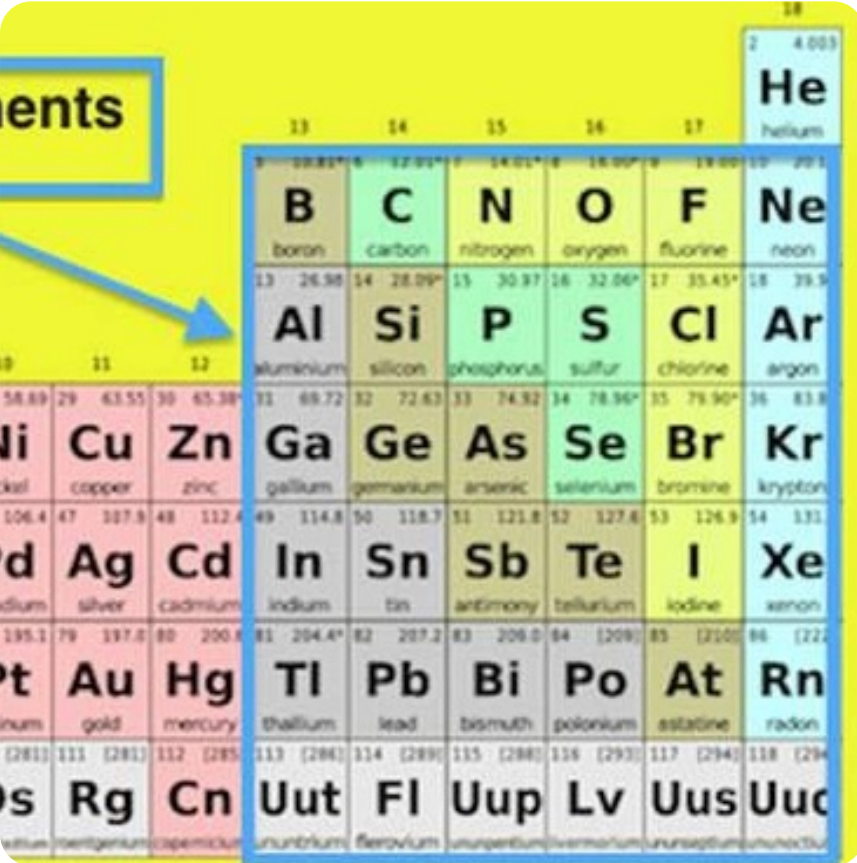


INORGANIC CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER



The image shows a periodic table with the p-block elements (groups 13 to 18) highlighted in a blue box. A blue arrow points from the word 'p-block' to the highlighted region.

						13	14	15	16	17	18
						B	C	N	O	F	Ne
						boron	carbon	nitrogen	oxygen	fluorine	neon
						Al	Si	P	S	Cl	Ar
						aluminium	silicon	phosphorus	sulfur	chlorine	argon
Li	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
lithium	copper	zinc	gallium	germanium	arsenic	selenium	bromine	krypton			
Rb	Ag	Cd	In	Sn	Sb	Te	I	Xe			
rubidium	silver	cadmium	indium	tin	antimony	tellurium	iodine	xenon			
Cs	Au	Hg	Tl	Pb	Bi	Po	At	Rn			
cesium	gold	mercury	thallium	lead	bismuth	polonium	astatine	radon			
Fr	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo			
francium	roentgenium	copernicium	ununtrium	flerovium	ununpentium	livermorium	ununseptium	ununoctium			

STUDY MATERIAL

p-Block Elements (group 13 to 18)

ENGLISH MEDIUM

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p-BLOCK ELEMENTS

IMPORTANT CONCEPTS :

- | | |
|---|---|
| 1. Back bonding | 2. Dimerisation |
| 3. Inert pair effect | 4. Oxyacids |
| 5. Hydrolysis | 6. Allotropes |
| 7. Silicates and Silicones | 8. Drying agent and bleaching agents |
| 9. Reactions and compounds (Group 13-18) | |

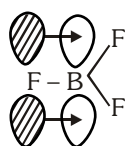
1. BACK BONDING

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

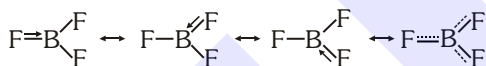
Conditions for back bonding :

- One bonded atom must possess vacant orbital and the other bonded atom must possess lone pair.
- Both bonded atoms must belong to 2nd period or one bonded atom must belong to 2nd period and the other must belong to 3rd period.

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



F-donor
B-acceptor



$$(B-F) \text{ B.O} = 4/3 = 1.33$$

Types of back bonding :

Based on type of orbital involved in overlapping

2 types of back bonding is possible

- $p\pi-p\pi$ back bonding
- $p\pi-d\pi$ back bonding

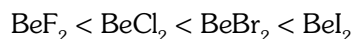
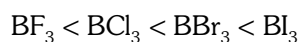
(1) **$p\pi-p\pi$ back bonding** : It is formed by the sidewise overlapping of two p orbitals.

Order of strength : $2p-2p > 2p-3p > 2p-4p \dots\dots$

Size of orbital \uparrow extent of B.B. \downarrow

It is used to explain following observations :-

- Abnormal bond length and bond energy of B-F bond in BF_3 .
- Lewis acidic order of **Boron** and **Beryllium** halides.



