01 p-Block Elements - Group 13 to18

Inert Pair Effect :

	Group-13	Group-14	Group-15
(group oxidation state)	$\underset{+3}{ns^2np^1}$	$\underset{+4}{ns^2np^2}$	$\underset{+5}{ns^2np^3}$

- While moving down the group the stability of lower oxidation state (2 less than group oxidation state) progressively increases and for the last element of the group the stability of lower oxidation state increases than the group oxidation state. **This is called inert pair effect.**

  Reason : As we move down the group there is presence of d & f-orbitals in inner shells which have poor shielding effect hence Z_{eff} increases. As a result the ns^2 electron pair becomes more and more tightly held to the nucleus and becomes inert /passive towards bonding.
- For the last element group oxidation state is highly oxidising in nature.

  Examples :
  1. $PbCl_2$ is more stable than $PbCl_4$.
  2. $TlCl$ is more stable than $TlCl_3$.
  3. $GaCl_3$ is more stable than $TlCl_3$.
  4. $SnCl_4$ is more stable than $PbCl_4$.
  5. Thallium (III) iodide does not exist.
  6. PbF_4, $PbCl_4$ exist but $PbBr_4$ and PbI_4 does not exist.
  7. Among pentahalides of Bi only BiF_5 exists due to strong oxidising nature of Pb^{+4} and strong reducing nature of I^-, PbI_4 does not exist while Cl^- and F^- cannot reduce Pb^{+4}

Back Bonding :

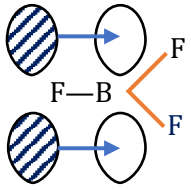
Definition : It is an additional bond which is formed between 2 adjacent bonded atoms in a covalent molecule/ion by collateral overlapping.

Conditions for back bonding :

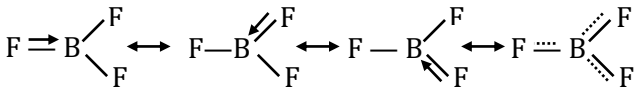
(i) One bonded atom must possess vacant orbital and the other bonded atom must possess lone pair.

(ii) Both bonded atoms must belong to 2^{nd} period or one bonded atom must belong to 2^{nd} period and other belong to 3^{rd} period.

As a result of back bonding between the bonded atoms, bond length decreases and bond energy increases.



F-donor
B-acceptor



(B–F) Bond Order = 4/3 = 1.33

Types of back bonding :

Based on type of orbitals involved in overlapping.

2 types of back bonding is possible.

(1) pπ-pπ back bonding.

(2) pπ-dπ back bonding.

(1) pπ-pπ back bonding : It is formed by the sidewise overlapping of two p orbitals.

Order of strength : 2p – 2p > 2p – 3p > 2p – 4p .....

Size of orbital ↑ Extent of B.B. ↓

It is used to explain following observations :-

(i) Lewis acidic order of **Boron** and **Beryllium** halides.

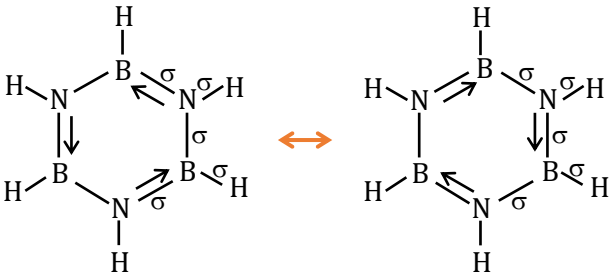
$BF_3 < BCl_3 < BBr_3 < BI_3$ $BeF_2 < BeCl_2 < BeBr_2 < BeI_2$

∵ Extent of back bonding ↓ ∴ Lewis acidic strength ↑

(ii) Hybridisation : If a lone pair participates in back bonding then it is not considered in hybridisation.

Ex. $B_3N_3H_6$ (inorganic benzene or borazine or borazole).

Hybridisation of B as well as N is sp^2.



Inorganic benzene is more reactive than organic benzene as in it the **bonds** are **polar,** although overall molecule is non-polar.

(iii) If back bonding is present in the molecule then tendency to form dimer or polymer decreases.

Ex. BF_3, BeF_2

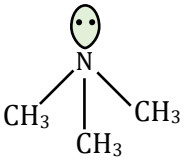
(2) pπ-dπ back bonding :

It is formed by the side wise overlapping between 2p and 3d orbitals.

It is used to explain the following observations :

(i) Hybridisation

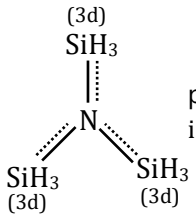
Ex. Trimethyl amine **$(CH_3)_3N$**



Back bonding is not possible due to absence of vacant orbital

- Hybridisation of N is sp^3
- Structure is trigonal pyramidal
- It is a stronger Lewis base (due to presence of l.p.)

Trisilyl amine **$(SiH_3)_3N$**



pπ—dπ back bonding is possible

- Hybridisation of N is sp^2
- Structure is trigonal planar
- It is a weaker Lewis base

(ii) Acidic strength

$CH_3—\ddot{O}—H$

Methyl alcohol

- No back bonding in conjugate base
- Less acidic

$SiH_3—\ddot{O}—H$

Silyl alcohol

- Back bonding present in conjugate base
- More acidic

Dimerisation/Polymerisation :

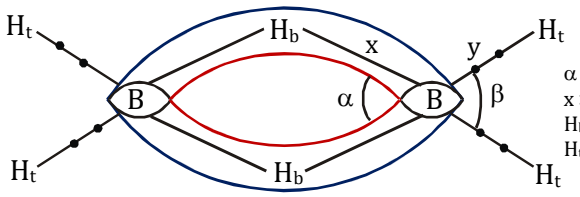
Types of Dimerisation

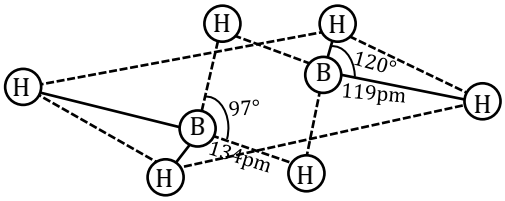
by 3 centre -2e⁻ bond eg. B_2H_6, $(BeH_2)_2$, $(BeH_2)_n$, $Al_2(CH_3)_6$, $Ga_2(CH_3)_6$

by 3 centre -4e⁻ bond eg. $(BeCl_2)_2$, $(BeCl_2)_n$, $(AlCl_3)_2$, $(ICl_3)_2$

(I) By banana bond or by 3 centre–2e⁻ bond or by e⁻ deficient bond

(i) B_2H_6





2 centre–2e⁻ bonds = 4

3 centre–2e⁻ bonds = 2structure of diborane, B_2H_6

Hybridisation state of boron is sp^3

It is electron deficient molecule and act as a Lewis acid.

All four terminal hydrogen and two boron atoms are present in same plane both bridging H are present in perpendicular plane.

If substitution reaction takes place then maximum four terminal hydrogen atoms can be substituted.

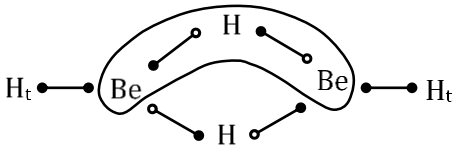
$$B_2H_6 + 4CH_3–Cl \rightarrow B_2H_2(CH_3)_4 + 4HCl$$

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

Hybridisation state of Be is sp^2

Planar

Electron deficient molecule

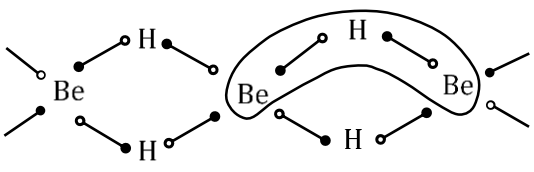


(iii) $(BeH_2)_n$ (polymer of BeH_2 in solid state)

Hybridisation state of Be is sp^3

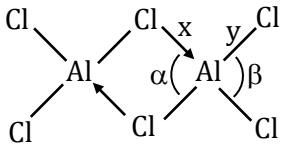
Non-planar

Electron deficient molecule



(II) By-coordinate bond / 3 centre–4e⁻ bond

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



$\alpha < \beta$; Order of bond angle

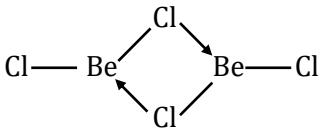
x > y ; Order of bond length

Hybridisation state of Al is sp^3

Non-planar

Octet of Al is complete so it is not e^- deficient

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

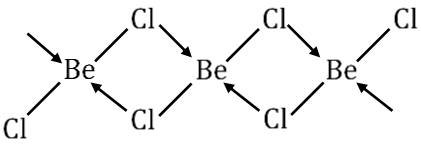


Hybridisation state of Be is sp^2

Planar

Electron deficient molecule

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

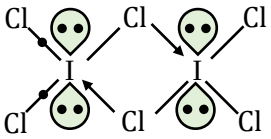


Hybridisation state of Be is sp^3

Non-planar

Octet of Be is complete so it is not e^- deficient

(iv) I_2Cl_6 (dimer of ICl_3)



Hybridisation state of I is sp^3d^2

Planar

e^- rich molecule (12 e^-)

Note :

(i) BCl_3, BBr_3 & 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 presence of back bonding.

(iii) AlF_3 cannot form dimer due to its ionic nature.

BEGINNER'S BOX-1

1. In BF_3 :

(1) B-F bond has double bond character and this bond is delocalised

(2) All the B–F bonds are single covalent in nature

(3) Bond energy and bond length of B–F bond indicate its single bond character

(4) All the bonds are ionic

CPB228

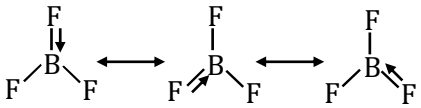
2. In BF_3, the B–F bond length is 1.30Å, when BF_3 is allowed to be treated with Me_3N, it forms an adduct,

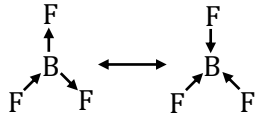
$[Me_3N \rightarrow BF_3]$. The bond length of B–F in the adduct is :

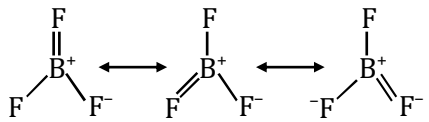
(1) Greater than 1.30Å (2) Smaller than 1.30Å (3) Equal to 1.30Å (4) None of these

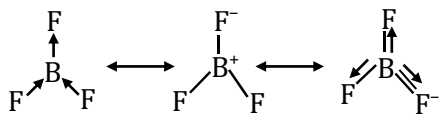
CPB229

3. Which of the following structures correctly represents the boron trifluoride molecule :

(1) 

(2) 

(3) 

(4) 

CPB230

4. Trisilylamine [$\ddot{N}(SiH_3)_3$] has a :-
(1) Planar geometry (2) Tetrahedral geometry
(3) Pyramidal geometry (4) None of these

CPB231

5. In which of the following molecule, vacant orbitals do not participate in bonding:-
(1) B_2H_6 (2) Al_2Cl_6 (3) $[H_3N.BF_3]$ (4) Si_2H_6

CPB232

6. In which of the following compounds B–F bond length is shortest?
(1) BF_4^- (2) $BF_3 \leftarrow NH_3$ (3) BF_3 (4) $BF_3 \leftarrow N(CH_3)_3$

CPB233

7. In diborane –
(1) 2 bridged hydrogen and four terminal hydrogen are present
(2) 3 bridged and three terminal hydrogen are present
(3) 4 bridged hydrogen atoms are not in the same plane
(4) 1 bridged hydrogen and 1 terminal hydrogen are present

CPB234

8. How many 2C-2e$^-$ bonds and 3C-2e$^-$ bonds are present in diborane ?
(1) 2 and 4 (2) 2 and 2 (3) 4 and 2 (4) 4 and 4

CPB235

Oxy Acid :

Compounds having **X-O-H** bonds are **Oxyacids**

Acidic Oxide + H_2O $\longrightarrow$ Oxyacids

Non-Metallic Oxide + H_2O $\longrightarrow$ Oxyacid

Example :

$CO_2 + H_2O \longrightarrow H_2CO_3$ Carbonic Acid

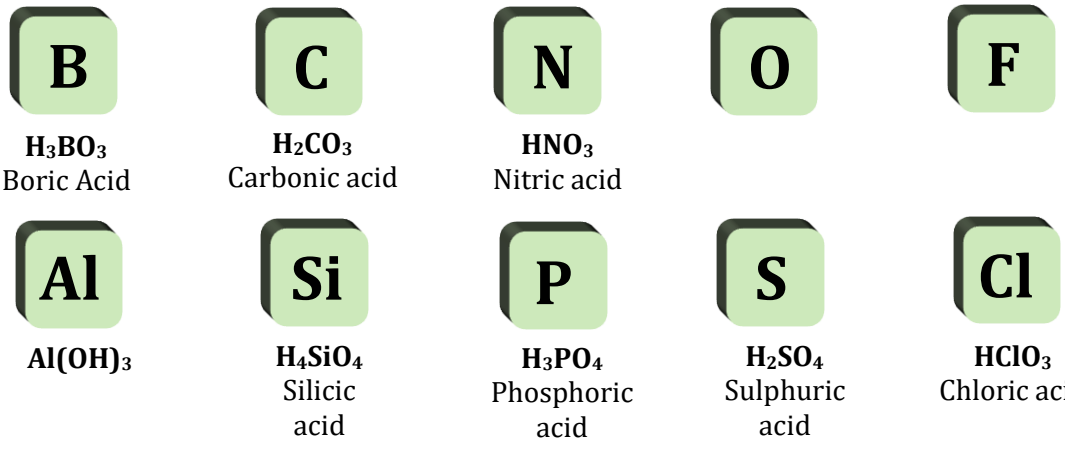
$SO_3 + H_2O \longrightarrow H_2SO_4$ Sulphuric Acid

$SO_2 + H_2O \longrightarrow H_2SO_3$ Sulphurous Acid

Suffix $\rightarrow$ Highest O.S. = ic acid

$\rightarrow$ Lower O.S. = ous acid

Parent 'ic' acids



H_3BO_3 Boric Acid

H_2CO_3 Carbonic acid

HNO_3 Nitric acid

$Al(OH)_3$

H_4SiO_4 Silicic acid

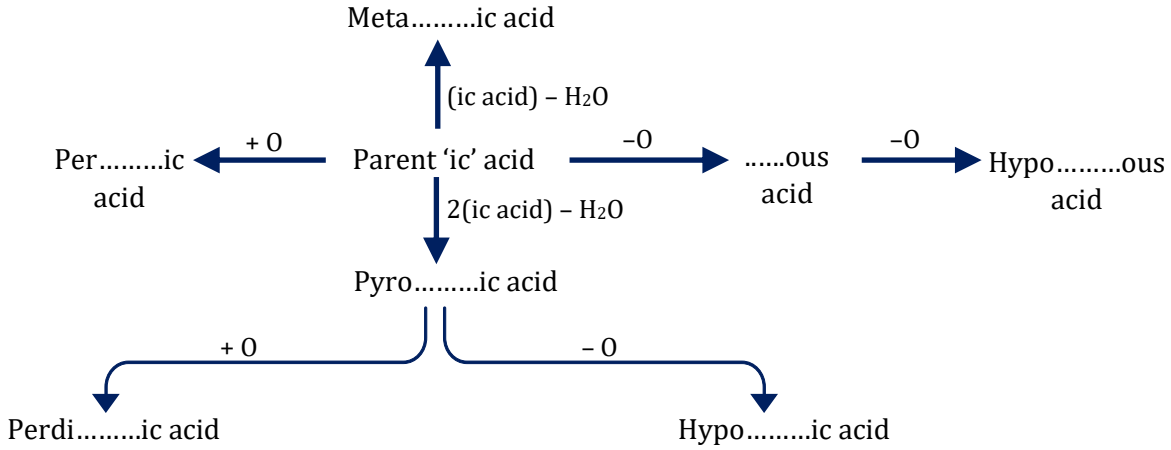
H_3PO_4 Phosphoric acid

H_2SO_4 Sulphuric acid

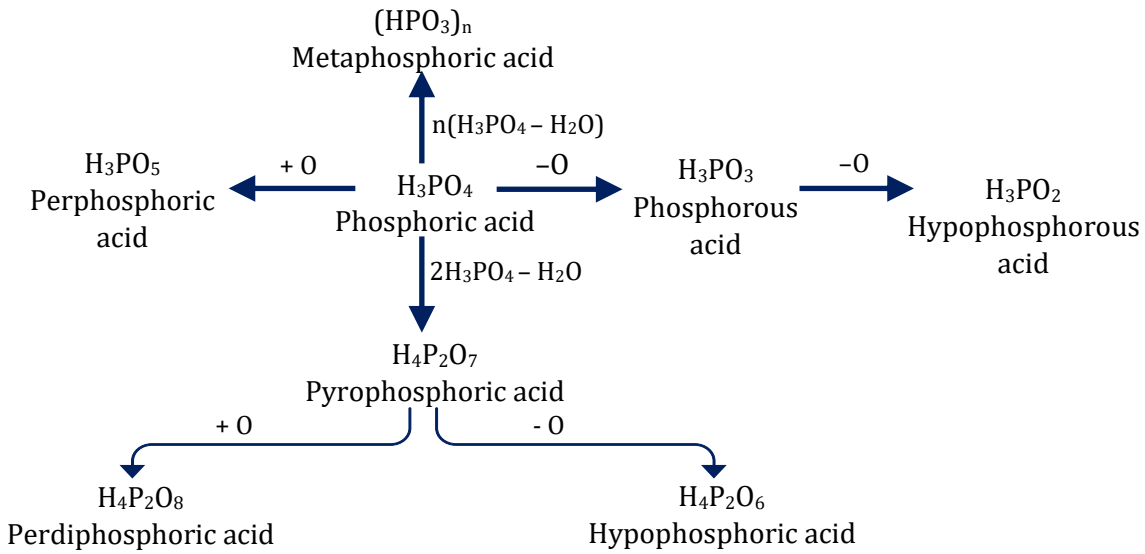
$HClO_3$ Chloric acid

Note :

Halogens form parent 'ic' acid in +5 O.S. instead of +7.



