g)$$

(b) Large scale preparation : It can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.

(c) Industrially method : Dioxygen is obtained from air by first removing carbon dioxide and water vapour and then, the remaining gases are liquefied and fractionally distilled to give dinitrogen and dioxygen.

Properties:

(i) Dioxygen is a colourless and odourless gas.

(ii) Its solubility in water is to the extent of 3.08 cm^3 in 100 cm^3 water at 293 K which is just sufficient for the vital support of marine and aquatic life.

(iii) It liquefies at 90 K and freezes at 55 K.

(iv) Oxygen atom has three stable isotopes: ^{16}O, ^{17}O and ^{18}O. Molecular oxygen, O_2 is unique in being paramagnetic inspite of having even number of electrons.

(v) Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases. Its combination with other elements is often strongly exothermic which helps in sustaining the reaction. However, to initiate the reaction, some external heating is required as bond dissociation enthalpy of oxgyen-oxygen double bond is high (493.4 kJ $mol^{\ominus 1}$). Some of the reactions of dioxygen with metals, non-metals and other compounds are as follows :

$2Ca + O_2 \rightarrow 2CaO$

$4Al + 3O_2 \rightarrow 2Al_2O_3$

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

$C + O_2 \rightarrow CO_2$

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Some compounds are catalytically oxidised. For example,

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

Uses:

(i) It's importance in normal respiration and combustion processes, oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel.

(ii) Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering.

(iii) The combustion of fuels, e.g., hydrazines in liquid oxygen, provides tremendous thrust in rockets.

Simple Oxides:

A binary compound of oxygen with another element is called oxide. In many cases one element forms two or more oxides. The oxides vary widely in their nature and properties. Oxides can be simple (e.g., MgO, Al_2O_3) or mixed (Pb_3O_4, Fe_3O_4).

Types of simple oxide : Simple oxides can be classified on the basis of their acidic, basic or amphoteric character.

Acidic oxide : An oxide that combines with water to give an acid is termed acidic oxide (e.g., SO_2, Cl_2O_7, CO_2, N_2O_5). For example, SO_2 combines with water to give H_2SO_3, an acid.

$SO_2 + H_2O \rightarrow H_2SO_3$

As a general rule, only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character (e.g., Mn_2O_7, CrO_3).

Basic oxide : The oxides which give a base with water are known as basic oxides (e.g., Na_2O, CaO, BaO). In general, metallic oxides are basic. For example, CaO combines with water to give $Ca(OH)_2$, a base.

$CaO + H_2O \rightarrow Ca(OH)_2$

Amphoteric oxide:

Some metallic oxides exhibit a dual behaviour. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides. They react with acids as well as alkalies. For example, Al_2O_3 reacts with acids as well as alkalies.

$Al_2O_3(s) + 6HCl(aq) + 9H_2O(\ell) \rightarrow 2[Al(H_2O)_6]^{3\oplus}(aq) + 6Cl^{\ominus}(aq)$

$Al_2O_3(s) + 6NaOH(aq) + 3H_2O(\ell) \rightarrow 2Na_3[Al(OH)_6](aq)$

Neutral oxide:

There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and N_2O.

Ozone:

(i) Ozone is an allotropic form of oxygen and is diamagnetic.

(ii) It is too reactive to remain for long in the atmosphere at sea level. At a height of about 20 kilometres, it is formed from atmospheric oxygen in the presence of sunlight. This ozone layer protects the earth's surface from an excessive concentration of ultraviolet (UV) radiations.

Threats to ozone layer

(i) Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

(ii) Another threat to this ozone layer is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

Preparation:

When a slow dry stream of oxygen is passed through a silent electrical discharge, conversion of oxygen to ozone (10%) occurs. The product is known as ozonised oxygen.

$$3O_2 \rightarrow 2O_3 \quad \Delta H^{\ominus}\,(298\ K) = +142\ kJ\ mol^{\ominus 1}$$

Since the formation of ozone from oxygen is an **endothermic** process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition. If concentration of ozone greater than 10 percent is required, a battery of ozonisers can be used, and pure ozone (b.p. –112.4°C) can be condensed in a vessel surrounded by liquid oxygen.

Illustration 8:

Ozone is thermodynamically unstable with respect to oxygen. Explain?

Solution:

Because its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen.

Note:

$2F_2 + 2H_2O \longrightarrow 4HF + O_2$
$F_2 + 3H_2O \longrightarrow 6HF + O_3$
} Ozonised oxygen } is separated by passing into spiral tube cooled by liq. air. Ozone condenses at –112.4°C.
[b.p. of O_2 –183°C ; b.p. of liq. air is –190°C]

Properties

(i) Pure ozone is a pale blue gas, dark blue liquid and violet-black solid.

(ii) Ozone has a characteristic fishy smell and in small concentrations it is harmless.

Toxic effect:

(a) Toxic enough (more toxic than KCN). It's intense blue colour is due to the absorption of red light.

(b) However, if the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.

Oxidizing properties

It is one of best oxidising agent, in acid solution, its standard, reduction potential value is 2.07 V.

$$O_3 + 2H^{\oplus} + 2e \longrightarrow O_2 + H_2O \quad E^\circ = +2.07\ V$$

It is next to F_2. [above 2.07 V, only F_2, F_2O are there]

It is not really surprising, therefore, high concentrations of ozone can be dangerously explosive. Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent. For example, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.

$$PbS(s) + 4O_3(g) \rightarrow PbSO_4(s) + 4O_2(g)$$

$$2I^{\ominus}(aq) + H_2O(\ell) + O_3(g) \rightarrow 2OH^{\ominus}(aq) + I_2(s) + O_2(g)$$

(i) Metal Sulphides to Sulphates.

$MS + 4O_3 \longrightarrow MSO_4 + 4O_2$ [M = Pb, Cu, Zn, Cd]

(ii) $2HX + O_3 \longrightarrow X_2 + H_2O + O_2$ [X = Cl, Br, I]

(iii) $NaNO_2 + O_3 \longrightarrow NaNO_3 + O_2$

$Na_2SO_3 + O_3 \longrightarrow Na_2SO_4 + O_2$

$Na_2AsO_3 + O_3 \longrightarrow Na_3AsO_4 + O_2$

(iv) Moist S, P, As + $O_3 \Rightarrow$

$S + H_2O + 3O_3 \longrightarrow H_2SO_4 + 3O_2$

$2P + 3H_2O + 5O_3 \longrightarrow 2H_3PO_4 + 5O_2$

$2As + 3H_2O + 5O_3 \longrightarrow 2H_3AsO_4 + 5O_2$

(v) Moist $I_2 \longrightarrow HIO_3$, whereas dry iodine $\longrightarrow I_4O_9$ (yellow)

$I_2 + 5O_3 + H_2O \longrightarrow 2HIO_3 + 5O_2$

$2I_2 + 9O_3 \longrightarrow I_4O_9 + 9O_2$ (I_4O_9 exists as $I^{3\oplus}$ and $3IO_3^{\ominus}$)

(vi) $2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$

$2K_4[Fe(CN)_6] + O_3 + H_2O \longrightarrow 2K_3[Fe(CN)_6] + 2KOH + O_2$

$2FeSO_4 + O_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + O_2 + H_2O$

(vii) (a) $2KI\ (acidified) + O_3 + 2HCl \longrightarrow I_2 + 2KCl + H_2O + O_2$

(b) $2KI\ (neutral) + O_3 + H_2O \longrightarrow \underbrace{I_2 + 2KOH}_{KI+KOI} + O_2$ } O_3 is estimated by this reaction

$KI + KOI + 2HCl \longrightarrow 2KCl + I_2 + H_2O$

$I_2 + 2S_2O_3^{2\ominus} \longrightarrow S_4O_6^{2\ominus} + 2I^{\ominus}$

(c) alk. { $KI + 4O_3 \longrightarrow KIO_4 + 4O_2$

$KI + 3O_3 \longrightarrow KIO_3 + 3O_2$

(viii) Hg loses its fluidity (tailing of Hg)

$2Hg + O_3 \longrightarrow Hg_2O + O_2$

similarly $2Ag + O_3 \longrightarrow \underset{\text{(Brown)}}{Ag_2O} + O_2$

(ix) $BaO_2 + O_3 \longrightarrow BaO + 2O_2$

$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

$Na_2O_2 + O_3 + H_2O \longrightarrow 2NaOH + 2O_2$

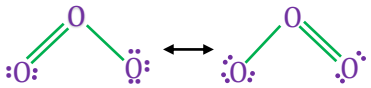
(x) $2KOH + 5O_3 \longrightarrow 2KO_3 + 5O_2 + H_2O$

In all above reaction O_3 gives up O_2 but some reactions are there which consumes all O-atom.

