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An Initiative by अमरउजाला

16th GROUP ELEMENTS

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O

S

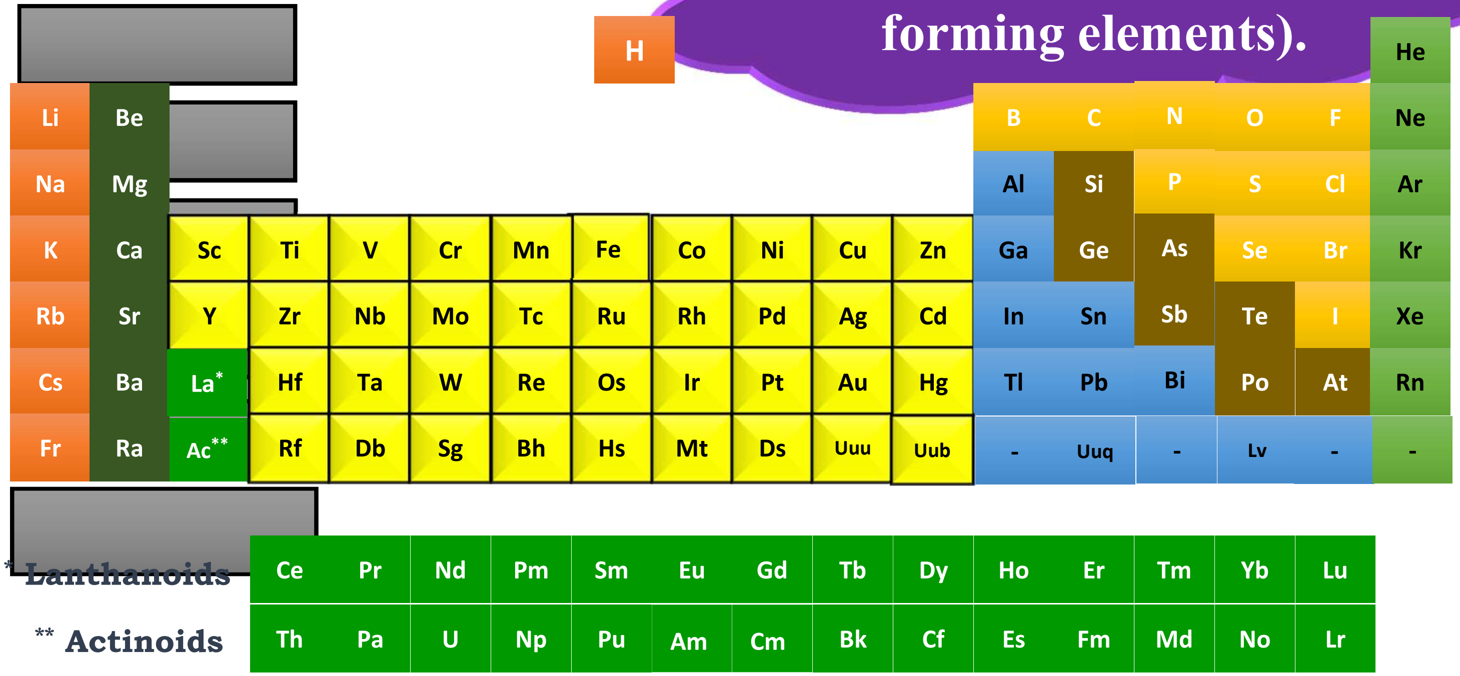
Se

Te

Po

Lv

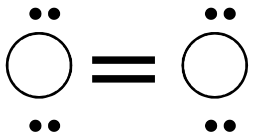
The first four elements are also called as chalcogens (ore forming elements).



							H										He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Uuu	Uub	-	Uuq	-	Lv	-	-
* Lanthanoids			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
** Actinoids			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

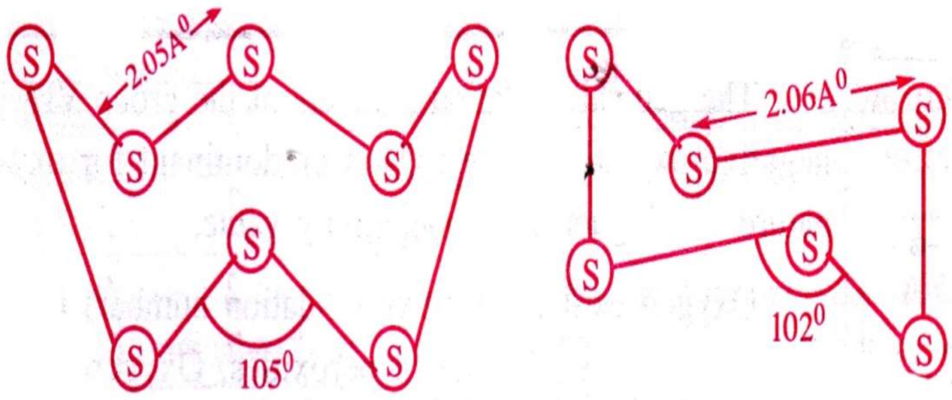
Physical state:

- Oxygen is a gas while others are solids. This is because oxygen exists as diatomic molecule due to its ability to form stable multiple bonds.
- While sulphur, selenium and tellurium exist as puckered 8 atom rings as they are incapable of forming bonds due to large size.



$\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}=\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}$

Physical state:



Puckered ring S_8 molecule

S_6 Chair molecule

Structure of sulphur molecules

Physical state:

- The tendency to exist in 8 atom rings is greatest with sulphur and decreases down the group.
- The special stability of the eight membered rings in sulphur is due to sp^3 -hybridization of sulphur atoms involving both bonding and non-bonding pairs of electrons.
- Above 1000^0c , sulphur exists as S_2 molecule only, which has structure like O_2 .

Metallic and non metallic character:

$$\left.\begin{array}{l}\mathbf{O}\\ \mathbf{S}\end{array}\right\}\text{ Non-metals}$$

$$\left.\begin{array}{l}\mathbf{Se}\\ \mathbf{Te}\end{array}\right\}\text{ Metalloids}$$

P_o ⟶ Radio active element

Physical properties:

The atomic radii of Group 16 elements is smaller than the atomic radii of Group 15 because of increase in the effective nuclear charge.

Atomic radii:

Hence atomic size increases down the group.

O < S < Se < Te < Po

Atomic size

Elements	Elec. Config.	Diagram
O	[He] $2s^2\ 2p^4$	
S	[Ne] $3s^2\ 3p^4$	
Se	[Ar] $3d^{10}\ 4s^2\ 4p^4$	
Te	[Kr] $4d^{10}\ 5s^2\ 5p^4$	

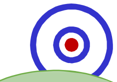
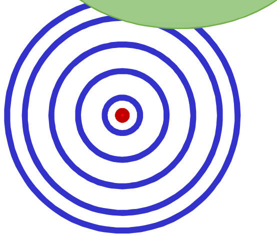
Physical properties: Ionisation energy

- The ionisation energy values decrease gradually on descending the group as the atomic number and size increase.

I.E: O > S > Se > Te > Po

- Ionisation energy values of the group 16 elements are relatively low compared to the Corresponding elements of adjacent group.

Ionization energy

Elements	Elec. Config.	Diagram
O	[He] 2s^2 2p^4	
S	[Ne] 3s^2 3p	
Se	[Ar] 3d	
Te	[Kr] 4d^{10} 5s^2 5p^4	

The energy required to remove a loosely bound electron from the outermost shell of an atom in the gaseous state is called as *ionization energy.*

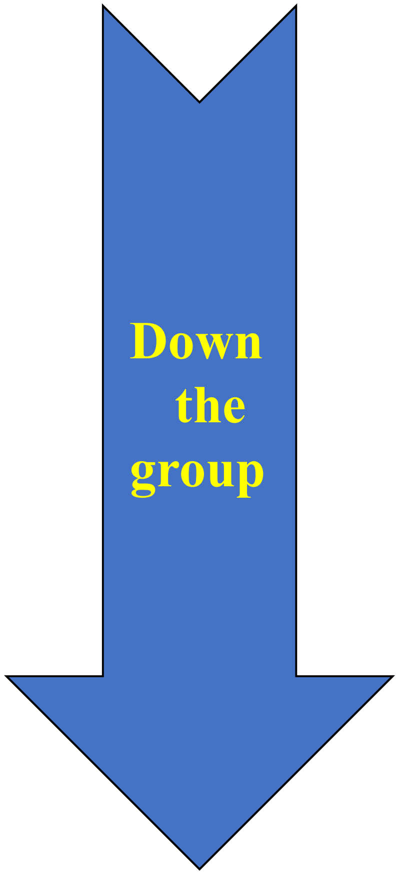
Down the group

At. Number(Z) ↑es

Nucleus size ↑es

Atomic size ↑es

Ionization Energy ↓es



Physical properties:

Electron Gain Enthalpy:

- Group 16 elements have high electron gain enthalpy. On moving from oxygen to sulphur the EA_1 value increases and then decreases from ‘S’ to Po .