Example :

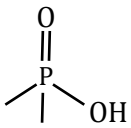


Structures of Oxyacid :

Rules to Draw Structures of Oxyacids :

1. No. of '-H' = No. of '-OH' (Except oxyacids of Phosphorus).

2. For oxy acids of Phosphorus :



3. If Central atom belongs to : 2^{nd} period $\rightarrow$ sp^2 hybridisation

3^{rd} period $\rightarrow$ sp^3 hybridisation

4. For Oxyacids or oxides having **two Central atom** :

(a) If calculated OS < Max OS $\rightarrow$ X-X

(b) If calculated OS = Max OS $\rightarrow$ X-O-X

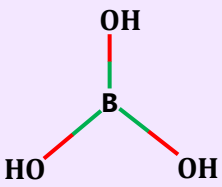
(c) If calculated OS > Max OS $\rightarrow$ X-O-O-X

5. If oxyacid have only **one Central atom** and **calculated OS > Max OS $\rightarrow$ X-O-O-H**

Max OS = Valence electrons
Calculated OS = OS using Formula

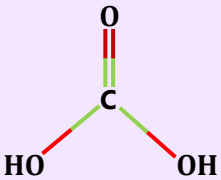
Example :

Boric Acid
H_3BO_3



Basicity = 1*

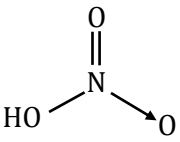
Carbonic Acid
H_2CO_3



Basicity = 2

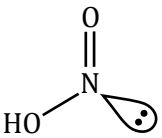
Oxyacid of Nitrogen

Nitric acid (HNO_3)



Basicity = 1

Nitrous acid (HNO_2)

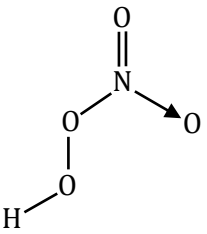


Basicity = 1

Pernitric acid (HNO_4)

Calculated OS > Max OS

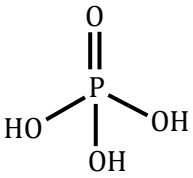
→ X-O-O-H



asicity = 1

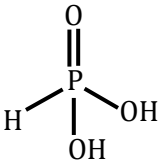
Oxyacid of Phosphorus :

Orthophosphoric acid/ Phosphoric acid (H_3PO_4)



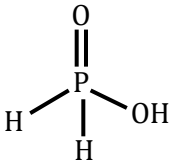
Basicity = 3

Orthophosphorus acid/ Phosphorus acid/ Phosphonic acid (H_3PO_3)



Basicity = 2*

Hypophosphorus acid/ Phosphinic acid (H_3PO_2)

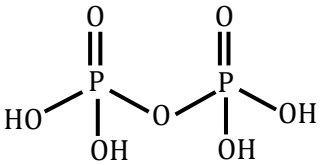


Basicity = 1*

Pyrophosphoric acid/ Diphosphoric acid ($H_4P_2O_7$)

Calculated OS = Max OS

→ X-O-X

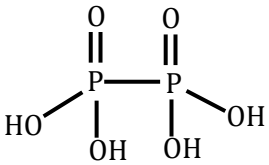


Basicity = 4

Hypophosphoric acid ($H_4P_2O_6$)

Calculated OS < Max OS

→ X-X



Basicity = 4

Perdiphosphoric Acid ($H_4P_2O_8$)

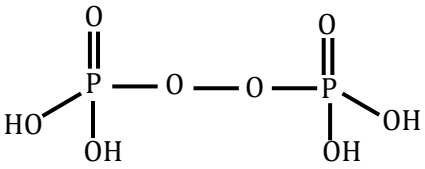
Calculated OS > Max OS

→ X-O-O-X

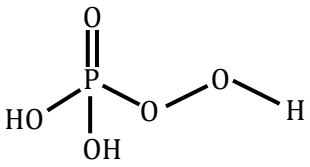
Perphosphoric Acid (H_3PO_5)

Calculated OS > Max OS

→ X-O-O-H



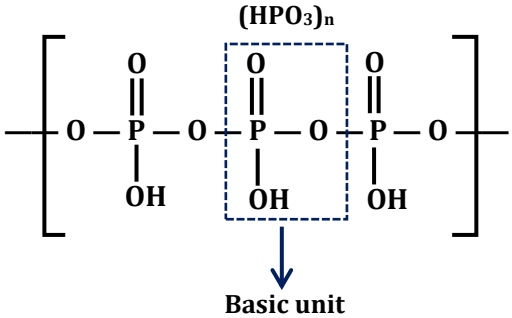
Basicity = 4

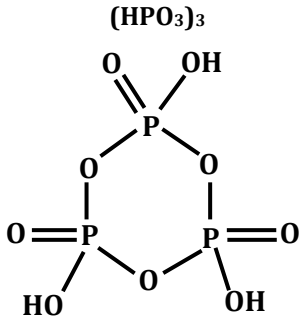


Basicity = 3

Metaphosphoric acid (HPO_3)

Metaphosphoric acid exists as dimer, cyclic trimer or polymer.

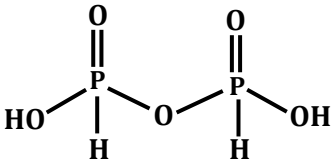




Cyclic Trimetaphosphoric Acid

Pyrophosphorous acid ($H_4P_2O_5$)

Calculated OS < Max OS $\rightarrow$ ~~X — X~~ $\rightarrow$ X — O — X



Basicity = **2***

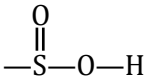
Types of Oxyacids of Sulphur

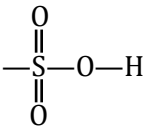
Normal

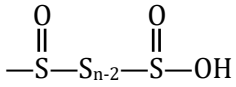
- In which oxidation state of sulphur is +2, +4, +6

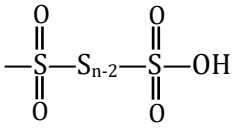
Thio

- In which oxidation state of sulphur is +3, +5

Suffix – ous $\Rightarrow$ 

Suffix – ic $\Rightarrow$ 

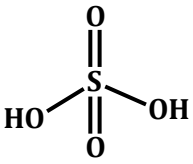
Suffix – Thionous $\Rightarrow$ 

Suffix – Thionic $\Rightarrow$ 

n = no. of sulphur atom

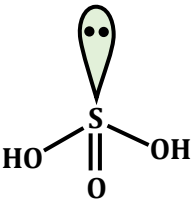
Oxyacids of Sulphur :

Sulphuric acid
(H_2SO_4)



Basicity = 2

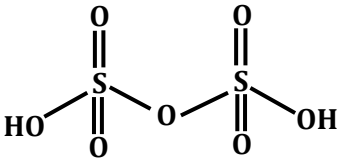
Sulphurous acid
(H_2SO_3)



Basicity = 2

Pyrosulphuric acid/Oleum

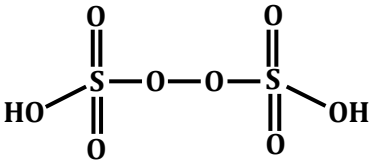
Oleum ($H_2S_2O_7$)
Calculated OS = Max OS
→ X-O-X



Basicity = 2

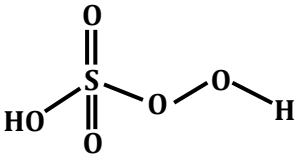
Peroxodisulphuric acid/
Marshall's Acid ($H_2S_2O_8$)

Calculated OS > Max OS
→ X-O-O-X



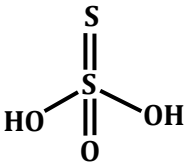
Basicity = 2

Peroxomonosulphuric Acid/
Persulphuric acid/
Caro's Acid (H_2SO_5)
Calculated OS > Max OS
→ X-O-O-H



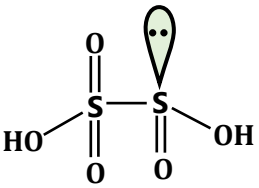
Basicity = 2

Thiosulphuric acid
($H_2S_2O_3$)



Basicity = 2

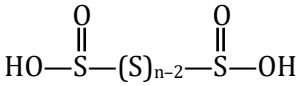
Pyrosulphurous acid
($H_2S_2O_5$)



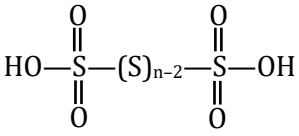
Basicity = 2

Oxy acids containing (S-S linkage)

Polythionous
$H_2S_nO_4$
O.S. = +3



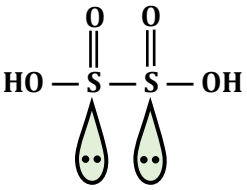
Polythionic
$H_2S_nO_6$
O.S. = +5



[Number of S–S-linkage = Number of Sulphur atom-1]

Dithionous Acid

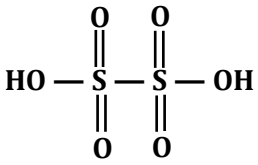
$H_2S_2O_4$



Basicity = 2

Dithionic Acid

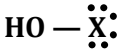
$H_2S_2O_6$

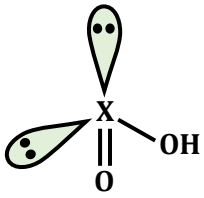


Basicity = 2

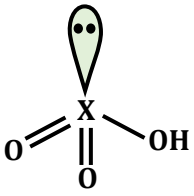
Oxyacid of Halogens :

Element	Hypohalous Acid (HOX)	Halous Acid (HXO_2)	Halic Acid (HXO_3)	Perhalic Acid (HXO_4)
F	HOF	-	-	-
Cl	HOCl	$HClO_2$	$HClO_3$	$HClO_4$
Br	HOBr	-	$HBrO_3$	$HBrO_4$
I	HOI	-	HIO_3	HIO_4

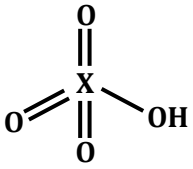




sp^3, Bent

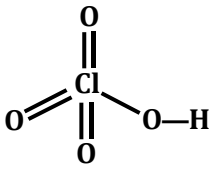


sp^3, Pyramidal



sp^3, tetrahedral

Perchloric Acid ($HClO_4$)



Number of peroxy(-O-O-) linkage = 0

Not a True per acid

Heating effect of oxyacid :

(i) Heating effect of Phosphoric Acid :-

$$2H_3PO_4 \xrightarrow[-H_2O]{200^\circ C} H_4P_2O_7 \xrightarrow[-H_2O]{600^\circ C} (HPO_3)_2 \xrightarrow[\text{Red hot}\ -H_2O]{\Delta} P_2O_5$$

(ii) Heating effect of Boric Acid :-

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow[-H_2O]{100^\circ C} \underset{\text{Meta Boric acid}}{HBO_2} \xrightarrow[-H_2O]{\Delta} \underset{\text{Boric Anhydride or Boron sesquioxide}}{B_2O_3}$$

Anhydride :

When water is completely removed from oxyacid

Types of Anhydrides :-

(a) Normal anhydride

Non-metal oxide which is obtained on removal of water from one type of oxyacid

$H_3PO_4 \xrightarrow{\Delta} P_2O_5 + H_2O$

$H_2CO_3 \xrightarrow{\Delta} CO_2 + H_2O$

(b) Mixed anhydride

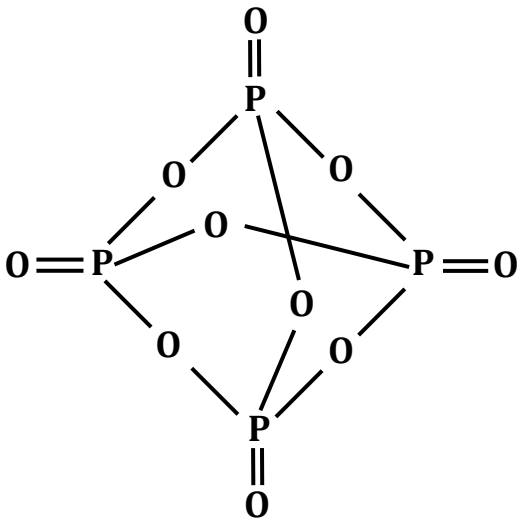
Non-metal oxide which is obtained on removal of water from two types of oxyacids

$HNO_3 + HNO_2 \xrightarrow{\Delta} N_2O_4 + H_2O$

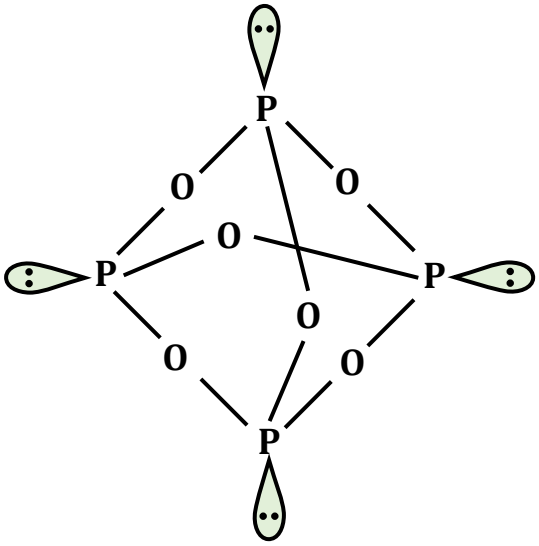
$HClO_3 + HClO_4 \xrightarrow{\Delta} Cl_2O_6 + H_2O$

Oxides Of Phosphorus

$(P_2O_5)_2/P_4O_{10}$

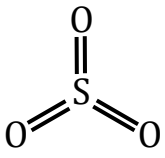


$(P_2O_3)_2/P_4O_6$

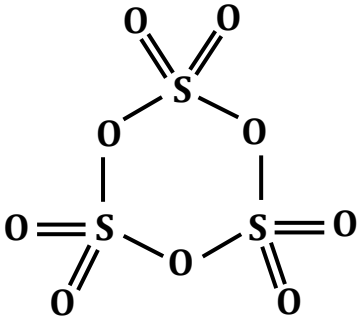


Oxides of Sulphur

(SO_3) Sulphur Trioxide



$(SO_3)_3$ /(S_3O_9) / Solid SO_3



Heating effect of oxyacid :-

Heating effect of "-ous acid"

(i) $\overset{+3}{H}NO_2 \xrightarrow{\Delta} \overset{+5}{H}NO_3 + \overset{+2}{N}O$

(ii) $H_3\overset{+3}{P}O_3 \xrightarrow{\Delta} H_3\overset{+5}{P}O_4 + \overset{-3}{P}H_3$

(iii) $\overset{+1}{H}ClO \xrightarrow{\Delta} \overset{+5}{H}ClO_3 + \overset{-1}{H}Cl$

Acidic Nature of oxyacid :-

If Central Atom is same ⇒ Acidic Nature ∝ Oxidation Number

(i) $HNO_2 < HNO_3$ **(ii)** $H_2SO_4 > H_2SO_3$ **(iii)** $HClO < HClO_2 < HClO_3 < HClO_4$

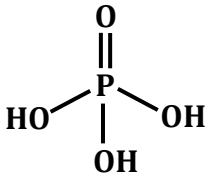
If Central Atom is different ⇒ Acidic Nature ∝ Electronegativity

(i) $H_3BO_3 < H_2CO_3 < HNO_3$ **(ii)** $HClO_3 > HBrO_3 > HIO_4$

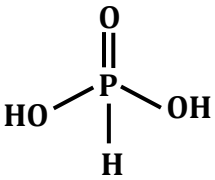
Reducing Nature of oxyacid :-

In Oxyacids of Phosphorus ⇒ Reducing Nature ∝ No. of P-H bonds

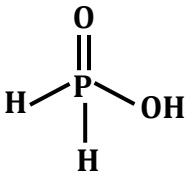
Order of reducing nature ⇒ H_3PO_2 > H_3PO_3 > H_3PO_4



Number of P–H Bond = 0



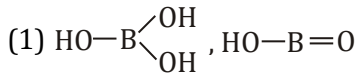
Number of P–H Bond = 1

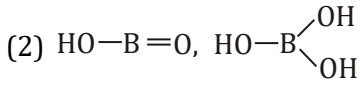


Number of P–H Bond = 2

BEGINNER'S BOX-2

1. Structures of metaboric acid and orthoboric acid respectively are :

(1) 

(2) 

(3) Both the above

(4) None

CPB236

2. Hypophosphorus acid (H_3PO_2) is –

(1) Tribasic acid (2) Dibasic acid (3) Monobasic acid (4) Not acidic at all

CPB237

3. The correct order of decreasing acid strength of oxy acids of group 15 elements is :

(1) $HNO_3 > H_3SbO_4 > H_3AsO_4 > H_3PO_4$ (2) $H_3PO_4 > H_3AsO_4 > H_3SbO_4 > HNO_3$

(3) $HNO_3 > H_3PO_4 > H_3AsO_4 > H_3SbO_4$ (4) $HNO_3 > H_3AsO_4 > H_3PO_4 > H_3SbO_4$

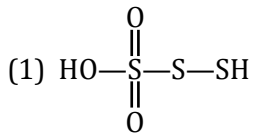
CPB238

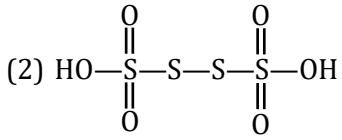
4. Which one of the following is a mixed anhydride :

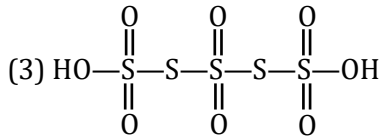
(1) NO (2) NO_2 (3) N_2O_3 (4) N_2O_5

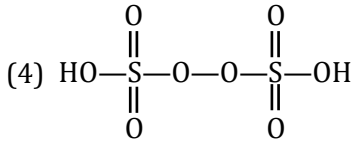
CPB239

5. The structure of peroxodisulphuric acid is :

(1) 

(2) 

(3) 

(4) 

CPB240

6. Number of S–S bond in $H_2S_nO_6$

(1) n (2) (n–1) (3) (n–2) (4) (n+1)

CPB241

7. Ga^+ acts as a reducing agent because –

(1) Ga^{3+} state is less stable than Ga^{+1} (2) Ga^{3+} state is more stable than Ga^{+1}

(3) Ga^{3+} convert into Ga^{+1} (4) None of the above

CPB242

8. In inert pair effect which pair of electrons are said to be inert

(1) 2 electrons of (n–1)s (2) 2 electrons of (n–1)d

(3) 2 electrons of np (4) 2 electrons of ns

CPB243

Hydrolysis - Mechanism and Hydrolysis of Some Important Covalent Molecules :

$$A-B+H_2O\longrightarrow A-O-H+H-B$$

Hydrolysis of covalent compound is Lewis Acid – Lewis Base reaction in which H_2O acts as Lewis Base.

Only those compounds undergo hydrolysis at room temperature, in which vacant orbital is present on more electropositive element.

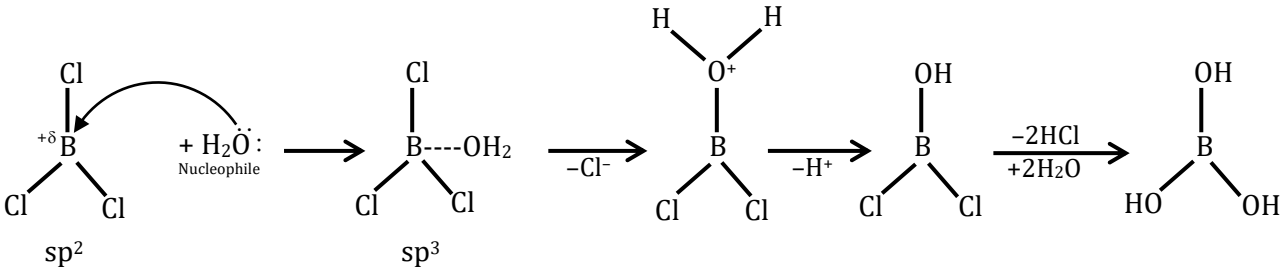
(Weaker base goes out and a stronger base substitutes it.)

Example :

(i) $BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl\uparrow$ (White Fumes)

or H_3BO_3

(Ortho Boric Acid)



For hybridisation of transition state

Reactant	⟶	Transition state
sp	⟶	sp^2
sp^2	⟶	sp^3
sp^3	⟶	sp^3d

Example :

(i) $BBr_3 + 3H_2O \longrightarrow B(OH)_3 + 3HBr\uparrow$

or H_3BO_3

(Ortho Boric Acid)

(ii) $SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl\uparrow$ (White Fumes)

(Silicic Acid)

(iii) $AlCl_3 + 6H_2O \longrightarrow \underbrace{[Al(H_2O)_6]^{3+}}_{\text{Ionic compound due to hydration}} + 3Cl^-\uparrow$

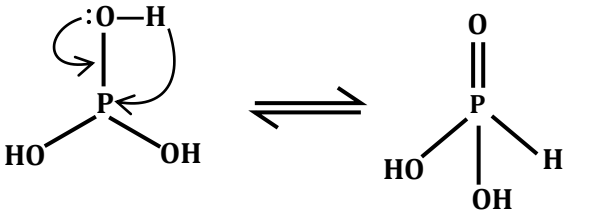
(iv) $CCl_4 + 4H_2O \longrightarrow$ No Hydrolysis

(v) $NCl_3 + H_2\ddot{O} \longrightarrow NH_3 + \underset{\text{Hypochlorous Acid}}{3HOCl}$

(vi) $SF_6 + H_2O \longrightarrow$ No hydrolysis

(vii) $PCl_3 + 3H_2\ddot{O} \longrightarrow P(OH)_3 + 3HCl$

Hydrolysis is followed by Tautomerism.