\therefore extent of back bonding \downarrow

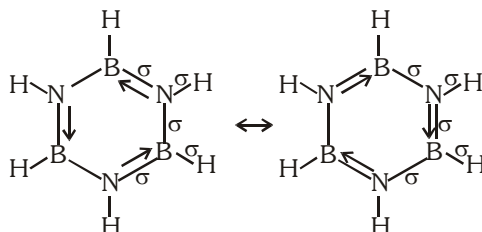
\therefore Lewis acidic strength \uparrow

Pre-Medical

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

Ex. $B_3N_3H_6$ (inorganic benzene or borazene 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.
- (d) If back bonding is present in the molecule then tendency to form dimer or polymer decreases.
Ex. BF_3 , BeF_2

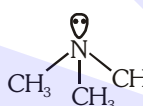
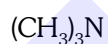
(2) $p\pi-d\pi$ back bonding :

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

It is used to explain following observations :

(a) Hybridisation

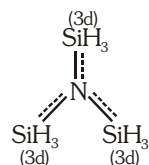
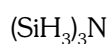
Ex. Trimethyl amine



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 lp)

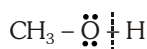
Trisilyl amine



$p\pi-d\pi$ back bonding is possible

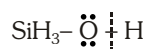
- Hybridisation of N is sp^2
- Structure is trigonal planar
- It is a weaker lewis base

(b) Acidic strength



Methyl alcohol

- No back bonding in conjugate base
- Less acidic



Silyl alcohol

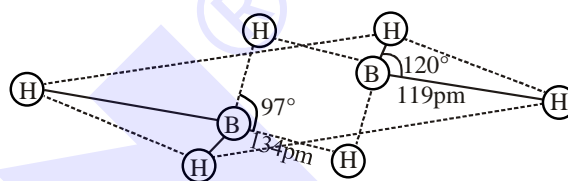
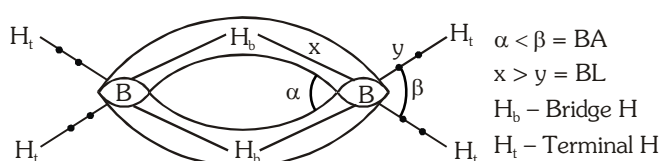
- Back bonding present in conjugate base
- More acidic

2. DIMERISATION / POLYMERISATION

Types of Dimerisation	
by 3-centre-2e ⁻ bond	by 3-centre-4e ⁻ bond
eg. B ₂ H ₆	eg. (BeCl ₂) ₂
(BeH ₂) ₂	(BeCl ₂) _n
(BeH ₂) _n	(AlCl ₃) ₂
Al ₂ (CH ₃) ₆	(ICl ₃) ₂
Ga ₂ (CH ₃) ₆	

(A) By banana Bond or by 3-Centre-2e⁻ bond or by e⁻ deficient bond

(a) B₂H₆



2-Centre-2e⁻ bonds = 4

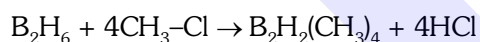
3-Centre-2e⁻ bonds = 2

structure of diborane, B₂H₆

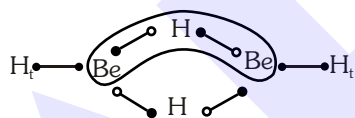
Hybridisation state of boron is sp³

It is electron deficient molecule and act as 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 only four terminal hydrogen atom will be substituted.

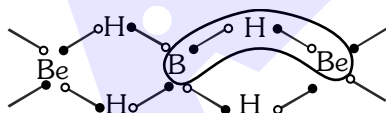


(b) (BeH₂)₂ (dimer of BeH₂ in vapour state)



- Hybridisation state of Be is sp²
- Planar
- electron deficient molecule

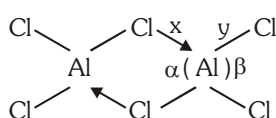
(c) (BeH₂)_n (polymer of BeH₂ in solid state)



- Hybridisation state of Be is sp³
- Non-planar
- electron deficient molecule

(B) By-coordinate Bond / 3-Centre-4e⁻ bond

(a) Al₂Cl₆ (dimer of AlCl₃ in liquid or solid state)



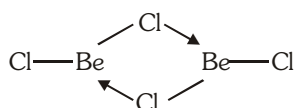
$\alpha < \beta$; Order of bond angle

$x > y$; Order of bond length

Hybridisation state of Al is sp³

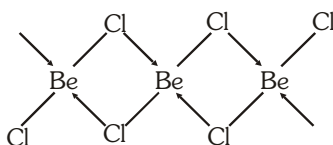
Non-planar

octet of Al is complete so it is not e⁻ deficient

(b) $(\text{BeCl}_2)_2$ (dimer of BeCl_2 in vapour state)

 Hybridisation state of Be is sp^2

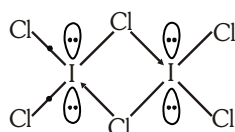
Planar

electron deficient molecule

(c) $(\text{BeCl}_2)_n$ (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

(d) 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
2. In BF_3 , the B-F bond length is 1.30 \AA , when BF_3 is allowed to be treated with Me_3N , it forms an adduct, $[\text{Me}_3\text{N} \rightarrow \text{BF}_3]$. The bond length of B-F in the adduct is :
 - (1) Greater than 1.30 \AA
 - (2) Smaller than 1.30 \AA
 - (3) Equal to 1.30 \AA
 - (4) None of these
3. Which of the following structures correctly represents the boron trifluoride molecule :

(1)

(3)

(2)

(4)
4. Trisilylamine $[\ddot{\text{N}}(\text{SiH}_3)_3]$ has a :-
 - (1) Planar geometry
 - (2) Tetrahedral geometry
 - (3) Pyramidal geometry
 - (4) None of these
5. In which of the following molecule, vacant orbitals do not participate in bonding:-

(1) B_2H_6
(2) Al_2Cl_6
(3) $[\text{H}_3\text{N} \cdot \text{BF}_3]$
(4) Si_2H_6

6. In which of the following compounds B-F bond length is shortest?
 (1) BF_4^- (2) $\text{BF}_3 \leftarrow \text{NH}_3$ (3) BF_3 (4) $\text{BF}_3 \leftarrow \text{N}(\text{CH}_3)_3$
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
8. How many $2\text{C}-2e^-$ bonds and $3\text{C}-2e^-$ bonds are present in diborane ?
 (1) 2 and 4 (2) 2 and 2 (3) 4 and 2 (4) 4 and 4

3. INERT PAIR EFFECT

- (group oxidation state) Group-13 Group-14 Group-15
- ns^2np^1 ns^2np^2 ns^2np^3
 $\underline{+3}$ $\underline{+4}$ $\underline{+5}$
- 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 becomes even greater than the group oxidation state. **This is called inert pair effect.**

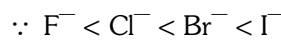
Group-13		Group-14		Group-15	
B	+3	C	+4	N	+5
Al	+3	Si	+4	P	+5
<hr/>					
Ga	+3 > +1	Ge	+4 > +2	As	+5 > +3
In	+3 > +1	Sn	+4 > +2	Sb	+5 > +3
Tl	+3 < +1	Pb	+4 < +2	Bi	+5 < +3

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 to participate in bonding.