S > Se > Te > Po > O

MCQs

1. Decreasing order of atomic radius of 16th group elements is….

a) O > S > Se > Te

b) O < S < Se < Te

[✓ **c) Te > Se > S > O**]

d) Se > Te > S > O

2) Oxygen required more ionization energy than…..

a) N

[✓ b) S]

c) F

d) P

Physical properties:

Electron negativity:

- **Down the group electro negativity decreases due to increase in atomic size. Oxygen is second most electro negative element after Fluorine.**

Po < Te < Se < S < O

Electronegativity

Elements	**Elec. Config.**	**Diagram**	**E.N.**
O	**[He] $2s^2\ 2p^4$**		
S	**[Ne] $3s^2\ 3p^4$**		
Se	**[Ar] $3d^{10}\ 4s^2\ 4p^4$**		
Te	**[Kr] $4d^{10}\ 5s^2\ 5p^4$**		**2.1**

The tendency of an atom in a compound to attract a shared pair of electrons towards itself is called as *electronegativity*.

Down the group

At. Number(Z)	↑es
Nucleus size	↑es
Atomic size	↑es
Electronegativity	↓ es

Down the group

Melting point & Boiling points:

M.P & B.P increase gradually with increase in atomic number but Po has less MP & BP than Te. Because greater inert pair effect van der Waal's forces of attraction will be less when compared with Te.

M.P order: $O < S < Se < Te > Po$

B.P order: $O < S < Se < Te > Po$

The large difference in the melting point of oxygen and sulphur is due to a change from diatomic O_2 to octaatomic S_8 which increases magnitude of van der Waal's forces.

Catenation:

Oxygen & sulphur show the property of catenation. Peroxides & poly sulphides are fairly stable. Catenation ability is second highest for sulphur, after carbon.

Allotropy

All the Group 16 elements exhibit allotropy.

Oxygen	**Oxygen, Ozone**
Sulphur	**Rhombic, Monoclinic, plastic, amorphous**
Selinium	**Red (non-metalic) Grey (Metallic)**
Tellurium	**Crystalline & amorphous**
Polonium	**α and β (Both metallic)**

MCQs

1) As you go down a group, the atomic size______?

a) Decrease

[✓ **b) Increases**]

c) Either (a) or (b)

d) None

2) Down the group, ionization enthalpy _______ ?

[✓ a) Decreases]

b) Increases

c) Either (a) or (b)

d) None

3) ______is the most electronegative element in Group 16th elements?

a) Polonium

b)Tellurium

c) Selenium

[✓ d) Oxygen]

OXIDATION STATES

Oxidation states (O.S.)

Element	+ve O.S.	– ve O.S.
O	+1, +2	– 2, – 1
S	+ 2, +4, +6	– 2
Se	+ 2, +4, +6	– 2
Te	+2, +4, +6	– 2
Po	+2, +4, +6	–

Common oxidation state = -2

Along with -2 except oxygen other elements shows +2,+4,+6

Oxygen shows +ve oxidation state with ‘F’

In OF_2 shows = +2

In O_2F_2 shows = +1

Along with these oxidation states oxygen can exhibit

-1 in peroxides Ex: H_2O_2

-1/2 in superoxides Ex: KO_2

Positive Oxidation State

Oxygen atom in the ground state	2*s* [↑↓]	2*p* [↑↓] [↑] [↑]	There are no d-orbitals excitation not easy
Sulphur atom in the ground state	3*s* [↑↓]	3*p* [↑↓] [↑] [↑]	3d [ ] [ ] [ ] [ ] [ ] Two unpaired electrons account for an oxidation state of +2
Sulphur atom in the first excited state	[↑↓]	[↑] [↑] [↑]	[↑] [ ] [ ] [ ] [ ] Four unpaired electrons account for an oxidation state of +4

Sulphur atom in the second excited state	↑	↑ ↑ ↑	↑ ↑ □ □ □ **Six unpaired electrons account for an oxidation state of + 6**

- **Stability of + 6 O.S decreases down the group due to INERT PAIR EFFECT.**
- **+ 4 compounds exhibit both oxidizing and reducing properties**
- **+ 6 compounds are only oxidizing agents**
- **As +ve O.S. increases, covalent character increases and ionic character decreases.**

E		Example	– Ve O.S.	
		OF_2	– 1	
		O_2F_2	– 2	
	+4	SF_4		

The tendency to show – 2 oxidation state decreases down the group.

Except oxygen, all other elements have vacant d – orbitals.

Po does not show – 2 oxidation state but show +2 state.

The tendency to form +4 oxidation state increases down the group.

Maximum Covalency:

- Maximum covalency of oxygen atom is 4.
- Due to the availability of vacant d orbitals except oxygen of this group shows maximum covalency ‘6’.

In the form of ice, but more number of times it shows 2 due to absence of d-orbitals.

MCQs

1) The stability of +6 states decreases down a group due to _____ effect.

a) Ion pair

b) Reactive pair

[✓ c) Inert pair]

d) None

2) Group 16 elements show _______ oxidation states.

a) +1,+3,-5

b) +1, +2,+5

[✓ c) +2,+4,+6,-2]

d) None

3) An example of O^{1-} is _____.

[✓ a) H_2O_2]

b) H_2O

c) NO_2

d) None

4) Polonium does not show ______ state.

- **a) +2**
- **b) +4**
- **c) +6**
- **[✓ d) -2]**

Chemical properties:

- **The reactivity of Group 16 elements decreases from oxygen to polonium O>S>Se>Te>Po.**

Hydrides:

- The binary compounds of hydrogen with chalcogens are called hydrides.
- General formula is H_2M.

All these hydrides are covalent compounds.

Characteristics of hydrides of group VIA elements

Hydride	Name	M-H bond length	M-H bond energy	Bond angle	Enthalpy of formation	Boiling point
H_2O	Water	$0.97A^0$	498 kJ mol^{-1}	104.5^0	-120 kJ mol^{-1}	373K
H_2S	Hydrogen sulphide	$1.33A^0$	368 kJ mol^{-1}	92.5^0	-10 kJ mol^{-1}	213K

Charaacterisitics of hydrides of group VIA elements

Hydride	Name	M-H bond length	M-H bond enegry	Bond angle	Enthalpy of formation	Boiling point
H_2Se	Hydrogen selenide	$1.48A^0$	289 kJ mol^{-1}	91^0	43 kJ mol^{-1}	231K
H_2Te	Hydrogen telluride	$1.73A^0$	192 kJ mol^{-1}	90^0	77 kJ mol^{-1}	271K

Hydrides: Preparation

H_2O is obtained by burning hydrogen in the atmosphere of oxygen, while H_2S, H_2Se & H_2Te are obtained by the action of acids on sulphides, selenides and tellurides.

$$FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$$

$$Na_2Se + H_2SO4 \longrightarrow Na_2SO_4 + H_2Se$$

The shape of H_2M type hydride is angular and the hybridisation is sp^3 .

Hydrides: Physical state

Water is colourless, odourless liquid while other hydrides are colourless, poisonous gases with bad odours.

Hydrides: Volatility

- Water has low volatility as hydrogen bonding brings association.
- H_2S has high volatility as no hydrogen bonding is present.
- Volatility decreases from H_2S to H_2Te due to increase in molecular masses of the hydrides.

Hydrides: Covalent character

- The electro negativity difference between M and H decreases, the covalent character increases from H_2S to H_2Te.

Hydrides: Thermal stability

Thermal stability depends on M-H bond dissociation energy.

Atomic size increases from H_2O to H_2Te.

∴ The tendency to dissociate M-H bond decreases.

Hydrides	H_2O	H_2S	H_2Se	H_2Te
Δ_{diss}(M-H) kJ mol^{-1}	463	347	276	238

Hydrides: Acidic nature

The aqueous solutions of these hydrides behave as weak acids. The acidic strength increases from H_2O to H_2Te .

Order: $H_2O < H_2S < H_2Se < H_2Te$

Hydrides: Reducing nature

All hydrides, except H_2O, act as reducing agents. The reducing nature increases from H_2O to H_2Te .This is due to weakening of M-*H* bond as the bond length increases with increase of size of M atom.

Order: $H_2O < H_2S < H_2Se < H_2Te$

MCQs

1)The order of boiling point of hydrides of 16th group is…..