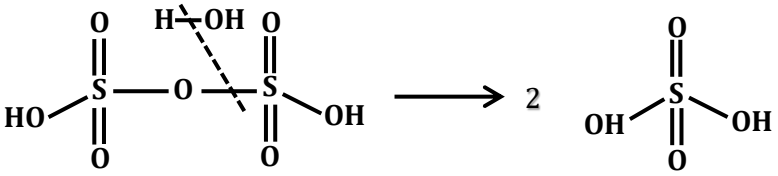


Phosphorous Acid (H_3PO_3)

Hydrolysis of Oxyacids :

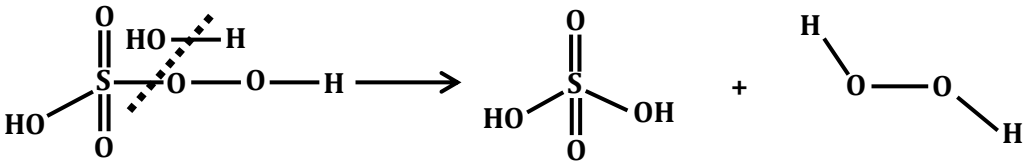
1. Pyrosulphuric Acid (Oleum)

$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$



2. Peroxomonosulphuric Acid (Caro's Acid)

$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$

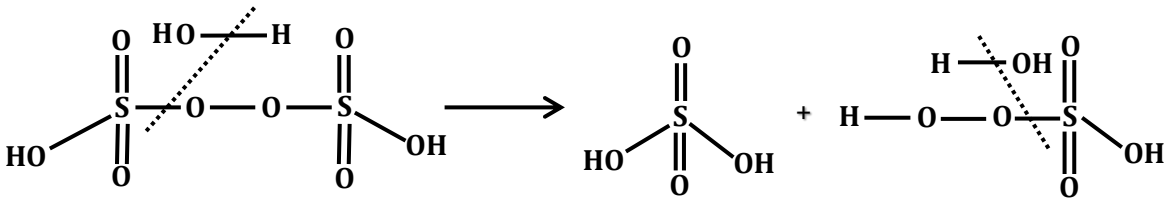


Note :

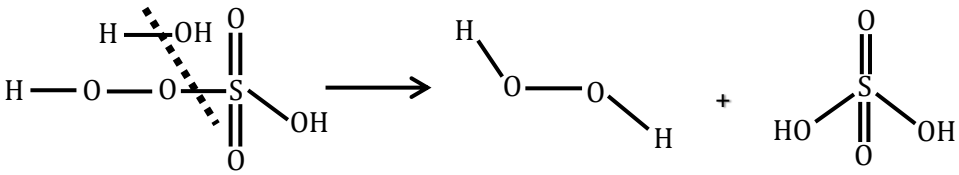
If Cal. OS > Max. OS, than on complete hydrolysis one of the product is H_2O_2 and other is Parent 'ic' acid.

3. Peroxodisulphuric Acid (Marshall's Acid)

$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$



$H_2SO_5 \xrightarrow{+H_2O} H_2SO_4 + H_2O_2$



$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$

$\xrightarrow{+H_2O} H_2SO_4 + H_2O_2$

Generally, one of the product of complete hydrolysis is oxyacid of more electropositive element in same Oxidation State.

$B^{+3} \longrightarrow H_3BO_3$ $S^{+4} \longrightarrow H_2SO_3$ $C^{+4} \longrightarrow H_2CO_3$

$S^{+6} \longrightarrow H_2SO_4$ $N^{+3} \longrightarrow HNO_2$ $Cl^{+1} \longrightarrow HClO$

$N^{+5} \longrightarrow HNO_3$ $Cl^{+3} \longrightarrow HClO_2$ $Si^{+4} \longrightarrow H_4SiO_4$

$Cl^{+5} \longrightarrow HClO_3$ $P^{+3} \longrightarrow H_3PO_3$ $Cl^{+7} \longrightarrow HClO_4$

$P^{+5} \longrightarrow H_3PO_4$

If element of odd group has even OS or element of even group has odd OS, than disproportionation reaction takes place

$N^{+4} \longrightarrow HNO_2 + HNO_3$ $S^{+5} \longrightarrow H_2SO_3 + H_2SO_4$ $P^{+4} \longrightarrow H_3PO_3 + H_3PO_4$

where $+3 < x < +5$

$Cl^{+2} \longrightarrow HClO + HClO_2$ $Cl^{+4} \longrightarrow HClO_2 + HClO_3$ $Cl^{+6} \longrightarrow HClO_3 + HClO_4$

Hydrolysis of Interhalogen Compounds :

1. $XX' + H_2O \longrightarrow HOX + HX'$ $\quad ClF + H_2O \longrightarrow HOCl + HF$

Electronegativity of $\Rightarrow$ X < X'

2. $XX'_3 + H_2O \longrightarrow HXO_2 + HX'$ $\quad ClF_3 + H_2O \longrightarrow HClO_2 + HF$

3. $XX'_5 + H_2O \longrightarrow HXO_3 + HX'$ $\quad ClF_5 + H_2O \longrightarrow HClO_3 + HF$

4. $XX'_7 + H_2O \longrightarrow HXO_4 + HX'$ $\quad IF_7 + H_2O \longrightarrow HIO_4 + HF$

Q. Write the complete hydrolysed products in the following :

1. $IF_7 + H_2O \longrightarrow HIO_4 + HF$

2. $ClF_5 + H_2O \longrightarrow HClO_3 + HF$

3. $BrF_5 + H_2O \longrightarrow HBrO_3 + HF$

4. $IF_5 + H_2O \longrightarrow HIO_3 + HF$

5. $BrCl + H_2O \longrightarrow HBrO + HCl$

6. $BrF + H_2O \longrightarrow HBrO + HF$

Degree of Hydrolysis $\propto$ Covalent character

$NaCl < MgCl_2 < AlCl_3 < SiCl_4$

$LiCl < BeCl_2 < BCl_3 < CCl_4$ — No hydrolysis

$BF_3 < BCl_3 < BBr_3 < BI_3$

$NCl_3 > PCl_3 > AsCl_3 > SbCl_3 > BiCl_3$

$SF_6 < SeF_6$ — No hydrolysis

Some Special Cases

(I) Hydrolysis of BX_3

BF_3 undergoes partial hydrolysis.

$4BF_3 + 3H_2O \longrightarrow 3H[BF_4] + B(OH)_3$

While BCl_3, BBr_3 and BI_3 undergoes complete hydrolysis.

$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl$ $\quad$ $BBr_3 + 3H_2O \longrightarrow B(OH)_3 + 3HBr$

$BI_3 + 3H_2O \longrightarrow B(OH)_3 + 3HI$

Note:

BCl_4^-, BBr_4^- and BI_4^- are unstable due to large size of surrounding atoms.

(II) Hydrolysis of SiX_4

SiF_4 undergoes partial hydrolysis.

$3SiF_4 + 4H_2O \longrightarrow 2H_2SiF_6 + H_4SiO_4$

While $SiCl_4$, $SiBr_4$ and SiI_4 undergoes complete hydrolysis.

$SiCl_4 + 4H_2O \longrightarrow H_4SiO_4 + 4HCl$ $\quad$ $SiBr_4 + 4H_2O \longrightarrow H_4SiO_4 + 4HBr$

$SiI_4 + 4H_2O \longrightarrow H_4SiO_4 + 4HI$

Hydrolysis of grp-15 chlorides

$NCl_3 + H_2O \longrightarrow NH_3 + HOCl$

$PCl_3 + H_2O \longrightarrow H_3PO_3 + 3HCl$

$AsCl_3 + H_2O \longrightarrow H_3AsO_3 + 3HCl$

$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$

Antimonyl Chloride

$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$

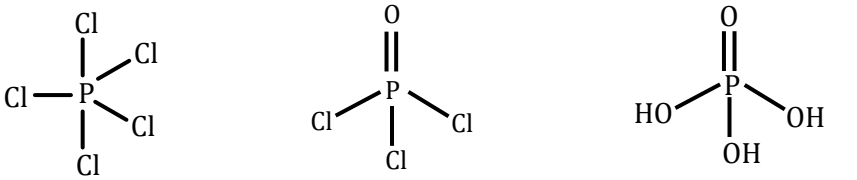
Bismuthyl Chloride

(White ppt also known as white pearl)

Partial hydrolysis of PCl_5

i. $\mathbf{PCl_5 + H_2O \longrightarrow 2\,HCl + POCl_3}$

$\mathbf{+ 3H_2O \longrightarrow H_3PO_4 + 3\,HCl}$



(III) Hydrolysis of Xenon Fluorides :

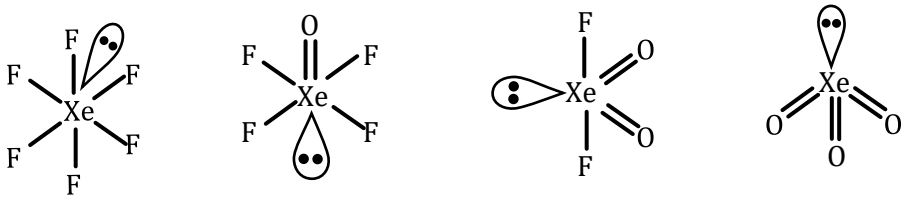
(i) $2XeF_2 + 2H_2O \longrightarrow 2Xe + O_2 + 4HF$

(ii) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

(iii) $XeF_4 + 2H_2O \longrightarrow Xe + XeO_3 + O_2 + 4HF$

Partial hydrolysis of XeF_6

$\mathbf{XeF_6 \xrightarrow{+H_2O} XeOF_4 + 2HF \xrightarrow{+H_2O} XeO_2F_2 + 2HF \xrightarrow{+H_2O} XeO_3 + 2HF}$



Reaction of H_2O with Ionic compounds

$A^{+x}B^{-y} + H^+OH^- \longrightarrow A(OH)_x + BH_y \uparrow$

(I) Nitrides

(i) $Li_3N \xrightarrow{+H_2O} LiOH + NH_3 \uparrow$ **(ii)** $Mg_3N_2 \xrightarrow{+H_2O} Mg(OH)_2 + NH_3 \uparrow$

(II) Phosphides

(i) $Ca_3P_2 \xrightarrow{+H_2O} Ca(OH)_2 + PH_3 \uparrow$

Hydrolysis of Ionic Compounds :

(III) Carbides

(i) Methanides (C^{-4} Units) : Produce CH_4 on reacting with water.

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

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

(ii) Acetylides (C_2^{-2} Units) : Produce C_2H_2 on reacting with water.

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

(iii) Allylides (C_3^{-4} Units) : Produce C_3H_4 on reacting with water.

$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + C_3H_4$ (Propyne)

Reaction between Non-metals and water

Non-Metal + $H_2O \longrightarrow$ "-ous" Oxyacid + Lowest O.S. Product

(i) $Cl_2 + H_2O \longrightarrow HOCl + HCl$

Mechanism :

$Cl\text{—}Cl + H\text{—}OH \longrightarrow HOCl + HCl$

(ii) $Br_2 + H_2O \longrightarrow HOBr + HBr$

(iii) $I_2 + H_2O \xrightarrow{\Delta} HOI + HI$ (Does not takes place at room temperature)

(iv) $F_2 + H_2O \longrightarrow 2HF + \frac{1}{2} O_2$

'F_2' is the only non-metal that can oxidise H_2O as it is a powerful oxidising agent. Other halogens & non-metals undergo disproportionation with water in basic medium. (Redox reaction)

O_3 is also produced in small amount & mixture of O_2 & O_3 is known as ozonised oxygen.

Reaction between Non-metals and water in alkaline medium

Non- Metals show disproportionation reaction with water in alkaline medium (aqueous NaOH).

Non-Metal + $NaOH_{(aq)} \longrightarrow$ "-ous" Oxidation State product + Lowest Oxidation State Product

(i) $Cl_2 + NaOH_{(aq)} \longrightarrow NaOCl + NaCl$

H_2O

$HOCl + HCl$

$NaOH_{(aq)}$

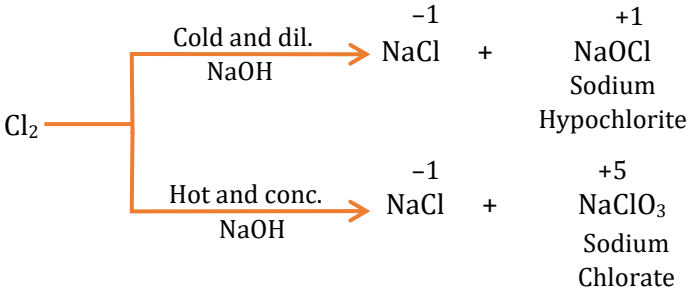
Reaction between Non-metals and water (in alkaline medium)

X_2 (Cl_2, Br_2, I_2)

Cold and dil. NaOH → NaX + $NaOX$ Sodium Hypohalite

Hot and conc. NaOH → NaX + $NaXO_3$ Sodium Halate

Reaction between Non-metals and water (in alkaline medium)



(ii) P_4 + NaOH → PH_3 (−3) + NaH_2PO_2 (+1) Sodium Hypophosphite

(iii) S_8 + NaOH → H_2S (−2) + $Na_2S_2O_3$ (+2) Sodium Thiosulphate

BEGINNER'S BOX-3

1. Which of the following statements is correct :

(1) Aluminium carbide as well as beryllium carbide produce methane gas on treatment with water

(2) On reacting with water, calcium carbide (CaC_2) produces acetylene while magnesium carbide (Mg_2C_3) gives propyne

(3) Both (1) and (2)

(4) None of the above

CPB244

2. (a) $Al \xrightarrow[\text{High temp.}]{N_2} A$ (b) $Al \xrightarrow[\text{High temp.}]{C} B$

Product A and B on hydrolysis yields respectively.

(1) Ammonia and acetylene (2) Ammonia and methane

(3) Nitric oxide and acetylene (4) None

CPB245

3. The hydrolysis of PCl_3 produces :

(1) $H_3PO_3 + HClO$ (2) $H_3PO_3 + HCl$ (3) $H_3PO_4 + HCl$ (4) $PH_3 + HClO$

CPB246

4. The number of molecules of water needed to convert one molecule of P_2O_5 into orthophosphoric acid is :

(1) 2 (2) 3 (3) 4 (4) 5

CPB247

5. Which of the following halides does not hydrolysed?

(1) NCl_3 (2) $SiCl_4$ (3) CCl_4 (4) PCl_3

CPB248

6. Consider the following reactions :

(i) $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$ (ii) $SF_4 + 3H_2O \rightarrow H_2SO_3 + 4HF$

(iii) $BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$ (iv) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

Then according to given information the incorrect statement is

(1) During the (i) reaction the hybridisation of 15th group element does not change

(2) During the (ii) reaction the hybridisation of 16th group element has been change

(3) During the (iii) reaction the hybridisation of 13th group element does not change

(4) During the (iv) reaction the hybridisation of 18th group element does not change

CPB249

7. Give the name of final product in following reaction.

$SiCl_4 \xrightarrow{\text{Hydrolysis}}$ product

(1) Silicic Acid (2) Dichlorido di hydroxo silicate

(3) Silicones (4) Silicone carbide

CPB250

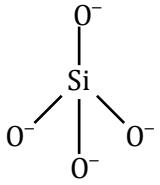
Compounds of silicon :

(I) Silicates

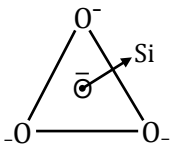
Naturally occurring minerals.

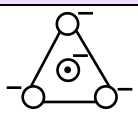
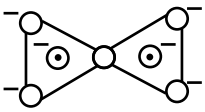
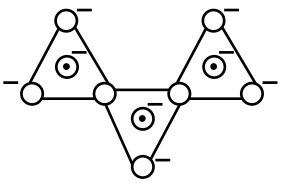
Si and O atoms have poor tendency to form π bond, so these silicates anion have tendency to form polymer.

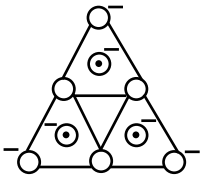
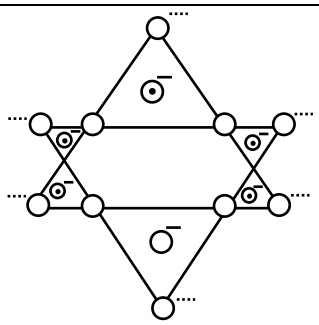
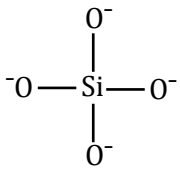
Basic structural unit is SiO_4^{-4}.



sp^3 hybridised



Silicate	No. of shared oxygen per unit	General formula	Structure	Example
Ortho silicate	0	SiO_4^{-4}		Zircon ($ZrSiO_4$)
Pyro silicate	1	$Si_2O_7^{-6}$		Hemi morphite $Zn_3Si_2O_7.Zn(OH)_2.2H_2O$)
Single chain silicate	For terminal unit-1 For centre unit-2	$(SiO_3^{-2})_n$ But not true formula of single chain silicate		$Ca_2Cu_2Si_3O_{10}$ (Kinoite)

Cyclic silicate	2	$(SiO_3^{-2})_n$ True formula of cyclic silicate		Beryl ($Be_3Al_2Si_6O_{18}$)
Sheet silicate	3	$(Si_2O_5^{-2})_n$		Talc $(Mg_3(OH)_2)(Si_2O_5)_2$
3-D silicate	4	$(SiO_2)_n$		Silica (SiO_2)

Some important example of silicates

(i) Sodium Zeolite $[Na_2Al_2Si_2O_8]/[Na_2O.Al_2O_3 . 2SiO_2.xH_2O]$

(i) It is a 3-D silicate

(ii) It is used as :

(a) An ion exchanger for softening of hard water.

(b) A catalyst in petrochemical industries for cracking of hydrocarbon & isomerisation.

Ex. ZSM-5 (Zeolite) is used to convert ethyl alcohol into petrol.

(ii) Silicon dioxide (SiO_2)/Silica

Occurs in different forms like quartz, cristobalite and tridymite.

Almost non-reactive due to strong Si–O bond.

However, it is attacked by NaOH and HF

Quartz is used to develop accurate clocks, modern radio & TV broadcasting & mobile radio communication.

Silica gel is used as drying agent.

Kieselguhr is amorphous form of silica which is used in filtration plants.

(i) $2NaOH + SiO_2 \longrightarrow \underset{\text{water glass}}{Na_2SiO_3} + H_2O$

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

$SiF_4 + 2HF \longrightarrow \underset{\substack{\text{hexa fluro}\\\text{silicic acid}}}{H_2[SiF_6]}$ } **Etching of glass.**

(II) Silicones

Silicones are organosilicone polymer which contain R_2SiO as a repeating unit.

Properties :

(i) Silicones are chemically inert due to the presence of strong sigma bond.

(ii) Silicones have water repelling nature due to presence of alkyl group.

(iii) Silicones are electric insulator due to absence of free electrons.