(i) $3SO_2 + O_3 \longrightarrow 3SO_3$

(ii) $3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O$

Bonding in ozone : In ozone the two oxygen-oxygen bond lengths in the ozone molecule are identical (128 pm) and the molecule is angular as expected with a bond angle of about 117°. It is a resonance hybrid of two main forms given below :



Absorbent : (i) Turpentine oil (ii) Oil of cinnamon

Quantitative method for the estimating on Ozone : Ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate.

Uses :

(i) Sterilising water

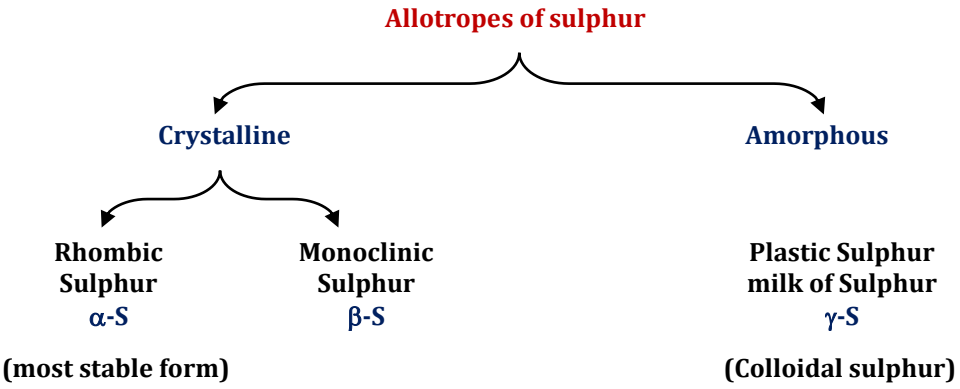
(ii) Detection of position of the double bond in the unsaturated compound.

(iii) It is used as a germicide, disinfectant and for sterilising water.

(iv) It is also used for bleaching oils, ivory, flour, starch, etc.

(v) It acts as an oxidising agent in the manufacture of potassium permanganate.

Allotropic forms of sulphur:

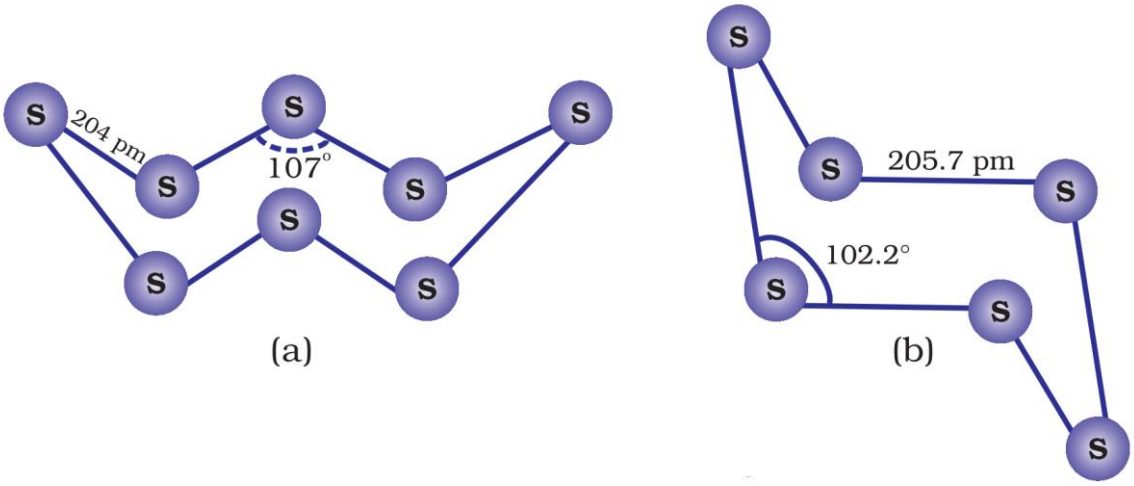


Sulphur forms numerous allotropes of which the yellow rhombic (α-sulphur) and monoclinic (β -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

$$\alpha\text{-sulphur} \underset{<369K}{\overset{>369K}{\rightleftharpoons}} \beta\text{-sulphur}$$

At 369 K both the forms are stable. This temperature is called transition temperature.

Both rhombic and monoclinic sulphur have S_8 molecules. These S_8 molecules are packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape.



The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades. In cyclo-S_6 , the ring adopts the chair form and the molecular dimensions are as shown in Fig. (b). At elevated temperatures (~1000 K), S_2 is the dominant species and is paramagnetic like O_2.

Note:

Viscosity of 'S' with temperature :

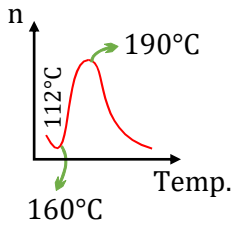
m.p. of 'S' ⟶112.8°C.

> 112.8°C to 160°C ⇒ slow decreases due to

S_8 rings slip and roll over one another easily.

> 160°C, increases sharply due to breaking of

S_8 rings into chains and polymerses into large size chain.



Sulphur dioxide:

Preparation

Sulphur dioxide is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:

$S(s) + O_2(g) \rightarrow SO_2(g)$

laboratory method by treating a sulphite with dilute sulphuric acid.

$SO_3^{2\ominus}(aq) + 2H^{\oplus}(aq) \rightarrow H_2O(\ell) + SO_2(g)$

Other preparation :

$Cu + 2H_2SO_4\ (conc.) \longrightarrow CuSO_4 + 2H_2O + SO_2$

$Hg + H_2SO_4 \longrightarrow HgSO_4 + H_2O + SO_2$

$2Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + H_2O + SO_2$

$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$

$(Charcoal)C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$

$NaHSO_3 + H_2SO_4 \longrightarrow NaHSO_4 + H_2O + SO_2$

Industrial method, by-product of the roasting of sulphide ores.

$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$

The gas after drying is liquefied under pressure and stored in steel cylinders.

Properties

(i) Sulphur dioxide is a colourless gas with pungent smell.

(ii) It is highly soluble in water.

(iii) It liquefies at room temperature under a pressure of two atmospheres and boils at 263 K.

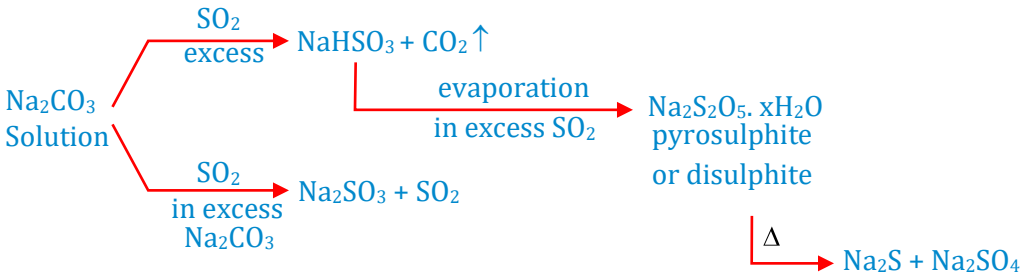
(iv) **Acidic character:** sulphur dioxide, when passed through water, forms a solution of sulphurous acid.

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

It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.

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

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



In its reaction with water and alkalies, the behaviour of sulphur dioxide is very similar to that of carbon dioxide. Sulphur dioxide reacts with chlorine in the presence of charcoal (which acts as a catalyst) to give sulphuryl chloride, SO_2Cl_2. It is oxidised to sulphur trioxide by oxygen in the presence of vanadium(V) oxide catalyst.

$$SO_2(g) + Cl_2(g) \xrightarrow[\text{of charcoal}]{\text{in presence}} SO_2Cl_2(\ell)$$

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

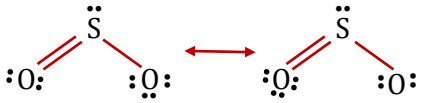
Reducing properties:

When moist, sulphur dioxide behaves as a reducing agent. For example, it converts iron(III) ions to iron(II) ions and decolourises acidified potassium permanganate(VII) solution; the latter reaction is a convenient test for the gas.

$$2Fe^{3\oplus} + SO_2 + 2H_2O \rightarrow 2Fe^{2\oplus} + SO_4^{2\ominus} + 4H^{\oplus}$$

$$5SO_2 + 2MnO_4^{\ominus} + 2H_2O \rightarrow 5SO_4^{2\ominus} + 4H^{\oplus} + 2Mn^{2\oplus}$$

Bonding in SO_2 : The molecule of SO_2 is angular. It is a resonance hybrid of the two canonical forms:



Uses:

(i) It is used for refining petroleum and sugar

(ii) It is used in bleaching wool and silk

(iii) It is used as an anti-chlor, disinfectant and preservative. Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide. Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic chemicals.