- For the last element group oxidation state is highly oxidising in nature.

Examples :

- PbCl_2 is more stable than PbCl_4 .
- TlCl is more stable than TlCl_3 .
- GaCl_3 is more stable than TlCl_3 .
- SnCl_4 is more stable than PbCl_4 .
- Thallium (III) iodide does not exist.
- PbF_4 , PbCl_4 exist but PbBr_4 and PbI_4 does not exist.
- Only BiF_5 exists among pentahalides of Bi



reducing nature

due to strong oxidising nature of Pb^{+4} and strong reducing nature of Br^- and I^- , PbBr_4 and PbI_4 does not exist while Cl^- and F^- can not reduce Pb^{+4}

4. OXY ACID

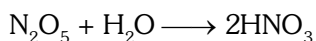
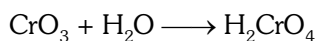
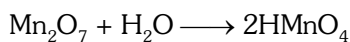
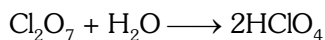
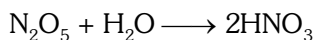
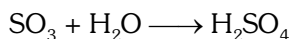
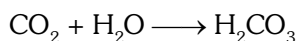
Inorganic acid which contain at least one Z-OH bond are known as oxyacids.
 (Z is generally a non metal)

Acidic oxide

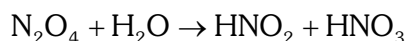
- or $\text{Non metallic oxide} + \text{H}_2\text{O} \rightleftharpoons \text{Oxyacids}$

Non metallic oxide
 Anhydrides of oxyacids

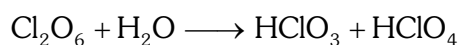
When an acidic oxide form one type of oxy acid on reaction with H_2O then it is a simple anhydride



When an acidic oxide on reaction with H_2O forms 2 types of oxy acids, then it is a mixed anhydride.



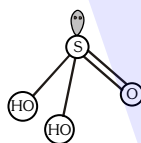
(N_2O_4 is mixed anhydride of HNO_2 & HNO_3)



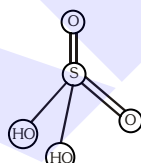
(Cl_2O_6 is mixed anhydride of $HClO_3$ and $HClO_4$)

Pyro	Meta	Per oxy acid	Hypo	
↓ 2 mole oxy acid ↓ -H ₂ O pyro acid	↓ 1 mole oxy acid ↓ -H ₂ O meta acid	↓ Z—O—O—H	↓ Ous acid ↓ -O Hypo us acid	↓ ic acid (Pyro ic acid) ↓ -O Hypo ic acid
Ex. $H_2S_2O_5$ $H_2S_2O_7$ $H_4P_2O_7$	Ex. HPO_3 HBO_2	Ex. H_2SO_5 $H_2S_2O_8$ HNO_4	Ex. HOX H_3PO_2	Ex. $H_4P_2O_6$

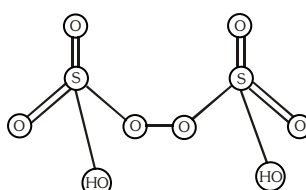
OXY ACIDS OF SULPHUR



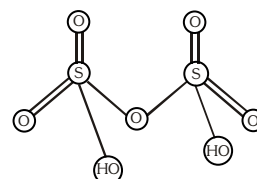
Sulphurous acid
(H_2SO_3)



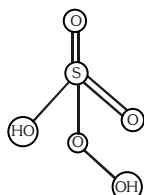
Sulphuric acid
(H_2SO_4)



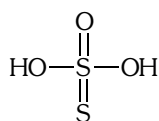
Peroxo disulphuric acid
(Marshall's acid)
($H_2S_2O_8$)



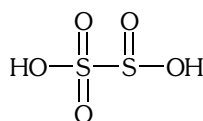
Pyro sulphuric acid/oleum
($H_2S_2O_7$)



Peroxo
monosulphuric acid
(Caro's acid)
(H_2SO_5)

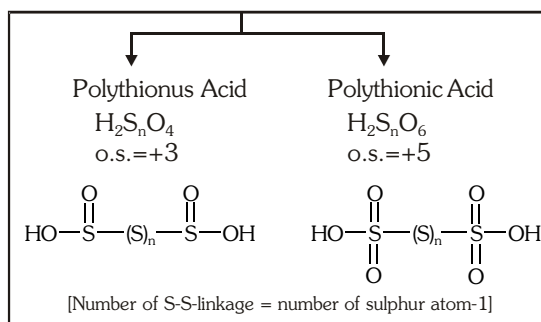


Thiosulphuric
acid
($H_2S_2O_3$)



Pyro sulphurous
acid
($H_2S_2O_5$)