Preparation :

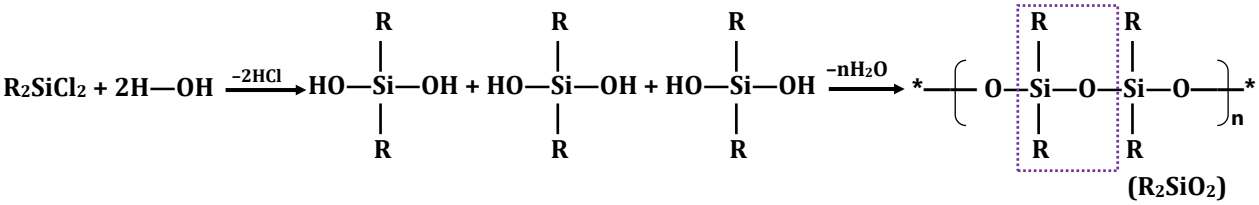
Alkyl chloro silane $\xrightarrow{\text{hydrolysis}}$ product $\xrightarrow{\text{condensation}}$ silicones

R_3SiCl : Used to stop chain length of silicones

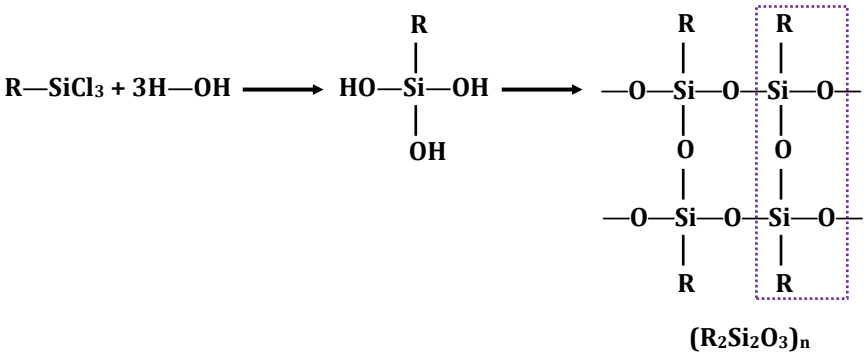
R_2SiCl_2 : Used to form single chain silicones

$RSiCl_3$: Used to form cross link silicones

(i) Linear chain silicone (Single chain silicones)



(ii) Cross linked silicone/Double chain silicone



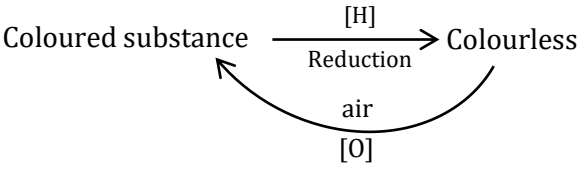
Bleaching Agents :

Bleaching can be done by Oxidation or by Reduction

(I) Permanent Bleaching (by Oxidation)

Coloured substance $\xrightarrow[\text{Oxidation}]{[O]}$ Colourless

(II) Temporary Bleaching (by Reduction)



(I) Permanent Bleaching (by Oxidation)

(i) O_3 (Dry bleach) $\quad O_3 \longrightarrow O_2 + [O]$

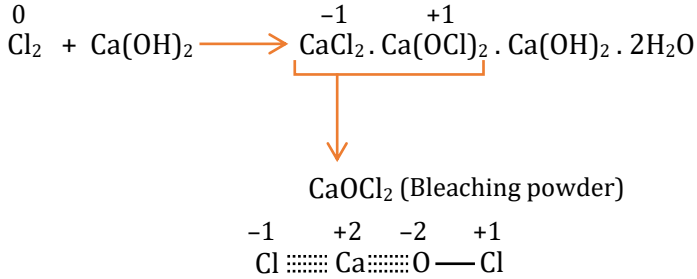
(ii) H_2O_2 (with moisture) $\quad H_2O_2 \longrightarrow H_2O + [O]$

(iii) Cl_2 (with moisture) $\quad Cl_2 + H_2O \longrightarrow HCl + HOCl$

Note :

Aqueous solution of Chlorine turns litmus paper red but afterwards the red color disappears.

Bleaching powder



$CaOCl_2 + H_2O \longrightarrow CaCl_2 + [O]$

(II) Temporary Bleaching (by Reduction)

(i) SO_2 (with moisture) $\qquad SO_2 + \text{Moisture} \longrightarrow [H]$

Dehydrating Agents :

Dehydrating Agents are used to absorb the moisture

Example:

P_4O_{10}, Conc.H_2SO_4, CaO, Anhydrous $CaCl_2$

$$\text{Acid} \xrightarrow[\text{Agent}]{\text{Dehydrating}} H_2O + \text{Oxide}$$

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

(Laboratory Preparation of CO)

ii. $\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow[H_2SO_4]{\text{Conc.}} CO + CO_2 + H_2O$

iii. $\begin{matrix}COOH\\|\\CH_2\\|\\COOH\\\text{Malonic Acid}\end{matrix} \xrightarrow[H_2SO_4]{\text{Conc.}} \underset{\substack{\text{Carbon}\\\text{Suboxide}}}{C_3O_2} + 2H_2O$

O=C=C=C=O

Charring of sugar

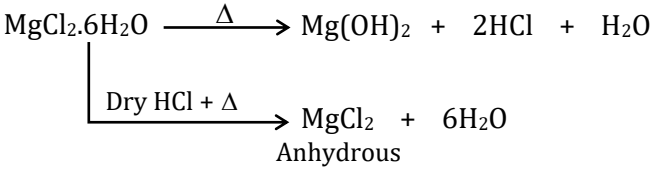
iv. $C_{12}H_{22}O_{11} \xrightarrow[H_2SO_4]{\text{Conc.}} 11H_2O + \underset{\text{Mass}}{\overset{\text{Black}}{C}}$

v. $2HNO_3 \xrightarrow{P_2O_5} N_2O_5$

Some extra points :

(i) NH_3 cannot be dried by conc. H_2SO_4, P_4O_{10} and $CaCl_2$

(ii) $MgCl_2.6H_2O$ and $AlCl_3.6H_2O$ cannot be dried by heating alone.

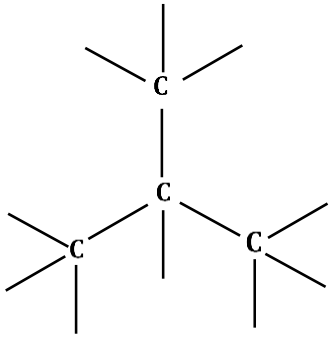
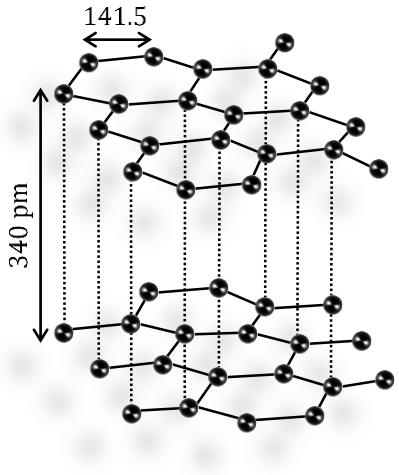


Allotropes :

(A) Allotropes of carbon

Allotropes of Carbon

Crystalline	Amorphous
Ex. Diamond	Ex. Coke
Graphite	Charcoal
Fullerene	Coal, C-lamp black

DIAMOND	GRAPHITE
	
Each carbon atom is bonded with four other carbon atoms	Each carbon atom is bonded with three other carbon atoms
sp^3 hybridisation	sp^2 hybridisation
Tetrahedral structure	Hexagonal layer structure
Insulator due to the absence of free electrons	Conductor due to the presence of delocalised electrons
Hard due to the presence of strong sigma bond and 3D structure	Soft due to the presence of weak van der Waals forces between two layers
Density = 3.35 gm/cm^3	Density = 2.22 gm/cm^3
High melting point (giant molecule)	Low melting point
Bond length (C—C) = 1.54Å	Bond length (C—C) = 1.41Å

Special Point :

(i) Thermodynamically graphite is more stable than diamond.

(ii) Aqueous solution of graphite is known as **aquadag**.

(iii) Graphite is also known as **plumbago (used in lead pencil)**

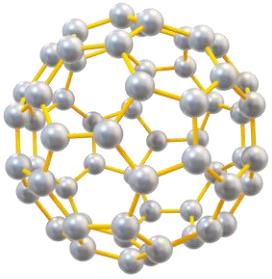
(iv) Graphite is used as a dry lubricant.

(v) **Hardest allotrope** of carbon is diamond, **softest allotrope** is lamp black, **purest allotrope** is fullerene

Dangling Bond

- Diamond and Graphite are not the purest allotropes of carbon because some surface carbon atoms have free valency.
- These carbon atoms form new bonds with impurities.
- These new bonds are known as Dangling Bond.

Fullerene

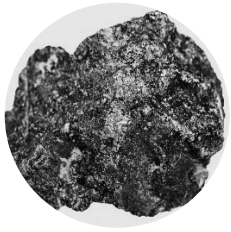


- C-60 & C-70 are common forms of fullerene.
- C-60 is also known as Buckminster fullerene (Bucky ball)
- There are 32 rings < 12 pentagonal rings, 20 hexagonal rings
- Each carbon atom bonded with 3 other carbon by sigma & double bond (resonance)
- sp^2 hybridisation & aromatic in nature
- It is a purest allotrope of carbon. (Dangling bond absent)

(B) Allotropes of Phosphorus

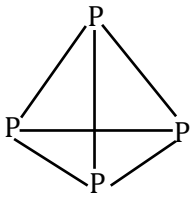
White Phosphorus

Red Phosphorus

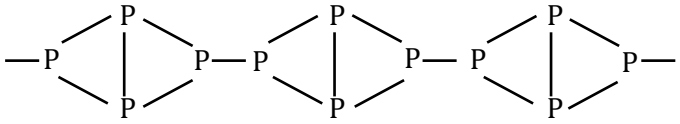


Black Phosphorus

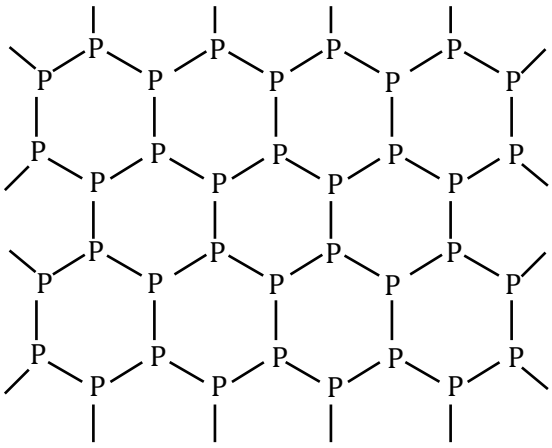
(i) White Phosphorus



(ii) Red Phosphorus

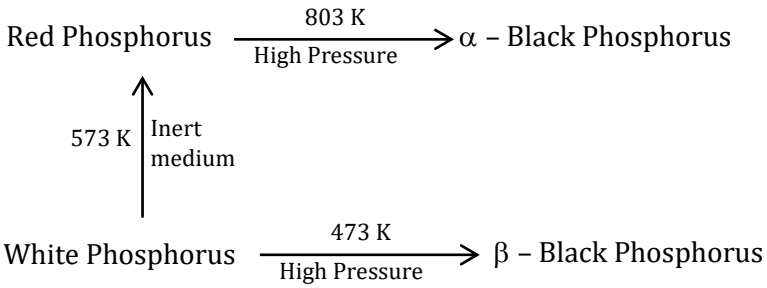


(iii) Black Phosphorus

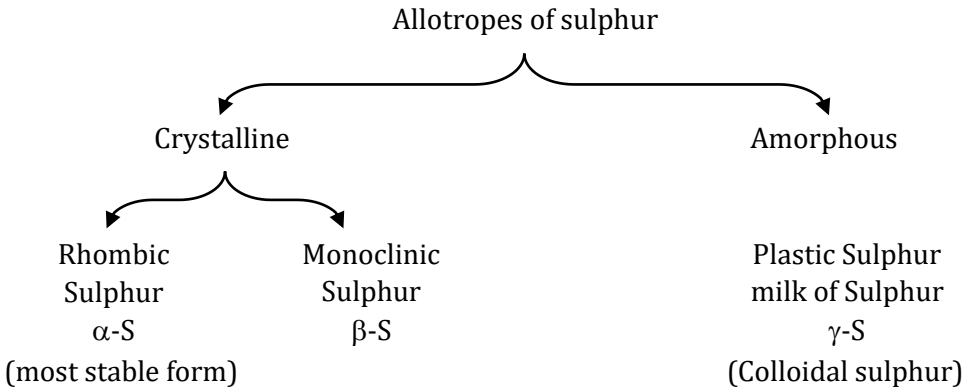


S.N.	Properties	White Phosphorus	Red Phosphorus
1.	Physical state	Waxy Solid	Brittle Powder
2.	Physiological action	Poisonous	Non-Poisonous
3.	Solubility in water	Insoluble	Insoluble
4.	Solubility in CS_2	Soluble	Insoluble
5.	Stability	Unstable	More Stable than White Phosphorus
6.	Phosphorescence	Glows in dark	Does not glow in dark

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

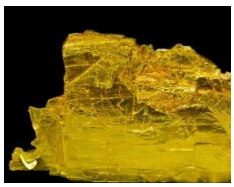


(C) Allotropes of Sulphur



$$\alpha - S \underset{< 95.6^\circ C}{\overset{> 95.6^\circ C}{\rightleftharpoons}} \beta - S$$

Rhombic Sulphur



Monoclinic Sulphur

Plastic Sulphur

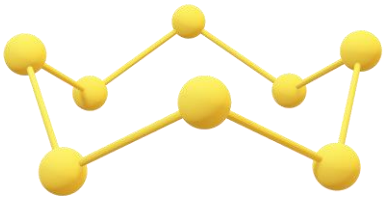
Note :

(i) Both α –S and β -S are soluble in CS_2 but insoluble in water.

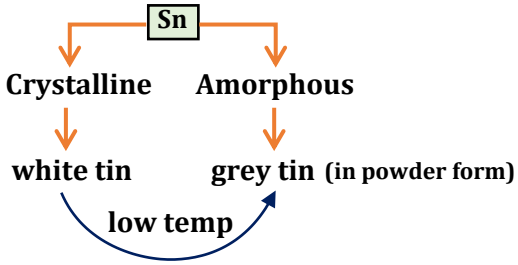
(ii) Both are puckered crown shape having S_8 units.

(iii) S_2 is paramagnetic sulphur which exist in vapour form at high temperature.

(iv) S_6 is chair form of sulphur.



(D) Allotropes of Tin



BEGINNER'S BOX-4

1. Silicones have the general formula
(1) SiO_4^{4-} (2) $Si_2O_7^{6-}$ (3) $(R_2SiO)_n$ (4) $(SiO_3)_n^{2-}$
CPB251

2. Glass or silica is soluble in :
(1) $HClO_4$ (2) HF (3) Aqua-regia (4) H_2SO_4
CPB252

3. $Si_2O_7^{6-}$ anion is obtained when
(1) No oxygen of a SiO_4^{-4} tetrahedron is shared with another SiO_4^{-4} tetrahedron
(2) One oxygen of a SiO_4^{-4} tetrahedron is shared with another SiO_4^{-4} tetrahedron
(3) Two oxygen of a SiO_4^{-4} tetrahedron is shared with another SiO_4^{-4} tetrahedron
(4) Three or all four oxygen of a SiO_4^{-4} tetrahedron is shared with another SiO_4^{-4} tetrahedron
CPB253

4. Consider the following route of reactions
R_2SiCl_2 + Water $\rightarrow$ (A) $\xrightarrow{\text{polymerisation}}$ (B)
Compound(B) in above reaction is
(1) Dimer silicone (2) Linear chain silicone
(3) Cross linked silicone (4) Polymerisation of (A) does not occur
CPB254

5. $(Si_2O_5)_n^{2n-}$ anion is obtained when
(1) No oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron
(2) One oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron
(3) Two oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron
(4) Three oxygen of a SiO_4^{4-} tetrahedron is shared with another SiO_4^{4-} tetrahedron
CPB255

6. What is true about various allotropes of carbon ?
(1) Diamond is thermodynamically more stable than graphite
(2) Both diamond and graphite are good conductor of electricity
(3) Diamond is harder than graphite
(4) Both graphite and fullerene are artificial allotropes of C
CPB256

7. Different layers in graphite are held together by :
(1) Ionic bonding (2) Metallic bonding
(3) Covalent bonding (4) Vander Waal's forces
CPB257

8. Which of the following is not related with white phosphorous ?
(1) It is more reactive than red phosphorous (2) It glows in dark
(3) It is highly poisonous (4) It is insoluble in both water and CS_2
CPB258

BORON FAMILY (GROUP-13) :

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.

General characteristics

(I) Physical properties :

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. Rest of the member are soft metals with low melting point and high electrical conductivity. Gallium with low melting point (303 K), can exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures. Density of the elements increases down the group from boron to Thallium.

(II) Oxidation state

(i) These elements show +1 and +3 oxidation states.

(ii) B & Al shows only +3 oxidation state. While other elements show +1 and +3 oxidation state.

(iii) +1 oxidation state is more stable on moving down the group due to increase in inert pair effect.

(iv) Relative stability of M^+ and M^{3+} ions may be given as :

$B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$

$B^{+} < Al^{+} < Ga^{+} < In^{+} < Tl^{+}$

Tl^+ ion is more stable than Tl^{3+} ion and thus, Tl^{3+} ion changes to Tl^+ ion therefore acting as an oxidising agent.

Tl^{3+} compounds + $2e^- \longrightarrow$ Tl^+ compounds

(III) Chemical properties

(i) Reactivity towards air

Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. 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.

$$2E_{(s)} + 3\,O_{2(g)} \xrightarrow{\Delta} 2\,E_2O_{3(s)};\ 2E_{(s)} + N_{2(g)} \xrightarrow{\Delta} 2\,EN_{(s)}.$$

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.

Chemistry of Boron- Orthoboric Acid, Borax :

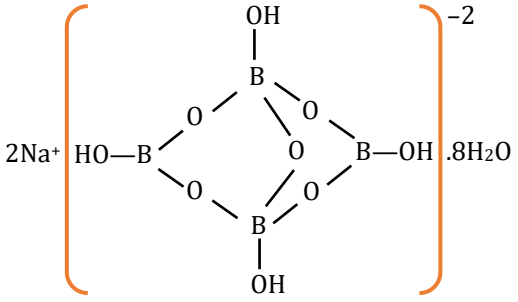
(I) Structure of Boron : Elemental boron exists in B_{12} form.

(II) Chemical Properties : It exists in five allotropes, four of which are crystalline and one is amorphous. All crystalline forms are very hard made up of clusters of B_{12} units. All crystalline forms are black in appearance and chemically inert. However, it is attacked at high temperature by strong oxidising agents such as a mixture of hot and concentrated H_2SO_4 and HNO_3 or Na_2O_2. But amorphous form is brown and chemically active.

(III) Compounds of Boron :

(i) Borax ($Na_2B_4O_7.10H_2O$)

$2Na^+\,[B_4O_5\,(OH)_4]^{-2}.8H_2O$



Important points :

B–O–B linkage = 5

Total B–O bonds = 14

Two B-sp^2 hybridised

Two B-sp^3 hybridised

Methods of Preparation

(I) From orthoboric acid

Borax is obtained by the action of Na_2CO_3 on orthoboric acid.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2\uparrow$$

Properties :

(i) Borax is a white powder, less soluble in cold water due to stable H-bonds within the molecule of borax, but more soluble in hot water, due to breaking of H-bonds present in borax, so that new H-bonds can easily form with water molecule.

(ii) Its aqueous solution is alkaline because of its hydrolysis to weak acid H_3BO_3 and strong alkali NaOH.

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

(iii) Action of heat.

When borax powder is heated, it first swells due to loss of water in the form of steam but at 740°C it converts into colourless transparent borax bead.

$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7$ $\qquad$ $Na_2B_4O_7 \xrightarrow{740°C} 2NaBO_2 + B_2O_3$ (borax bead)

Borax-bead test :

Borax reacts with certain metal salts such as, Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+} etc. to form coloured metaborates. The colour of the metaborates can be used to identify the metallic ions (cations) in salts.

$$Na_2B_4O_7{\cdot}10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{740°C} \underbrace{2NaBO_2 + B_2O_3}_{\text{glassy mass}} ; CuO + B_2O_3 \longrightarrow Cu(BO_2)_2 \text{ (blue bead)}$$

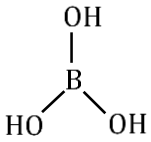
Ni^{2+} - Brown, Cu^{2+} - Pale blue, Co^{2+} - Dark blue, Mn^{2+} - Pink, Cr^{3+} - Green.

Uses : It is used

1. In borax bead test
2. In purifying gold
3. As flux during welding of metals
4. In the production of glass.

(II) Ortho Boric acid [H_3BO_3/$B(OH)_3$]

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



Methods of preperation :

(i) It is precipitated by acidfying an aqueous solution of borax.