Hydrogen Sulphide (H_2S) Sulphurated hydrogen:

Preparation:

By the action of dil. HCl or H_2SO_4 on iron pyrites.

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S\uparrow$$

Note:

Drying agent for this gas : fused $CaCl_2$, Al_2O_3 (dehydrated) P_2O_5 etc. But not H_2SO_4, because

$$H_2SO_4 + H_2S \longrightarrow 2H_2O + SO_2 + S$$

Properties:

It is a colourless gas having an offensive smell of rotten eggs.

(a) It burn in air with blue flame

$$2H_2S + O_2 \longrightarrow 2H_2O + S$$

If the air supply is in excess

$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2$$

(b) It is a mild acid.

$$H_2S \longrightarrow H^{\oplus} + SH^{\ominus}\ ,\ SH^{\ominus} \longrightarrow H^{\oplus} + S^{\ominus 2}$$

(c) It act as a reducing agent. It reduces halogen into corresponding hydroacid.

$$H_2S + X_2 \longrightarrow 2HX + S$$

Tests of H_2S:

(a) Unpleasant odour resembling that of rotten eggs.

(b) It turns lead acetate into paper black

$$(CH_3COO)_2Pb + H_2S \longrightarrow PbS\downarrow\text{(Black)} + 2\,CH_3COOH$$

(c) It gives a violet colouration with a alkaline solution of sodium nitroprusside.

Structure of H_2S:

(a) Similar to structure of water molecule i.e. V– shaped structure with bond length (H–S) 1.35A° and bond angle (H–S–H) is 92.5°

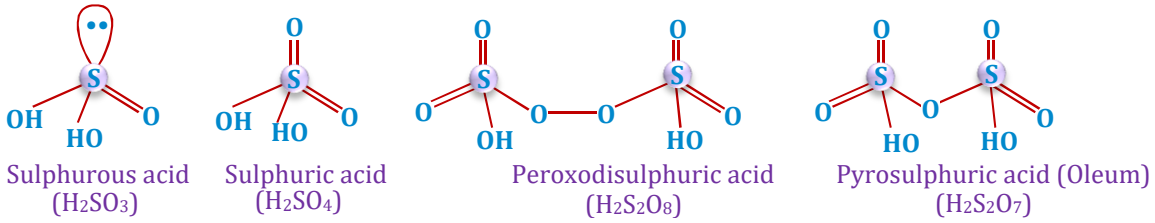
Uses

(a) It is mainly employed in salt analysis for the detection of cation.

(b) Reducing agent for H_2SO_4, $KMnO_4$, $K_2Cr_2O_7$, O_3, H_2O_2, $FeCl_3$

Oxoacids of Sulphur:

Sulphur formss a number of oxoacids such as H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_xO_6$ (x = 2 to 5), H_2SO_4, $H_2S_2O_7$, H_2SO_5, $H_2S_2O_8$. Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the form of their salts. Structures of some important oxoacids are shown in Fig.



Structures of some important oxoacids of sulphur

Sulphuric Acid:

Sulphuric acid is one of the most important industrial chemicals worldwide.

Industrial Manufacturing (Contact process)

Steps involved :

(i) Burning of sulphur or sulphide ores in air to generate SO_2.

(ii) Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5):

The SO_2 produced is purified by removing dust and other impurities such as arsenic compounds. The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

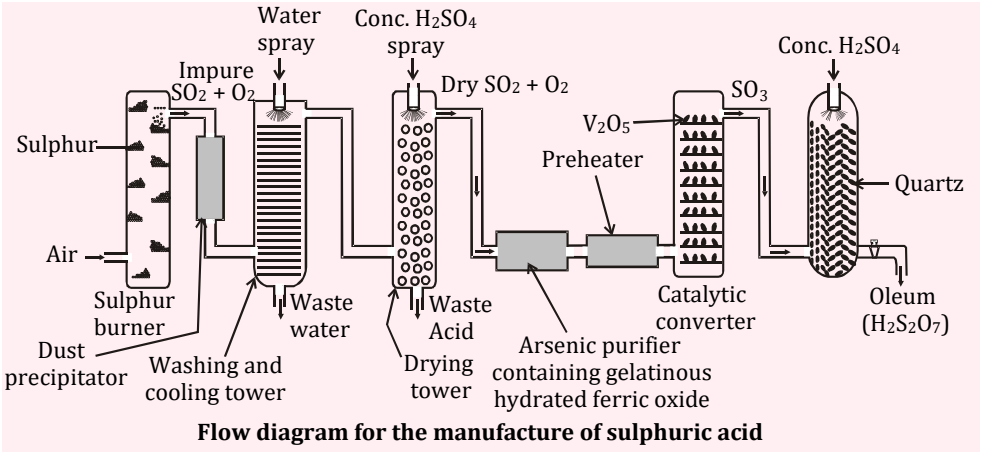
$$2SO_2(g)+O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \qquad \Delta_rH^{\ominus}=-196.6\ kJ\ mol^{\ominus 1}$$

The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low otherwise rate of reaction will become slow. In practice, the plant is operated at a pressure of 2 bar and a temperature of 720 K.

(iii) Absorption of SO_3 in H_2SO_4 to give Oleum ($H_2S_2O_7$) :

The SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce oleum. Dilution of oleum with water gives H_2SO_4 of the desired concentration. In the industry two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (Oleum)



Flow diagram for the manufacture of sulphuric acid

The sulphuric acid obtained by Contact process is 96-98% pure.

P_2O_5 is stronger dehydrating agent than H_2SO_4.

$H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$

Properties

(i) Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K.

(ii) The acid freezes at 283 K and boils at 611 K.

(iii) It dissolves in water with the evolution of a large quantity of heat. Hence, care must be taken while preparing sulphuric acid solution from concentrated sulphuric acid. The concentrated acid must be added slowly into water with constant stirring.

Chemical properties:

The chemical reactions of sulphuric acid are as a result of the following characteristics:

(a) low volatility
(b) strong acidic character
(c) strong affinity for water
(d) ability to act as an oxidising agent.

Acidic character:

In aqueous solution, sulphuric acid ionises in two steps.

$H_2SO_4(aq) + H_2O(\ell) \rightarrow H_3O^{\oplus}(aq) + HSO_4^{\ominus}(aq) : K_{a_1}$ = Very large ($K_{a1} > 10$)

$HSO_4^{\ominus}(aq) + H_2O(\ell) \rightarrow H_3O^{\oplus}(aq) + SO_4^{2\ominus}(aq); K_{a_2} = 1.2 \times 10^{\ominus 2}$

The larger value of Ka_1 ($Ka_1 > 10$) means that H_2SO_4 is largely dissociated into $H^{\oplus}$ and $HSO_4^{\ominus}$. Greater the value of dissociation constant (K_a), the stronger is the acid.

The acid forms two series of salts: normal sulphates (such as sodium sulphate and copper sulphate) and acid sulphates (e.g., sodium hydrogen sulphate). Sulphuric acid, because of its low volatility can be used to manufacture more volatile acids from their corresponding salts.

$$2MX + H_2SO_4 \longrightarrow \underset{(M = Metal)}{2HX} + M_2SO_4 (X = F, Cl, NO_3)$$

Dehydrating Property:

Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compounds; it is evident by its charring action on carbohydrates.

$$C_{12}H_{22}O_{11} \xrightarrow[\text{Conc.}]{H_2SO_4} 12C + 11H_2O$$

$$C_6H_{12}O_6 \xrightarrow[-6H_2O]{H_2SO_4} 6C$$

$$(COOH)_2 \xrightarrow[-H_2O]{H_2SO_4} CO + CO_2$$

$$HCO_2H \xrightarrow[-H_2O]{} CO$$

Oxidizing Nature :

Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2.

