

General Chemistry – II

Unit – II

P- Block Elements

2.1 Carbon family – Group study – Comparative study of Elements with respect to Valency, Oxides, Halides, Hydrides and Oxyacids – Catenation – Comparison of Properties of Carbon and Silicon – Silicates – Classification and Structure – Silicones – Preparation, Properties and Uses.

2.2 Nitrogen family - Group study – Comparative study of N, P, As, Sb and Bi with respect to Oxides, Oxyacids, Halides and Hydrides – Hydrazine and Hydroxylamine - Preparation, Properties, structure and Uses.

2.3 Oxygen family – Group study – Comparative study of O, S, Se and Te with respect to Catenation, Oxides, Halides, Hydrides and Oxyacids – Anomalous Behaviour of Oxygen – Oxyacids of Sulphur (Structure only) – Peracids of Sulphur – Preparation, Properties and Structure – Differences Between permonosulphuric Acid and Perdisulphuric Acid.

P-BLOCK ELEMENTS - CARBON FAMILY

GENERAL CHARACTERISTICS

ELECTRONIC CONFIGURATION

Element	Atomic No.	Electronic configuration	Valence shell configuration
Carbon	6	[He] $2s^2 2p^2$	$2s^2 2p^2$
Silicon	14	[Ne] $3s^2 3p^2$	$3s^2 3p^2$
Germanium	32	[Ar] $3d^{10} 4s^2 4p^2$	$4s^2 4p^2$
Tin	50	[Kr] $4d^{10} 5s^2 5p^2$	$5s^2 5p^2$
Lead	82	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$	$6s^2 6p^2$

METALLIC CHARACTER

C and Si are non metals, Ge is a metalloid and Sn and Pb are metals.

APPEARANCE

C is black , Si is light-brown, Ge greyish white, Sn and Pb are silvery white.

DENSITY

Density increases with the increase in atomic number due to increase in mass per unit volume.

MELTING POINTS AND BOILING POINTS

The melting points and boiling points decrease from carbon to lead but carbon and silicon have very high melting and boiling points due to their giant structure.

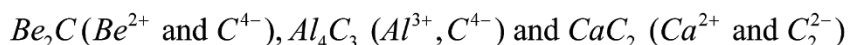
OXIDATION STATES

C	Si	Ge	Sn	Pb
(+2) < +4	(+2) < +4	+2 < +4	+2 < +4	+2 > +4

1. The compounds of Ge and Sn in +2 oxidation state are reducing in nature. Since their higher oxidation states +4 are more stable
2. The compounds of Pb in +4 oxidation state are powerful oxidising in nature. Since +2 oxidation state of Pb is more stable
3. The compounds in +2 oxidation state are ionic in nature and in +4 oxidation state are covalent in nature (Fajan's rule)

NEGATIVE OXIDATION STATES

Carbon forms and in certain compounds e.g.



IONISATION ENERGY

It decreases from C to Sn . For Pb it is slightly higher than Sn.

ELECTRONEGATIVITY VALUES

The values decrease from C to Pb but not in a regular manner probably due to filling of d-orbitals in Ge and Sn and f-orbitals in Pb.

CATENATION

It is the tendency of an element to form long chains of identical atoms. The greater the strength of element-element bond, the greater is the strength of catenation.

Bond	C–C	Si–Si	Ge–Ge	Sn–Sn
Bond kJ/mole	353.3	225.7	167.2	155.0

ALLOTROPY

All the elements except Pb show allotropy.

Allotropic forms of carbon - Diamond, Graphite and Fullerene

Amorphous forms of carbon - coal, charcoal etc.

Silicon (Si) - crystalline and amorphous

Tin (Sn) - grey tin, white tin and rhombic tin

Germanium - two crystalline forms

VALENCY

All elements exhibit tetravalency. In case of Carbon 406 kJ/ mole of energy is required for promotion of 2s electron to 2p. Formation of two extra bonds provide this energy .

INERT- PAIR EFFECT

On descending the group, the stability of +4 oxidation state decreases and that of +2 oxidation state increases.

ATOMIC AND IONIC RADII

Both increase from C to Pb

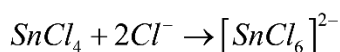
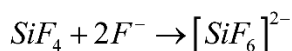
ATOMIC VOLUME

Atomic volume shows a regular increase from C to Pb.

FORMATION OF COMPLEXES

C does not give any complex due to non availability of empty d orbitals in valence shell.

The valence shell of Si and other elements contain d-orbitals and can accommodate more than 8 and can therefore form complexes. e.g.,



The hybridisation in these complexes is which is octahedral.

REACTIVITY

Increases from C to Pb.

MULTIPLE BONDING

Carbon forms $p\pi - p\pi$ multiple bonds with itself and with S, N and O. Other elements show negligible tendency of this type due to their large size. Others form $d\pi - p\pi$ multiple bonds.

FORMATION OF COMPOUNDS

HYDRIDES

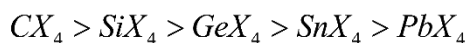
All form covalent hydrides. Their number and ease of formation decreases down the group.

- Hydrides of carbon are known as Alkanes, Alkene or Alkynes.
- Hydrides of Si and Ge are known Silanes and Germanes but their number is limited.
- The only hydrides of Sn and Pb are SnH_4 (Stannane) and PbH_4 (Plumbane).
- Their thermal stability decreases down the group.
- Their reducing character increases down the group.

HALIDES

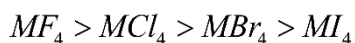
All the elements give tetrahedral and covalent halides of the type MX_4 except $PbBr_4$ and PbI_4 , since PbI_4 is strong oxidising and Br^- and I^- are strong reducing agent. SnF_4 is ionic.

- Stability - Order of thermal stability with common halogen



Order of thermal stability with common metals

2. Hydrolysis - Except other tetrahalides are hydrolysed



Ease of hydrolysis $SiX_4 > GeX_4 > SnX_4 > PbX_4$

CX_4 are not hydrolysed due to absence of vacant d-orbitals in valence shell of carbon.

DIHALIDES

Except carbon other elements form dihalides of the type MX_2 which are more ionic and have higher melting points and boiling points e.g. $SnCl_2$ is a solid whereas $SnCl_4$ is a liquid at room temperature.