$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3\downarrow$

$Na_2B_4O_7 + HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3\downarrow$

Properties:

It is a weak monobasic acid soluble in water and in aqueous solution the boron atom completes its octet by accepting OH^- from water molecules:

$B(OH)_3\,(aq) + 2H_2O(\ell) \rightleftharpoons [B(OH)_4]^-\,(aq) + H_3O^+\,(aq)$. $\qquad$ $pK_a = 9.25$.

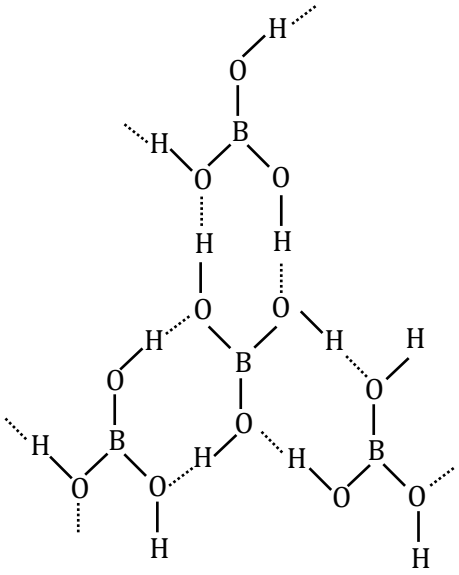
It therefore, functions as a Lewis acid and not as a proton donor like most acids.

Heating effect :

When heated it first forms metaboric acid (HBO_2) and then boron trioxide.

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{100°C} HBO_2 \xrightarrow{160°C} H_2B_4O_7 \xrightarrow{\text{red hot}} B_2O_3$$

Orthoboric acid is greasy to touch, less soluble in cold water but more soluble in hot water. In the solid state, the $B(OH)_3$ units are hydrogen bonded together into two dimensional sheets with almost hexagonal symmetry. The layers are quite a large distance apart (3.18 Å) and thus the crystal breaks quite easily into very fine particles.



Test for Borate radical :

When boric acid is heated with ethyl alcohol, the evolved gas is burned forming a green edged flame.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{ethyl borate (volatile)}}{B(OC_2H_5)_3} + 3H_2O$$

Uses :

(i) It is an antiseptic and its water solution is used as an eyewash.

(ii) It is also used in glass, enamel and pottery industry.

(III) Diborane (B_2H_6)

Binary compounds of B with H are called boron hydrides or boranes.

Preparation :

(i) $4BF_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3LiF + 3AlF_3$

(ii) $2NaBH_4 + I_2 \xrightarrow{\text{ether}} B_2H_6 + 2NaI + H_2$ (Laboratory Method)

(iii) $2BF_3 + 6NaH \xrightarrow{453K} B_2H_6 + 6NaF$ (Industrial method)

Properties :

(i) B_2H_6 is colourless gas and highly reactive (boiling point 180 K).

(ii) It catches fire spontaneously in air and explodes with O_2. Reaction with oxygen is extremely exothermic.

$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$ $\qquad \Delta H = -1976$ KJ/mol

Mixture of diborane with air or oxygen inflame spontaneously producing large amount of heat. Diborane has a higher heat of combustion per unit weight of fuel than most other fuels. It is therefore used as a rocket fuel.

At red-hot, the boranes decomposes to give boron and hydrogen.

(iii) Reaction with water is instantaneous.

$$B_2H_6 + 6H_2O \longrightarrow 2B(OH)_3 + 6H_2$$

(iv) The electron deficient 3c-2e⁻ B–H–B bridges are sites of nucleophilic attack.

Small amines such as NH_3, CH_3NH_2 and $(CH_3)_2NH$ give unsymmetrical cleavage of diborane.

$$B_2H_6 + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+ + [BH_4]^-$$

Large amines such as $(CH_3)_3N$ and pyridine give symmetrical cleavage of diborane.

$$2(CH_3)_3N + B_2H_6 \longrightarrow 2H_3B \leftarrow N(CH_3)_3$$

The reaction with ammonia depends on conditions.

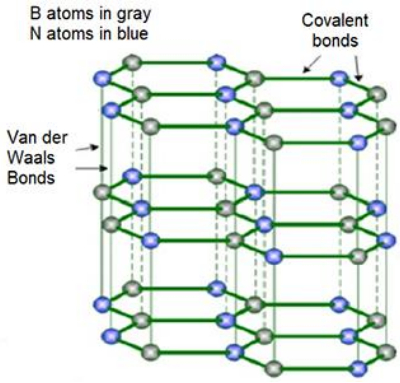
$$B_2H_6 + NH_3 \xrightarrow[\text{low temperature}]{\text{Excess } NH_3} B_2H_6 . 2NH_3 \text{ or } [H_2B(NH_3)_2]^+ [BH_4]^- \text{ (ionic compound).}$$

$$B_2H_6 + NH_3 \xrightarrow[\text{higher temperature(>200°C)}]{\text{Excess } NH_3} (BN)_x \textbf{ boron nitride/Inorganic graphite/Borazone}$$

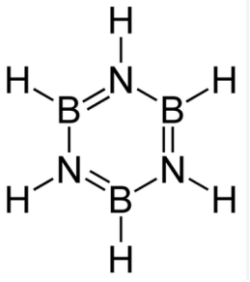
$$B_2H_6 + NH_3 \xrightarrow[\text{higher temperature(>200°C)}]{\text{Ratio } 2NH_3:1B_2H_6} B_3N_3H_6 \textbf{ borazine/Inorganic benzene/Borazole}$$

Borazine is much more reactive than benzene. Borazine readily undergoes addition reactions which do not occur with benzene. Borazine also decomposes slowly and may be hydrolysed to NH_3 and boric acid at elevated temperature. If heated with water, $B_3N_3H_6$ hydrolyses slowly.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3NH_3 + 3H_3BO_3 + 3H_2O$$



Borazone



Borazole

Chemistry of Aluminium :

Compounds of Aluminium

(a) Aluminium chloride – $AlCl_3$:

It is a colourless crystalline solid, soluble in water. It is covalent. Anhydrous $AlCl_3$ is a deliquescent white solid.

Preparation :

(i) By dissolving aluminium, Al_2O_3, or $Al(OH)_3$ in dilute HCl :

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow$$

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

The solution obtained is filtered and crystallized when the crystals of $AlCl_3.6H_2O$ are obtained.

(ii) By heating a mixture of Al_2O_3 and coke and passing chlorine over it.

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 \text{ (anhydrous)} + 3CO\uparrow$$

Alum :

(I) Alums are double salt with their general formula $M_2SO_4.M'_2(SO_4)_3.24H_2O$
where M = monovalent radical like Na^+, K^+, NH_4^+ and M' = Trivalent radical like Al^{+3}, Cr^{+3}. Fe^{+3}.

(II) The different alums are -

(i) Potash alum - $K_2SO_4.Al_2(SO_4)_3.24H_2O$
(ii) Chrome alum - $K_2SO_4.Cr_2(SO_4)_3.24H_2O$
(iii) Iron alum - $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$
(iv) Ammonium alum - $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$

(III) In alums each metal ion is surrounded by six water molecules.

(IV) Lithium does not form alum because Li ion is too small to have a coordination number of six.

Properties :

(i) It is a white crystalline solid highly soluble in water.
(ii) On heating it swells up.
(iii) Its aqueous solution is acidic in nature because it gives H_2SO_4 on hydrolysis.
(iv) It is a double salt and its aqueous solution gives test of all the constituents ions.

Uses :

(i) Alum is used to stop bleeding.
(ii) It is used for purification of water.
(iii) It is used as a mordant in dyeing industry.
(iv) Alum is used for tanning of leather.

BEGINNER'S BOX-5

1. Which of the following can be detected by the borax-bead test ?
(1) Ni^{2+} (2) Co^{2+} (3) Pb^{+2} (4) Both (1) and (2)
CPB259

2. A mixture of boric acid with ethyl alcohol burns with green edged flame due to the formation of –
(1) Ethyl borax (2) Ethyl borate (3) Methyl borax (4) Methyl borate
CPB260

3. The hydrolysis of borax produces –
(1) An acidic medium
(2) A basic medium
(3) A neutral medium
(4) An acidic or an neutral medium
CPB261

4. In alums, each metal ion is surrounded by–
(1) Two water molecules
(2) Four water molecules
(3) Six water molecules
(4) Eight water molecules
CPB262

5. Which of the following is false statement :-
(1) Boranes are easily hydrolysed
(2) $LiAlH_4$ reduces BCl_3 to borane
(3) B_2H_6 is a Lewis acid
(4) B_2H_6 does not react with air
CPB263

6. Inorganic graphite is :-
(1) $B_3N_3H_6$ (2) B_2H_6 (3) BN (4) BF_3
CPB264

7. Tl shows a core of
(1) Noble gas configuration
(2) Noble gas + 10 electron configuration
(3) Noble gas + 14 f electron + 10 d electron configuration
(4) None of these

CPB265

8. Which is correct about diborane-
(1) Highly toxic liquid (2) Inflammable in air
(3) Have 4 bridge bond (4) Has 4C-3e⁻ bond.

CPB266

9. Nature of boric acid H_3BO_3 is-
(1) Weak acid (2) Amphoteric (3) Strong base (4) None

CPB267

10. Borax bead is –
(1) $Na_2B_4O_7.10H_2O$ (2) $NaBO_2 + B_2O_3$
(3) $Na_2[B_4O_5(OH)_4].8H_2O$ (4) All

CPB268

CARBON FAMILY (GROUP-14) :

Introduction

- Carbon and silicon are non-metals, germanium is metalloid whereas tin and lead are soft metals with low melting points.

General Characteristics

Physical properties

- All group 14 elements are solid.
- They have higher melting point and boiling point than 13 group elements.

Chemical properties

Reaction with O_2

- All elements when heated with O_2 form two types of oxide (MO and MO_2).
- SiO only exist at high temperature.

Reactivity towards H_2O

- C, Si and Ge do not react with H_2O.
- Sn decomposes steam to form dioxide and H_2 gas.
  $Sn + 2H_2O$ (steam) $\longrightarrow SnO_2 + 2H_2$
- Pb is unaffected by H_2O due to formation of protective layer of oxide.

Catenation property

- Tendency of self-linkage is called catenation of an atom.
- C has maximum tendency of catenation due to formation of strong C–C bond.
- On moving down the group tendency of catenation decreases due to increase in size.
- Lead does not show catenation.

Compounds of Carbon (Oxides of Carbon Family) :

(A) Carbon Monoxide (CO)

(I) Preparation

(i) It is formed together with CO_2, when carbon or carbonaceous matter is oxidized by air or oxygen. It is also produced when CO_2 is reduced by red- hot carbon; this reaction is of importance in metal extractions.

$$C_{(s)} + CO_{2(g)} \longrightarrow 2CO_{(g)}$$

(ii) In the laboratory it can be prepared by dehydrating methanoic acid with concentrated sulphuric acid.

$$HCOOH_{(liq)} \xrightarrow[conc.H_2SO_4]{373K} CO_{(g)} + H_2O$$

(iii) If oxalic acid is dehydrated in the same way, CO_2 is formed as well.

$$H_2C_2O_4 \xrightarrow[-H_2O]{conc.H_2SO_4,\Delta} CO + CO_2$$

(iv) 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**.

$$C_{(s)} + H_2O_{(g)} \xrightarrow{473—1273K} CO_{(g)} + H_{2(g)}$$

(water gas)

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.

(II) Physical Properties

(i) Carbon monoxide is a colourless, odourless gas which burns in air with a blue flame, forming CO_2. It is sparingly soluble in water and is a neutral oxide. CO is toxic, because it forms a complex with haemoglobin in the blood and this complex is more stable than oxy-haemoglobin. This prevents the haemoglobin in the red blood corpuscles from carrying oxygen round the body. This causes oxygen deficiency, leading to unconsciousness and then death.

Estimation of CO

$$I_2O_5 + CO \longrightarrow 5CO_2 + I_2 \text{ (violet)}$$

$$I_2 \xrightarrow{+ Na_2S_2O_3} \text{Titration with Hypo Solution}$$

$$2NaI + Na_2S_4O_6$$

(Colourless)

(B) Carbon Dioxide (CO_2)

(I) Preparation :

(i) Complete combustion of carbon containing compounds.

$$CH_4 + O_2 \longrightarrow CO_2 + H_2O$$

(ii) In the laboratory it can be conveniently made by the action of dilute hydrochloric acid on marble chips.

$$CO_3^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \longrightarrow CO_{2(g)} + H_2O_{(\ell)}$$

(iii) Industrially it is produced as a by-product during the manufacturing of quicklime and in fermentation processes.

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}; \qquad C_6H_{12}O_{6(aq)} \longrightarrow 2C_2H_5OH_{(aq)} + 2CO_{2(g)}$$

(glucose)

(II) Properties :

(i) It is a colourless, odourless and heavy gas which dissolves in its own volume of water at ordinary temperature and pressure. Like all gases, it dissolves much more readily in water when the pressure is increased and this principle is used in the manufacturing of soda water and fizzy drinks.

(ii) CO_2 is easily liquefied (critical temperature = 31.1°C) and a cylinder of the gas under pressure is a convenient fire extinguisher. When the highly compressed gas is allowed to expand rapidly solid carbon dioxide ('dry ice') is formed. Solid carbon dioxide sublimes at –78°C and, since no massy liquid is produced, it is a convenient means of producing low temperatures.

(iii) Carbon dioxide is the acid anhydride of carbonic acid, which is a weak dibasic acid and ionises in two steps as follows : $H_2CO_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons HCO_3^-{}_{(aq)} + H_3O^+_{(aq)}$

$HCO_3^-{}_{(aq)} + H_2O_{(\ell)} \rightleftharpoons CO_3^{2-}{}_{(aq)} + H_3O^+_{(aq)}$

H_2CO_3 / HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42.

A solution of carbonic acid in water will slowly turn blue litmus red and when the solution is boiled, all the CO_2 is evolved.

(iv) Carbon dioxide readily reacts with alkalies forming the carbonate and, if CO_2 is in excess, the hydrogen carbonate. This is the basis of the lime-water test for CO_2 gas.

$Ca(OH)_{2(aq)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(liq)}$; $CaCO_{3(s)} + H_2O_{(liq)} + CO_{2(g)} \rightarrow Ca(HCO_3)_{2(aq)}$

The above reaction accounts for the formation of temporarily hard water.

(v) 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 :

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

By this process plants make food for themselves as well as for animals and human beings. 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 greenhouse effect and thus, raise the temperature of the atmosphere which might have serious consequences.

(vi) Gaseous CO_2 is extensively used to carbonate soft drinks. Being heavy and non–supporter of combustion it is used as fire extinguisher. A substantial amount of CO_2 is used to manufacture urea.

BEGINNER'S BOX-6

1. Which element has less tendency to show catenation ?
(1) C (2) Si (3) Ge (4) Sn

CPB269

2. Which of the following statement is false :
(1) Dry ice is solid CO_2
(2) CO_2 is weakly acidic
(3) CO_2 and SiO_2 are linear molecules
(4) CO_2 is a gas while SiO_2 is solid

CPB270

3. CO is :
(1) Reductant (2) Poisonous gas (3) Neutral to litmus (4) All

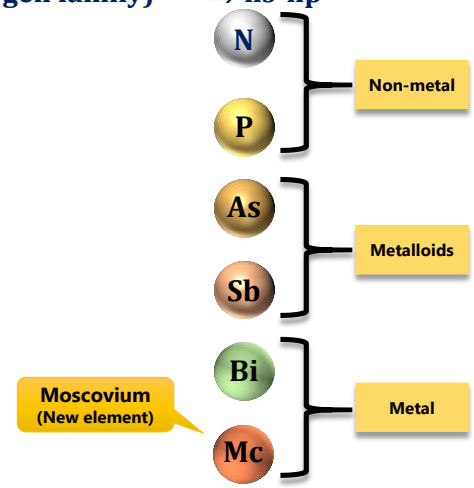
CPB271

4. Which is/are true statements :
(1) Both CO_2 and SiO_2 are acidic oxides
(2) CO is toxic because it forms a complex with haemoglobin in the blood
(3) In CO_2 $p\pi$-$p\pi$ bond is present while in SiO_2 π bond is absent.
(4) All are true statements

CPB272

NITROGEN FAMILY (GROUP-15) :

Group-15 (Nitrogen family) $\Rightarrow ns^2np^3$



- These are also called Pnictogen Family.
- Pnictogen = Suffocating

(I) Physical State

The first element **Nitrogen**, is a **gas.**

The second member **Phosphorus**, is a **soft waxy solid**, however, can pass readily into vapour state.

The **remaining elements are solids**. These are hard and possess metallic lustre.

Q. Why N_2 is inert at room temperature but phosphorus is highly reactive?

Due to larger bond dissociation energy of N_2 molecule it is inert at room temperature but P_4 molecule due to great angular strain is highly unstable and reactive.

Even at room temperature its slow combustion takes place when exposed in air thats why it glows in dark.

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

Anomalous behavior of Nitrogen

Nitrogen differs from the rest of the members of this group due to its small size, high EN, high IE and ability to form $p_\pi - p_\pi$ bond with itself and with other elements. Heavier elements of this group do not form p_π-p_π bonds.

1. Non-availability of d-orbitals
2. Small size
3. High electronegativity
4. Ease of formation of multiple bonds

(II) Oxidation state

- The **common** oxidation states of these elements are **–3, +3 and +5**.
- The tendency to exhibit **–3** oxidation state **decreases** down the group due to the increase in size and metallic character.
- The **stability of +3** oxidation state **increases** and that of **+5** oxidation state **decreases** on moving down from N to Bi **(due to Inert Pair Effect).**
- In the case of nitrogen, all oxidation states from +1 to + 4 tend to disproportionate in acid solution.

$$\mathbf{3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO}$$

- In case phosphorus nearly-all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid.

(III) Oxides

$$E + O_2 \xrightarrow[\text{(limited)}]{} E_2O_3$$

Acidic Nature ∝ Electronegativity ∝ Oxidation State.

$$E + O_2 \xrightarrow[\text{(excess)}]{} E_2O_5$$

Decreasing acidic nature

Increasing acidic nature

N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3
N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5

- Stability of oxides of higher oxidation states decreases down the group
- Thus, N_2O_5 is quite stable while **Bi_2O_5 is not known** (due to inert pair effect)
- Besides these three types of oxides, nitrogen forms two more oxides **N_2O and NO (these are neutral)**.
- The reluctance of **P, As, Sb & Bi** to enter into $p\pi - p\pi$ multiple bonding leads to cage structure for these oxides & they **exist as dimers E_4O_6 & E_4O_{10}.** [E = Elements of 15th group]

(IV) Hydrides

- All elements of this group form volatile hydrides of the type **MH_3**, which have **pyramidal** shape with a lone pair of electrons.

$$E + H_2 \longrightarrow EH_3$$

- All the hydrides are **colourless** gases.
- The **poisonous** nature increases from NH_3 to BiH_3.
- **NH_3 is highly soluble** in water due to hydrogen bonding but other hydrides are less soluble.

NH_3	Bond Angle ↓
PH_3	Bond Length ↑
AsH_3	Thermal Stability ↓
SbH_3	Reducing Nature ↑
	Basic Character ↓

Melting point order :

Expected: $NH_3 < PH_3 < AsH_3 < SbH_3$

Actual: $PH_3 < AsH_3 < SbH_3 < \textcircled{NH_3}$

Boiling point order :

Expected: $NH_3 < PH_3 < AsH_3 < SbH_3$

Actual: $PH_3 < AsH_3 < \textcircled{NH_3} < SbH_3$

(V) Halides

$E + X_2 \longrightarrow EX_3$ (limited) $E + X_2 \longrightarrow EX_5$ (excess)

- NF_3 is the only stable trihalide of Nitrogen.
- Nitrogen do not form Pentahalide (NX_5).
- BiF_5 is the only pentahalide of Bismuth which exists.
- Trihalides except BiF_3 are predominantly covalent in nature.