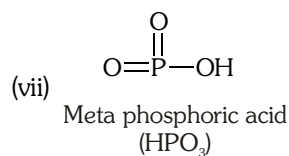
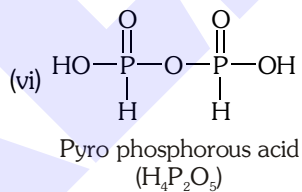
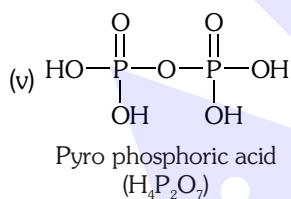
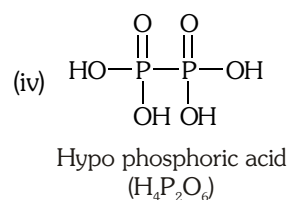
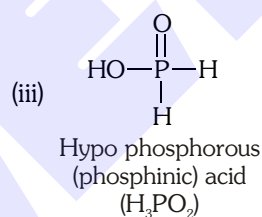
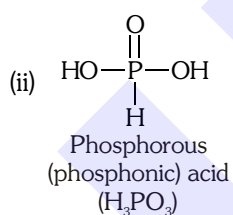
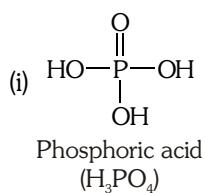
OXY ACIDS OF SALT CONTAINING S-S LINKAGE



Important points :

$H_2S_2O_3$	}	(S-S bond)
$H_2S_2O_4$		
$H_2S_2O_5$		
$H_2S_2O_6$		
$H_2S_2O_7 \rightarrow [S-O-S]$		
$H_2S_2O_8 \rightarrow [S-O-O-S]$		

OXY ACID OF PHOSPHORUS

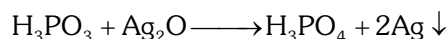
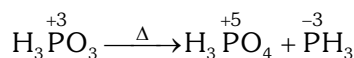
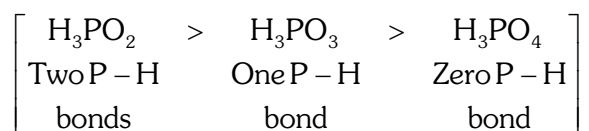


OXY ACIDS OF HALOGENS

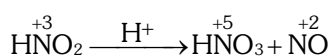
Hypohalous Acid	Halous Acid	Halic Acid	Per halic Acid
$HO-X$	$O=X-OH$	$HO-X \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$	$HO-X \begin{smallmatrix} \diagup O \\ \diagdown O \\ \diagup O \\ \diagdown O \end{smallmatrix}$
+1 $HOCl$ $HOBr$ HOI	+3 $HClO_2$ — —	+5 $HClO_3$ $HBrO_3$ HIO_3	+7 $HClO_4$ $HBrO_4$ HIO_4

Some important points

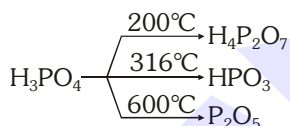
- (1) Oxy acid of phosphorus having +1 & +3 oxidation state (having P-H bond) can act as reducing agent and give disproportionation reaction on heating.


Order of reducing nature.


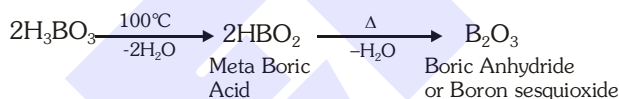
Note : Nitrogen compound having +1 & +3 oxidation state gives disproportionation reaction in acidic medium.



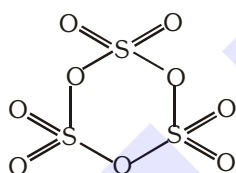
- (2) Heating effect of phosphoric acid



- (3) Heating effect of boric acid

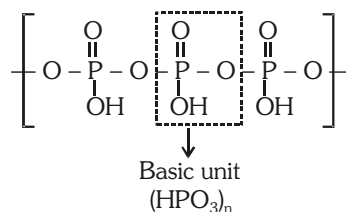
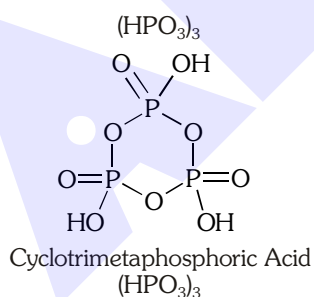


- (4) SO_3 exists as a cyclic trimer (S_3O_9)



6 S=O bonds
3 S-O-S bonds
S is sp^3 hybridised
Non planar molecule

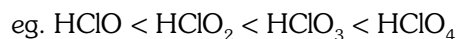
- (5) Metaphosphoric acid exists as dimer, cyclic trimer or polymer



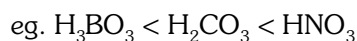
- (6) Acidic nature of oxy acids.

General concept :

- (i) For same element $\left(\begin{array}{l} \text{Acidic nature} \\ \text{of oxyacids} \end{array} \right) \propto \left(\begin{array}{l} \text{Oxidation number of} \\ \text{active element} \end{array} \right)$

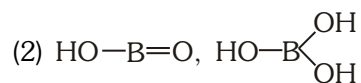
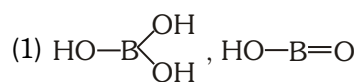


- (ii) For different elements (Acidic nature of oxyacids \propto EN of active element)



BEGINNER'S BOX-2

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



(3) Both the above

(4) None

2. Hypophosphorus acid (H_3PO_2) is –

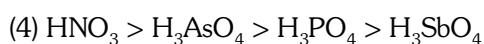
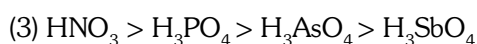
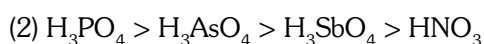
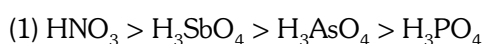
(1) Tribasic acid

(2) Dibasic acid

(3) Monobasic acid

(4) Not acidic at all

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



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

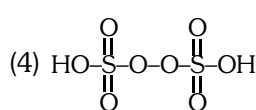
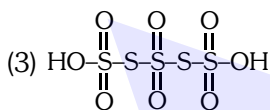
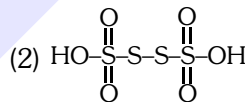
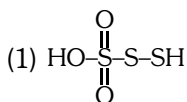
(1) NO

(2) NO_2

(3) N_2O_3

(4) N_2O_5

5. The structure of peroxodisulphuric acid is :



6. Number of S-S bond in $\text{H}_2\text{S}_n\text{O}_6$

(1) n

(2) (n-1)

(3) (n-2)

(4) (n+1)

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

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

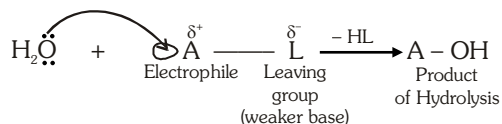
5. HYDROLYSIS

Hydrolysis is a nucleophilic substitution reaction in which H_2O acts as a nucleophile.