a) $H_2O < H_2S < H_2Se < H_2Te$

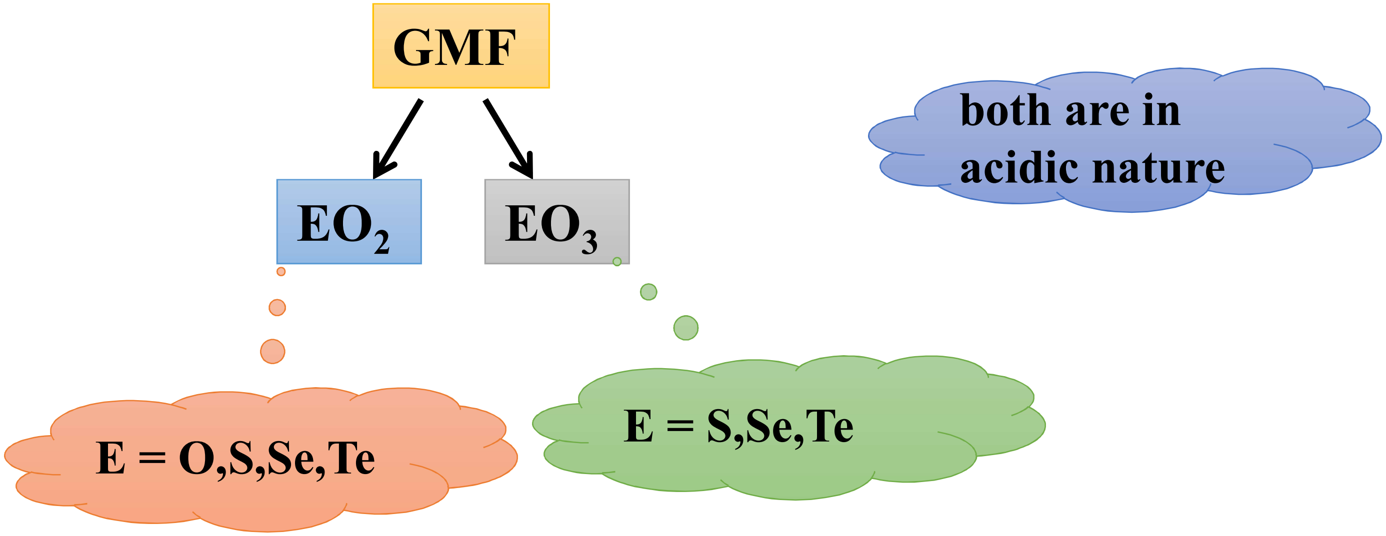
b) $H_2O > H_2S > H_2Se > H_2Te$

[✓ c) $H_2O > H_2Te > H_2Se > H_2S$]

d) $H_2Te > H_2Se > H_2S > H_2O$

Oxides:

Binary compounds of oxygen with 16th group elements are oxides.



GMF

EO_2

EO_3

E = O,S,Se,Te

E = S,Se,Te

both are in acidic nature

Physical state of oxides:

At room temperature

O_3
SO_2
gases

SeO_2
TeO_2
Solid

Reducing properties of oxides:

Decreases from SO_2 to TeO_2

Reducing agent

Oxidising agent

Halides:

Binary compounds of halogens with 16th group elements are halides.

Halides

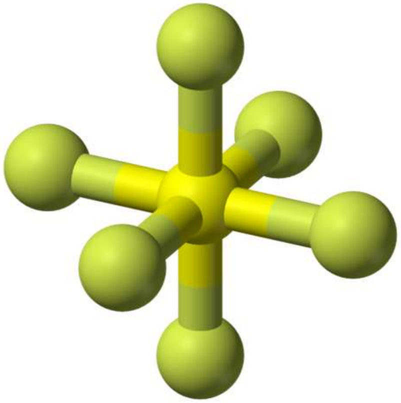
- **E_2X_2**
- **EX_2**
- **EX_4**
- **EX_6**

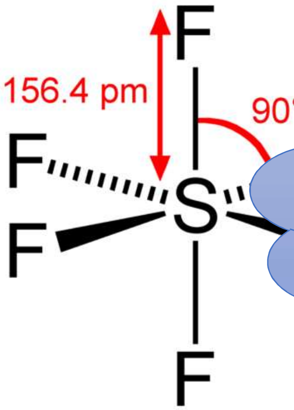
Oxygen forms only O_2F_2 and OF_2

Stability of Halides:

- The stability of halides decreases from F^- to
- Amongst hexa halides, hexa fluorides are the only stable halides.
- All hexa fluorides are gaseous in state with octahedral in shape..

SF_6 is the most stable hexahalide.



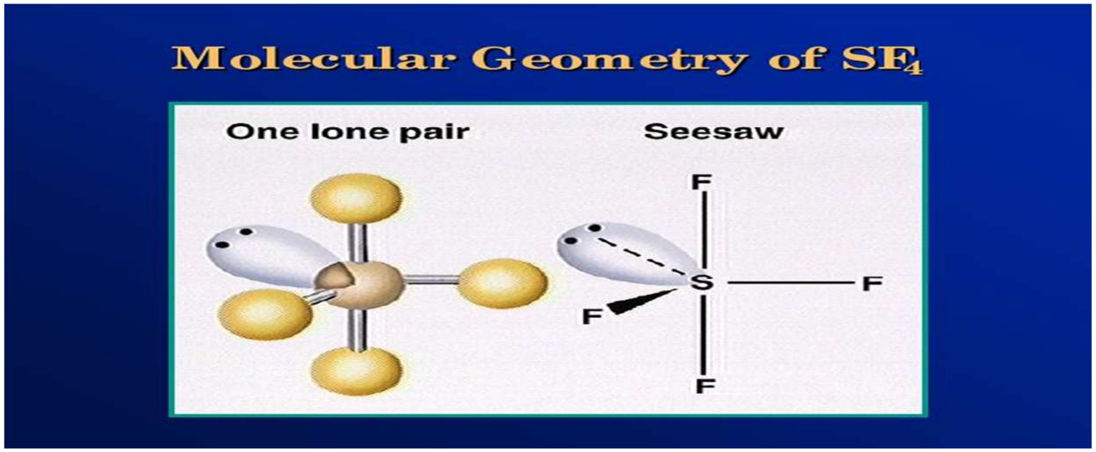


In all hexa halides central atom under goes SP^3d^2 hybridization

Tetra fluorides:

- SF_4 → gas
- SeF_4 → liquid
- TeF_4 → Solid

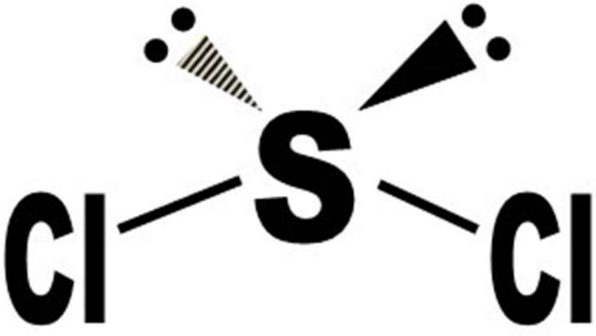
All are have SP^3d hybridation and see-saw in shape



Dihalides:

GMF : MX_2

- **All elements except Se form dichlorides and dibromides.**
- **These are SP^3 hybridised with angular in shape.**



Mono Halides:

It is a dimeric form of mono halides

GMF : M_2X_2

Ex: S_2F_2, S_2Cl_2, S_2Br_2, $SeCl_2$ and Se_2Br_2

All mono halides under goes disproportionation reaction

Ex:

$$2SeCl_2 \rightarrow SeCl_4 + 3Se$$

MCQs

1) The hybridisation of ‘S’ in SF_4

a) SP_3

[✓ b) SP^3d]

c) dSP^2

d) SP^3d_2

Four types of oxides based on nature

Types of Oxides	Reactivity of oxides	Examples of Oxide
Basic Oxide	Neutralise hydrochloric acid	Na_2O, K_2O, MgO, CaO, CrO, CuO, Ti_2O,Fe_2O_3
Acidic Oxide	Neutralise caustic soda solution	B_2O_3, CO_2, NO_2, P_4O_6, P_4O_{10}, SO_2, SO_3, Cl_2O, Cl_2O_7
Amphoteric oxide	Neutralise hydrochloric acid as well as caustic soda solution	Ge_2O_3, Sb_4O_6, TeO_2, Al_2O_3, BeO, ZnO, SnO_2, PbO_2

SULPHUR

Occurrence of sulphur

	Types	Examples
i)	Sulphides	copper pyrites (Cu_2S), iron pyrites (FeS_2), zinc blende (ZnS), cinnabar (HgS), galena (PbS), etc
ii)	Sulphates	Gypsum ($CaSO_4.2H_2O$), Epsom salt ($MgSO_4$ $.7H_2O$), Barytes ($BaSO_4$), Glauber's ($Na_2SO_4.10H_2O$), etc.

ALLOTROPIC FORMS OF SULPHUR

It exists in several allotropic forms.

- **All these are non-metallic.**

Allotropes of sulphur are :

(a) α- Sulphur or Rhombic sulphur

(b) β- Sulphur or monoclinic sulphur or prismatic sulphur.

(c) γ- Monoclinic sulphur.

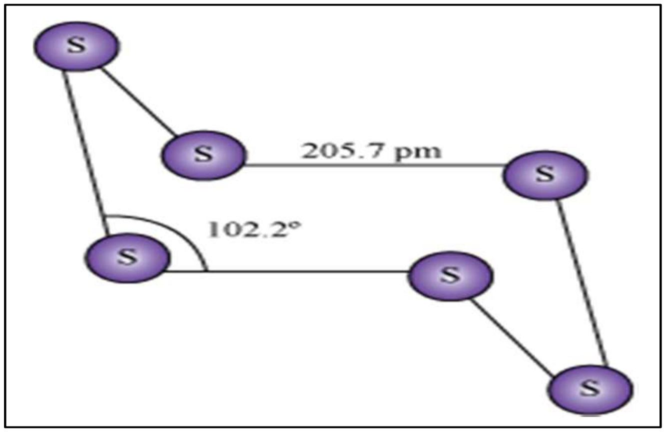
(d) χ- Sulphur or plastic sulphur.