Compounds of Nitrogen :

(I) Nitrogen (N_2)

(i) Preparation

Dinitrogen is produced commercially by the liquefaction and fractional distillation of air. Liquid nitrogen distils out first leaving behind liquid oxygen.

Reaction between ammonium chloride and sodium nitrite

$$NH_4Cl + NaNO_2 \xrightarrow{\Delta} NaCl + NH_4NO_2$$

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

By heating ammonium nitrite or Ammonium Dichromate

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

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


Heating of Metal Azide (to obtain very pure N_2)

$$2Ba(N_3)_2 \xrightarrow{\Delta} 2Ba + 3N_2$$

(ii) Properties

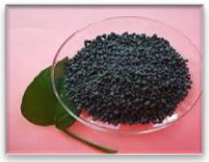
Nitrogen combines with calcium carbide to form calcium cyanamide at 1000°C

$$CaC_2 + N_2 \xrightarrow{\Delta} \underset{\text{Nitrolim}}{CaCN_2} + C$$

The mixture of calcium cyanamide and carbon is technically known as nitrolim and is used as fertilizer.

$$CaCN_2 + 3H_2O \longrightarrow Ca(OH)_2 + NH_2CONH_2$$

$$NH_2CONH_2 + 2H_2O \longrightarrow (NH_4)_2CO_3$$



Nitrolim

(iii) Uses

(a) It is also used where the presence of an inert atmosphere is required (iron and steel industry, inert diluent for reactive chemicals).

(b) Liquid nitrogen is used as a refrigerant to preserve biological materials, in freezing food articles and in cryosurgery.

(II) Ammonia (NH_3)

(i) Preparation

(a) By the hydrolysis of metal cyanamide (Cyanamide process)

$CaCN_2 + 3H_2O \longrightarrow Ca(OH)_2 + NH_2CONH_2$

Urea on treatment with caustic soda form ammonia.

$NH_2CONH_2 + 2NaOH \longrightarrow Na_2CO_3 + 2NH_3$

Urea

(b) Ammonium salts on reaction with base gives NH_3

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

$(NH_4)_2SO_4 + NaOH \longrightarrow NH_3 + H_2O + Na_2SO_4$

(c) By Haber's process (A commercial method)

$N_2 + 3H_2 \underset{\text{Iron oxide}+K_2O \text{ \& } Al_2O_3}{\overset{500^0C,200atm}{\rightleftharpoons}} 2NH_3$ ($\Delta H°_f = -46.1$ kJ mol^{-1})

According to Le–Chatelier's principle, the optimum conditions for the better yield of ammonia are–

(i) High pressure : 200 atm

(ii) Low temperature : The working temperature is 450 – 550° C

(iii) Catalyst : Finely divided iron with some amount of molybdenum as a promotor.

(ii) Properties

(a) It is colourless gas with pungent odour.

(b) Ammonia gas is highly soluble in water its aqueous solution is weakly basic due to the formation of OH^- ions

$NH_{3(g)} + H_2O \longrightarrow NH_4^+{}_{(aq)} + OH^-_{(aq)}$

(c) It forms salts with acids.

$NH_3 + HCl \longrightarrow NH_4Cl \uparrow$ (Thick white fumes) Ammonium Chloride

$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$ Ammonium Sulphate

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

$ZnSO_{4(aq)} + 2NH_4OH_{(aq)} \longrightarrow Zn(OH)_{2(s)} + (NH_4)_2SO_{4(aq)}$

White ppt

$FeCl_{3(aq)} + NH_4OH_{(aq)} \longrightarrow Fe_2O_3.xH_2O_{(s)} + NH_4Cl_{(aq)}$

Brown ppt

(e) Due to the presence of lone pair on NH_3 it act as a ligand and is used to detect the presence of metal ions.

$Cu^{2+}{}_{(aq)} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4]^{2+}{}_{(aq)}$

Blue Deep blue

$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]Cl_{(aq)}$

White ppt Colourless

(f) Reaction with Cl_2

With Excess amount of Cl_2

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

With Excess amount of NH_3

$NH_3 + Cl_2 \longrightarrow NH_4Cl + N_2$

(g) Reaction with Nessler's reagent: A reddish brown ppt. is formed.

$2KI + HgCl_2 \longrightarrow HgI_2 + 2KCI$

Alkaline solution of K_2HgI_4 is called Nessler's reagent which gives brown ppt. with NH_3, called iodide of Millon's base.

$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow H_2NHgOHgI + 7KI + 2H_2O$

Brown ppt

(iii) Uses

(a) Used in refrigeration **(b)** Manufacturing of fertilizers, explosives, urea etc.

(III) Oxides of nitrogen

Name	Formula	Preparation	Properties
Dinitrogen Monoxide	N_2O	$NH_4NO_3 \longrightarrow N_2O + H_2O$	Neutral, Colourless
Nitrogen Monoxide	NO	$NO_2^- + Fe^{+2} \xrightarrow{H_2SO_4} Fe^{+3} + NO + H_2O$	Neutral, Colourless
Dinitrogen Trioxide	N_2O_3	$NO + N_2O_4 \longrightarrow N_2O_3$	Acidic, Blue solid
Nitrogen Dioxide	NO_2	$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + NO_2 + O_2$	Acidic, Brown gas
Dinitrogen Tetraoxide	N_2O_4	$2NO_2 \rightleftharpoons N_2O_4$	Acidic, Colourless solid/ liquid
Dinitrogen Pentaoxide	N_2O_5	$HNO_3 + P_4O_{10} \longrightarrow HPO_3 + N_2O_5$	Acidic, Colourless solid

Nitric Acid (HNO_3) :

(I) Preparation

(i) In the laboratory, nitric acid is prepared by heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

(ii) Ostwald's Process (Modern Process)

The mixture of ammonia and air when passed over platinum gauze catalyst at 500K, the ammonia is oxidised to nitric oxide.

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

The nitric oxide is then oxidised to nitrogen dioxide by air which is cooled to 50° C and absorbed in water.

$$2NO + O_2 \longrightarrow 2NO_2$$
$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$
$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

Note :

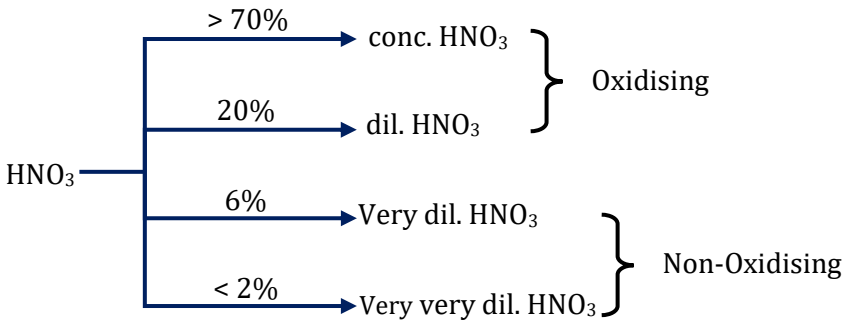
HNO_3 can be concentrated by distillation upto **68%** by mass further concentrated to **98%** can be achieved by dehydration with **conc. H_2SO_4**.

(II) Properties

Anhydrous nitric acid is a colourless fuming liquid.

But **HNO_3** appears yellow on standing due to dissolved **NO_2.**

It is a powerful oxidising agent.



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

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

Oxidising Nature of HNO_3 with Metals :

(i) The products of reduction depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

M (If M is **More** reactive than Hydrogen)
- conc. HNO_3 → Metal Nitrate + NO_2
- dil. HNO_3 → Metal Nitrate + N_2O
- very dil. HNO_3 → Metal Nitrate + NH_3 Or NH_4NO_3

Metal (M) (If M is **Less** reactive than Hydrogen)
- conc. HNO_3 → Metal Nitrate + NO_2
- dil. HNO_3 → Metal Nitrate + NO
- very dil. HNO_3 → No reaction

Zn
- conc. HNO_3 → $Zn(NO_3)_2 + NO_2$
- dil. HNO_3 → $Zn(NO_3)_2 + N_2O$
- very dil. HNO_3 → $Zn(NO_3)_2 + NH_4NO_3$

Cu
- conc. HNO_3 → $Cu(NO_3)_2 + NO_2$
- dil. HNO_3 → $Cu(NO_3)_2 + NO$
- very dil. HNO_3 → No reaction

(ii) Fe, Al, Cr do not dissolve in concentrated nitric acid because of the formation of a passive film on the surface.

(iii) Au & Pt are not affected by conc. HNO_3.

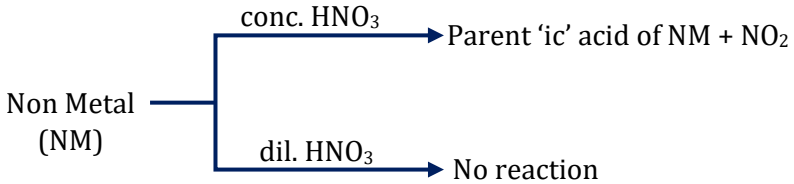
(iv) Au and Pt can be dissolved only in aqua regia (HCl + HNO_3)

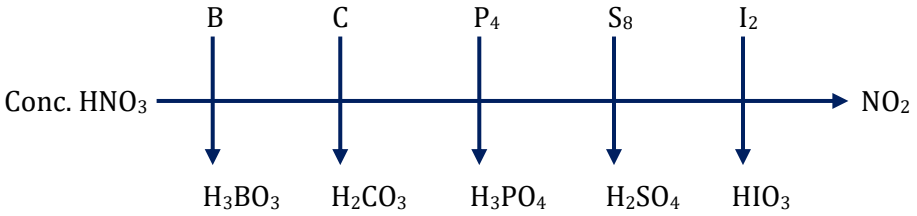
Au + aqua regia $\longrightarrow$ $H[AuCl_4]$

Pt + aqua regia $\longrightarrow$ $H_2[PtCl_6]$

Oxidising Nature of HNO_3 with Non-Metals :

(i) The nascent oxygen oxidises various non-metals to their corresponding highest oxyacids.





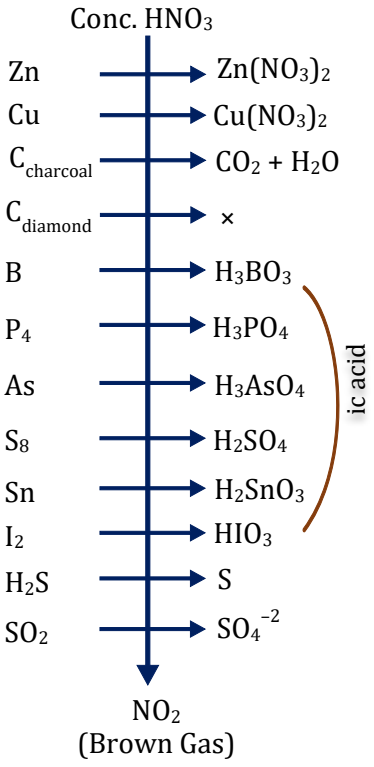
Oxidation of metalloids:

(i) Metalloids like non-metals also form highest oxyacids.

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

Summary :- Oxidising nature of HNO_3

Types of Metal	Conc. HNO_3	Dil. HNO_3	Very dil. HNO_3
Negative SRP metal	Metal nitrate + NO_2	Metal nitrate + N_2O	Metal nitrate + NH_4NO_3/ (NH_3)
Positive SRP metal & Pb	Metal nitrate + NO_2	Metal nitrate + NO	×
Metalloids, Non-metals & Sn	ic -acid + NO_2	×	×



(iii) Uses

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

(b) Another major use is in the pickling of stainless steel and etching of metals.

(c) As an oxidizer in rocket fuels.

Compounds of Phosphorus :

(1) Phosphine (PH_3)

(I) Preparation

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

In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$ (Laboratory Method)

(sodium hypophosphite)

Note:

To produce pure PH_3 it is absorbed in HI and form PH_4I, which on treating with KOH produce PH_3

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

(II) Properties

PH_3 due to the presence of P_2H_4 or P_4 vapours is highly inflammable and produce smoke. i.e. why it is used in warfare to produce smoke.

It is weakly basic like ammonia gives phosphonium compounds.

$PH_3 + HBr \longrightarrow PH_4Br$

When absorbed in copper sulphate or mercuric chloride, corresponding phosphides are obtained.

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

$3HgCl_2 + 2\ PH_3 \longrightarrow Hg_3P_2 + HCl$

(III) Uses

Used in warfare to produce smoke of Phosphorus Pentaoxide.

In Holme Signal ($Ca_3P_2 + CaC_2$) used in Sea.

(2) Phosphorus Halide

(I) Phosphorus Trihalide (PCl_3)

(i) Preparation

$P_4 + 6Cl_2 \longrightarrow 4PCl_3$

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

(ii) Properties

Colourless oily liquid and hydrolysis in the presence of moisture.

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

Reacts with organic compound containing –OH group.

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

$3CH_3CH_2OH + PCl_3 \longrightarrow H_3PO_3 + 3C_2H_5Cl$

(II) Phosphorus Pentahalide (PCl_5)

(i) Preparation

$P_4 + 10Cl_2 \longrightarrow 4PCl_5$

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

(ii) Properties

It is yellowish white powder and in moist air, it hydrolyses to $POCl_3$ and finally converted into PCl_5

$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$

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

When heated, it sublimes but decomposes on strong heating.

$PCl_5 \longrightarrow PCl_3 + Cl_2$

Reacts with organic compound containing –OH group

$CH_3COOH + PCl_5 \longrightarrow H_3PO_4 + CH_3COCl$

$CH_3CH_2OH + PCl_5 \longrightarrow H_3PO_4 + C_2H_5Cl$

CONCEPTUAL CORNER

Q.1 Why BiH_3 is the strongest reducing agent amongst all the hydrides of Group 15 elements ?

Ans. In hydrides of nitrogen family on moving down the group M–H bond length increases so bond strength decreases hence tendency to release hydrogen increases and reducing nature increases.
Increasing order of reducing nature is $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

Q.2 Write the reaction of thermal decomposition of sodium azide.

Ans. Thermal decomposition of sodium azide gives dinitrogen gas.
$2NaN_3 \rightarrow 2Na + 3N_2$

Q.3 Why N_2 is less reactive at room temperature?

Ans. N_2 is less reactive at room temperature because of the high bond enthalpy of N≡N bond.

Q.4 Why does $R_3P = O$ exist but $R_3N = O$ does not (R = alkyl group)?

Ans. Due to presence of vacant d orbital phosphorous can form five covalent bond, while nitrogen restricts its covalency to four due to absence of vacant d orbitals.

Q.5 Why does nitrogen show catenation properties less than phosphorus?

Ans. N–N bond is weaker than the single P–P bond due to high interelectronic respulsion of non-bonding electrons as a result the catenation tendency is weaker in nitrogen.

Q.6 Mention the conditions required to maximise the yield of ammonia.

Ans. In accordance with Le Chatelier's principle, high pressure 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), a temperature of ~ 700 K and the 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.

Q.7 How does ammonia react with a solution of Cu^{2+}?

Ans. The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule 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 Cu^{2+}.

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

Q.8 Illustrate how copper metal can give different products on reaction with HNO_3.

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

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

Q.9 Why is nitrogen di-oxide paramagnetic in gaseous state but the solid obtained on cooling it is diamagnetic.

Ans. NO_2 contains odd number of electrons in its valence shell. On cooling it forms dimer and converted to stable N_2O_4 which is a colourless solid and diamagnetic in nature.

Q.10 Why NH_3 gas cannot be dried by passing over P_2O_5, $CaCl_2$ and H_2SO_4 ?

Ans. $CaCl_2 + 8NH_3 \longrightarrow CaCl_2.8NH_3$

$P_2O_5 + 6NH_3 + 3H_2O \longrightarrow 2(NH_4)_3PO_4$

$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$

So it is dried by passing over quick lime (CaO).

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

Q.11 Why inert atmosphere of CO_2 is taken in the formation of PH_3 by the reaction of white phosphorous with conc. NaOH solution.

Ans. To decrease the partial pressure of O_2 in atmosphere.

Q.12 Why does PCl_3 fumes in moisture?

Ans. PCl_3 hydrolyses in the presence of moisture giving fumes of HCl

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

Q.13 What happens when PCl_5 is heated?

Ans. When heated, it sublimes but decomposes on stronger heating

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

Q.14 Can PCl_5 act as an oxidising as well as reducing agent? Justify.

Ans. It can act as an oxidising as well as reducing agent due to oxidising nature of P(V) and reducing nature of Cl^-

BEGINNER'S BOX-7

1. Which of the following halide of nitrogen is stable?

(1) NF_3 (2) NCl_3 (3) NBr_3 (4) NI_3

CPB273

2. The nitrogen oxide(s) that does not contain N–N bond(s) is

(1) N_2O (2) N_2O_3 (3) N_2O_4 (4) N_2O_5

CPB274

3. What is false about N_2O_5 ?

(1) It is anhydride of HNO_3
(2) It is a powerful oxidizing agent
(3) Solid N_2O_5 is called nitronium nitrate
(4) Structure of N_2O_5 contains no [N → O] bond

CPB275

4. Which of the following process is not involved in Ostwald's process for the manufacture of HNO_3?

(1) $4NH_3(g) + 5O_2(g) \xrightarrow[500K,9bar]{Pt} 4NO(g) + 6H_2O(g)$

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

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

(4) $NO_2 \xrightarrow{\text{low temp.}} N_2O_4$

CPB276

5. Which of the following salts give NH_3 in alkaline medium?
(1) $(NH_4)_2CO_3$ (2) $(NH_4)_2SO_4$ (3) NH_4Cl (4) All of the above

CPB277

6. Which of the following reaction is suitable for obtaining very pure nitrogen?
(1) $NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$
(2) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$
(3) $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$
(4) All of the above

CPB278

7. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a
(1) Dimerisation reaction (2) Disproportionation reaction
(3) Condensation reaction (4) Precipitation reaction

CPB279

8. Which of the following gas is highly poisonous and has strong rotten fish like smell ?
(1) NH_3 (2) PH_3 (3) HNO_3 (4) None

CPB280

9. Which of the following properties does not match with N_2.
A. Odourless B. Tangy taste C. Non toxic gas D. Highly soluble in water
E. Used in liquid state as refrigerant.
(1) A,B,D (2) B,D (3) B,D,E (4) A,B,C,D

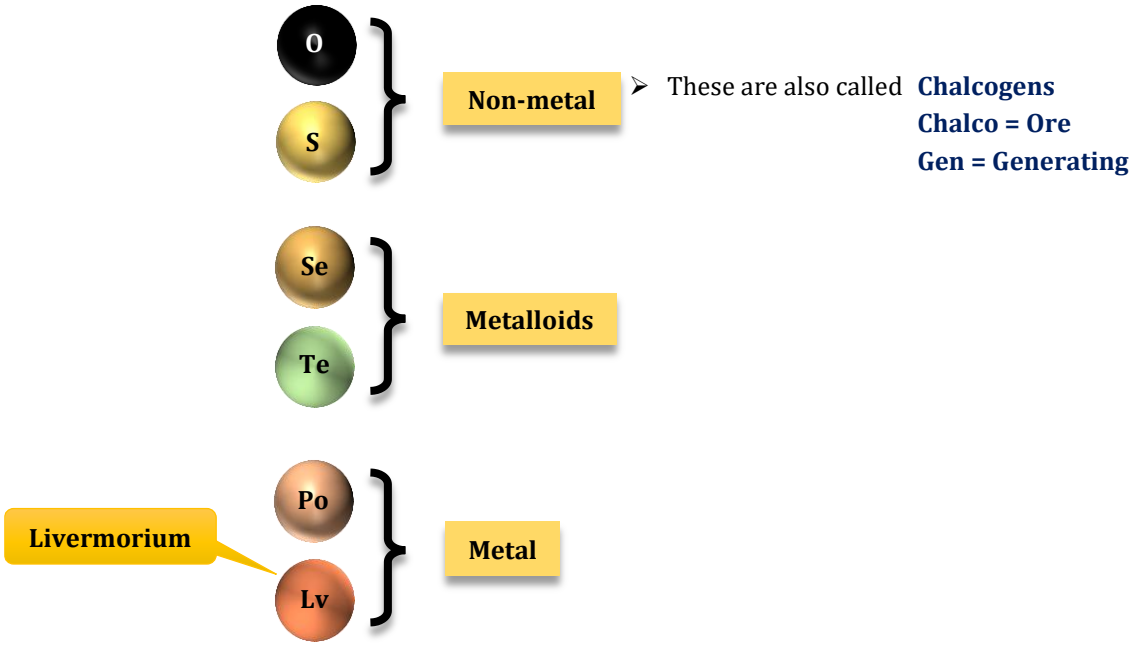
CPB281

10. Which paramagnetic gas is evolved if lead nitrate is heated.
(1) O_2 (2) NO (3) Both (4) None

CPB282

OXYGEN FAMILY (GROUP-16) :

Group-16 (Oxygen Family) $\Rightarrow ns^2np^4$



Note :

(i) Except Oxygen all other members are solid.