C, Si and Ge form trihalides of the type MHX_3 . Pb and Sn do not form trihalides of the type MHX_3

OXIDES

They form two types of oxides

Mono-oxides of the type MO

CO (neutral) and SiO , GeO , SnO , PbO (all basic)

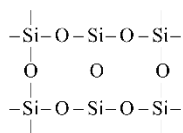
CO forms a number of coordination compounds with transition metals e.g. $Ni(CO)_4$, $Fe(CO)_5$ and $Cr(CO)_6$

Dioxides of the type MO_2

Acidic - CO_2 , SiO_2

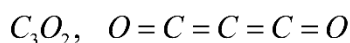
Amphoteric - GeO_2 , SnO_2 and PbO_2

CO_2 is linear, gas at ordinary temperature. Solid CO_2 is known dry ice or drikold. SiO_2 is solid with three dimensional network having Si bonded to four oxygen atoms tetrahedrally and covalently.

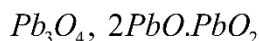


The bond energy of $\text{Si}-\text{O}$ bond is 368 kJ/mol, therefore SiO_2 is chemically inert and has high melting point. GeO_2 , SnO_2 and PbO_2 all are network solids. PbO_2 is a powerful oxidising agent

Carbon also gives **suboxide**



Lead also gives **mixed oxide**

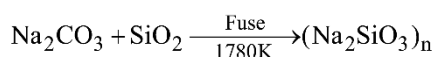


ACIDS

All elements give acids of the type H_2MO_3 e.g. H_2CO_3 (carbonic acid), H_2SiO_3 (silicic acid), H_2SnO_3 (metastannic acid), H_2PbO_3 (meta plumbic acid). Carbonic acid forms two series of salts, bicarbonates (HCO_3^-) and carbonates (CO_3^{--}).

SILICATES

Silicates are metal derivatives of silicic acid H_2SiO_3 and can be obtained by fusing metal oxides or metal carbonates with sand e.g.



TYPE OF SILICATES

Silicates contain tetrahedral formed by sp^3 hybridisation, depending upon the number of O-atoms shared between tetrahedra and fashion, Silicates have been classified into following groups

3. **Orthosilicates** - They contain discrete SiO_4^{4-} tetrahedra, Examples are phenacite Be_2SiO_4 , willimite Zn_2SiO_4 , zircon ZrSiO_4 , forsterite Mg_2SiO_4 .

4. **Pyrosilicates** - Here two tetrahedra units are joined by one oxygen atom forming a large discrete $Si_2O_7^{6-}$. Examples are thortveitite $Se_2(Si_2O_7)$, hemimorphite $Se_2(Si_2O_7)$.

5. **Chain silicates** - Here two oxygen atoms per SiO_4 tetrahedra are shared giving polymeric anion chains. Discrete unit is $(SiO_3^{2-})_n$. Examples: synthetic sodium silicate, Na_2SiO_3 lithium silicate Li_2SiO_3 , natural spodumene $LiAl(SiO_3)_2$, jadeite $NaAl(SiO_3)_2$, enstatite $MgSiO_3$ and diopside $CaMg(SiO_3)_2$.

6. **Double chains** - Here two simple chains are held together by shared oxygen atoms. The discrete unit is $(Si_4O_{11}^{6-})_n$. Example mineral tremolde $Ca_2Mg_5Si_4O_{11}(OH)_2$.

Double chains silicates is also called amphibole

- **Cyclic silicates** - Here two oxygen atoms per SiO_4^{4-} tetrahedra are shared giving discrete unit $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$. Example Beryl $Be_3Al_2Si_6O_{18}$

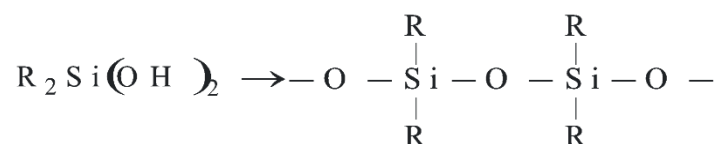
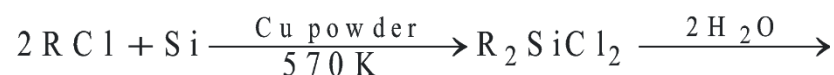
- **Sheet-silicates** - Here three oxygen atoms per tetrahedra are shared giving two dimensional sheet having discrete unit $(Si_2O_5^{2-})_n$. Example

Talc $Mg(Si_2O_5)_2 Mg(OH)_2$, Kaolin $Al_2(OH)_4(Si_2O_5)$.

- **Framework silicates** - Here all four oxygen atoms of each tetrahedra are shared. Example are quartz, zeolites, tridymite and cristobalite.

SILICONES

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



Silicone

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

Comparison between carbon and silicon:

Size

As expected silicon is larger than carbon due to the presence of a second shell: i.e., C = $1s^2 2s^2 2p^2$ while Si = $1s^2 2s^2 2p^6 3s^2 3p^2$. A comparison of the relative sizes of carbon and silicon are given in [Table](#).

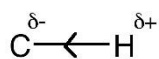
Coordination number

Carbon is known to have a coordination number of 2, 3, and 4 in its compounds depending on the hybridization. A coordination number of 1 can also be considered for CO and CN^- . Four-coordinate carbon may be considered to be coordinatively saturated. In contrast, in the absence of overwhelming steric bulk, silicon is observed to have coordination numbers of 3, 4, 5, and 6. Examples of five and six-coordinate silicon include $\text{Si}(\text{acac})_2\text{Cl}$ and SiF_6^{2-} , respectively. Coordination numbers of higher than 4 have been ascribed to the use of low-lying *d* orbitals; however, calculations show these are not significant. Instead, hypervalent silicon is better described by the formation of 3-center molecular orbitals.

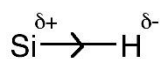
Electronegativity The electronegativities of silicon and carbon are given in [Table](#) along with hydrogen. Since carbon is more electronegative than hydrogen the C-H bond is polarized towards carbon resulting in a more protic hydrogen ([Figurea](#)). In contrast, the lower electronegativity of silicon results in a more hydridic hydrogen ([Figureb](#)). This difference is reflected in the reaction chemistry of SiH_4 versus CH_4 .

Selected Pauling electronegativity values.