$Cu + 2H_2SO_4(conc.) \rightarrow CuSO_4 + SO_2 + 2H_2O$

$HBr\ /HI + H_2SO_4\ (conc.) \rightarrow Br_2/I_2 + SO_2 + H_2O$

$3S + 2H_2SO_4(conc.) \rightarrow 3SO_2 + 2H_2O$

$C + 2H_2SO_4(conc.) \rightarrow CO_2 + 2SO_2 + 2H_2O$

$2P + 5H_2SO_4\ (conc.) \rightarrow H_3PO_4 + 5SO_2$

H_2SO_4 & SO_3 :

$$\overbrace{SO_2 + Cl_2}^{\text{Both gas}} \longrightarrow SO_2Cl_2$$

$$H_2SO_4 + 2PCl_5 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$$

SO_2Cl_2 ↓ good chlorinating agent

Uses :

Sulphuric acid is a very important industrial chemical. A nation's industrial strength can be judged by the quantity of sulphuric acid it produces and consumes. It is needed for the manufacture of hundreds of other compounds and also in many industrial processes. The bulk of sulphuric acid produced is used in the manufacture of fertilisers (e.g., ammonium sulphate, superphosphate). Other uses are in:

(i) petroleum refining
(ii) manufacture of pigments, paints and dyestuff intermediates
(iii) detergent industry
(iv) metallurgical applications (e.g., cleansing metals before enameling, electroplating and galvanising
(v) storage batteries
(vi) in the manufacture of nitrocellulose products and
(vii) as a laboratory reagent.

Sodium Thiosulphate:

Preparation:

(i) Na_2SO_3 solution + S (powder) $\xrightarrow{\text{boiling}} Na_2S_2O_3 \xrightarrow{\text{evaporation}} Na_2S_2O_3.5H_2O$, monoclinic crystal

SO_2 passed: $Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2$; $2NaHSO_3 + Na_2CO_3 \longrightarrow Na_2SO_3 + H_2O + CO_2$

Na_2CO_3 excess

(ii) Na_2SO_4 (Salt cake) + $4C$ (Coke) $\xrightarrow{\text{roasting}} Na_2S + 4CO$

↓ SO_2 passed into it

$Na_2S_2O_3$ $[3SO_2 + 2Na_2S \longrightarrow 2Na_2S_2O_3 + S]$

(iii) $2Na_2S + Na_2CO_3 + 4SO_2 \longrightarrow 3Na_2S_2O_3 + CO_2$

(iv) $6NaOH + 4S \longrightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

$3Ca(OH)_2 + 12\ S \longrightarrow CaS_2O_3 + 2CaS_5 + 3H_2O$

(v) $Na_2SO_3 + Na_2S + I_2 \longrightarrow Na_2S_2O_3 + 2NaI$ (spring reaction)

(vi) $2Na_2S + 2O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2NaOH$

[Na_2S is readily oxidised in air giving rise to $Na_2S_2O_3$]

Properties: (i) $4Na_2S_2O_3 \xrightarrow{\Delta} Na_2S_5 + 3Na_2SO_4$

(ii) $Na_2S_2O_3 + 2H^{\oplus} \longrightarrow H_2S_2O_3 \xrightarrow{\Delta} H_2O + SO_2 + S\downarrow$ (White turbidity)

Reaction: (i) $Na_2S_2O_3 + I_2 \longrightarrow S_4O_6^{2\ominus} + 2I^{\ominus}$

+ Cl_2 – water $\longrightarrow SO_4^{2\ominus} + S + 2HCl$

+ Br_2 – water $\longrightarrow SO_4^{2\ominus} + S + 2HBr$

+ $4OI^{\ominus} + 2OH^{\ominus} \longrightarrow 2SO_4^{2\ominus} + 4I^{\ominus} + H_2O$

+ $4Cl_2 + 5H_2O \longrightarrow \underbrace{Na_2SO_4 + H_2SO_4 + 8HCl}_{2NaHSO_4}$

Halogen family:

Group 17 Elements (F, Cl, Br, I, At, Ts):

These are collectively known as the halogens (Greek halo means salt and genes means born i.e., salt producers). Astatine and tennessine are radioactive elements.

Occurrence:

(i) Fluorine and chlorine are fairly abundant while bromine and iodine less so.

(ii) Fluorine is present mainly as insoluble fluorides (fluorspar CaF_2, cryolite Na_3AlF_6 and fluoroapatite $3Ca_3(PO_4)_2.CaF_2$) and small quantities are present in soil, river water plants and bones and teeth of animals.

(iii) Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but is mainly sodium chloride solution (2.5% by mass).

(iv) The deposits of dried up seas contain these compounds, e.g., sodium chloride and carnallite, $KCl.MgCl_2.6H_2O$. Certain forms of marine life contain iodine in their systems; various seaweeds, for example, contain upto 0.5% of iodine and Chile saltpetre contains upto 0.2% of sodium iodate.

(v) Tennessine is a synthetic radioactive element. Its symbol is Ts, atomic number 117, atomic mass 294 and electronic configuration [Rn] $5f^{14}6d^{10}7s^2\ 7p^5$. Only very small amount of the element could be prepared. Also its half life is in milliseconds only. That is why its chemistry could not be established.

Electronic Configuration:

The electronic configuration of outermost shell 17^{th} group element is (ns^2np^5).

Atomic and ionic radii : F < Cl < Br < I

Ionisation Enthalpy : F > Cl > Br > I

Most Negative Electron Gain Enthalpy : Cl > F > Br > I

It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2p orbitals of fluorine and thus, the incoming electron does not experience much attraction.

Electronegativity : F > Cl > Br > I

Physical Properties:

(i) Their melting and boiling points steadily increase with atomic number.

(ii) All halogens are coloured. For example, F_2 is a yellow gas, Cl_2 greenish yellow gas, Br_2 red liquid and I_2 violet coloured solid. Reason : Decrease in HOMO-LUMO gap.

(iii) Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.

(iv) **Bond energy order ;** $Cl_2 > Br_2 > F_2 > I_2$

A reason for this anomaly is the relatively large electron-electron repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2.

Table: Atomic and Physical Properties of Halogens

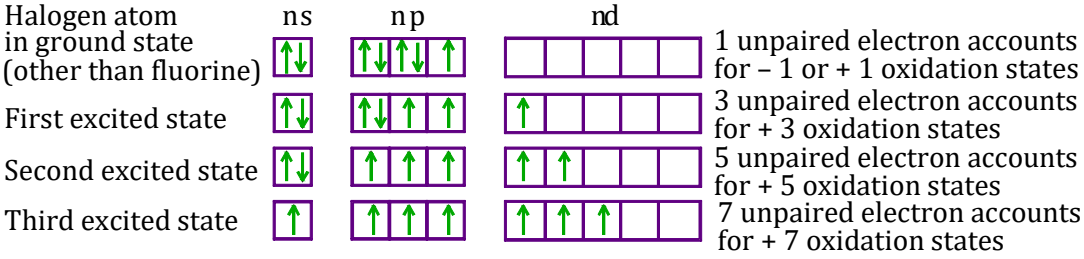
Property	F	Cl	Br	I	At[a]
Atomic number	9	17	35	53	85
Atomic mass/g mol^{-1}	19.00	35.45	79.90	126.90	210
Electronic configuration	$[He]2s^2 2p^5$	$[Ne]3s^2 3p^5$	$[Ar]3d^{10}4s^2 4p^5$	$[Kr]4d^{10}5s^2 5p^5$	$[Xe]4f^{14}5d^{10}6s^2 6p^5$
Covalent radius/pm	64	99	114	133	–
Ionic radius X^-/pm	133	184	196	220	–
Ionisation enthalpy/kJ mol^{-1}	1680	1256	1142	1008	–
Electron gain enthalpy, /kJ mol^{-1}	–333	–349	–325	–296	2.2
Electronegativity[b]	4	3.2	3.0	2.7	–
$\Delta_{Hyd}H(X^-)$/kJ mol^{-1}	515	381	347	305	–
	F_2	**Cl_2**	**Br_2**	**I_2**	**–**
Melting point/K	54.4	172.0	265.8	386.6	–
Boiling point /K	84.9	239.0	332.5	458.2	–
Density/g cm^{-3}	1.5 (85)[c]	1.66(203)[c]	3.19(273)[c]	4.94(293)[d]	–
Distance X–X/pm	143	199	228	266	–
Bond dissociation enthalpy/(kJ mol^{-1})	158.8	242.6	192.8	151.1	–
$E^{\ominus}/V$[e]	2.87	1.36	1.09	0.54	–

[a]Radioactive; [b]Pauling scale; [c]For the liquid at temperatures (K) given in the parentheses; [d]solid; [e]The half-cell reaction is $X_2(g) + 2e^- \rightarrow 2X^-(aq)$.