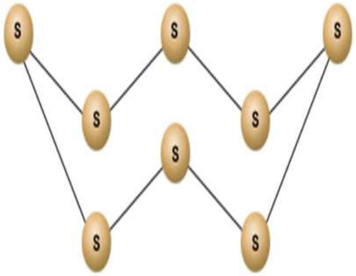
α and β sulphur are most important

ALLOTROPIC FORMS OF SULPHUR

α,β and γ Forms of sulphur are crystalline in nature and possess puckered ring structures (S_8) (crown configuration)

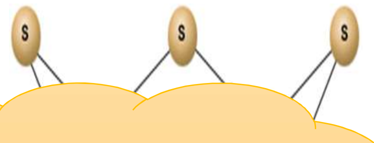
It also exist in S_6 form(chair form)





i) Rhombic sulphur

Roll sulphur $\xrightarrow[CS_2]{\text{evapouration}}$ Rhombic sulphur



Insoluble in water, readily soluble in CS
extent in benzene, alcohol and ethers.

M.P: 385.8K and
specific gravity: 2.06

It is the most common and most stable form of Sulphur.

It is also called as α-sulphur or octahedral sulphur.

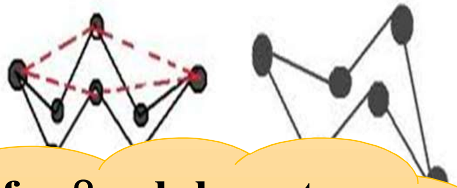
Eight sulphur atoms in a molecule form puckered ring in a crown shape.

ii) Monoclinic

M.P: 392K and
specific gravity: 1.98

Rhombic

ii) coo



Heating of α,β sulpher at
1000k S_2 is formed
which is paramagnetic
nature like O_2.

It is also called as β-sulphur or prismatic s

Below 369 K, it exists as α-sulphur

Above 369 K, it exists as β-sulphur

At 369 K, both α-sulphur and β-sulphur are stable.

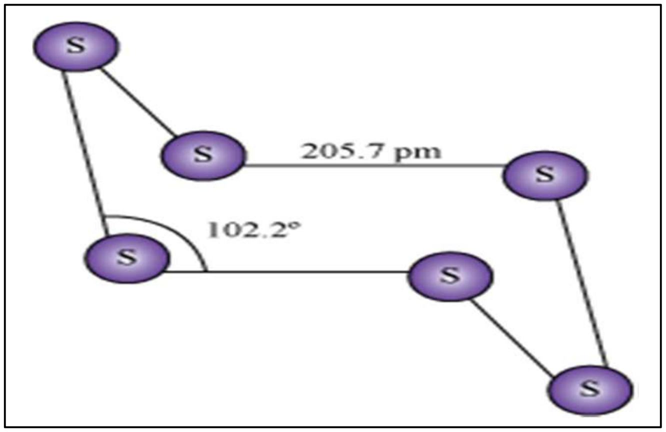
Therefore, 369K is called the transition temperature.

iii) Cyclo–S_6 sulphur

The ring has a chair form.

S-S bond length is 207.7pm

The bond angle is 102.2^0



iv) Small S_n molecular sulphur

These are unstable.

They exist in the form of sulphur vapours as S_2 and S_3 molecules.

S_3 has Cherry red colour.

S_2 has violet colour.

MCQs

1. ______ sulphur is the most stable form of sulphur.

a) Monoclinic

[✓ b) Rhombic]

c) Colloidal

d) None of these

2. ________ is the transition temperature of monoclinic sulphur.

[✓ a) 369K]

b) 359K

c) 319K

d) None of these

PREPARATION OF SULPHUR DIOXIDE

Preparation Sulphur dioxide

$$S_8 + 8O_2 \xrightarrow{\Delta} 8SO_2$$

Stored in steel cylinders

Laboratory method

$$Cu_{(s)} + 2H_2SO_4 \longrightarrow CuSO_{4(aq)} + 2H_2O_{(l)} + SO_{2(g)}$$

$$Na_2SO_{3(aq)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + 2H_2O_{(l)} + SO_{2(g)}$$

Industrial method

$$4FeS_{2(s)} + 11O_2 \xrightarrow{\Delta} 2Fe_2O_3 + 8SO_2$$

SO_2 as a reducing agent

$I_2 + 2H_2O + SO_2 \longrightarrow 2HI + H_2SO_4$

$\underset{\text{orange}}{K_2Cr_2O_7} + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{\text{green}}{Cr_2(SO_4)_3} + H_2O$

$2FeCl_3 + SO_2 + 2H_2O \longrightarrow 2FeCl_2 + H_2SO_4 + 2HCl$

$5SO_2 + 2KMnO_4 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

Properties:

- Colourless gas
- Pungent smell
- Highly soluble in water
- It is a anhydride of H_2SO_3 (sulphurous acid)

$$SO_{2\,(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3\,(aq)}$$

Chemical properties:

due to intermediate oxidation state H_2SO_3 acts as both reducing agent and oxidising agent

SO_2 as an oxidizing agent

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S\downarrow$$

$$4FeCl_2 + SO_2 + 4HCl \longrightarrow 4FeCl_3 + 2H_2O + S\downarrow$$

Action of NaOH on SO_2

$$2NaOH + SO_2 \longrightarrow Na_2SO_3$$

sodium sulphite

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

Sodium Hydrogen sulphite

Action of Cl_2 on SO_2

$$SO_{2(g)} + Cl_{2(g)} \longrightarrow SO_2Cl_{2(l)}$$

sulphuryl chloride

Action of O_2 on SO_2

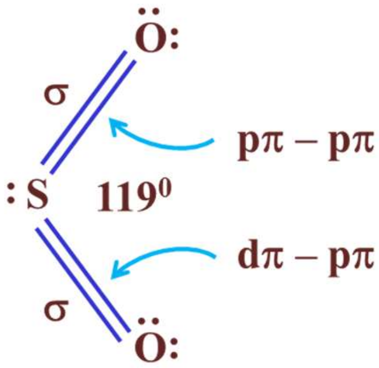
$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$$

Structure of SO_2 molecule :

- SO_2 molecules have a bent shaped structure with O – S – O bond angle of 119°.
- Sulphur in SO_2 is sp^2 hybridized forming three hybrid orbitals. Due to lone pair electrons, bond angle is reduced from 120° to 119°.
- In the structure, each oxygen atom is bonded to sulphur by a σ and π bond.

Structure of SO_2 molecule :

- The σ bonds between S and O are formed by sp^2 – p overlapping.
- One of π bonds arises from pπ – pπ overlapping while other from dπ – pπ overlap.
- Both of the S – O bonds are identical.



MCQs

1) $4\,FeS_2 + 11\,O_2 \longrightarrow 2$ ____________ + 8 ____________.

a) Fe_3O_4, SO_3

b) FeO, SO_2

[✓ c) Fe_2O_3, SO_2]

d) none of these

2) $SO_2 + Cl_2 \longrightarrow$ ______________

a) $SOCl_2$

[✓ **b)** SO_2Cl_2]

c) S_2Cl_2

d) none of these

3) SO_2 is a /an _________ agent.

a) oxidizing

b) reducing

[✓ c) both (a) and (b)]

d) none of these

4) **Sulphur in SO_2 is ________hybridized.**

a) sp^3

b) sp

c) dsp^2

[✓ d) sp^2]

OXOACIDS OF SULPHUR

Oxoacids of Sulphur

- **Among VI A group elements, S, Se and Te form oxyacids.**
- **The oxoacids of sulphur are more numerous.**
- **The oxoacids of sulphur are classified into four series**
  - **a) Sulphurous acid series**
  - **b) Sulphuric acid series**
  - **c) Thionic acid series**
  - **d) Peroxy acid series**

Oxoacids of Sulphur

- The hybridisation of ‘S’ in all oxyacids is Sp^3
- Oxoacids of Sulphur with S – S linkage are called thioacids.
- Salt of Caro’s acid is called permonosulphate and salt of Marshall’s acid is perdisulphate or persulphate.

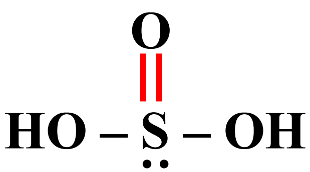
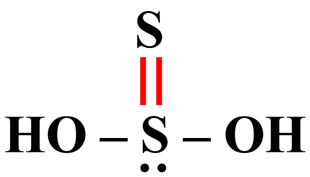
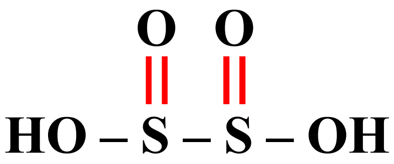
  Basicity of all oxo acids of sulphur is 2.
- Distillation of $H_2S_2O_8$ with water gives H_2SO_5 which on further hydrolysis gives H_2O_2

- **Hybridization of sulphur in**

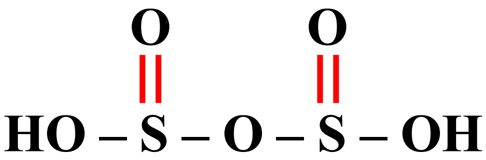
  SO_3^{-2}, SO_4^{-2}, $S_2O_3^{-2}$, $S_2O_4^{-2}$ ions is Sp^3

- **Hypo reduces cupric salts to cuprous salts and auric salts to aurous salts. The formulae of complex compounds formed in these reactions are $Na[Cu_6(S_2O_3)_5]$ and $Na_3[Au(S_2O_3)_2]$**