Element	Pauling scale
C	2.5
H	2.1
Si	1.8



(a)



(b)

Relative polarization of C-H and Si-H bonds.

Bond energies

The E-E and E-O bond energies for carbon and silicon are given in [Table](#). The bond energy for a C-C bond is slightly greater than for a C-O bond, while the Si-O bond is significantly stronger than the Si-Si bond. This difference is reflected in the chemistry of silicon versus carbon compounds. The chemistry of carbon is dominated by catenation: the ability of a chemical element to form a long chain-like structure via a series of covalent bonds. Although silicon does form Si-Si bonds, they are far more reactive than their C-C analogs, and polymers of silicon are predominantly comprised of Si-O chains (as a result of the very strong bond).

Selected bond energies for carbon and silicon.

Element	E-E bond energy (kJ/mol)	E-O bond energy (kJ/mol)
C	356	335
Si	230	370

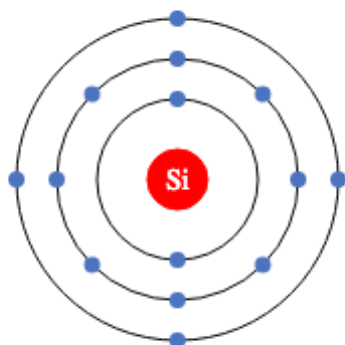
Multiple bonds

While unsaturated compounds for carbon (i.e., alkenes and alkynes) are common, the analogous silicon compounds (disilenes) were only reported in 1981, and disilynes in 2004. The Si=Si double bond lengths are 2.14 - 2.29 Å which is 5 - 10% shorter than the Si-Si single bond lengths. This bond shortening is less than *ca.* 13% in carbon compounds.

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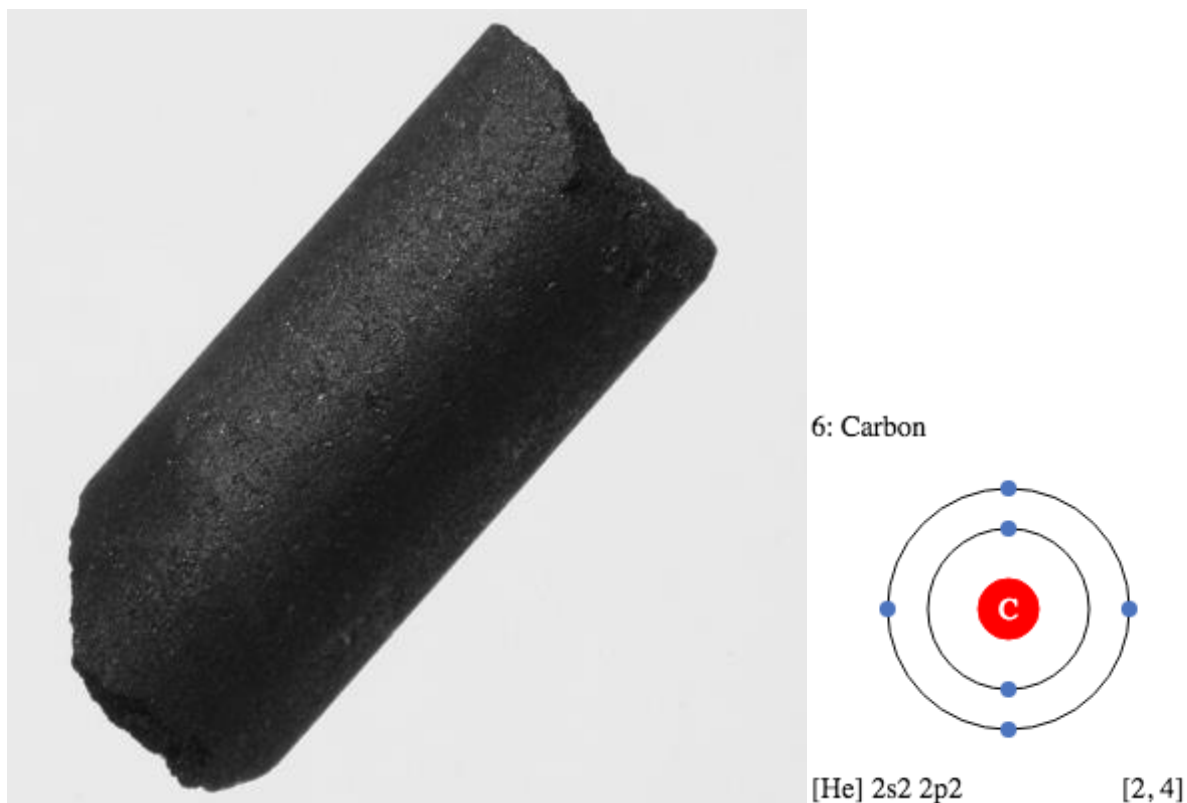
14: Silicon



[Ne] 3s² 3p²

[2, 8, 4]

14 Si Silicon



P-BLOCK ELEMENTS - NITROGEN FAMILY

GENERAL CHARACTERISTICS

The group 15 of the periodic table consists of nitrogen, phosphorous, arsenic, antimony and bismuth. These elements are known as **pnictogens** and their compounds as **pnicomides**.

ELECTRONIC CONFIGURATION

Element	At. No.	Electronic configuration	Valence shell
Nitrogen	7	[He] 2s ² 2p ³	2s ² 2p ³
Phosphorous	15	[Ne] 3s ² , 3p ³	3s ² 3p ³
Arsenic	33	[Ar] 3d ¹⁰ , 4s ² 4p ³	4s ² 4p ³

Antimony	51	[Kr] 4d ¹⁰ , 5s ² 5p ³	5s ² 5p ³
Bismuth	83	[Xe] 4f ¹⁴ , 5d ¹⁰ 6s ² 6p ³	6s ² 6p ³

METALLIC CHARACTER

N, P(non metals), As, Sb(metalloids), Bi(metal)

PHYSICAL STATE

Nitrogen is first element after hydrogen to be a diatomic gas in normal form. All other elements in the group are normally solids.

ATOMICITY

N₂ is diatomic while others are tetra-atomic M₄

MELTING AND BOILING POINTS

The melting point increases from nitrogen to arsenic. The boiling points increase regularly on moving down the group.

DENSITY

Density increases down the group.