Chemical Properties:

Oxidation states :

(i) All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit +1, +3, +5 and +7 oxidation states also as explained below :



(ii) The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g., in interhalogens, oxides and oxoacids.

(iii) The oxidation states of +4 and +6 occur in the oxides and oxoacids of chlorine and bromine.

(iv) The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only –1 oxidation state.

Chemical reactivity:

(i) All the halogens are highly reactive.

(ii) They react with metals and non-metals to form halides and the reactivity of the halogens decreases down the group. i.e. the order is $F_2 > Cl_2 > Br_2 > I_2$

(iii) The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. In general, a lower atomic number halogen oxidises halide ions of higher atomic number.

$F_2 + 2X^{\ominus} \rightarrow 2F^{\ominus} + X_2$ (X = Cl, Br or I)

$Cl_2 + 2X^{\ominus} \rightarrow 2Cl^{\ominus} + X_2$ (X = Br or I)

$Br_2 + 2I^{\ominus} \rightarrow 2Br^{\ominus} + I_2$

The decreasing oxidising ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials, which are dependent on the parameters as follows :

$$\frac{1}{2}X_2(g) \xrightarrow{1/2\,\Delta_{diss}H^{\ominus}} X(g) \xrightarrow{\Delta_{eg}H^{\ominus}} X^{-}(g) \xrightarrow{\Delta_{hyd}H^{\ominus}} X^{\ominus}(aq)$$

(1) Reactivity towards water

The relative oxidising power of halogens can further be illustrated by their reactions with water. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reaction of iodine with water is nonspontaneous. In fact, $I^{\ominus}$ can be oxidised by oxygen in acidic medium; just the reverse of the reaction is observed with fluorine.

$2F_2(g) + H_2O(l) \rightarrow 4H^{\oplus}(aq) + 4F^{\ominus}(aq) + O_2(g)$

$X_2(g) + H_2O(l) \rightarrow HX(aq) + HOX(aq)$

(where X = Cl or Br)

$4I^{\ominus}(aq) + 4H^{\oplus}(aq) + O_2(g) \rightarrow 2I_2(s) + 2H_2O(l)$

Note:

Anomalous behaviour of fluorine

(i) Fluorine is anomalous in many properties. For example, ionisation enthalpy, electronegativity, and electrode potentials are all higher for fluorine than expected from the trends set by other halogens. Also, ionic and covalent radii, m.p. and b.p., enthalpy of bond dissociation and electron gain enthalpy are quite lower than expected.

(ii) Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements).

(iii) It forms only one oxoacid while other halogens form a number of oxoacids.

(iv) Hydrogen fluoride is a liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

Reason for the anomalous behaviour of fluorine:

The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of d orbitals in valence shell.

Properties of Hydrogen Halides				
Property	**HF**	**HCl**	**HBr**	**HI**
Melting point/K	190	159	185	222
Boiling point/K	293	189	206	238
Bond length (H – X)/pm	91.7	127.4	141.4	160.9
$\Delta_{diss} H^{\ominus}$/kJ mol^{-1}	57.4	432	363	295
pK_a	3.2	-7.0	-9.5	-10.0

(2) Reactivity towards hydrogen :

They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine. Hydrogen halides dissolve in water to form hydrohalic acids. Some of the properties of hydrogen halides are :

(i) The acidic strength order : HF < HCl < HBr < HI

(ii) The stability order of these halides : H–F > H–Cl > H–Br > H–I.

(3) Reactivity towards oxygen :

(i) Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF_2 and O_2F_2. However, only OF_2 is thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.

(ii) Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7.

(iii) A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br.

(iv) The higher oxides of halogens tend to be more stable than the lower ones.

(v) Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.

(vi) The bromine oxides, Br_2O, BrO_2 , BrO_3 are the least stable halogen oxides (middle row anomally) and exist only at low temperatures. They are very powerful oxidising agents.

(vii) The iodine oxides, 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.

(4) Reactivity towards metals :

Halogens react with metals to form metal halides. For example, bromine reacts with magnesium to give magnesium bromide.

$Mg(s) + Br_2(l) \rightarrow MgBr_2(s)$

The ionic character of the halides decreases in the order MF > MCl > MBr > MI where M is monovalent metal. If a metal exhibits more than one oxidation state, the halides in higher oxidation state will be more covalent than the one in lower oxidation state. For example, $SnCl_4$, $PbCl_4$, $SbCl_5$ and UF_6 are more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$ and UF_4 respectively.

(5) Reactivity of halogens towards other halogens :

Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types XX′ , XX_3', XX_5' and XX_7' where X is a larger size halogen and X′ is smaller size halogen.

Fluorine:

Method of Preparation:

Moissan process : [By electrolysis of KHF_2 (which is obtained from CaF_2)]

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$ { KF decreases the m.p. of the mix. depending upon the composition, due to formation of KHF_2. }

$HF + KF \longrightarrow KHF_2$

$KHF_2 \xrightarrow{\text{Electrolysis}} H_2$ (at cathode) + F_2 (at anode)

Bromine:

$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$

Iodine:

From Sea-weed process : Sea weed $\xrightarrow{\Delta}$ Ash $\longrightarrow$ Iodide dissolved in boiling water $\xrightarrow{H_2O_2\,[O]}$ I_2 $\longrightarrow$ Solvent extraction $\longrightarrow$ Evaporation $\longrightarrow$ Pure I_2

Chlorine:

Chlorine was discovered in 1774 by Scheele by the action of HCl on MnO_2.

In 1810 Davy established its elementary nature and suggested the name chlorine on account of its colour (Greek, chloros = greenish yellow).

Preparation:

(i) By electrolysis of aq. NaCl :

$2NaCl + 2H_2O \longrightarrow 2NaOH + \underset{\text{at cathode}}{H_2} + \underset{\text{(anode)}}{Cl_2}$

$\underset{\text{(Molten)}}{2NaCl} \xrightarrow{\text{Electrolysis}} \underset{\text{(cathode)}}{2Na} + \underset{\text{(anode)}}{Cl_2}$

(ii) By heating manganese dioxide with concentrated hydrochloric acid.

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

However, a mixture of common salt and concentrated H_2SO_4 is used in place of HCl.

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

(iii) By the action of HCl on potassium permanganate.

$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

Manufacture of chlorine:

(i) **Deacon's process :** By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

(ii) **Electrolytic process :** Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode. It is also obtained as a by–product in many chemical industries.

Physical Properties:

(i) It is a greenish yellow gas with pungent and suffocating odour.
(ii) It is about 2-5 times heavier than air.
(iii) It can be liquefied easily into greenish yellow liquid which boils at 239 K.
(iv) It is soluble in water.

Chemical Properties:

Reaction with metals and Non-Metals :

Chlorine reacts with a number of metals and non-metals to form chlorides.

$2Al + 3Cl_2 \rightarrow 2AlCl_3$

$P_4 + 6Cl_2 \rightarrow 4PCl_3$

$2Na + Cl_2 \rightarrow 2NaCl$

$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$

$2Fe + 3Cl_2 \rightarrow 2FeCl_3$

Reaction with hydrogen:

It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.

$H_2 + Cl_2 \rightarrow 2HCl$

$H_2S + Cl_2 \rightarrow 2HCl + S$

$C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C$

Reaction with ammonia:

With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.

$\underset{(excess)}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$

$NH_3 + \underset{(excess)}{3Cl_2} \longrightarrow \underset{(explosive)}{NCl_3} + 3HCl$

Reaction with alkalies:

With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

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

(cold and dilute)

$6\ NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

(hot and conc.)

but on acidification the disproportionated product gives back the same element.

$X^{\ominus} + OX^{\ominus} + 2H^{\oplus} \longrightarrow X_2 + H_2O$

$5X^{\ominus} + XO_3^{\ominus} + 6H^{\oplus} \longrightarrow 3X_2 + 3H_2O$

[X = Cl, Br, I]

Reaction with slaked lime:

With dry slaked lime it gives bleaching powder.

$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$

The composition of bleaching powder is $Ca(OCl)_2.CaCl_2.Ca(OH)_2.2H_2O$.

Note:

In general the average formula of Bleaching power is $CaOCl_2$. or $Ca(OCl)Cl$.