Condition for hydrolysis :

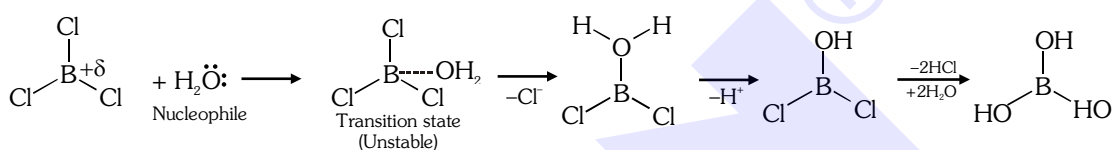
For hydrolysis electrophile should have vacant orbital it undergoes through $\text{S}_\text{N}2$ mechanism

Mechanism of hydrolysis : ($\text{S}_\text{N}2$ mechanism)



- Weaker base goes out and a stronger base substitutes it.

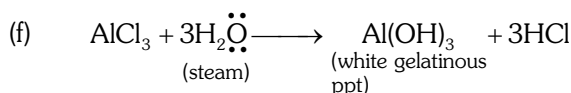
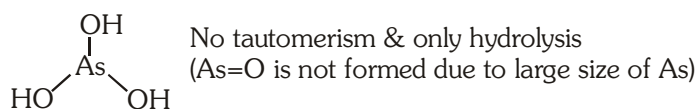
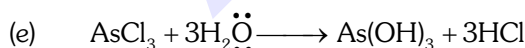
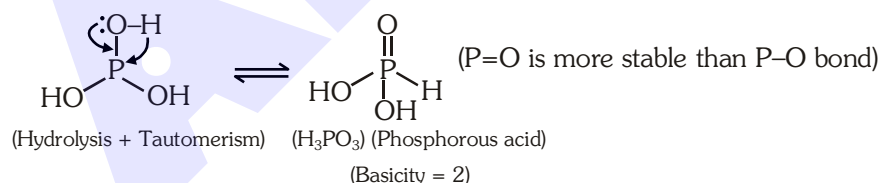
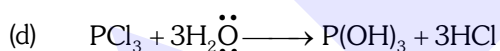
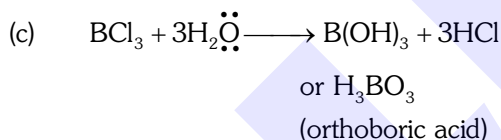
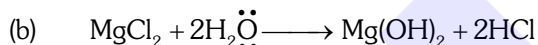
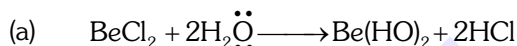
Example

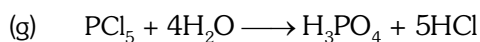


- In general hydrolysis is a non redox reaction.

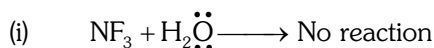
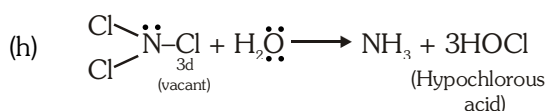
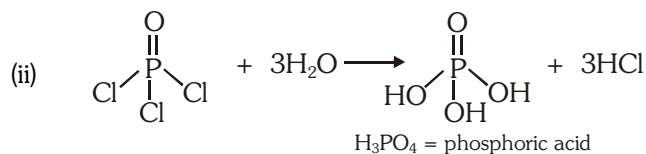
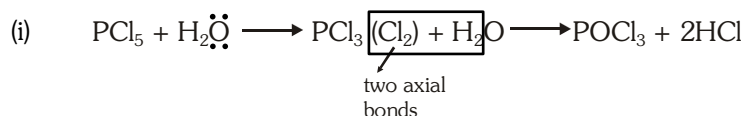
Important examples of hydrolysis

1. Hydrolysis of some important covalent molecules.





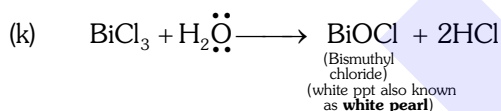
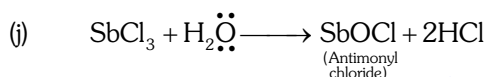
Hydrolysis of PCl_5 complete in two steps :-



(due to absence of vacant orbitals in the valence shell of Nitrogen)

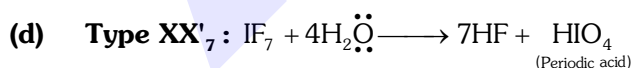
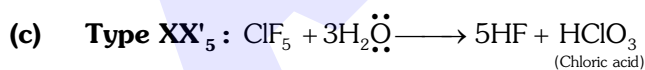
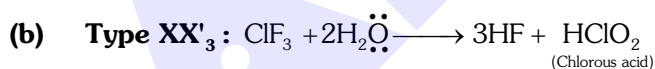
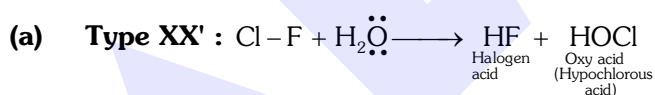
• **Partial hydrolysis**

SbCl_3 and BiCl_3 undergo partial Hydrolysis due to ionic character.