ATOMIC RADII

Atomic radii increases with increase in atomic number.

COVALENT RADII

Covalent radii increases in a regular fashion down the group.

ALLOTROPY

All the elements (except bismuth) show allotropy.

Nitrogen - a-nitrogen, b-nitrogen

Phosphorus - white, Red, scarlet, violet, a-black, b-black

Arsenic - Grey, Yellow, Black

Antimony - Metallic, Yellow, Explosive

OXIDATION STATE

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

Nitrogen has a wide range of oxidation states

Oxidation state	Example
+5	N ₂ O ₅ , HNO ₃ ,
+4	NO ₂ , N ₂ O ₄
+3	HNO ₂ , , NF ₃
+2	NO
0	N ₂
-1	NH ₂ OH, NH ₂ F
-2	N ₂ H ₄
-3	NH ₃ , ,

NEGATIVE OXIDATION STATES

-3 oxidation state is exhibited by other elements also. Ca₃P₂, Na₃As, Zn₃Sb₂

INERT PAIR EFFECT

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

IONISATION ENERGY

Ionisation energy of nitrogen is very high due to small atomic radius. The ionisation energy decreases down the group.

ELECTRONEGATIVITY

The electronegativity decreases from nitrogen to bismuth.

CATENATION

They exhibit the property of catenation but due to weak M–M bond to less extent than 14 group elements.

Bond C–C N–N P–P As–As

kJ/mol 353.3 163.7 201.6 147.4

REACTIVITY

Elemental nitrogen is highly unreactive largely because of its strong triple bond. (almost as inert as noble gases).

While phosphorus is extremely reactive and kept in water. It is inflammable and can be ignited at 45°C. It shows green luminescence or glow in dark on account of its slow oxidation. This glow phenomenon is known as phosphorescence.

MULTIPLE BOND FORMATION

Only nitrogen has a tendency to form pp—pp multiple bonds. Others forms dp—pp multiple bonds easily.

COMPOUNDS OF GROUP 15 ELEMENTS

HYDRIDES

All the elements of this group form hydrides of the type MH_3 which are covalent and pyramidal in shape.

Some properties follow the order which are

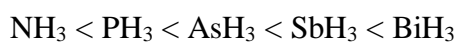
$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Ammonia Phosphine Arsine Stabene Bismuthene

- Ease of formation

- Stability
- Basic character
- Solubility
- Bond angle (NH_3 107.5° ; PH_3 92° , AsH_3 91° , SbH_3 90°)
- Strength of M – H bond
- Dipole moment
- Decomposition temperature

Some properties follow the order



- Reducing character
- Covalent character
- Poisonous character
- Rate of combustion

Boiling points : $\text{BiH}_3 > \text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$

HALIDES

All the elements of this group form trihalides of the type MX_3 and except nitrogen all form pentahalides of the type MX_5

MX_3 M = N, P, As, Sb, Bi and X = F, Cl, Br or I

MX_5 when X = F, M can be P, As, Sb and Bi
when X = Cl, M can be P, As and Sb

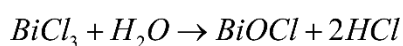
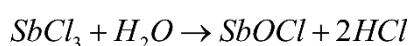
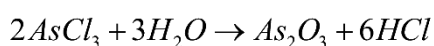
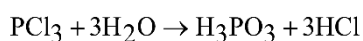
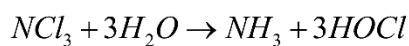
when X = Br, M can be P

NF_3 is a colourless, odourless gas and the most stable of this series. It has low reactivity.

NCl_3 is a yellow oily liquid that reacts with water to form ammonia and hypochlorous acid.

NI₃ is shock sensitive and decomposes explosively when touched.

HYDROLYSIS



- Ease of hydrolysis BiCl₃ > SbCl₃ > AsCl₃ > PCl₃ > NCl₃
- Trihalides except BiF₃ are covalent in nature
- Trihalides have pyramidal structure.

PENTAHALIDES

As nitrogen does not contain vacant d-orbitals in the second shell and cannot expand its outer shell hence it does not form pentahalides.

- The hybridisation in pentahalides is sp³d (trigonal bipyramidal)
- Thermally less stable than trihalides
- Act as Lewis acids $PCl_5 + Cl^- \rightarrow [PCl_6]^-$
- On complete hydrolysis they produce acids $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

OXIDES

All the elements of this group form oxides of the type M₂O₃ and M₂O₅. either by direct combination with O₂ or indirectly.

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

Oxides of P $P_2O_5 (P_4O_{10})$ $P_2O_3 (P_4O_6)$
strongly acidic

Oxides of As As_2O_5 As_2O_3
Amphoteric

Oxides of Sb Sb_2O_5 Sb_2O_3
Amphoteric

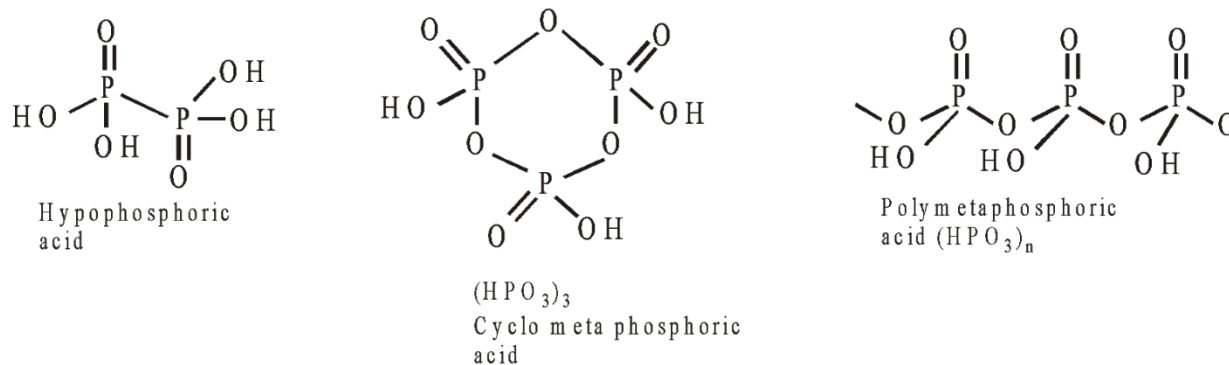
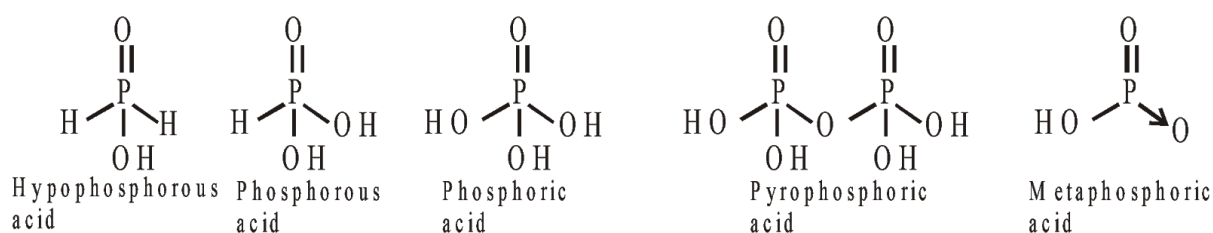
Oxides of Bi Bi_2O_5 Bi_2O_3
Basic