Reaction with hydrocabon

Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons. For example,

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{UV} \underset{\text{Methyl Chloride}}{CH_3Cl} + HCl$$

$$\underset{\text{Ethene}}{C_2H_4} + Cl_2 \xrightarrow{\text{Room temperature}} \underset{\text{1,2-dichloroethane}}{C_2H_4Cl_2}$$

Note:

Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

(i) It oxidises ferrous to ferric and sulphite to sulphate. Chlorine oxidises sulphur dioxide to sulphur trioxide and iodine to iodate. In the presence of water they form sulphuric acid and iodic acid respectively.

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

$Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$

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

$I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$

(ii) It is a powerful bleaching agent; bleaching action is due to oxidation.

$Cl_2 + H_2O \rightarrow 2HCl + [O]$

Coloured substance + [O] $\rightarrow$ Colourless substance

Uses:

(i) Bleaching woodpulp (required for the manufacture of paper and rayon), bleaching cotton and textiles.

(ii) Extraction of gold and platinum.

(iii) Manufacture of dyes, drugs and organic compounds such as CCl_4, $CHCl_3$, DDT, refrigerants, etc.

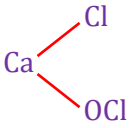
(iv) Sterilising drinking water.

(v) Preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

(vi) It bleaches vegetable or organic matter in the presence of moisture.

Note:

Bleaching effect of chlorine is permanent.

Bleaching Powder : 

Preparation. : $Cl_2(g) + \underset{\text{Slaked lime}}{Ca(OH)_2} \xrightarrow{40°C} Ca(OCl)Cl + H_2O$

(a) On long standing it undergoes

(i) auto oxiation $6Ca(OCl)Cl \longrightarrow Ca(ClO_3)_2 + 5CaCl_2$

(ii) $2Ca(OCl)Cl \xrightarrow[\text{Cat.}]{CoCl_2} 2CaCl_2 + O_2\uparrow$

(iii) $Ca(OCl)Cl + H_2O \longrightarrow Ca(OH)_2 + Cl_2$

Oxidising Properties:

$CaOCl_2 + H_2S \longrightarrow S + CaCl_2 + H_2O$

$CaOCl_2 + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + CaCl_2 + H_2O$

$CaOCl_2 + KNO_2 \longrightarrow CaCl_2 + KNO_3$

$3CaOCl_2 + 2NH_3 \longrightarrow 3CaCl_2 + 3H_2O + N_2$

$CaOCl_2 + 2KI + 2HCl \longrightarrow CaCl_2 + 2KCl + H_2O + I_2$

$CaOCl_2 + 2KI + 2AcOH \longrightarrow CaCl_2 + 2KOAc + H_2O + I_2$

$CaOCl_2 + Na_3AsO_3 \longrightarrow Na_3AsO_4 + CaCl_2$

Reaction with acid:

$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$

$Ca(OCl)Cl + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$

$Ca(OCl)Cl + CO_2 \longrightarrow CaCO_3 + Cl_2$

Note:

ClO_2 does not dimerise because odd electron undergoes delocalisation (in its own vacant 3d-orbital)

Cl_2O_4 ($Cl.ClO_4$) is not the dimer of ClO_2. Actually it is Cl-perchlorate.

Hydrogen Chloride:

(i) Glauber prepared this acid in 1648 by heating common salt with concentrated sulphuric acid.
(ii) Davy in 1810 showed that it is a compound of hydrogen and chlorine.

Preparation:

Laboratory method : it is prepared by heating sodium chloride with concentrated sulphuric acid.

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

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

HCl gas can be dried by passing through concentrated sulphuric acid.

Properties:

(i) It is a colourless and pungent smelling gas. Due to strong affinity for water, conc. HCl pulls moisture of air towards self. The moisture forms droplets of water and hence, cloudy white fumes appear.
(ii) It is easily liquefied to a colourless liquid (b.p.189 K) and freezes to a white crystalline solid (f.p.159 K).
(iii) It is extremely soluble in water
(iv) **Acidic character :** It ionises as follows

$HCl(g) + H_2O(l) \rightarrow H_3O^{\oplus}(aq) + Cl^{\ominus}(aq)$ $K_a = 10^7$

Its aqueous solution is called hydrochloric acid. High value of dissociation constant (K_a) indicates that it is a strong acid in water. It reacts with NH_3 and gives white fumes of NH_4Cl.

$NH_3 + HCl \rightarrow NH_4Cl$

Note:

Aqua regia When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

$Au + 4H^{\oplus} + NO_3^{\ominus} + 4Cl^{\ominus} \rightarrow AuCl_4^{\ominus} + NO + 2H_2O$

$3Pt + 16H^{\oplus} + 4NO_3^{\ominus} + 18Cl^{\ominus} \rightarrow 3PtCl_6^{2\ominus} + 4NO + 8H_2O$

Reaction with salts:

Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogencarbonates, sulphites, etc.

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

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

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

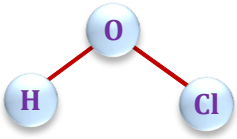
Uses:

(i) It is used in the manufacture of chlorine, NH_4Cl and glucose (from corn starch)
(ii) It is used for extracting glue from bones and purifying bone black
(iii) It is used in medicine and as a laboratory reagent.

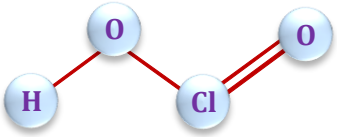
Oxoacids of Halogens:

(i) Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid.
(ii) The other halogens form several oxoacids.
(iii) Most of them cannot be isolated in pure state. They are stable only in aqueous solutions or in the form of their salts.

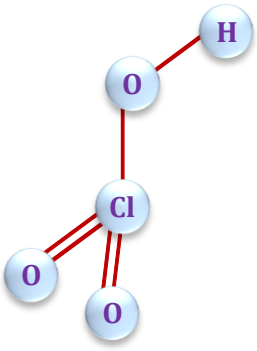
Oxoacids of Halogens				
Halic (I) acid (Hypohalous acid)	**HOF** (Hypofluorous acid)	**HOCl** (Hypochlorous acid)	**HOBr** (Hypobromous acid)	**HOI** (Hypoiodous acid)
Halic (III) acid (Halous acid)	— —	**HOClO** (Chlorous acid)	— —	— —
Halic (V) acid (Halic acid)	— —	**$HOClO_2$** (Chloric acid)	**$HOBrO_2$** (Bromic acid)	**$HOIO_2$** (Iodic acid)
Halic (VII) acid (Perhalic acid)	— —	**$HOClO_3$** (Perchloric acid)	**$HOBrO_3$** (Perbromic acid)	**$HOIO_3$** (Periodic acid)



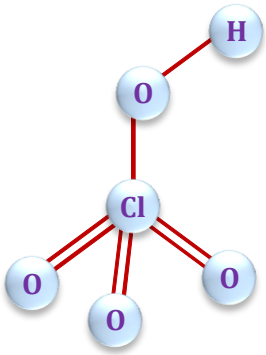
Hypochlorous acid



Chlorous acid



Chloric acid



Perchloric acid

The structures of oxoacids of chlorine

Interhalogen Compounds:

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as XX′ , XX_3', XX_5' and XX_7' where X is halogen of larger size and X′ of smaller size and X is more electropositive than X′. As the ratio between radii of X and X′ increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride should have maximum number of atoms as the ratio of radii between I and F should be maximum. That is why its formula is IF_7 (having maximum number of atoms).

$5IF \longrightarrow IF_5 + 2I_2$ [The overall system gains B.E. by 250 kJ/mol]

There are never more than two halogens in a molecule.

Bonds are essentially covalent and b.p. increases as the E.N. difference increases.

AX_5 & AX_7 type formed by large atoms like Br & I to accommodate more atoms around it.

The interhalogens are generally more reactive than the halogens (except F_2) due to weaker A–X bonds compared toX–X bond.