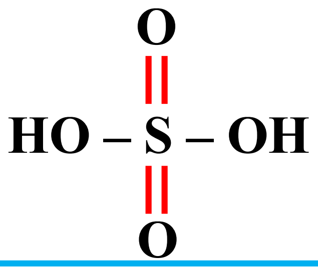
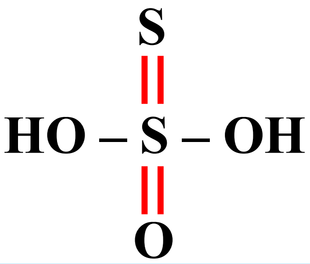
I. SULPHUROUS ACID SERIES

Oxoacid		Structure	Oxidation state
1.	Sulphurous acid H_2SO_3	 $\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\cdot\cdot}{S}}-OH}$	+4
2.	Thio sulphurous acid $H_2S_2O_2$	 $\mathrm{HO-\overset{\overset{S}{\|}}{\underset{\cdot\cdot}{S}}-OH}$	–2,+4
3.	Dithionous acid $H_2S_2O_4$ (hypo sulphurous acid)	 $\mathrm{HO-\overset{\overset{O}{\|}}{S}-\overset{\overset{O}{\|}}{S}-OH}$	+3

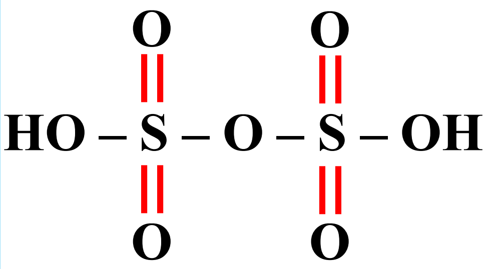
I. SULPHUROUS ACID SERIES

Oxoacid		Structure	Oxidation state
4.	Pyrosulphurous acid $H_2S_2O_5$	 $HO-\overset{\overset{O}{\|}}{S}-O-\overset{\overset{O}{\|}}{S}-OH$	+3, +5, AV=+4

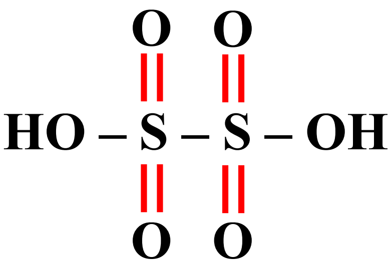
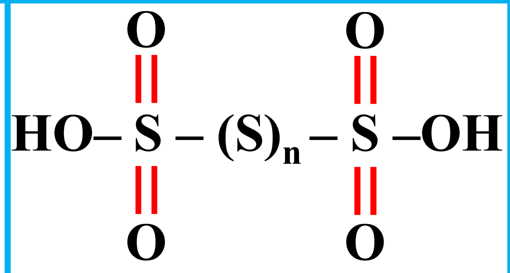
II. SULPHURIC ACID SERIES

Oxoacid		Structure	Oxidation state
1.	Sulphuric acid H_2SO_4 Also called oil of vitriol	 $HO-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-OH$	+6
2.	Thiosulphuric acid $H_2S_2O_3$	 $HO-\overset{\overset{S}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-OH$	–2, +6

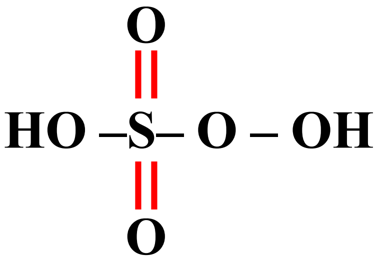
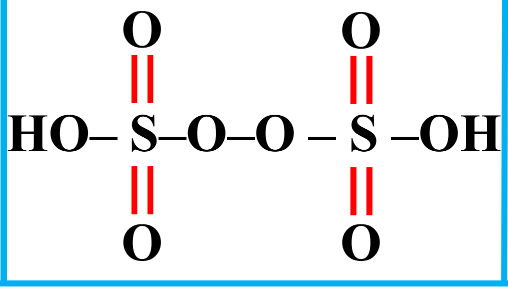
II. SULPHURIC ACID SERIES

Oxoacid		Structure	Oxidation state
3.	Pyrosulphuric acid or oleum $H_2S_2O_7$ also called disulphuric acid	 $HO-\overset{O}{\underset{O}{\overset{\parallel}{\underset{\parallel}{S}}}}-O-\overset{O}{\underset{O}{\overset{\parallel}{\underset{\parallel}{S}}}}-OH$	+6

III. THIONIC ACID SERIES

	Oxoacid	Structure	Oxidation state
1.	**Dithionic acid** $H_2S_2O_6$	 $HO-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-OH$	+5
2.	**Polythionic acid** $H_2(S)_{n+2}O_6$	 $HO-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-(S)_n-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-OH$	+5, (0)

IV. PEROXO ACID SERIES

Oxoacid		Structure	Oxidation state
1.	Peroxy monosulphuric acid or Caro’s acid H_2SO_5	 $HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-OH$	+6
2.	Peroxy disulphuric acid $H_2S_2O_8$ Marshall’s acid	 $HO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$	+6

MCQs

1. The molecular formula of Dithionic acid is __________.

a) $H_2S_2O_4$

b) H_2SO_3

[✓ c) $H_2S_2O_6$]

d) None of these

2. The molecular formula of Dithionous acid is ____________.

[✓ a) $H_2S_2O_4$]

b) H_2SO_3

c) $H_2S_2O_6$

d) None of these

3. Oxidation state of Sulphur in Caro's acid (H_2SO_5) is ___________.

a) + 3

b) –3

c) + 2

[✓ d) + 6]

4. ____________ is also called as oil of Vitriol.

a) H_2SO_3

[✓ b) H_2SO_4]

c) $H_2S_2O_6$

d) None of these

SULPHURIC ACID (H_2SO_4)
PART-1

Sulphuric acid:

- Sulphuric acid is a very important chemical used in industry.
- Because of its wide applications in industry, it is called ‘King of chemicals’. It is also called as ‘OIL OF VITRIOL’.
- There are two important methods of manufacturing sulphuric acid.

1) Lead chamber process

2) Contact process

Lead chamber process

Sulphuric acid was prepared earlier by lead chamber process, which is an example of homogeneous catalysis. Sulphur dioxide is oxidized with oxygen in the presence of nitric oxide as catalyst. This method is not in use now.

Lead chamber process

$2SO_2 + O_2 + 2H_2O \xrightarrow{NO} 2H_2SO_4$ **Net Reaction**

$2H_2O + NO \longrightarrow HNO_3 + 3H^+$

$S + O_2 \longrightarrow SO_2$ (oxidation of sulphur)

$2HNO_3 + 2SO_2 \longrightarrow H_2O + NO + NO_2 + 2SO_3$

$SO_2 + NO_2 \longrightarrow SO_3 + NO$

$SO_3 + H_2O \longrightarrow H_2SO_4$ **Sulphuric Acid**

Contact Process

Preparation of SO_2

i) Burning of sulphur (or) sulphide ores (like iron pyrites) in air to get SO_2

$$S_{(g)} + O_{2(g)} \xrightarrow{\Delta} SO_{2(g)}$$

ii) Sulphur dioxide required for the process is obtained by roasting of iron pyrities.

$$4FeS_{2(g)} + 11\ O_{2(g)} \xrightarrow{\Delta} 2Fe_2O_{3(s)} + 8SO_{2(g)}$$

Contact Process

Oxidation of SO_2 to SO_3

2. Sulphur dioxide is oxidised catalytically with atmospheric air to sulphur trioxide. The catalyst commonly used is vanadium pentoxide.

$$2SO_{2(g)} + O_{2(g)} \underset{\Delta}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_{3(g)}$$

$$\Delta H = -196.6 \text{ kJ/mole}$$

Catalysts are often poisoned in contact process.
Hence gases used must be pure.

Contact Process

Oxidation of SO_2 to SO_3

- The SO_2 to SO_3 is reversible, exothermic leads to a decrease in volume in forward direction.
- Hence, low temperature and high pressure are favourable.
- In practice, the plant is operated at 2 bar pressure and 720K.

Dissolution of SO_3 in H_2SO_4

3. Sulphur trioxide formed is absorbed in conc. Sulphuric acid to get oleum, which is diluted with water to obtain concentrated sulphuric acid.

$$SO_{3(g)} + H_2SO_4 \longrightarrow \underset{\text{(oleum)}}{H_2S_2O_7}$$

96-98% pure
is obtained.

Dilution of oleum, $H_2S_2O_7$

$$H_2S_2O_7 + H_2O_{(l)} \longrightarrow 2H_2SO_4$$

Sulphuric Acid

- **Sulphuric acid is dense, colourless oily liquid with a specific gravity 1.84 at room temperature.**

- **It freezes at 283 K and boils at 610 K. It is soluble in water, but the dissolution is largely exothermic.**

- **Hence care is to be taken while preparing an aqueous solution. The concentrated acid must be added slowly to water with constant stirring.**

- **Sulphuric acid is less volatile and hence it is used to prepare volatile acids from their corresponding salts.**

Hot conc. H_2SO_4 is moderately strong oxidising agent(strength in between H_3PO_4 and HNO_3).

$$2KF+H_2SO_{4(Conc.)}\rightarrow 2HF+K_2SO_4$$

$$2NaNO_3+H_2SO_{4(Conc.)}\rightarrow 2HNO_3+Na_2SO_4$$

$$Cu+2H_2SO_{4(Conc.)}\rightarrow CuSO_4+2H_2O+SO_2$$

$$C+2H_2SO_{4(Conc.)}\rightarrow CO_2+2H_2O+2SO_2$$

It is very good dehydrating agent. It removes water from carbohydrates as

$$S+2H_2SO_{4(Conc.)}\rightarrow 3SO_2+2H_2O$$

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

Bulk of sulphuric acid is used in manufacturing fertilizers.