OXYACIDS OF N AND P

Both form a number of oxy acids which are as follows:

		Oxidation number	Basicity
Hyponitrous acid	$H_2N_2O_2$	+1	
Nitroxyl acid	$H_4N_2O_4$	+2	
Nitrous acid	HNO_2	+3	
Nitric acid	HNO_3	+5	
Peroxyntoric acid	HNO_4	+5	
Hydronitrous acid	H_2NO_2	+2	
Hypophosphorus acid	H_3PO_2	+1	1
Phosphorus acid	H_3PO_3	+3	2

Orthophosphoric acid	H_3PO_4	+5	3
Pyrophosphoric acid	$\text{H}_4\text{P}_2\text{O}_7$	+5	4
Meta phosphoric acid	HPO_3	+5	1
Hypophosphoric acid	$\text{H}_4\text{P}_2\text{O}_6$	+4	4

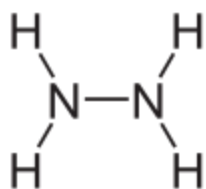


Hydrazine Formula - Hydrazine Uses, Properties, Structure and Formula

Hydrazine Formula

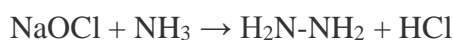
Hydrazine is an inorganic base which is an important reagent in the preparation of many nitrogen compounds.

Formula and structure: The chemical formula of hydrazine is NH_2NH_2 . Its molecular formula is N_2H_4 , and its molar mass is 32.04 g/mol. The chemical structure is shown below, consisting of two NH_2 groups covalently attached. Each of the N-NH_2 groups adopts a pyramidal shape.



Occurrence: Hydrazine is produced naturally by some microorganisms such as yeast, bacteria and fungi, as it is an intermediate in the anaerobic oxidation of ammonia.

Preparation: The commercial production of hydrazine is by the Raschig process, in which sodium hypochlorite solution is treated with excess ammonia to form a chloramine intermediate, which then gives the final hydrazine product along with hydrochloric acid.



It can also be prepared in a related process by using urea ($\text{H}_2\text{N-CO-NH}_2$) instead of ammonia:



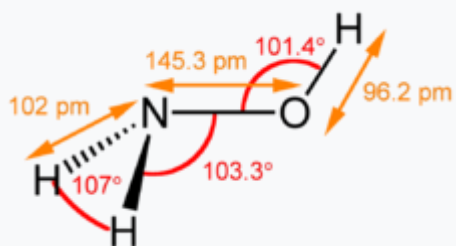
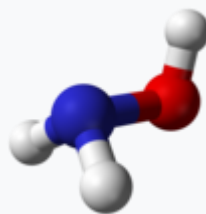
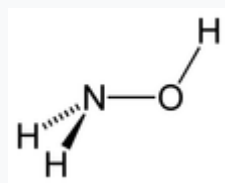
Physical properties: Hydrazine is a colorless and dense liquid with a strong odor of ammonia. It has a density of 1.02 g/mL and a boiling point of 114 °C. It is highly flammable and soluble in water.

Chemical properties: Hydrazine is a highly reactive base and reducing agent, and is widely used in organic synthesis. Hydrazine is a moderate base, while its aqueous solutions are highly alkaline. It reacts violently with oxidants, acids, metals and metal oxides, creating a potential fire and explosion hazard. When heated to decomposition, it emits toxic fumes of nitrogen oxide, ammonia and hydrogen, which can also lead to fires and explosions.

Uses: Hydrazine is used for many industrial applications including preparation of polymer foams, polymerization catalysts, pesticides and the gas used in air bags. Several important pharmaceuticals are based on hydrazine and its derivatives. Hydrazine is also used in various rocket fuels, in power plants, in organic synthesis and in fuel cells as a safer alternative to hydrogen.

Hydroxylamine is an *inorganic compound* with the *formula* NH_2OH . The pure material is a white, unstable *crystalline, hygroscopic* compound. However, hydroxylamine is almost always provided and used as an aqueous solution. It is used to prepare *oximes*, an important functional group. It is also an intermediate in biological *nitrification*. In biological nitrification, the oxidation of NH_3 to hydroxylamine is mediated by the *enzyme ammonia monooxygenase* (AMO). *Hydroxylamine oxidoreductase* (HAO) further oxidizes hydroxylamine to nitrite.

Hydroxylamine



Properties

Chemical formula

NH₂OH

Molar mass

33.030 g·mol⁻¹

Appearance

Vivid white, opaque crystals

Density

1.21 g cm⁻³ (at 20 °C)[2]

Melting point

33 °C (91 °F; 306 K)

Boiling point

58 °C (136 °F; 331 K) /22 mm Hg (decomposes)

<i>log P</i>	-0.758
<i>Acidity (pK_a)</i>	6.03 (NH ₃ OH ⁺)
<i>Basicity (pK_b)</i>	7.97
Structure	
<i>Coordination geometry</i>	Trigonal at N
<i>Molecular shape</i>	Tetrahedral at N
<i>Dipole moment</i>	0.67553 D
Thermochemistry	
<i>Heat capacity (C)</i>	46.47 J K ⁻¹ mol ⁻¹
<i>Std entropy (S^o₂₉₈)</i>	<i>molar</i> 236.18 J K ⁻¹ mol ⁻¹
<p>Uses. Hydroxylamine and its salts are commonly used as reducing agents in myriad organic and inorganic reactions. They can also act as antioxidants for fatty acids</p>	

P – Block element OXYGEN FAMILY

GENERAL CHARACTERISTICS

The elements oxygen, sulphur, selenium, tellurium and polonium belong to group VIA or 16 group of periodic table.