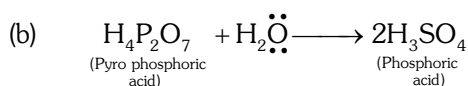
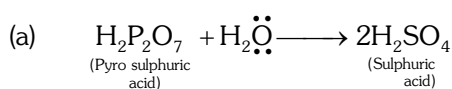


2. Hydrolysis of interhalogen compounds (XX'_n)

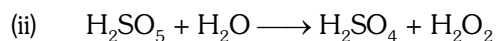
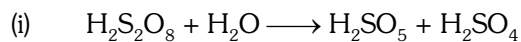
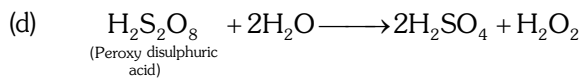
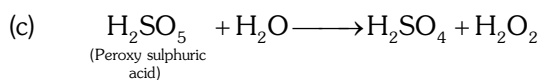
where X – large size Halogen (less EN atom), X' – small size Halogen (more EN atom)



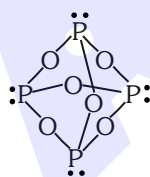
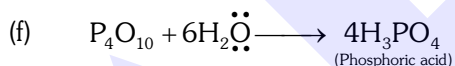
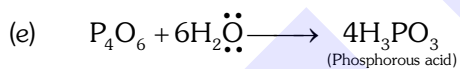
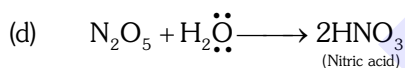
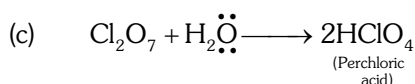
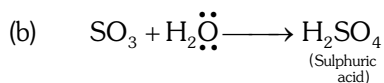
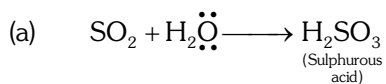
3. Hydrolysis of pyro and peroxy oxy acids



Pre-Medical

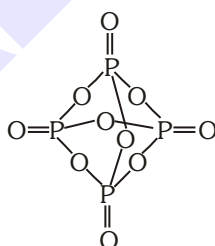


4. Hydrolysis of Acidic oxides


 sp^3 hybrid 'P'

6 P–O–P bonds

P = O bond is absent

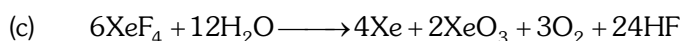
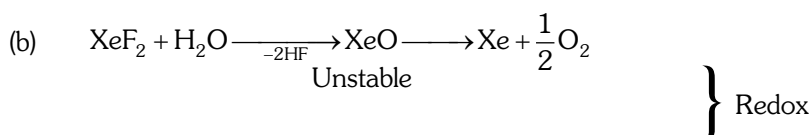
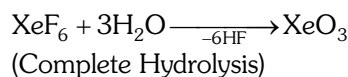
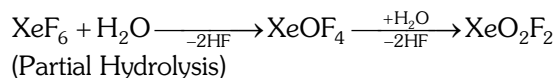

 sp^3 hybrid 'P'

6 P–O–P bonds

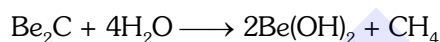
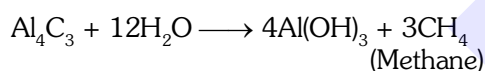
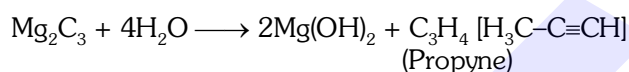
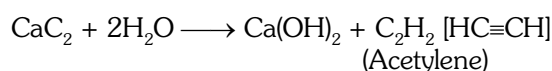
4 P = O bonds

5. Hydrolysis of xenon fluorides

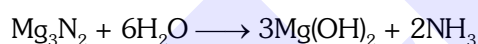
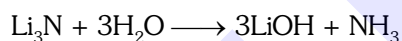
- (a) Hydrolysis of XeF_6 is a non redox reaction and it can undergo partial as well as complete hydrolysis.

**6. Hydrolysis of ionic compounds**

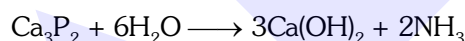
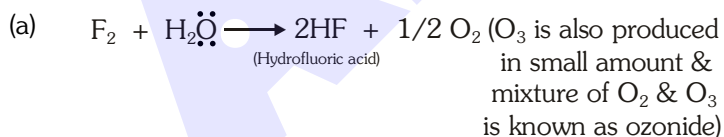
- (a) **Carbides**



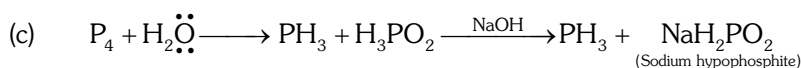
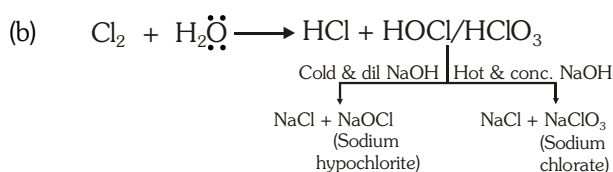
- (b) **Nitrides**



- (c) **Phosphides**

**7. Hydrolysis of non-metals and halogen**

- 'F₂' 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)



BEGINNER'S BOX-3

- Which of the following statements is correct :
 - Aluminium carbide as well as beryllium carbide produce methane gas on treatment with water
 - On reacting with water, calcium carbide (CaC_2) produces acetylene while magnesium carbide (Mg_2C_3) gives propyne
 - Both 1 & 2
 - None of the above
- $\text{Al} \xrightarrow{\text{N}_2} \text{A}$
High temp.
 - $\text{Al} \xrightarrow{\text{C}} \text{B}$
High temp.

Product A and B on hydrolysis yields respectively.