- It is also used in petroleum refining,
- detergent industry,
- manufacture of paints pigments,
- electroplating process,
- galvanization process,
- manufacture of nitrocellulose,
- storage batteries
- and also as a laboratory reagent.

- Sulphuric acid is a strong diprotic acid (Ka_1>10 and Ka_2 ia 1.2 $\times 10^{-2}$. It forms two types of salts (hydrogensulphate and sulphate)upon neutralization.

$$H_2SO_4 + NaOH \rightarrow NaHSO_4 \quad + H_2O$$

Sodium
Hydrogen sulphate

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 \quad + 2H_2O$$

Sodium sulphate

- Concentrated sulphuric acid is a strong dehydrating agent. It removes water from organic compounds and chars carbohydrates.

$$C_2H_5OH \xrightarrow[H_2SO_4]{165^0C} C_2H_4 + H_2O$$

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

- Hot concentrated sulphuric acid is a moderately strong oxidant.

- **It is less powerful than HNO_3, but more powerful than H_3PO_4 in its oxidation ability.**

- **It oxidises metals and non-metals and is reduced to sulphur dioxide.**

MCQs

1. Sulphuric acid is prepared by ____________ process.

a) Haber’s

[✓ **b) Contact**]

c) Deacon’s

d) None of these

2. Sulphuric acid is prepared by ____________ process.

[✓ a) Lead chamber]

b) Carbon chamber

c) Oxygen chamber

d) None of these

3. $H_2S_2O_7$ is known as ________________

a) Hydrosulphuric acid

[✓ b) Oleum]

c) Sulphonic acid

d) None of these

4. $C + 2H_2SO_4 \longrightarrow$ __________ + __________ $+ 2H_2O$.

a) CO, SO_3

[✓ b) CO_2, SO_2]

c) CO_2, SO_3

d) CO_2, SO_3

5. $HCOOH \xrightarrow{\text{conc. } H_2SO_4} H_2O + \_\_\_\_\_\_\_\_\_\_$

a) CO_2

b) HCHO

[✓ c) CO]

d) CO_2, SO_3

6. $P_4O_{10} + 2H_2SO_4 \rightarrow$

a) H_3PO_3

[✓ b) H_3PO_4]

c) $H_4P_2O_6$

d) CO_2, SO_3

7. $C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12$ ______________ $+ 11H_2O$

a) CO

[✓ b) C]

c) $H_4P_2O_6$

d) HCOOH

PHOSPHORUS

Symbol

P

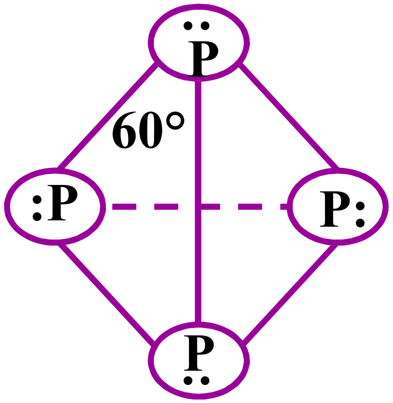
Atomic Number

15

Phosphorus

Allotropic forms of phosphorus

White phosphorus



- Common variety of phosphorus.
- Consists of P_4
- Four P-atoms lie at the corners of the regular tetrahedron
- Each phosphorus bonded to each of the three P-atom by covalent bonds.
- It is poisonous.

Allotropic forms of phosphorus

White phosphorus

- **White phosphorus is a translucent white waxy solid.**
- **It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence).**
- **It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3**

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$$

(Sodium hypophosphite)

- **and it is less stable**

Allotropic forms of phosphorus

White phosphorus

- **It readily catches fire in air to give dense white fumes of P_4O_{10}.**

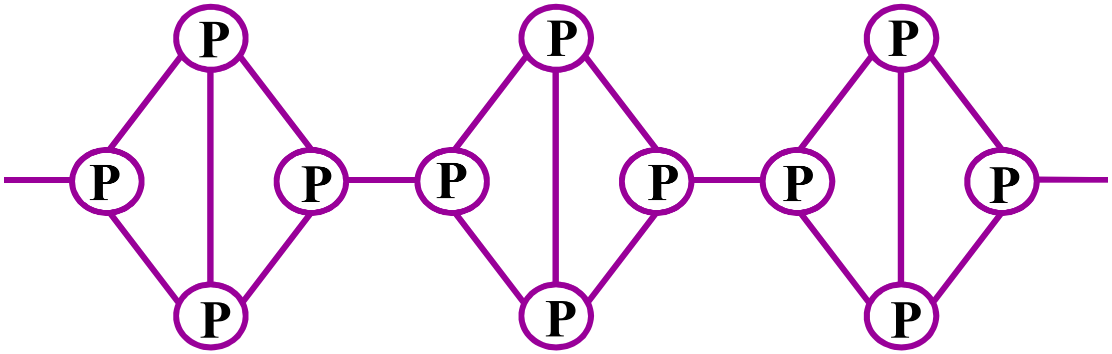
$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

- **It consists of discrete tetrahedral P_4 molecules are held by Vander Waal's forces.**

Allotropic forms of phosphorus

Red phosphorus

- It is polymeric.



- It is non poisonous.

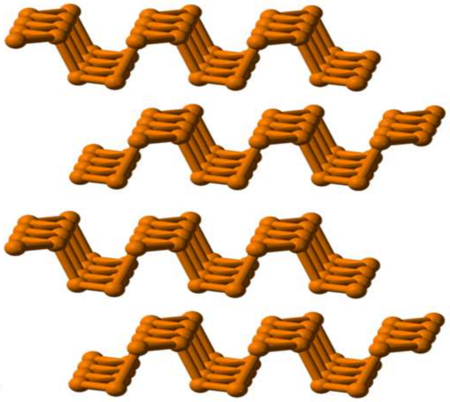
Allotropic forms of phosphorus

Red phosphorus

- It is obtained by heating white “P” at 573 K in an inert atmosphere for several days.
- It Possesses iron grey lustre.
- It is odourless.
- non-poisonous and insoluble in water as well as in carbon disulphide.
- Chemically, red phosphorus is much less reactive than white phosphorus.
- It is polymeric, consisting of chains of P_4 tetrahedral linked together through covalent bonds.

Allotropic forms of phosphorus

Black phosphorus



- It is thermodynamically most stable form
- It has a layered structure
- It has mainly two forms α - Black and β - Black
- Red phosphorus gives α - Black phosphorus
- White phosphorus gives β - Black phosphorus
- It does not get oxidized easily with air
- It can be sublimed in air and has opaque monoclinic or rhombohedral crystals.
- It does not oxide in air. **β**- black phosphorus is prepared by heating white phosphorus at 473K under high pressure.

Allotropy

Arsenic → Allotropic forms are

Grey metallic **Yellow** **Black**

Antimony → Allotropic forms are

Metallic antimony **Yellow or α – antimony** **Explosive antimony**

- Out of the three, the stable forms are yellow and metallic antimony

Bi → radioactive and emits α rays half life 1.9×10^{19} years

Question

What happens when phosphorus is heated with concentrated NaOH solution in an inert atmosphere of CO_2

Answer:

$$P_4 + 3\ NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3\uparrow$$

MCQs

1. Phosphorus exists in white, ______and black forms.

[✓ a) Red]

b) Blue

c) Grey

d) None

2. α- Black phosphorus is obtained from ______ phosphorous.

- **a) White**
- **b) Blue**
- [✓ **c) Red**]
- **d) None**

3. ______ is the most thermodynamically stable form of phosphorus.

a) White

[✓ **b) Black**]

c) Red

d) None

4. ______dose not show allotropy.

a) N

b) P

c) As

[✓ d) Bi]

5. α –nitrogen has ____________packing.

[✓ **a) Simple cubic**]

b) Hexagonal

c) Both

d) none

6. _________antimony is less stable.

a) Metalic

[✓ b) Explosive]

c) Yellow

d) none

7. Half life of Bismuth is ________years.

[✓ a) 1.9×10^{19}]

b) 1.9×10^{22}

c) 1.5×10^{10}

d) 1.9×10^{9}

PHOSPHINE

Preparation of Phosphine

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

Calcium phosphide		Calcium hydroxide	phosphine

$$Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3\uparrow$$

Calcium phosphide		Calcium chloride	phosphine

From phosphorus

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$$

White Phosphorus

Phosphine

Sodium hypophosphite

From phosphonium iodide

$$PH_4I + KOH \rightarrow KI + H_2O + PH_3$$

Phosphonium iodide

Phosphine

THE PROPERTIES OF PHOSPHINE

- It is a colourless gas with fish smell and is highly poisonous.
- It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.
- It is slightly soluble in water.
- The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2.