(ii) All these elements exhibit allotropy.

(iii) Oxygen show **Anomalous Behavior** due to small size, high Electronegativity, absence of d-orbitals and tendency to form $p_\pi - p_\pi$ bonds.

1. Oxidation State :

Stability of +2 O.S. ↑ as we move down the group.

Oxygen show -2 to +2 oxidation state.

S, Se and Te show +4 and +6 generally.

Stability of +4 O.S. ↑ while that of +6 ↓ down the group.

Grp-16 elements show +6 O.S. show with Oxygen and Fluorine.

Compounds in +4 and +6 O.S. are covalent in nature.

2. Reaction with Hydrogen :

$E + H_2 \longrightarrow H_2E$

H_2O	Bond Angle ↓
H_2S	Bond Length ↑
H_2Se	Thermal Stability ↓
H_2Te	Acidic Character ↑
↓	Reducing nature ↑

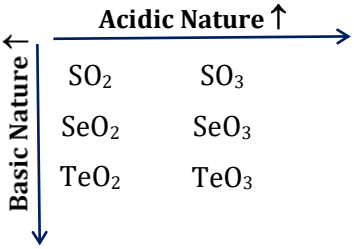
3. Reaction with oxygen :

$E + O_2 \longrightarrow EO_2$ or EO_3

O_3 and SO_2 are gases, while SeO_2 is solid.

Reducing property of dioxides decreases from SO_2 and TeO_2.

SO_2 is reducing while TeO_2 is an oxidizing agent.



4. Reaction with Halogen :

$E + X_2 \longrightarrow EX_2 / EX_4 / EX_6$

Stability of halides decreases in order $F^- > Cl^- > Br^- > I^-$.

They form dichlorides and dibromides.

SF_4 is gas, SeF_4 is liquid and TeF_4 is solid.

Amongst heaxahalides, hexafluorides are the only stable halides.

All hexafluorides are gaseous in nature.

Monohalides exist as dimer : S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2.

These dimeric forms undergo disproportionation.

$2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$

Compounds of Oxygen :

1. Oxygen (O_2)

(I) Preparation :

(i) By Heating Chlorates, Nitrates, Permanganate.

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

(ii) By thermal decomposition of oxides of metals which are present below hydrogen in the electrochemical series.

$2Ag_2O \xrightarrow{\Delta} 4Ag + O_2$ $\quad 2HgO \xrightarrow{\Delta} 2Hg + O_2$ $\quad 2PbO_2 \xrightarrow{\Delta} 2PbO + O_2$

(iii) By decomposition of H_2O_2

$H_2O_{2(aq)} \xrightarrow{\Delta} H_2O_{(l)} + O_{2(g)}$

(iv) Commercially it is manufactured by Water and Air.

Electrolysis of water leads to the release of hydrogen at cathode and oxygen at anode.

$2H_2O_{(l)} \xrightarrow[\text{Traces of acid/base}]{\text{Electrolysis}} 2H_{2(g)} + O_{2(g)}$

(II) Properties

It is a colourless and odourless gas.

It is paramagnetic in nature.

It liquefies at 90 K and freeze at 55 K.

Metals and non-metals (except Noble elements like Au, Pt). undergo combustion with O_2. The combustion is associated with liberation of large amount of energy.

$ZnS + O_2 \longrightarrow ZnO + SO_2$ $\quad C_2H_4 + O_2 \longrightarrow CO_2 + H_2O$

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

Some compounds are catalytically oxidized

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

$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$ (Deacon's process)

2. Ozone (O_3)

O_3 is an allotropic form of oxygen.

(I) Preparation :

$3O_2 \xrightarrow[\text{To prevent decomposition of } O_3]{\text{Silent electric discharge}} 2O_3$ $\quad (\Delta H = +142\ kJ/mol)$

Maximum 10% conversion of Oxygen to Ozone occurs.

(10% O_3 + 90% O_2) max.

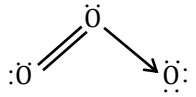
(II) Properties :

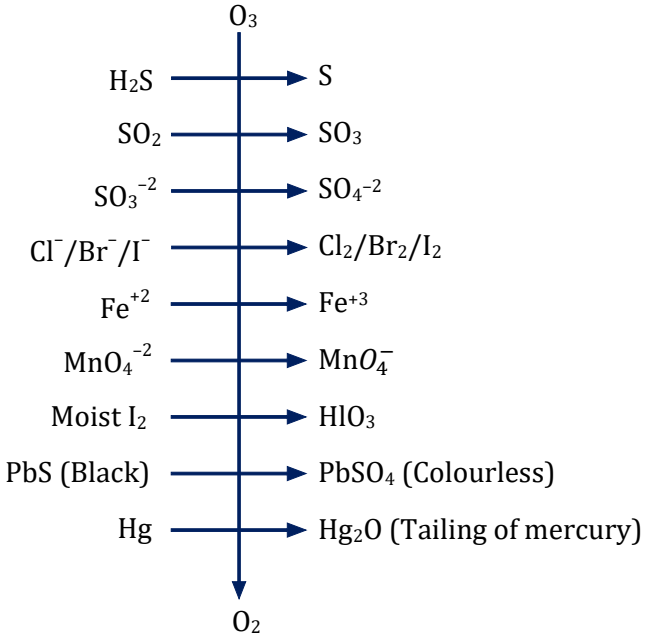
Gas ⟶ Pale blue $\quad$ Liquid ⟶ Blue $\quad$ Solid ⟶ Violet (Black Crystal)

Stronger Oxidising agent than O_2

Diamagnetic, Bent shape

It acts as an oxidising agent





Tailing of mercury

Hg doesn't stick to container surface as surface tension is more.

O_3 is passed over Hg to form Hg_2O (some amount). Remaining Hg separates and goes towards borders of container (away from Hg_2O). 'Tail like appears hence named 'tailing' of mercury. Also, is a confirmatory test of O_3.

$$Hg + O_3 \longrightarrow Hg_2O$$

(III) Uses :

O_3 and H_2O_2 are used to remove black stains of old paintings

Pb	+	H_2S	$\longrightarrow$	PbS
in paint		in air		Black
PbS	+	H_2O_2 / O_3	$\longrightarrow$	$PbSO_4$
Black				White

Note :

Supersonic jets are also responsible for O_3 layer depletion as they release NO gas.

$NO + O_3 \longrightarrow O_2 + NO_2$.

Estimation of O_3.

$$2KI + H_2O + O_3 \longrightarrow 2KOH + O_2 + I_2 \text{ (violet)}$$

$+ Na_2S_2O_3$ Titration with Hypo Solution

$$2NaI + Na_2S_4O_6$$
(Colourless)

Compounds of Sulphur :

1. Sulphur Dioxide (SO_2)

(I) Preparation :

By combustion of Sulphur in presence of Oxygen.

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

Burning Sulphur Smell

By reaction of metal sulphites with dilute HCl **(Laboratory method)**

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

Similarly, bisulphites also give SO_2 with dilute HCl

$NaHSO_3 + HCl \longrightarrow NaCl + SO_2 + H_2O$

(II) Properties :

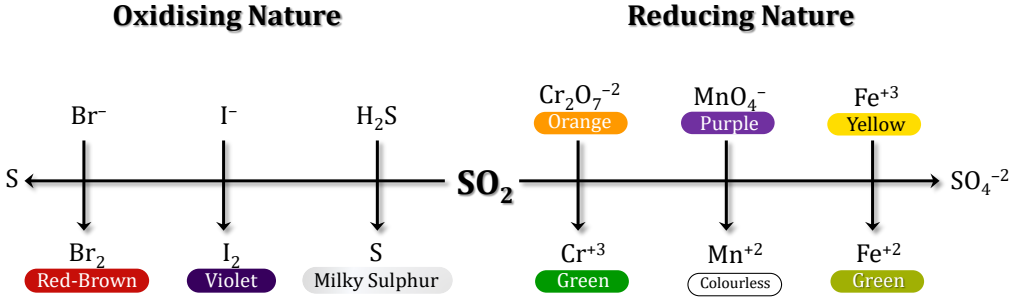
Colourless gas with pungent smell.

It is heavier than air and is highly soluble in water.

Acidic oxide and thus dissolve in water forming sulphurous acid.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

It can act as reducing as well as oxidising agent.



2. Hydrogen Sulphide (H_2S)

(I) Preparation :

It is prepared in Kipp's apparatus

$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$

(II) Properties :

Colourless gas with rotten egg smell.

Moderately soluble in water but solubility decreases with increasing temperature.

It gives black ppt with lead acetate.

$(CH_3COO)_2Pb + H_2S \longrightarrow \underset{\text{Black ppt}}{PbS} + 2CH_3COOH$

Reducing behaviour : Acts as a strong reducing agent as it decomposes evolving hydrogen.

$H_2S + SO_2 \longrightarrow H_2O + S$

3. Sulphuric Acid (H_2SO_4)

It is also known as **Oil of Vitriol** and **King of Chemicals**.

(I) Preparation :

Contact Process :

It involves three steps :

(i) Burning of Sulphur or sulphide ore in the presence of O_2.

$S + O_2 \longrightarrow SO_2$

(ii) Conversion of SO_2 to SO_3 in the presence of Catalyst (V_2O_5)

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3(g) \qquad \Delta H = -196.6\ KJmol^{-1}$

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.

(iii) Absorption of SO_3 in H_2SO_4 to give **oleum**

$SO_3 + H_2SO_4 \longrightarrow \underset{\text{Oleum}}{H_2S_2O_7}$

Dilution of Oleum :

$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

The Sulphuric acid obtained by contact process is 96-98 % pure.

Note :

In contact process, impurity of As_2O_3 is absorbed by $Fe_2O_3.xH_2O$.

(II) Properties :

(i) Colourless oily liquid.

(ii) Conc. H_2SO_4 is an O.A.

(iii) Conc. H_2SO_4 is a dehydrating agent

(iv) Conc. H_2SO_4 is strong acid ($Ka_1 + Ka_2$)

(Formal Charge on O α 1/stability of anion)

(v) Conc. H_2SO_4 is less volatile due to H-bonding

(vi) Dil. H_2SO_4 is acidic only (neither oxidising nor dehydrating)

Oxidising Nature

1. Conc. H_2SO_4 acts as mild oxidizing agent and reduces to SO_2

$M + \text{conc. } H_2SO_4 \longrightarrow \text{Metal sulphate} + SO_2 + H_2O$

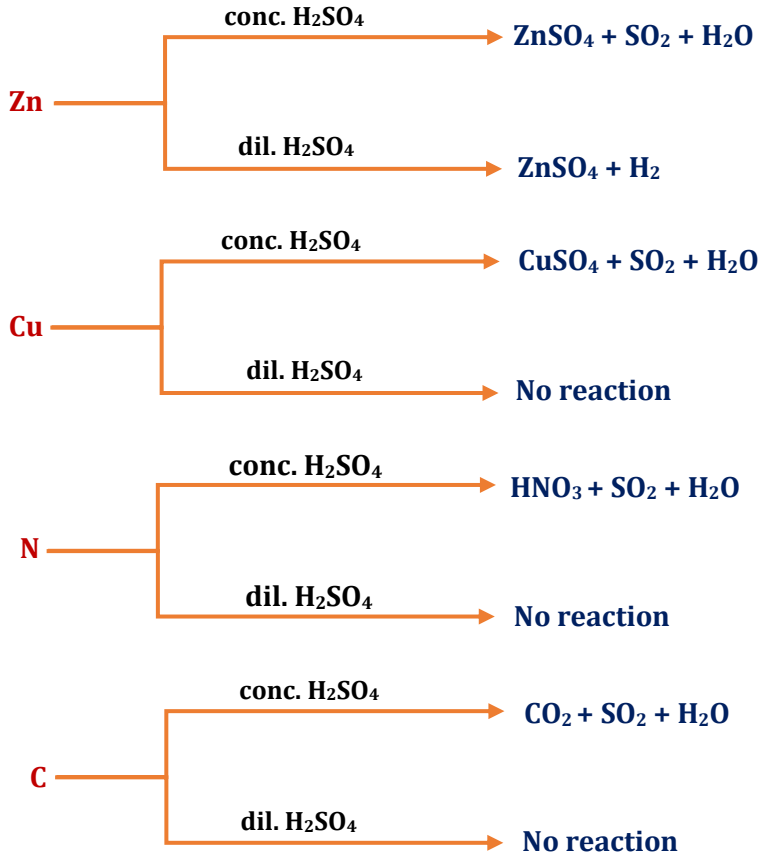
2. dil. H_2SO_4 doesn't act as oxidizing agent only as acid.

$M + \text{dil. } H_2SO_4 \longrightarrow \text{Metal sulphate} + H_2$

3. Only conc. H_2SO_4 reacts with non-metals.

$NM + \text{conc. } H_2SO_4 \longrightarrow \text{Anhydride of Parent 'ic' acid of NM} + SO_2$

Example :



(III) Uses :

(i) In petroleum refining — In fertilizer production

(ii) As drying agent for gases like HCl, Cl_2 — In storage batteries

NCERT QUESTIONS

Q.1 **H_2S is less acidic than H_2Te. Why?**

Ans. Due to the decrease in bond (E–H) dissociation enthalpy down the group, acidic character increases.

Q.2 **Why is H_2O a liquid and H_2S a gas?**

Ans. Hydrogen bonds are present between H_2O molecules while between H_2S molecules, vander Waal's forces are present.

Q.3 **Why is dioxygen a gas but sulphur a solid?**

Ans. Oxygen exist as a O_2 molecule while sulphur exist as a S_8 molecule and due to more molecular mass sulphur is solid.

Q.4 **Knowing the electron gain enthalpy values for $O \rightarrow O^-$ and $O \rightarrow O^{2-}$ as –141 and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^-?**

Ans. Consider lattice energy factor in the formation of compounds.

Q.5 **Which of the following does not react with oxygen directly? Zn, Ti, Pt, Fe**

Ans. Pt is a noble metal which does not react directly with oxygen.

Q.6 Complete the following reactions:

(i) $C_2H_4 + O_2 \rightarrow$ **(ii) $4Al + 3O_2 \rightarrow$**

Ans. (i) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ (ii) $4Al + 3O_2 \rightarrow 2Al_2O_3$

Q.7 How is O_3 estimated quantitatively?

Ans. When 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. This is a quantitative method for estimating O_3 gas.

Q.8 What happens when sulphur dioxide is passed through an aqueous solution of Fe(III) salt?

Ans. $2Fe^{+3} + SO_2 + 2H_2O \rightarrow 2Fe^{+2} + SO_4^{-2} + 4H^+$

Q.9 How is the presence of SO_2 detected?

Ans. It has colourless gas with pungent smell and decolourise acidified $KMnO_4$ solution.

Q.10 Write the conditions to maximise the yield of H_2SO_4 by Contact process.

Ans. 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.

Q.11 Why is $K_{a_2} << K_{a_1}$ for H_2SO_4 in water?

Ans. It is difficult to remove H^+ ion from HSO_4^- ion.

BEGINNER'S BOX-8

1. Which of the following is not oxidised by O_3?

(1) KI (2) $FeSO_4$ (3) $KMnO_4$ (4) K_2MnO_4

CPB283

2. In which of the following reaction conc. H_2SO_4 is not used as on oxidising agent?

(1) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$ (2) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$

(3) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$ (4) None

CPB284

3. Hot conc. H_2SO_4 acts as strong oxidising agent which of the following element is oxidised by conc. H_2SO_4 into two gaseous products?

(1) Cu (2) S (3) C (4) Zn

CPB285

4. HCOOH reacts with conc.H_2SO_4 to produce

(1) CO (2) CO_2 (3) NO (4) NO_2

CPB286

5. Regarding O_3 incorrect statement is-

(1) Ozone is a allotrope of oxygen

(2) In presence of sunlight formed by atmospheric oxygen

(3) In laboratory formed ozone is known as ozonised oxygen

(4) Formation of O_3 from O_2 is an exothermic process hence carried out in silent electric discharge tube

CPB287

6. What happens when SO_3 is passed through water-

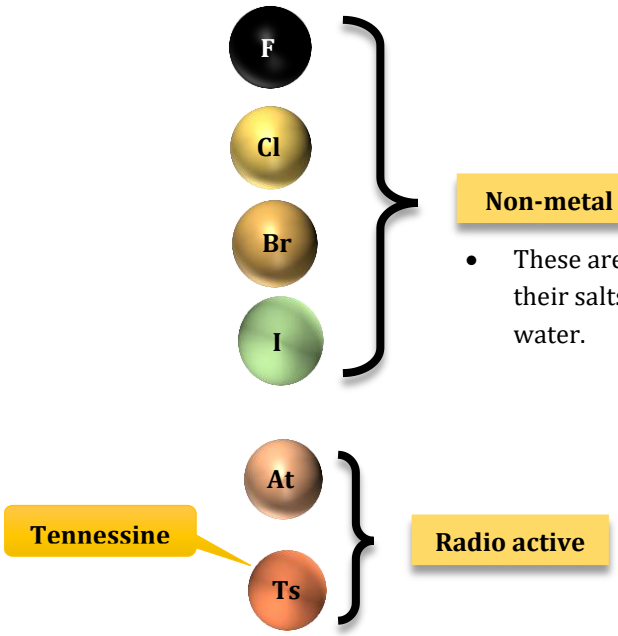
(1) H_2SO_4 (2) $H_2O + S$ (3) $H_2S + O_2$ (4) None

CPB288

HALOGEN FAMILY (GROUP-17) :

Introduction

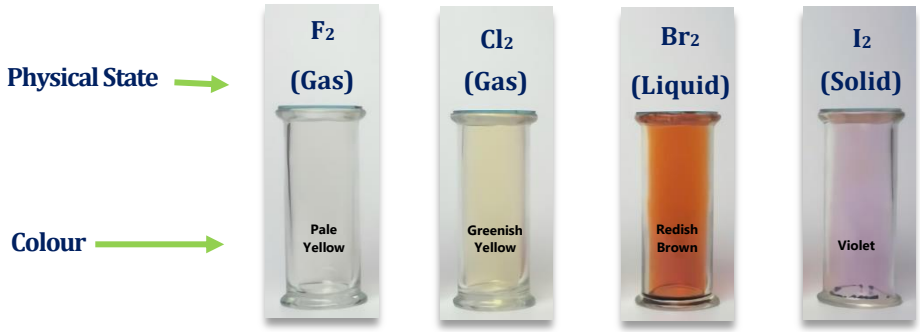
Group-17 (Halogen Family) $\Rightarrow ns^2np^5$



- These are called **Halogens** as their salts are usually found in sea water.