 - Ammonia and acetylene
 - Ammonia and methane
 - Nitric oxide and acetylene
 - None
- The hydrolysis of PCl_3 produces :
 - $\text{H}_3\text{PO}_3 + \text{HClO}$
 - $\text{H}_3\text{PO}_3 + \text{HCl}$
 - $\text{H}_3\text{PO}_4 + \text{HCl}$
 - $\text{PH}_3 + \text{HClO}$
- The number of molecules of water needed to convert one molecule of P_2O_5 into orthophosphoric acid is :
 - 2
 - 3
 - 4
 - 5
- Which of the following halides does not hydrolysed?
 - NCl_3
 - SiCl_4
 - CCl_4
 - PCl_3
- Consider the following reactions :
 - $\text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$
 - $\text{SF}_4 + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 + 4\text{HF}$
 - $\text{BCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{BO}_3 + 3\text{HCl}$
 - $\text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF}$

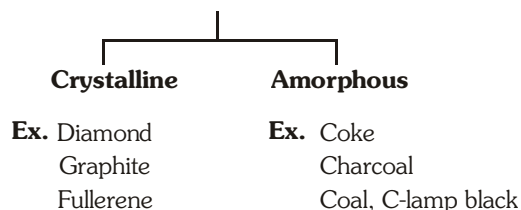
Then according to given information the incorrect statement is

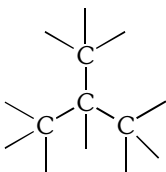
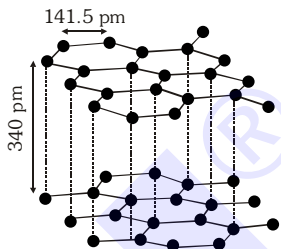
 - During the (i) reaction the hybridisation of 15th group element does not change
 - During the (ii) reaction the hybridisation of 16th group element has been change
 - During the (iii) reaction the hybridisation of 13th group element does not change
 - During the (iv) reaction the hybridisation of 18th group element does not change
- Give the name of final product in following reaction.

$$\text{SiCl}_4 \xrightarrow{\text{Hydrolysis}} \text{product}$$
 - Silicic Acid
 - dichlorido di hydroxo silicate
 - Silicones
 - Silicone carbide

6. ALLOTROPES

(A) Allotropes of Carbon



DIAMOND	GRAPHITE
	
Each carbon atom is bonded with four other carbon atoms sp^3 hybridisation tetrahedral structure	Each carbon atom is bonded with three other carbon atoms sp^2 hybridisation hexagonal layer structure
Insulator due to absence of free electrons	Conductor due to presence of delocalised electrons
Hard due to presence of strong sigma bond and 3D structure	Soft due to 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) = 1.54 \AA	Bond length (C—C) = 1.41 \AA

Special Point :

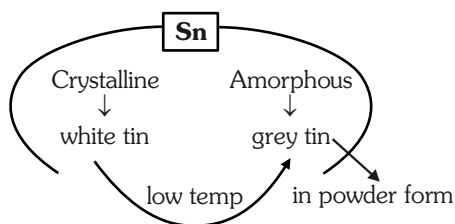
- (i) Thermodynamically graphite is more stable than diamond.
- (ii) Aqueous solution of graphite is known as **aquadag**.
- (iii) Graphite is also known as **plumbago (used in lead pencil)**
- (iv) Graphite use as a dry lubricants.
- (v) **Hardest allotrope** of carbon is diamond, **softest allotrope** is lamp black, **purest allotrope** is fullerene

Fullerene

- C-60 & C-70 are common forms of fullerene.
- C-60 is also known as Buckminster fullerene (Bucky ball)
- There are 32 rings $\begin{cases} 12 \text{ pentagonal} \\ 20 \text{ hexagonal} \end{cases}$
- Each carbon atom bonded with 3 other carbon by sigma & double bond (resonance)
- sp^2 hybridisation & aromatic in nature

Dangling Bond

In diamond or graphite some surface carbon atoms have free valency. These carbon atoms form new bonds with impurities. These new bonds are known as dangling bond.

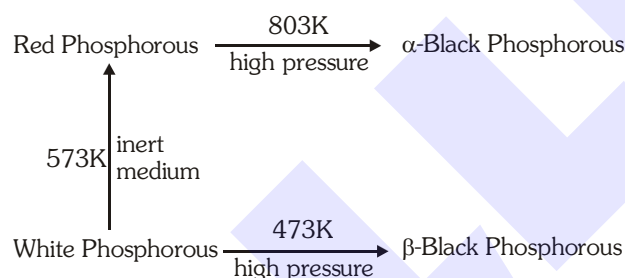
(B) ALLOTROPES OF TIN

(C) ALLOTROPES OF PHOSPHOROUS

(a) white/yellow phosphorous

(b) Red phosphorous

(c) Black phosphorous

White Phosphorous	Red Phosphorous
(1) Waxy solid (2) Poisonous (3) Soluble in CS_2 , Insoluble in water (4) Discrete units of P_4 are held by Vander Waal's forces (5) Less stable due to more angular strain (6) It glows in dark due to slow oxidation(phosphorecence)	(1) Brittle powder (2) Non poisonous (3) Insoluble in water & CS_2 (4) P_4 units are linked with each other through covalent bond (5) More stable than white phosphorous (6) It does not glow in dark

Order of stability or MP or density \rightarrow white < red < black

(D) ALLOTROPES OF SULPHUR

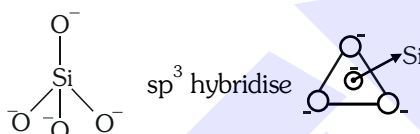
S	
Crystalline	Amorphous
Rhombic sulphur (α -S) (most stable form) Monoclinic sulphur (β -S) $\alpha\text{-S} \xrightleftharpoons[<95.6^\circ\text{C}]{>95.6^\circ\text{C}} \beta\text{-S}$ 95.6°C = transition Temp. both are soluble in CS_2 but insoluble in water	Milk of sulphur Plastic sulphur (γ -S) Colloidal sulphur $\underset{\text{RA}}{\text{H}_2\text{S}} + \underset{\text{OA}}{2\text{HNO}_3} \xrightarrow{\text{Redox}} \text{S} + 2\text{NO}_2 + 2\text{H}_2\text{O}$

- II. (a) density of $\alpha S > \beta S$
- (b) Both are puckered crown shape having S_8 units
- (c) S_2 is paramagnetic sulphur which exist in vapour form at high temperature.
- (d) S_6 is chair form of S