Preparation:

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions, For e.g.,

$$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{473K} 2ClF$$

$$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573K} 2ClF_3$$

$$\underset{\text{(equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl$$

$$I_2 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow 2ICl_3$$

$$\underset{\text{(diluted with water)}}{Br_2 + 3F_2} \longrightarrow 2BrF_3$$

$$Br_2 + \underset{\text{(excess)}}{5F_2} \longrightarrow 2BrF_5$$

Properties:

Some properties of interhalogen compounds are given in Table below

Some Properties of Interhalogen Compounds			
Type	**Formula**	**Physical stae and colour**	**Structure**
XX'_1	ClF	colourless gas	-
	BrF	pale brown gas	-
	IF[a]	Detected spectroscopically	-
	BrCl[b]	gas	-
	ICl	ruby red solid (α-form)	-
		brown red solid (β-form)	-
	IBr	black solid	
XX'_3	ClF_3	colourless gas	Bent T-shaped
	BrF_3	yellow green liquid	Bent T-shaped
	IF_3	yellow powder	Bent T-shaped
	ICl_3[c]	orange solid	Bent T-shaped
Xx'_5	IF_5	colourless gas but solid below 77 K	square pyramidal
	BrF_5	colourless liquid	square pyramidal
	ClF_5	colourless liquid	square pyramidal
Xx'_7	IF_7	colourless gas	pentagonal bipyramidal

[a]Very unstable; [b]The pure solid is known at room temperature; [c]Dimerises as Cl–bridged dimer (I_2Cl_6)

(i) These are all covalent molecules and are diamagnetic in nature.

(ii) They are volatile solids or liquids at 298 K except ClF which is a gas.

(iii) Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.

(iv) Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because X–X′ bond in interhalogens is weaker than X–X bond in halogens except F–F bond.

(v) All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX′), halite (when XX'_3), halate (when XX'_5) and perhalate (when XX'_7) anion derived from the larger halogen.

$XX' + H_2O \rightarrow HX' + HOX$

Their molecular structures are very interesting which can be explained on the basis of VSEPR theory. The XX'_3 compounds have the bent 'T' shape, XX'_5 compounds square pyramidal and IF_7 has pentagonal bipyramidal structures.

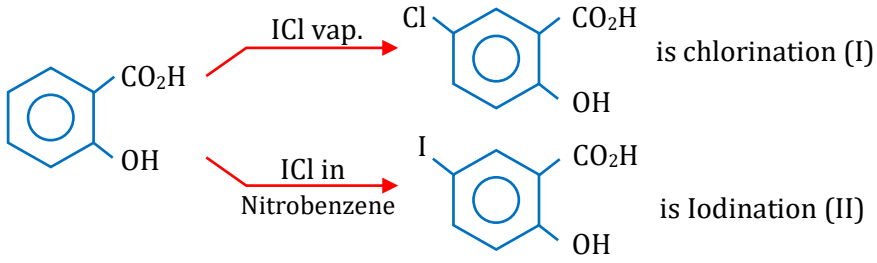
Uses:

(i) These compounds can be used as non aqueous solvents.

(ii) Interhalogen compounds are very useful fluorinating agents. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

$U(s) + 3ClF_3(l) \rightarrow UF_6(g) + 3ClF(g)$

One pecularity with ICl :



Polyhalides:

(i) $KI + I_2 \longrightarrow KI_3$

(ii) $ICl + KCl \longrightarrow K^{\oplus}[ICl_2]^{\ominus}$

(iii) $ICl_3 + KCl \longrightarrow K^{\oplus}[ICl_4]^{\ominus}$

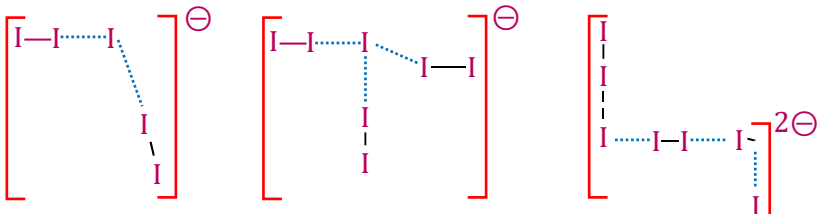
(iv) $IF_5 + CsF \longrightarrow Cs^{\oplus}[IF_6]^{\ominus}$

(v) $ICl + KBr \longrightarrow K^{\oplus}[BrICl]^{\ominus}$

$Rb[ICl_2] \xrightarrow{\Delta} RbCl + ICl$ [not $RbI + Cl_2$]

Here the products on heating depends on the lattice energy of the product halide. The lattice energy of alkali halide with smaller halogen is highest since the interatomic distance is least.

Structure of $I_5^{\ominus}$, $I_7^{\ominus}$, $I_8^{2\ominus}$



Ex. $[N(CH_3)_4]^{\oplus}I_7^{\ominus}$ Ex. Cs_2I_8

$I_3^{\ominus}$, $Br_3^{\ominus}$, $Cl_3^{\ominus}$ are known $Cl_3^{\ominus}$ compounds are very less stable.

Stability order : $I_3^{\ominus} > Br_3^{\ominus} > Cl_3^{\ominus}$ > depends upon the donating ability of $X^{\ominus}$.

NOTE- $F_3^{\ominus} \Rightarrow$ can not form due to absence of vacent orbital.

Pseudo Halogens:

There are univalent ion consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. E.g.

(i) Na-salts are soluble in water but Ag-salts are insoluble in water.

(ii) H-compounds are acids like HX.

(iii) Some anions can be oxidised to give molecules X_2.

Anions :	**Acids**	**Dimer**
$CN^{\ominus}$	HCN	$(CN)_2$
$SCN^{\ominus}$	HSCN(thiocyanic acid)	$(SCN)_2$
$SeCN^{\ominus}$		$(SeCN)_2$
$OCN^{\ominus}$	HOCN (cyanic acid)	
$NCN^{2\ominus}$(Bivalent)	H_2NCN (cyanamide)	
$ONC^{\ominus}$	HONC (Fulminic acid)	
$N_3^{\ominus}$	HN_3 (Hydrazoic acid)	

$CN^{\ominus}$ shows maximum similarites with $Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$

(i) forms HCN

(ii) forms$(CN)_2$

(iii) AgCN, $Pb(CN)_2$, are insoluble

(iv) Interpseudo halogen compounds ClCN, BrCN, ICN can be formed

(v) AgCN is insoluble in H_2O but soluble in NH_3

(vi) forms large no.of complexes.e.g. $[Cu(CN)_4]^{3\ominus}$ & $[CuCl_4]^{\ominus 3}$

Noble gases family:

Group 18 Elements (He, Ne, Ar, Kr, Xe, Rn, Og):

Occurrence:

(i) All the noble gases except radon and oganesson occur in the atmosphere.
Relative abundance : Ar is highest (Ne, Kr, He, Rn, Og)

(ii) Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent.

(iii) Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite.

(iv) The main commercial source of helium is natural gas.

(v) Xenon and radon are the rarest elements of the group.

(vi) Radon is obtained as a decay product of ^{226}Ra.

$$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$

(vii) Oganesson has been synthetically produced by collision of $^{249}_{98}Cf$ atoms and $^{48}_{20}Ca$ ions

$$^{249}_{98}CF + {}^{48}_{20}Ca \longrightarrow {}^{294}_{118}Og + 3n$$

Oganesson has its symbol Og, atomic number 118, atomic mass 294 and electronic configuration [Rn] $5f^{14}6d^{10}7s^27p^6$. Only very small amount of Og has been produced. Its half life is 0.7 milliseconds. Therefore, mainly predictions about its chemistry have been made

(viii) He liquid can exist in two forms. I-form when changes to II-form at λ-point temperature many physical properties change abruptly.

E.g.

(i) Sp. heat changes by a factor of 10

(ii) Thermal conductivity increases by 10^6 and it becomes 800 times faster than Cu

(iii) It shows zero resistance

(iv) It can flow up the sides of the vessel

Illustration 9:

Why 18 group element are termed as noble gas ?

Solution:

All these are gases and chemically unreactive. They form very few compounds. Because of this they are termed noble gases.

Electronic Configuration:

General electronic configuration of 18 group element is ns^2np^6 except helium which has $1s^2$.

Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

Ionisation Enthalpy:

Ionsiation energy decreases down the group with increase in atomic size.

He > Ne > Ar > Kr > Xe > Rn (I.E. order)

Due to stable electronic configuration these gases exhibit very high ionisation enthalpy.

Atomic Radii

Atomic radii increase down the group with increase in atomic number.

He < Ne < Ar < Kr < Xe < Rn (atomic radius order)

Electron Gain Enthalpy:

They have large positive values of electron gain enthalpy due to stable electronic configurations, and there for have no tendency to accept the electron

Melting point and boiling point

$$\underset{\left(-269^{\circ}C\right)}{\underset{\downarrow}{He}} < Ne < Ar < Kr < Xe < Rn \left(\text{Melting point order}\right)$$

B.P. order : He < Ne < Ar < Kr < Xe < Rn (Boiling point order)

Density order :

He < Ne < Ar < Kr < Xe < Rn (Density order)

Physical properties :

(i) All the noble gases are monoatomic.