These elements are known as **chalcogens** i.e. ore forming elements.

ELECTRONIC CONFIGURATION

Elements	At.No.	Electronic confg.	Valence shell electronic confg
Oxygen	8	[He]2s ² 2p ⁴	2s ² 2p ⁴
Sulphur	16	[Ne]3s ² 3p ⁴	3s ² 3p ⁴
Selenium	34	[Ar]4s ² 4p ⁴	4s ² 4p ⁴
Tellurium	52	[Kr]5s ² 5p ⁴	5s ² 5p ⁴
Polonium	84	[Xe]6s ² 6p ⁴	6s ² 6p ⁴

The oxygen differs from the rest of the elements due to its-

9. small size
10. higher electronegativity
11. absence of d atomic orbitals in valence shell
12. tendency to form multiple bonding

METALLIC AND NON METALLIC CHARACTER

O S Se Te Po
 └──────────┬──────────┘ └──────────┬──────────┘
 Non metals Metalloids
Metal (Radio active) t_{1/2} 138.4 days

ABUNDANCE

O > S > Se > Te > Po

Oxygen is the most abundant element. It constitutes 46.6% of earth's crust, 21% of air and 89.1% of ocean by weight. Sulphur forms about 0.052% of earth's crust.

DENSITY

Increases down the group regularly.

MELTING POINT AND BOILING POINT

Both show a regular increase down the group due to increase in molecular weight and Van der Waal's forces of attraction.

OXIDATION STATE

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

In OF₂ the oxidation state of oxygen is +2

IONISATION ENERGY

They possess a large amount of ionisation energy which decrease gradually from O to Po due to increase in size of atoms and increase in screening effect.

ELECTRON AFFINITY

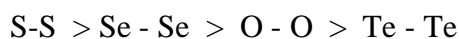
They have high electron affinity which decrease from O to Po. As the size of the atom increases the extra added electron feels lesser attraction by nucleus and electron affinity decreases.

ELECTRONEGATIVITY

It decreases down the group due to decrease in the effective nuclear charge down the group.

CATENATION

The tendency to form chains of identical atoms is known as catenation. It follows the order

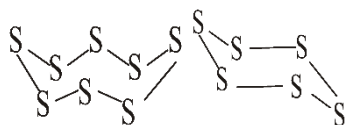


226 172 142 126 kJ/mol

The higher the bond strength, the higher is the catenation.

ATOMICITY

Oxygen is diatomic, sulphur and selenium octa atomic with puckered ring structure



Ring S₆

ALLOTROPY

All the elements exhibit allotropy

Oxygen - O₂ dioxygen and O₃ ozone

Sulphur - Rhombic (or α) sulphur S₈

Monoclinic (or β) sulphur S₈ (most stable)

Plastic (or λ) sulphur open chain

Colloidal (or δ) sulphur

The S_R changes to S_M above 95.4°C.

Selenium Rhombic Se₈, Monoclinic Se₈ (Grey)

Grey is the most stable consisting of regularly arranged spirals of Se atoms.

Tellurium Non metallic, Metallic (more stable)

Polonium α and β both metallic

ATOMIC RADII

Increases regularly from O to Po.

IONIC RADII

Increases regularly from O to Po

ATOMIC VOLUME

Increase regularly from O to Po

MULTIPLE BOND FORMATION

The tendency of these elements to form multiple bonds to C and N decreases down the group
eg. $S = C = S$ is moderately stable.

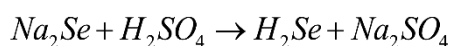
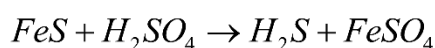
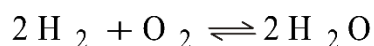
$Se = C = Se$ decomposes readily and

$Te = C = Te$ not known

COMPOUNDS OF SIX GROUP ELEMENTS

HYDRIDES

All these elements form stable hydrides of the type H_2M either by directly combining with hydrogen or by the action of acids on metal sulphides, Selenides and tellurides



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

$H_2O > H_2S > H_2Se > H_2Te$

104.5° 92.5° 91° 90° (all sp^3 hybridised)

← Stability, volatile character (from H_2S to H_2Te)

→ Poisonous nature, acidic character, reducing character.

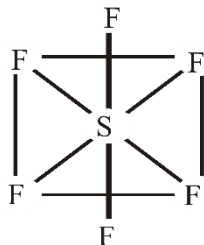
The weakening of $M - H$ bond with the increase in the size of M (not the electronegativity) explains the acid character of hydrides.

HALIDES

All these elements form a number of halides. The halides of oxygen are not very stable eg OF_2 , Cl_2O_7 , I_2O_5 etc.

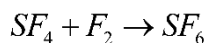
HEXAHALIDES

These are formed by fluorine only (not by Cl, Br, I) where elements exhibit maximum valency of +6. SF_6 , SeF_6 , TeF_6 are colourless gases with sp^3d^2 hybridisation and octahedral structure. These are covalent in nature. Due to bigger size of Cl, Br and I the coordination number of 6 is not achieved.

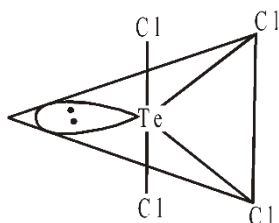


TETRAHALIDES

With the exception of SBr_4 , SI_4 and SeI_4 all tetrahalides are known. SF_4 is gaseous, SeF_4 is liquid and TeF_4 is solid. SCl_4 is unstable liquid. These have lewis acid character.

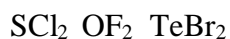


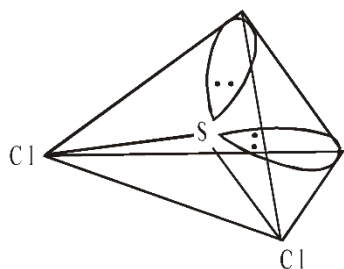
They have trigonal bipyramidal shape with sp^3d hybridization.