THE PROPERTIES OF PHOSPHINE

$$PH_3 \quad + \quad 4Cl_2 \longrightarrow PCl_5 \quad + \quad 3HCl$$

Phosphorus pentachloride

$$3CuSO_4 + \quad 2PH_3 \longrightarrow Cu_3P_2 \quad + \quad 3H_2SO_4$$

Copper phosphide

THE PROPERTIES OF PHOSPHINE

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

Mercuric chloride

Mercuric phosphide

$$4PH_3 \xrightarrow{\Delta} P_4 + 3H_2$$

$$PH_3 + HBr \rightarrow PH_4Br$$

phosphonium bromide

THE PROPERTIES OF PHOSPHINE

- 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.
- It is also used in smoke screens.

THE USES OF PHOSPHINE

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

Calcium carbide — **Acetylene**

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

Calcium phosphide — **Phosphine**

A mixture of Ca_3P_2 and CaC_2 is used in Holme's signal for navigation

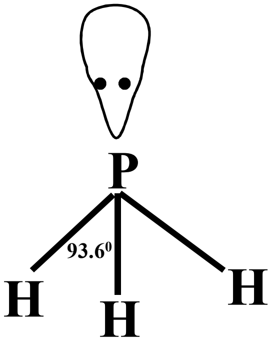
Question

Q3. Bond angle in PH^+_4 is higher than that of PH_3. Why?

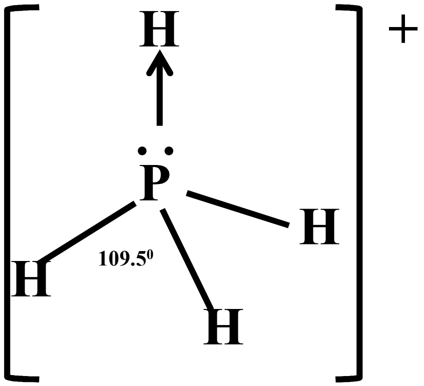
Answer:

In both PH_4^+ and PH_3, phosphorous atom is sp^3 hybridized. in PH^+_4, all the four orbitals are bonded where as in PH_3, there is a lone pair of electrons.

Due to a lone pair – bonded pair repulsion in PH_3, the bond angle is less than 109.5^0.



PH_3 (Pyramidal)



PH_4^+ (Tetrahedral)

Question

In what way can it be proved that PH_3 is basic in nature

Answer:

PH_3 reacts with acids like HI to form PH_4I which shows that it is basic in nature..

$$PH_3 + HI \longrightarrow PH_4I$$

Due to lone pair on phosphorous atom, PH_3 is acting as a Lewis base in the above reaction

MCQs

1. $P_4 + 3NaOH + H_2O \rightarrow$ ______ + ______

a) PH_3, $NaOH$

b) PH_3, H_3PO_4

[✓ c) PH_3, NaH_2PO_2]

d) None

2. $3CuSO_4 + 2PH_3 \rightarrow$ ______ + $3H_2SO_4$

a) Cu_2P_3

[✓ b) Cu_3P_2]

c) $Cu_3(PO_4)_2$

d) None

3. A mixture of ______ and ______ is used as Holme's signal.

a) PH_3, CH_4

b) PH_3, C_2H_6

[✓ c) CaC_2, Ca_3P_2]

d) PH_3, C_6H_6

4. ______ + $6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

a) AlP

b) Ca_2P_3

[✓ c) Ca_3P_2]

d) $Ca_3(PO_4)_2$

PHOSPHORUS TRICHLORIDE

Preparation of Phosphorus trichloride

$$P_4 + 6Cl_2 \xrightarrow{\Delta} \underset{\text{Phosphorus trichloride}}{4PCl_3}$$

$$P_4 + \underset{\text{Thionyl chloride}}{8SOCl_2} \xrightarrow{\Delta} \underset{\text{Phosphorus trichloride}}{4PCl_3} + 2S_2Cl_2 + 4SO_2$$

Properties of PCl_3

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

Phosphorous acid

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

Phosphorous penta chloride

Properties of PCl_3

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

Acetic acid **Acetyl chloride**

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

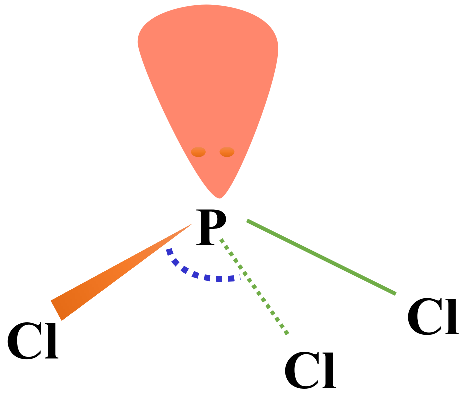
Ethanol **Chloroethane**

$$3AgCN + PCl_3 \longrightarrow P(CN)_3 + 3AgCl$$

Silver cyanide **Silver chloride**

Structure of PCl_3

- Pyramidal shape
- Phosphorus is sp^3 hybridised
- Phosphorus has lone pair of electron



MCQs

1. PCl_3 is ______ hybridized.

a) sp^2

b) sp

[✓ **c) sp^3**]

d) dsp^2

2. $PCl_3 + H_2O \rightarrow$ ______ + ______

a) PH_3,HCl

[✓ b) H_3PO_3,HCl]

c) H_3PO_4,HCl

d) H_3PO_3, Cl_2

3. PCl_3 has a ______ geometry.

a) Trigonal planar

b) Tetrahedral

c) Linear

[✓ d) Pyramidal]

4. $3CH_3COOH + PCl_3 \rightarrow 3$ ______ $+ H_3PO_3$

a) CH_3CH_2Cl

[✓ b) CH_3COCl]

c) CH_3COCH_3

d) None of these

PHOSPHORUS PENTACHLORIDE

Preparation of Phosphorus pentachloride

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

(excess) Phosphorus pentachloride

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

Sulfuryl chloride

Properties of PCl_5

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

Phosphorus oxychloride

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

Phosphoric acid

$$PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$$

Phosphorus trichloride

Properties of PCl_5

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

Ethanol **Chloroethane**

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

Acetic acid **Acetyl chloride**

PCl_5 as a powerful chlorinating agent

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

Silver chloride

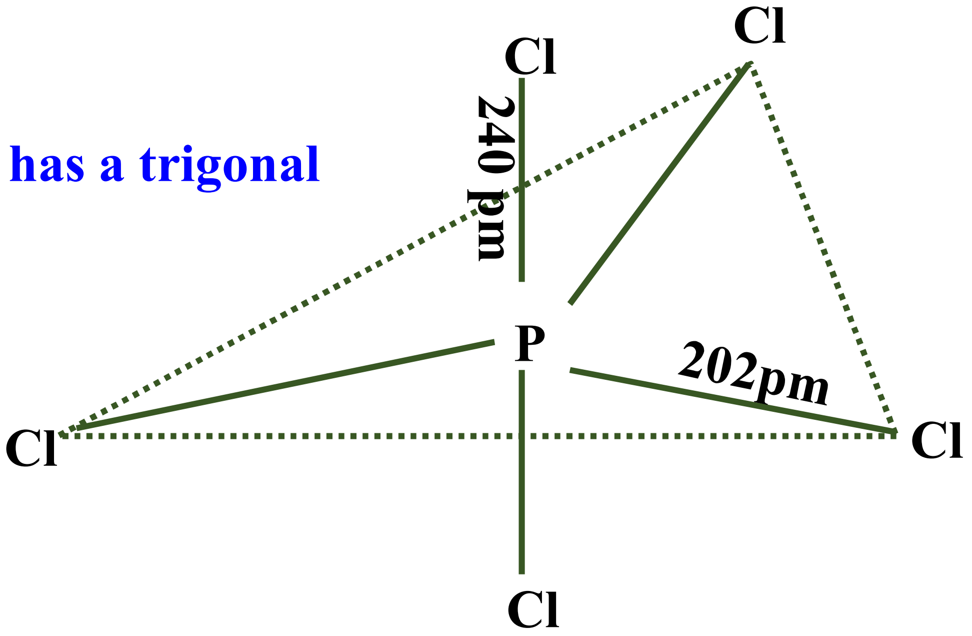
$$Sn + 2PCl_5 \longrightarrow SnCl_4 + 2PCl_3$$

Tin chloride

Structure of PCl_5

In gaseous and liquid phases, it has a trigonal bipyramidal structure.

In the solid state it exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral and the anion , $[PCl_6]^-$ is octahedral.



PCl_5 has a trigonal bi pyramidal structure

MCQs

1. 2Ag + PCl_5 → 2______ + ______.