Physical Properties :

Physical State



- The colour of the halogen is due to absorption of visible light by their molecules resulting in the excitation of outer electrons to higher energy levels.
- The colour deepness down the group.
- Halogens are diatomic covalent molecules.
- These, elements do not show allotropy.
- They do not show catenation.
- Anomalous behaviour of fluorine is due to Small size, high electronegativity, Non-availability of d-orbitals, low dissociation energy, Highest positive reduction potential.

Chemical Properties :

1. **Oxidation State :**
   - As fluorine is the most electronegative element so it always show (–1) oxidation state.
   - In fluorine d-orbitals are not available, so it can-not have any of higher oxidation state.
   - The common oxidation states of other halogens are –1, + 1, + 3, + 5, and +7.
   - Oxidation states of +4 and +6 are less common and occur in oxides and oxyacids. These oxides containing +4 or +6 oxidation state have odd electron bonds and are usually para-magnetic particularly in vapour phase.

2. Oxidising Nature :

$F_2 > Cl_2 > Br_2 > I_2$

- F_2 is a strong oxidizing halogen and it oxidises other halide ions in solution or even in solid phase.
- In general, a halogen oxidises halide ion of higher atomic number.

$F_2 + 2X^- \longrightarrow 2F^- + X_2$ (X = Cl, Br, I)

$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$ (X = Br, I)

$Br_2 + 2X^- \longrightarrow 2Br^- + X_2$ (X = I)

3. Reactivity :

- All halogens are chemically very reactive elements.
- They react with metal and Non-Metal to form halides.
- The reactivity of halogens goes on decreasing on moving down the group :

  $F_2 > Cl_2 > Br_2 > I_2$
- The high reactivity of fluorine is due to weak F-F bond, extremely high oxidising power and high electronegativity. Thus, Fluorine is also called **super halogen**.

4. Reaction with Hydrogen :

$E + H_2 \longrightarrow HE$

HF	Bond Length ↑
HCl	Thermal Stability ↓
HBr	Reducing nature ↑
HI	Acidic Character ↑

5. Reaction with Oxygen :

$E + O_2 \longrightarrow E_2O / E_2O_3 / E_2O_5 / E_2O_7$

- Fluorine form only two types of Oxide i.e. OF_2 and O_2F_2
- Chlorine forms the large number of oxides while iodine forms the least.
- Chlorine, Bromine, Iodine form various types of Oxide in different oxidation states ranging from +1 to +7
- The oxides in the higher oxidation states are more stable than lower oxidation states.
- The Stability of Oxides formed by Halogens varies as I > Cl > Br. This is due to **middle row anomaly**.
- Br_2O, BrO_2, BrO_3 are least stable halogen oxides, they are very powerful oxidizing agents.
- O_2F_2 is unstable and used in removing Pu as PuF_6 from spent nuclear fuel.

F	Cl	Br	I
OF_2	Cl_2O	Br_2O	
	ClO_2	BrO_2	I_2O_5
O_2F_2	Cl_2O_6	BrO_3	
	Cl_2O_7		

Compounds of Halogen Family :

Chemistry of Chlorine

Chloride minerals : Rock salt [NaCl], Sylvine (KCl), Horn silver [AgCl]

(I) Preparation

(i) By the action of HCl on MnO_2

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

(ii) By the action of HCl on $KMnO_4$

$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 3Cl_2$

Chlorine is produced industrially by the electrolysis of natural brine or aqueous solutions of NaCl.

(iii) By Deacon's Process :

$4HCl + O_2 \xrightarrow[(723K)]{CuCl_2} 2Cl_2 + 2H_2O$

(II) Physical Properties

(i) Chlorine is a yellowish-green gas.

(ii) Pungent suffocating smell.

(iii) Poisonous in nature.

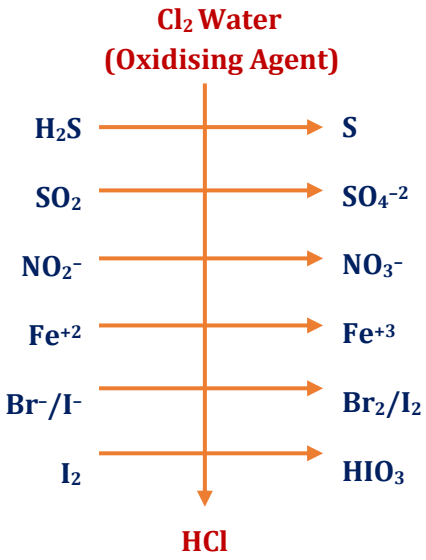
(iv) Produces headache if inhaled in small quantity and in excess proves fatal.

(III) Chemical Properties

Chlorine water acts as a good oxidant and permanent Bleaching agent.

$Cl_2 + H_2O \longrightarrow HCl + O$

Colored substances + [O] $\longrightarrow$ Colorless substance.



(IV) Uses

(i) Used in the purification of drinking water

(ii) Used as a bleaching agent for cotton fabrics, paper and rayon [Bleaching agent in presence of moisture]

(iii) Used as a germicide and disinfectant

Halogen Acids (HCl) :

(I) Preparation :

(i) By heating a halide with concentrated acid :

$NaCl + H_2SO_4 \xrightarrow{150^\circ C} NaHSO_4 + HCl$

$NaHSO_4 + NaCl \xrightarrow{550^\circ C} Na_2SO_4 + HCl$

HCl cannot be dried over P_2O_5 (P_4O_{10}) or quick lime since they react with HCl gas chemically.

$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$

$P_4O_{10} + 3HCl \longrightarrow POCl_3 + 3HPO_3$

HCl is, hence dried by passing through concentrated H_2SO_4.

(II) Properties :

(i) This is colourless, pungent smelling gas with acidic taste.

(ii) Its aqueous solution is called hydrochloric acid.

(iii) It reacts with NH_3 & gives white fumes of NH_4Cl.

$NH_3 + HCl \longrightarrow NH_4Cl$

Pseudo Halides

- They are uni-negative ions that have properties similar to those halide ions.
- They consist of two or more atoms of which at least one is nitrogen.
- They give salts resembling the halide salts.
- For example, the sodium salts are soluble in water, but the silver salts are not soluble.

Pseudo Halogens

- Since each halide ion has a corresponding halogen (for example bromide ion has bromine as the corresponding halogen), attempts have been made to isolate corresponding pseudo halogens.

Pseudo halide ion	Dimer (Pseudo halogen)
CN^- cyanide ion	$(CN)_2$ cynogen
SCN^- thiocyanate ion	$(SCN)_2$ thiocynogen
OCN^- cyanate ion	

- The well known pseudo halide is CN^-. It resemble Cl^-, Br^- and I^- in the following respects:
- It gives an acid HCN, hydrogen cyanide (prussic acid).
- It can be oxidised to form a molecule cyanogen CN–CN.
- CN^- ion forms a large number of complexes similar to halide complexes,

  Example : $[CuCl_4]^{2-}$ and $[Cu(CN)_4]^{2-}$, and $[CoCl_6]^{3-}$ and $[Co(CN)_6]^{3-}$.

Interhalogen Compounds :

Halogen combines with themselves to form a number of **Interhalogen compounds** like XX', XX'_3, XX'_5, XX'_7 Where X is a large size halogen and X' is small size halogen.

IF	**IF_3**	**IF_5**	**IF_7**
ICl	**ICl_3**	**ICl_5**	
IBr	**IBr_3**	**BrF_5**	
BrF	**$BrCl_3$**	**ClF_5**	
BrCl	**ClF_3**		
ClF			

Preparation :

$Cl_2 + F_2 \longrightarrow 2ClF$ $Cl_2 + 3F_2 \longrightarrow 2ClF_3$ $Cl_2 + I_2 \longrightarrow 2ICl$

$Br_2 + 3F_2 \longrightarrow 2BrF_3$ $I_2 + 3Cl_2 \longrightarrow 2ICl_3$ $Br_2 + 5F_2 \longrightarrow 2BrF_3$

Note:

Inter halogen compounds are more reactive than halogen (Except Flourine) due to bond polarity and less Bond Dissociation energy.

Uses :

(i) These compounds can be used as non-aqueous solvents.

(ii) Used as Flourinating agents.

(iii) ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

$$U_{(s)} + 3ClF_{3(l)} \rightarrow UF_{6(g)} + 3ClF_{(g)}$$

Test of halide ions :-

(i) $F^- \rightarrow$ etching of glass

(ii) Cl^- salts, Br^- salts, I^- salts $\xrightarrow[\text{Solution}]{AgNO_3}$ AgCl (White), AgBr (Pale Yellow), AgI (Yellow)

(iii) I_2 gives blue colour with starch solution

(iv) Layer test for Iodide (I^-) :

$$NaI + Cl_2 \longrightarrow I_2 + NaCl$$

(v) Layer test for Bromide (Br^-) :

$$NaBr + Cl_2 \longrightarrow Br_2 + NaCl$$

NCERT QUESTIONS

Q.1 **Covalent radius of fluorine is 64 pm but the bond length is not equal to 128 pm and that is 143 pm and bond energy is found to be comparable to I_2. Explain why ?**

Ans. This may be attributed to ℓ.p – ℓ.p repulsions due to small size of F atom.

Q.2 **Electron affinity of chlorine is more than F. Inspite of this F_2 is the better oxidising agent. Why ?**

Ans. SRP of F_2 is much higher than that of Cl_2 on account of smaller bond dissociation energy of F_2 molecule and high hydration energy of F^- ion.

Q.3 **Layer test of Br^- is successful with Cl_2 but not with I_2. Explain?**

Ans. Br^- is oxidised by Cl_2 but not by I_2

Q.4 **What is the difference between bleaching action of SO_2 and Cl_2**

Ans. The bleaching action of SO_2 is temporary because it takes place through reduction.
The bleaching action of Cl_2 is permanent because it takes place through oxidation

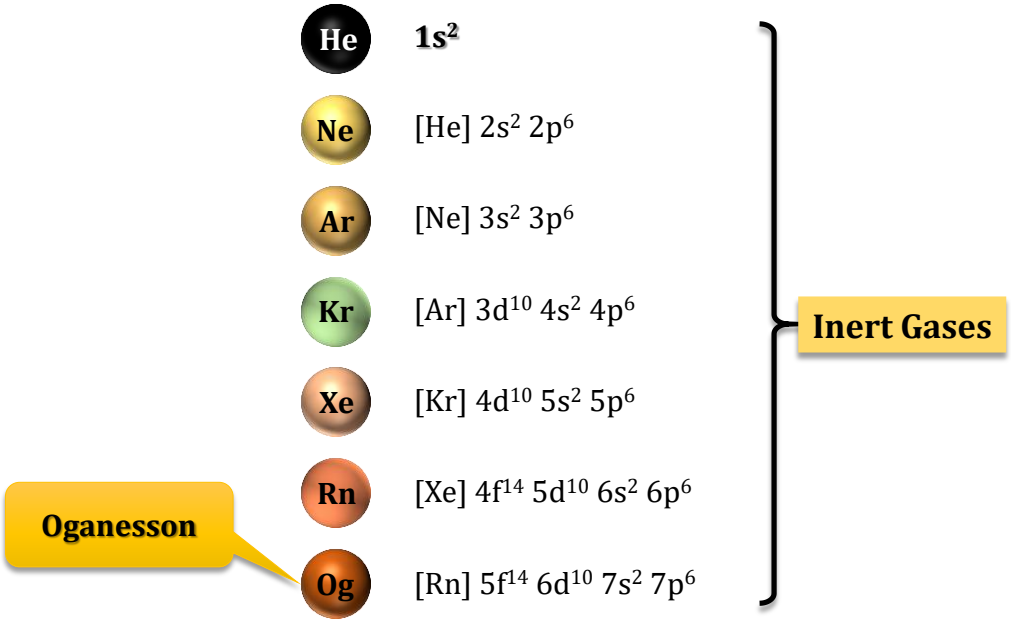
Q.5 **(a) When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. why ?**
(b) Chlorine water turns blue litmus red but solution becomes colourless after sometime.

Ans. (a) It forms H_2 gas. $Fe + 2\,HCl \longrightarrow FeCl_2 + H_2$.
Liberation of hydrogen prevents the formation of ferric chloride.
(b) Blue litmus change into red due to acidic nature ($Cl_2 + H_2O \rightarrow HOCl + HCl$) but it is bleaching agent, therefore, it decolourises the red litmus.

NOBLE GAS FAMILY (GROUP-18) :

Introduction

Group-18 (Noble Gas Family) $\Rightarrow$ ns^2np^6



- Oxidation state: 0, +2, +4, +6, +8
- Noble gases are inert due to stable configuration, high IP and ΔH_{eg} = +ve
- 1st inert gas compound was prepared by Neil Bartlett $Xe^+[PtF_6]^-$ similar to $O_2^+[PtF_6]^-$ because IP of Xe is approximately equal to O_2.

Properties of Noble Gases :

1. **Physical State**
   These gases are colourless, odourless and tasteless.
2. **Heating with Air**
   These gases neither burn nor support in burning.
3. **Atomicity**
   Since their combining capacity is very low they exist as a single atom hence they are monoatomic.
4. **Force of Attraction Between Atoms of Noble Gases**
   The Van der Waals forces between the atoms increases from He to Xe due to increase in polarizability. The ease of liquefaction of these gases increase with the increase in their atomic weights.
   All have low values of melting and boiling points. These values increase gradually as the atomic number increases.
   Melting point : He < Ne < Ar < Kr < Xe < Rn
   Boiling point : He < Ne < Ar < Kr < Xe < Rn
5. **Solubility in Water**
   These gases are sparingly soluble in water (8 to 40 ml per litre at 25°C).
   Solubility in water increases with increasing atomic number.
   He < Ne < Ar < Kr < Xe < Rn
6. **Electrical Conductivity**
   These gases have fairly high electrical conductivity. They produce characteristic coloured light when an electrical discharge is passed through them at low pressure.

Compounds of Noble Gases :

1. Xenon Flourides : XeF_2, XeF_4, XeF_6

Preparation :

$$\underset{2:1}{Xe + F_2} \xrightarrow[1\text{ bar}]{673\text{ K}} XeF_2 \qquad \underset{1:5}{Xe + 2F_2} \xrightarrow[7\text{ bar}]{873\text{ K}} XeF_4 \qquad \underset{1:20}{Xe + 3F_2} \xrightarrow[60\text{-}70\text{ bar}]{573\text{ K}} XeF_6$$

Properties of Xenon Fluoride

(a) XeF_2, XeF_4 and XeF_6 are colourless crystalline solids subliming readily at 298 K.

(b) They are powerful fluorinating agents. They are readily hydrolysed by even traces of water.

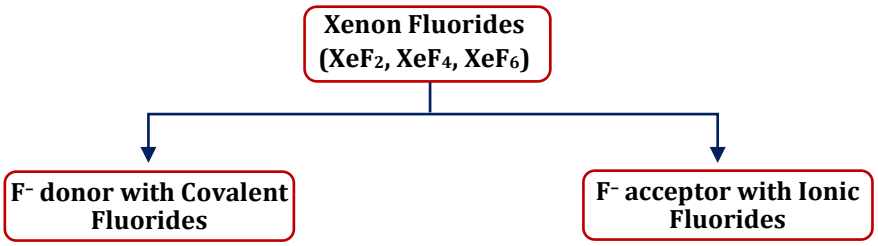
(c) The hydrolysis of XeF_2 can be represented by the equation.

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$$

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

(d) Xenon Flouride can act as as both F^- (Fluoride ion) donor and acceptors:



Ex. $XeF_4 + SbF_5 \rightarrow [XeF_3]^+[SbF_6]^-$

$XeF_6 + PF_5 \rightarrow [XeF_5]^+[PF_6]^-$

Ex. $XeF_6 + CsF \rightarrow [Cs]^+[XeF_7]^-$

$XeF_4 + NaF \rightarrow [Na]^+[XeF_5]^-$

2. Xenon - Oxygen compounds :

Prepared by Hydrolysis of XeF_4 and XeF_6

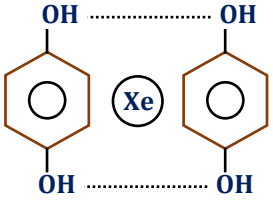
$XeO_3 \Longrightarrow$ colourless, explosive solid & trigonal pyramidal structure.

$XeOF_4 \Longrightarrow$ colourless, volatile liquid & square pyramidal structure.

3. Clathrate Compounds :

Larger inert gases like Kr, Xe etc. are packed into crystal structure of some organic compounds.

Xenon diquinol.



Noble Gases :

Uses of Inert Gases

Helium

(i) Non-inflammable light gas.

(ii) Filling balloons for meteorological observations.

(iii) Used in gas-cooled nuclear reactors.

(iv) Liquid He (BP = 4.2 K) is used as cryogenic agent for carrying out various experiments at low temperature.

(v) Used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and MRI system.

(vi) Used as diluent for O_2 in modern diving apparatus as it has very low solubility in blood.

Uses of Inert Gases

Neon :-

(i) Used in discharge tubes and fluorescent bulbs for ads.

(ii) Neon bulbs are used in botanical gardens and green houses.

Argon :

(i) Mainly used to provide an inert atmosphere in high temperature metallurgical processes, like arc welding of metals or alloys and for filling electric bulbs.

(ii) Used in laboratory for handling substances that are air-sensitive.

Xenon and Krypton :

(i) Used in light bulbs designed for special purposes

BEGINNER'S BOX-9

1. Which is correct

(1) $NaCl \xrightarrow{conc.H_2SO_4}$ yellow green gas (2) $NaBr \xrightarrow{conc.H_2SO_4}$ red brown vapour

(3) $NaF + Cl_2 \longrightarrow NaCl + F_2$ (4) All

CPB289

2. True statement about I^- will be

(1) Weak base (2) Strong nucleophile

(3) Strong reducing agent (4) All

CPB290

3. Which of the following is strong oxidising agent

(1) F_2 (2) Cl_2 (3) Br_2 (4) I_2

CPB291

4. The ion that cannot undergo disproportionation is

(1) ClO_4^- (2) ClO_3^- (3) ClO_2^- (4) ClO^-

CPB292

5. In the clatherates of xenon with water, the nature of bonding between xenon and water molecule is

(1) Covalent (2) Hydrogen bonding

(3) Co-ordinate (4) Dipole-induced dipole interaction

CPB293

6. XeF_2 reacts with PF_5 to give :

(1) XeF_6 (2) $[XeF]^+ [PF_6]^-$ (3) XeF_4 (4) $[PF_4]^+ [XeF_3]^-$

CPB294

7. The first compound of noble gases prepared by Neil-Bartlett was :-

(1) $Xe^+ [PtF_6]^-$ (2) XeF_4 (3) XeF_6 (4) $XeOF_4$

CPB295

8. Colour of F_2 is -

(1) Greenish - yellow (2) Light blue (3) Pink (4) Pale yellow

CPB296

9. Basis of formation of Bartlett compound is-

(1) Ionisation enthalpy (2) Solubility

(3) Boiling point (4) Color property

CPB297

BEGINNER'S BOX — ANSWERS KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7	8
	Ans.	1	1	1	1	4	3	1	3

BEGINNER'S BOX-2	Que.	1	2	3	4	5	6	7	8
	Ans.	2	3	3	2	4	2	2	4

BEGINNER'S BOX-3	Que.	1	2	3	4	5	6	7
	Ans.	3	2	2	2	3	4	1

BEGINNER'S BOX-4	Que.	1	2	3	4	5	6	7	8
	Ans.	3	2	2	2	4	3	4	4

BEGINNER'S BOX-5	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	4	2	2	3	4	3	3	2	1	2

BEGINNER'S BOX-6	Que.	1	2	3	4
	Ans.	4	3	4	4

BEGINNER'S BOX-7	Que.	1	2	3	4	5	6	7	8	9	10
	Ans.	1	4	4	4	4	3	2	2	2	1

BEGINNER'S BOX-8	Que.	1	2	3	4	5	6
	Ans.	3	3	3	1	4	1

BEGINNER'S BOX-9	Que.	1	2	3	4	5	6	7	8	9
	Ans.	2	4	1	1	4	2	1	4	1