(ii) They are colourless, odourless and tasteless.

(iii) They are sparingly soluble in water.

(iv) They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces.

(v) Helium has the lowest boiling point (4.2 K) of any known substance.

(vi) It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

Table: Atomic and Physical Properties of Group 18 Elements

Property	He	Ne	Ar	Kr	Xe	Rn*
Atomic number	2	10	18	36	54	86
Atomic mass/g mol^{-1}	4.00	20.18	39.95	83.80	131.30	222.00
Electronic configuration	$1s^2$	$[He]2s^22p^6$	$[Ne]3s^23p^6$	$[Ar]3d^{10}4s^24p^6$	$[Kr]4d^{10}5s^25p^6$	$[Xe]4f^{14}5d^{10}6s^26p^6$
Atomic radius/pm	120	160	190	200	220	–
Ionicsation enthalpy/kJ mol^{-1}	2372	2080	1520	1351	1170	1037
Electron gain enthalpy/kJ mol^{-1}	48	116	96	96	77	68
Density (at STP)/g cm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}
Melting point/K	–	24.6	83.8	115.9	161.3	202
Boiling point /K	4.2	27.1	87.2	119.7	165.0	211
Atmospheric content (% by volume)	5.24×10^{-4}	1.82×10^{-3}	0.934	1.14×10^{-4}	8.7×10^{-6}	–

* *radioactive*

Chemical Properties:

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases except helium ($1s^2$) have completely filled ns^2np^6 electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

Note:

The reactivity of noble gases has been investigated occasionally, In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2^{\oplus}\ PtF_6^{\ominus}$. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 $kJmol^{\ominus 1}$) was almost identical with that of xenon (1170 kJ $mol^{\ominus 1}$). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound $Xe^{\oplus}PtF_6^{\ominus}$ by mixing PtF_6 and xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised. The compounds of krypton are fewer. Only the difluoride (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g., RnF_2) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

Fluorides of xenon:

Preparation

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

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

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

$$XeF_4 + O_2F_2 \xrightarrow{143K} XeF_6 + O_2$$

Physical properties:

XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K.

Chemical properties:

(i) Hydrolysis : They are readily hydrolysed even by traces of water. For example, XeF_2 is hydrolysed to give Xe, HF and O_2.

$2XeF_2(s) + 2H_2O(l) \rightarrow 2Xe\,(g) + 4\,HF(aq) + O_2(g)$

Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

$XeF_6 + 3H_2O \rightarrow XeO_3 + 6\,HF$

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

$XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

Note:

Hydrolysis in alkaline medium

$2XeF_2 + 4OH^{\ominus} \longrightarrow 2Xe + 4F^{\ominus} + 2H_2O + O_2$

$XeF_6 + 7OH^{\ominus} \longrightarrow \underset{\text{Xenate ion}}{HXeO_4^{\ominus}} + 3H_2O + 6F^{\ominus}$

$2HXeO_4^{\ominus} + 2OH^{\ominus} \longrightarrow XeO_6^{4\ominus}\downarrow + Xe + 2H_2O + O_2$

(ii) As fluorinating agents : They are powerful fluorinating agents.

$2SF_4 + XeF_4 \longrightarrow 2SF_6 + Xe$

$Pt + XeF_4 \longrightarrow PtF_4 + Xe$

$NO + XeF_2 \longrightarrow NOF + Xe$

(iii) As fluoride donor

$XeF_2 + MF_5 \longrightarrow [XeF]^{\oplus}\,[MF_6]^{\ominus}(M = As, Sb, P)$

$XeF_6 + BF_3 \longrightarrow [XeF_5]^{\oplus}\,[BF_4^{\ominus}]$

$XeF_6 + HF \longrightarrow [XeF_5]^{\oplus}\,[HF_2]^{\ominus}$

(iv) As Fluoride acceptor

$XeF_6 + MF \longrightarrow M^{\oplus}\,[XeF_7]^{\ominus}$ (M = Na, K, Rb, Cs)

$2Cs^{\oplus}[XeF_7]^{\ominus} \xrightarrow[50°C]{\Delta} XeF_6 + Cs_2[XeF_8]$

$\underset{\text{(alkali metals fluoride)}}{XeF_4} + MF \longrightarrow M^{\oplus} + XeF_5^{\ominus}$

(v) Reaction with SiO_2

SiO_2 also converts XeF_6 into $XeOF_4$

$2XeF_6 + SiO_2 \longrightarrow SiF_4\uparrow + 2XeOF_4$

$XeO_3 + 2XeF_6 \longrightarrow 3XeOF_4$

Similarly, $XeO_3 + XeOF_4 \longrightarrow 2XeO_2F_2$

(vi) Oxidizing properties

H_2 reduces Xe – fluorides to Xe

$XeF_2 + H_2 \longrightarrow Xe + 2HF$ and so on

Xe - fluorides oxidise $Cl^{\ominus}$ to Cl_2 and $I^{\ominus}$ to I_2

$XeF_2 + 2HCl \longrightarrow 2HF + Xe + Cl_2$

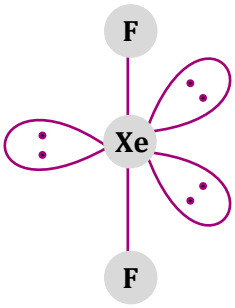
$XeF_4 + 4KI \longrightarrow 4KF + Xe + 2I_2$

Noble gas hydrate (clathrate compound) : Ar, Kr, Xe can form clathrate compounds but He, Ne cannot due to their smaller size.

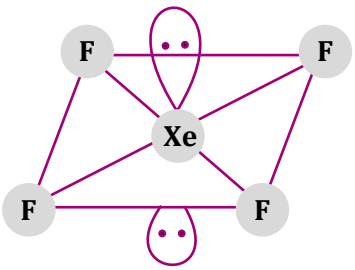
eg. $Xe \bullet 6H_2O$ } formed only when
$Ar \bullet 6H_2O$ } water freezes at high
$Kr \bullet 6H_2O$ } pressure together with noble gas

(a) Structure and bonding:

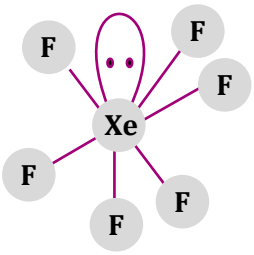
XeF_2 and XeF_4 have linear and square planar structures respectively. XeF_6 has seven electron pairs (6 bonding pairs and one lone pair) and would, thus, have a distorted octahedral structure as found experimentally in the gas phase. Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.



(a) Linear



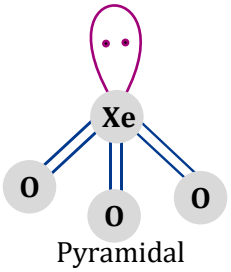
(b) Square plannar



(c) Distorted octahedral

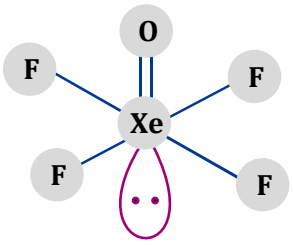
(b) Xenon-oxygen compounds

XeO_3 is a colourless, white hygroscopic explosive solid and has a pyramidal molecular structure.



Pyramidal

$XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure.



Square pyramidal

Uses of helium:

(i) He is a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations.
(ii) It is also used in gas-cooled nuclear reactors.
(iii) It is used in cryoscopy to obtain the very low temperature required for superconductor and laser (b.p. 4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures.
(iv) It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis.
(v) It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood. He is used in preference to N_2 to dil. O_2 in the gas cylinders used by divers. This is because N_2 is quite soluble in blood, so a sudden change in pressure causes degassing and gives bubbles of N_2 in the blood. This causes the painful condition called bends. He is slightly soluble so the risk of bends is reduced.

Uses of Neon:

(i) Ne is used in discharge tubes and fluorescent bulbs for advertisement display purposes.
(ii) Neon bulbs are used in botanical gardens and in green houses.

Uses of Argon:

(i) Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs.
(ii) It is also used in the laboratory for handling substances that are air-sensitive.

Uses of Xenon and Krypton:

There are no significant uses of Xenon and Krypton. They are used in light bulbs designed for special purposes.

Uses of Radon:

Used in radioactive research.
Used in treatment of cancer and other malignant growths.