DIHALIDES

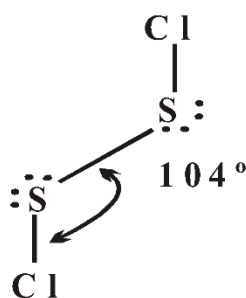
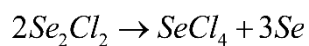
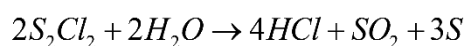
The dihalides eg SCl_2 , OF_2 , $TeBr_2$ are sp^3 , hybridised and have distorted bond angles due to electron pair repulsions





DIMERIC MONOHALIDES

The dimeric monohalides are given by sulphur and selenium eg S_2F_2 , S_2Cl_2 , Se_2Cl_2 , S_2Br_2 , Se_2Br_2 . These are slowly hydrolysed and undergo disproportionation.



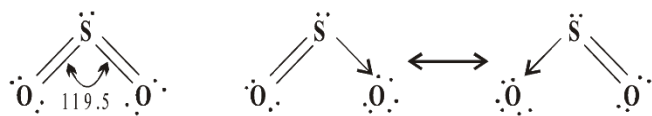
The monohalides have structure similar to H_2O_2 with distorted bond angle of sp^3 hybridisation

OXIDES

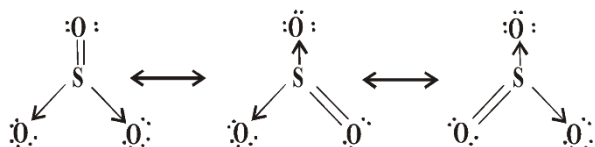
Ozone is considered as oxide of oxygen O. Oxides of other elements are as follows

Element	Mono Oxide	Dioxide	Tri Oxide
S	SO	SO ₂	SO ₃
Se	-	SeO ₂	SeO ₃
Te	TeO	TeO ₂	TeO ₃
Po	PoO	PoO ₂	-

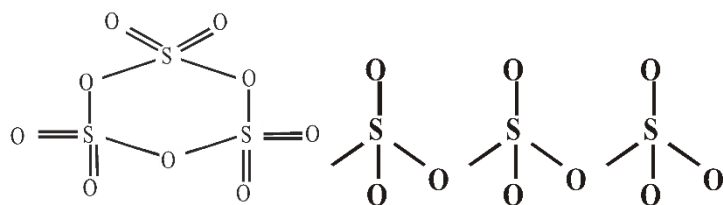
SO_2 is a gas having sp^2 hybridisation and V-shape.



SO_3 is a gas, sp^2 hybridised and planar in nature.

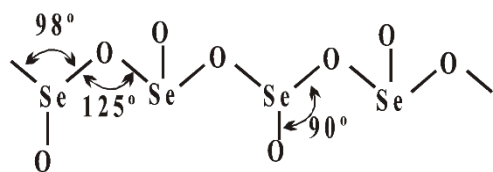


In solid state it exist as a **cyclic trimer** $(\text{SO}_3)_3$ α -form or as a linear chain cross linked sheets

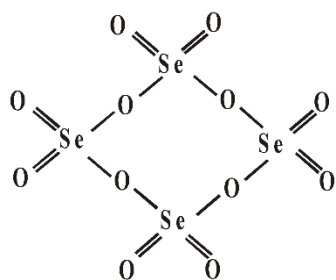


α -form β - and γ - form

SeO_2 volatile solid consists of non planar infinite chains



SeO_3 has tetrameric cyclic structure

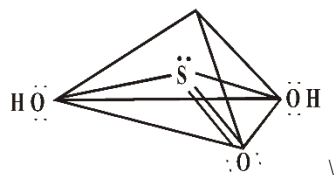


OXY ACIDS

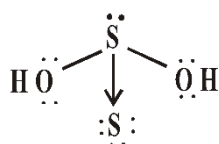
Sulphur forms four series of oxy acids

SULPHUROUS ACID SERIES

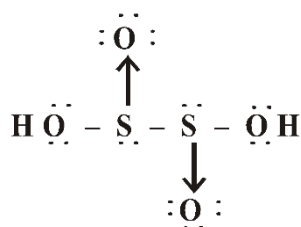
Sulphurous acid (H_2SO_3)



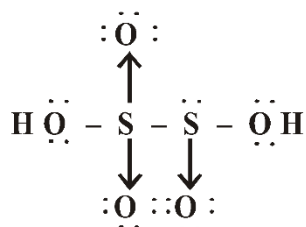
Thiosulphurous acid ($\text{H}_2\text{S}_2\text{O}_2$)



Hyposulphurous acid ($\text{H}_2\text{S}_2\text{O}_4$)

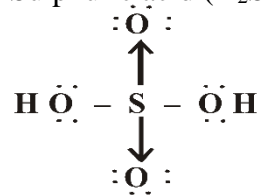


Pyrosulphurous acid ($\text{H}_2\text{S}_2\text{O}_5$)

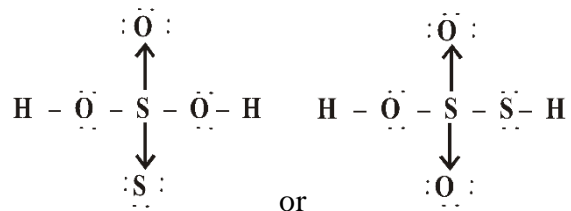


SULPHURIC ACID SERIES

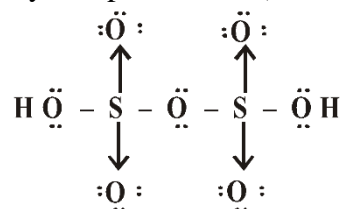
Sulphuric acid (H₂SO₄)



Thiosulphuric acid (H₂S₂O₃)

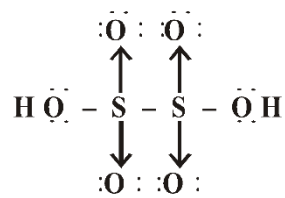


Pyrosulphuric acid (H₂S₂O₇)

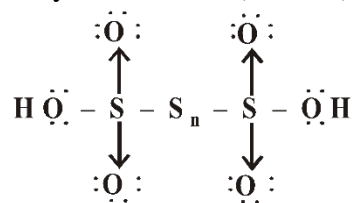


THIONIC ACID SERIES

Dithionic acid (H₂S₂O₆)