[✓ a) AgCl, PCl_3]

b) PCl_3, AgCl

c) AgCl, P_4

d) None of these

2. PCl_5 shows _______ geometry.

a) Tetrahedral

b) Square planar

[✓ c) Trigonal bipyramidal]

d) None

3. $P_4 + 10Cl_2 \rightarrow$ ______

a) PCl_3

[✓ b) PCl_5]

c) Both a & b

d) None of these

4. $CH_3COOH + PCl_5 \rightarrow$ ______ + ______ + HCl

a) CH_3CH_2Cl, H_3PO_4

b) CH_3CH_2Cl, $POCl_3$

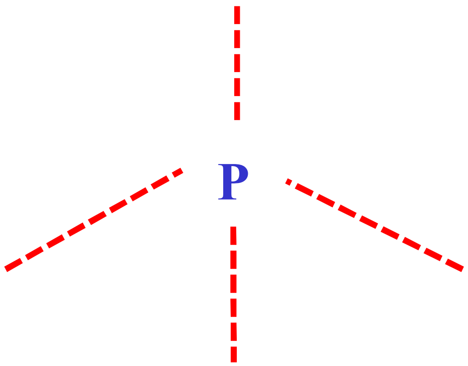
[✓ c) CH_3COCl, $POCl_3$]

d) CH_3COCl, H_3PO_3

OXOACIDS OF PHOSPHOROUS

Oxoacids of phosphorous

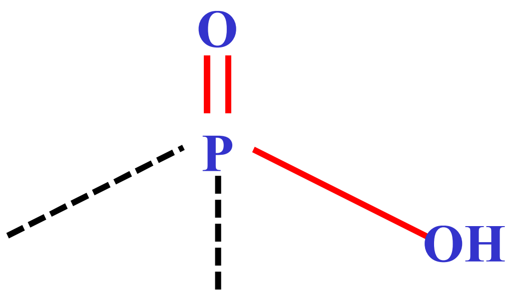
- **In oxy acids, phosphorus is tetrahedrally surrounded by other atoms .**



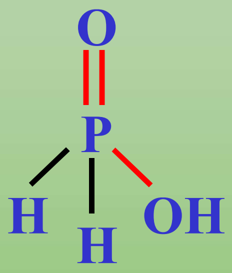
Oxyacids of phosphorous

General structure

- All these acids contain at least one P = O bond and one P–OH bond.



Hypophosphorous or phosphinic acid H_3PO_2

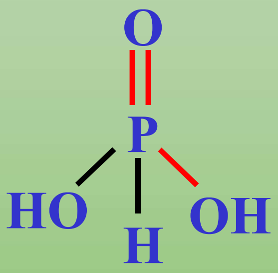
Oxyacid	**i) Hypophosphorus acid or** **Phosphinic acid (H_3PO_2)** **two P – H bonds, one P – OH bond and one P = O bond.**
Structure	
Oxidation state of P	**+1**

Hypophosphorous or phosphinic acid H_3PO_2

$$\underset{\text{White phosphorus}}{2P_4} + 3Ba(OH)_2 + 6H_2O \longrightarrow \underset{\text{ppt}}{3Ba(H_2PO_2)_2} + 2PH_3$$

$$Ba(H_2PO_2)_2 + H_2SO_4 \longrightarrow 2H_3PO_2 + \underset{\text{ppt}}{BaSO_4}$$

Orthophosphorus acid or Phosphonic acid H_3PO_3

Oxyacid	ii) Orthophosphorus acid(H_3PO_3) one P – H bond, two P – OH bonds and one P = O bond.
Structure	
Oxidation state of P	+3

Orthophosphorus acid H_3PO_3

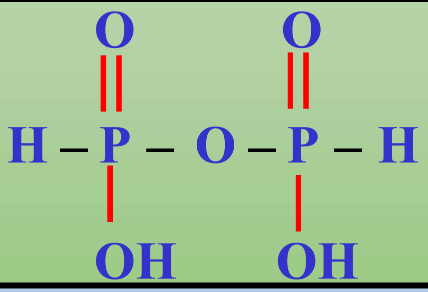
$$P_2O_3 + 3H_2O \longrightarrow 2H_3PO_3$$

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

Properties of H_3PO_3

$$4H_3PO_3 \xrightarrow{\Delta} \underset{\text{Ortho Phosphoric acid}}{3H_3PO_4} + \underset{\text{phosphine}}{PH_3}$$

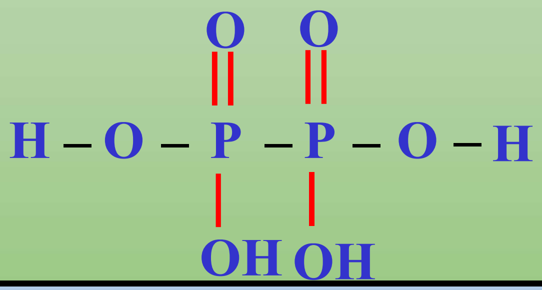
Pyrophosphorus acid ($H_4P_2O_5$)

Oxyacid	**iii) Pyrophosphorus acid ($H_4P_2O_5$)** **two P – H bonds,** **two P – OH bonds** **two P = O bonds** **one P – O – P bond**
Structure	 $H-\overset{\overset{O}{\Vert}}{\underset{\underset{OH}{\vert}}{P}}-O-\overset{\overset{O}{\Vert}}{\underset{\underset{OH}{\vert}}{P}}-H$
Oxidation state of P	**+3**

Pyrophosphorus acid ($H_4P_2O_5$)

$$PCl_3 + H_3PO_3 + 2H_2O \longrightarrow H_4P_2O_5 + 3HCl$$

Hypophosphoric acid ($H_4P_2O_6$)

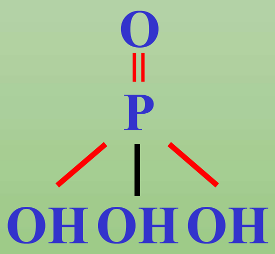
Oxyacid	iv) Hypophosphoric acid ($H_4P_2O_6$) four P – OH bonds, two P = O bonds, One P-P bond.
Structure	 $\mathrm{H-O-\underset{\underset{OH}{\mid}}{\overset{\overset{O}{\Vert}}{P}}-\underset{\underset{OH}{\mid}}{\overset{\overset{O}{\Vert}}{P}}-O-H}$
Oxidation state of P	+4

Hypophosphoric acid ($H_4P_2O_6$)

Properties of $H_4P_2O_6$

$$H_4P_2O_6 \xrightarrow{\Delta} H_3PO_3 + HPO_3$$

Orthophosphoric acid H_3PO_4

Oxyacid	v) Orthophosphoric acid (H_3PO_4) three P – OH bonds, one P = O bond.
Structure	
Oxidation state of P	+5

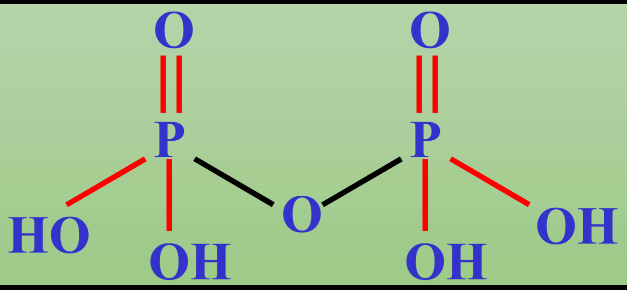
Orthophosphoric acid H_3PO_4

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 2H_3PO_4$$

$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$$

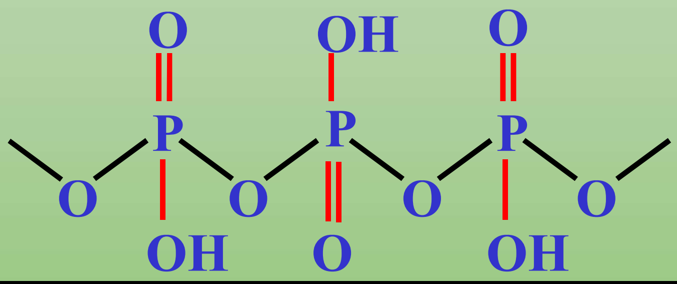
Pyrophosphoric acid $H_4P_2O_7$

Oxyacid	vi) Pyrophosphoric acid ($H_4P_2O_7$) four P – OH bonds, two P = O bonds, one P – O – P bond
Structure	
Oxidation state of P	+5

Pyrophosphoric acid $H_4P_2O_7$

$$2H_3PO_4 \xrightarrow{\Delta} H_4P_2O_7 + H_2O$$

Poly metaphosphoric acid $(HPO_3)_n$

Oxyacid	**vi) Poly metaphosphoric acid $(HPO_3)_n$**
Structure	
Oxidation state of P	**+5**

Polymetaphosphoric acid $(HPO_3)_n$

- **Polymetaphosphoric acid is prepared by heating mixture of phosphorus acid and Br_2 in a sealed tube.**
- **It is also called *glacial phosphoric acid*.**

Polymetaphosphoric acid $(HPO_3)_n$

Characteristics

Acids which contain P–H bonds have strong reducing tendency.

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

P – H bonds in oxoacids do not ionise to give H^+ ions.

Only H atoms attached to Oxygen in P–OH form ionise and cause basicity.

MCQs

1. The oxidation state of Phosphorus in poly metaphosphoric acid is…

a) +3

b) +1

c) +2

[✓ d) +5]

2. The oxidation state of Phosphorus in pyro phosphorus acid is…

a) +1

b) +2

[✓ c) +3]

d) +4

3. Hypo phosphoric acid is…

a) H_3PO_4

[✓ b) $H_4P_2O_6$]

c) $(HPO_3)_3$

d) H_2PO_5

4. In oxyacids, phosphorus is surrounded by...

a) Octahedrally

[✓ b) Tetrahedrally]

c) Both a & b

d) None of these

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