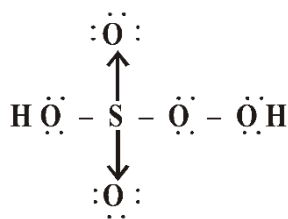
Polythionic acid (H₂S_nO₆)



(n=3, 4, 5H₂S₂O)

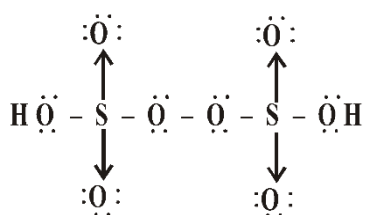
PEROXY ACID SERIES

Peroxomonosulphuric acid (H₂SO₅)



(Caro's Acid)

Peroxodisulphuric acid ($\text{H}_2\text{S}_2\text{O}_8$)



(Marshall's acid)

Oxyacids of Selenium - Selenous acid (H_2SeO_3), Selenic acid (H_2SeO_4)

Oxyacids of Tellurium - Tellurous acid (H_2TeO_3), Telluric acid (H_2TeO_4)

Anomalous behaviour of oxygen

Oxygen forms strong hydrogen bonding in H_2O which is not found in H_2S . Also, the maximum covalency of oxygen is four, whereas in a case of other elements of the group, the valence shells can be expanded and covalency exceeds four.

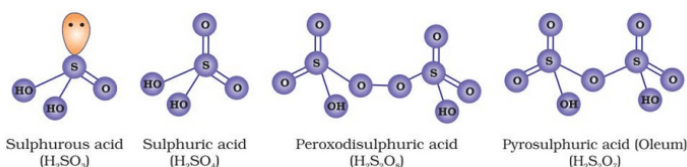
Reasons for the anomalous behaviour of oxygen are:

- Small size and high electronegativity
- Absence of d-orbitals

Oxoacids of Sulphur

Sulphur forms a variety of oxoacids. All oxoacids of sulphur are dibasic.

Sulphur forms a number of oxoacids such as H_2SO_3 , $\text{H}_2\text{S}_2\text{O}_3$, $\text{H}_2\text{S}_2\text{O}_4$, $\text{H}_2\text{S}_2\text{O}_5$, $\text{H}_2\text{S}_x\text{O}_6$ ($x = 2$ to 5), H_2SO_4 , $\text{H}_2\text{S}_2\text{O}_7$, H_2SO_5 , $\text{H}_2\text{S}_2\text{O}_8$. 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 the figure given below



Formula	Name	Important properties	Structural formula
H_2SO_3 (+4)	Sulphurous acid	Free acid does not exist diprotic, strong reducing agent	$\begin{array}{c} \cdot\cdot \\ O = \overset{\cdot\cdot}{S} - OH \\ \\ OH \end{array}$
H_2SO_4 (+6) (Oil of vitriol)	Sulphuric acid	Stable diprotic, dehydrating agent	$\begin{array}{c} O \\ \\ O = S - OH \\ \\ OH \end{array}$
$H_2S_2O_3$ (-2 and +6)	Thiosulphuric acid	Free acid does not exist but its salts e.g. $Na_2S_2O_3$ All quite stable reducing agent	$\begin{array}{c} S \\ \\ O = S - OH \\ \\ OH \end{array}$
$H_2S_2O_4$ (+3)	Dithionous acid		$\begin{array}{c} O \quad O \\ \quad \\ HO - S - S - OH \end{array}$
$H_2S_2O_6$ (+5)	Dithionic acid	Free acid is moderately stable but its salts are quite stable.	$\begin{array}{c} O \quad O \\ \quad \\ O = S - S = O \\ \quad \\ OH \quad OH \end{array}$
$H_2S_2O_7$ (+6) (Oleum)	Disulphuric acid (Pyrosulphuric acid)	Strong oxidising agent	$\begin{array}{c} O \quad O \\ \quad \\ O = S - O - S = O \\ \quad \\ OH \quad OH \end{array}$
H_2SO_5 (+6) (Caro's acid)	Peroxomonosulphuric acid (Its salts known as persulphates)	Stable crystalline solid, powerful oxidising agent	$\begin{array}{c} O \\ \\ HO - S - OOH \\ \\ O \end{array}$
$H_2S_2O_8$ (+6) (Marshals acid)	Peroxodisulphuric acid (its salts are known as disulphates)	Strong oxidising agent.	$\begin{array}{c} O \quad O \\ \quad \\ O = S - O - O - S = O \\ \quad \\ OH \quad OH \end{array}$

Differences between Caro's acid and Marshall's acid

Caro's Acid vs Marshall's Acid		
More Information Online WWW.DIFFERENCEBETWEEN.COM		
	Caro's Acid	Marshall's Acid
DEFINITION	Caro's acid is an inorganic acid containing a sulfate group and a peroxide group	Marshall's acid is an inorganic acid containing two sulfate groups and a peroxide group
STRUCTURAL FORMULA	$\text{HO-O-S(O}_2\text{)-OH}$	$\text{HO}_3\text{S-O-O-SO}_3\text{H}$
COMPOSITION	One sulfate group and one peroxide group	Two sulfate groups and one peroxide group
NAMING	After Heinrich Caro	After Hugh Marshall
USES	Cleaning, disinfection, oxidant, etc.	As a powerful oxidizing agent

Questions

Section A

2mark questions

1. What are Carbon family element? Give examples.
2. Definition: Electronic configuration of Carbon family element.
3. Write short notes on Oxyacids of Carbon family element?
4. Write notes on comparison of carbon and silicon?
5. What is hydrazine?
6. What is hydroxylamine?
7. Write short notes on hydrides of N family?
8. What is Peracids?
9. Comparative study of Oxygen family.
10. Definition: Electronegativity of oxygen.

SectionB

5mark questions

1. Explain the comparative study of carbon family element.
2. Explain comparison of carbon and silicon.
3. Explain the preparation properties structure and uses of hydrazine.
4. Explain the chemical properties of oxygen family element.
5. Explain the Oxyacids of Sulphur.

Section C

10mark questions

1. Discuss about comparative study of carbon family.

2.Explain the comparative study of N family.

3.Explain the comparative study of oxygen family.