7. Compounds of Silicone

(A) 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}



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 $Zn_3Si_2O_7 \cdot Zn(OH)_2 \cdot 2H_2O$
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
(1) Sodium Zeolite $[\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8]/[\text{Na}_2\text{O}.\text{Al}_2\text{O}_3.2\text{SiO}_2.x\text{H}_2\text{O}]$

- (i) It is a 3-D silicate
- (ii) It is used in
 - (a) as a ion exchanger for softening of hard water
 - (b) as a catalyst in petrochemical industries for cracking of hydrocarbon & isomerisation

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

(2) 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.
 - Kieselgur is amorphous form of silica which is used in filtration plants.
- (a) $2\text{NaOH} + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$
water glass
- (b) $\text{SiO}_2 + 4\text{HF} \rightarrow 2\text{H}_2\text{O} + \text{SiF}_4$
 $\text{SiF}_4 + 2\text{HF} \rightarrow \text{H}_2[\text{SiF}_6]$
hexa fluoro silicic acid
- This process is also known as **Etching of glass**.

(B) SILICONES

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

Properties :

- (i) Silicones are chemically inert due to 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.

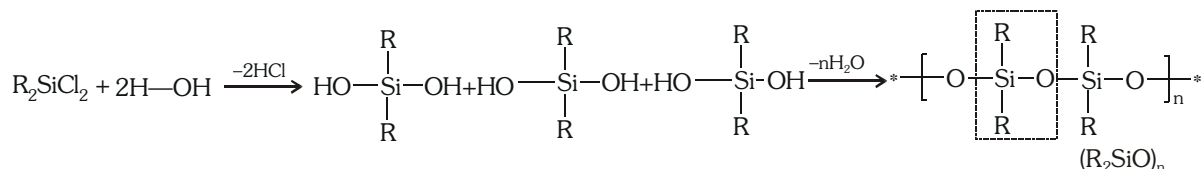
Preparation :

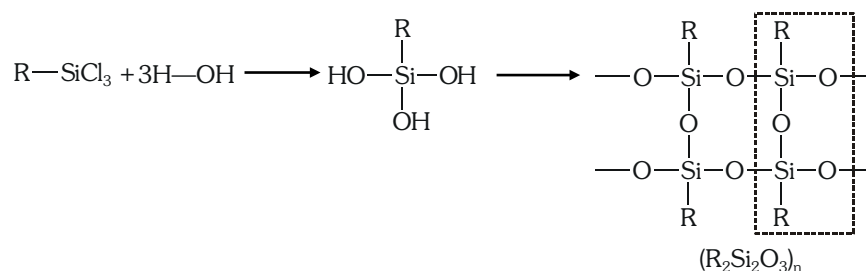
Alkyl chloro silane $\xrightarrow{\text{hydrolysis}}$ product $\xrightarrow{\text{condensation}}$ silicones

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

(a) Linear chain silicone (single chain silicones)


(b) Cross linked silicone/Double chain silicone**8. BLEACHING AGENTS**

Conversion of coloured substance into colourless substance by using a suitable bleaching agent is known as bleaching.

- Bleaching can be done by oxidation or reduction.
- Coloured substance $\xrightarrow[\text{Oxidation}]{[O]}$ Colourless
(Permanent bleaching)
- Coloured substance $\xrightarrow[\text{Reduction}]{[H]}$ Colourless
air
[O]
(Temporary bleaching)

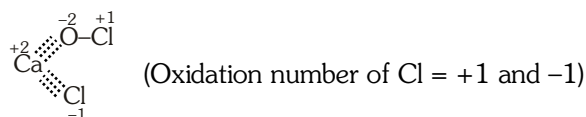
Examples of bleaching agents :

- | By oxidation | By Reduction |
|------------------------------|------------------------|
| (1) O_3 (Dry bleach) | SO_2 (with moisture) |
| (2) H_2O_2 (with moisture) | |
| (3) Cl_2 (with moisture) | |

- Bleaching powder** : Used in textile industries. Bleaches by oxidation.

$CaCl_2 \cdot Ca(OCl)_2 \cdot Ca(OH)_2 \cdot 2H_2O$ (average oxidation number of Cl = 0)

or

**9. DEHYDRATING AGENTS**

A compound which removes water from a substance.

Examples of dehydrating agents are : Conc. H_2SO_4 , P_4O_{10} , CaO , Anhydrous $CaCl_2$

- Acid $\xrightarrow[\text{agent}]{\text{dehydrating}}$ H_2O + Oxide

Example :

- $\text{HCOOH} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{H}_2\text{O} + \text{CO}$ (Lab preparation of CO)
- $\begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$ (Lab preparation of CO & CO₂)
- $\begin{array}{c} \text{COOH} \\ | \\ \text{CH}_2 \\ | \\ \text{COOH} \end{array} \xrightarrow{\text{conc. H}_2\text{SO}_4} 2\text{H}_2\text{O} + \text{O}=\text{C}=\text{C}=\text{C}=\text{O} \text{ (C}_3\text{O}_2\text{)}$
 (Malonic acid) (Carbon suboxide)
- Charring of sugar (dehydration) :
 $\text{C}_{12}\text{H}_{22}\text{O}_{11} \xrightarrow{\text{conc. H}_2\text{SO}_4} 11 \text{H}_2\text{O} + \text{C}$
 (Carbon black)
- $2\text{HClO}_4 \xrightarrow[\text{-H}_2\text{O}]{\text{P}_4\text{O}_{10}} \text{Cl}_2\text{O}_7$
- $2\text{HNO}_3 \xrightarrow[\text{-H}_2\text{O}]{\text{P}_4\text{O}_{10}} \text{N}_2\text{O}_5$

Some extra points :

- NH₃ can not be dried by conc. H₂SO₄, P₄O₁₀ and CaCl₂
- Alcohols, phenols can not be dried by metal hydrides.
- MgCl₂.6H₂O and AlCl₃.6H₂O can not be dried by heating alone.

BEGINNER'S BOX-4

- Silicones have the general formula
 (1) SiO₄⁴⁻ (2) Si₂O₇⁶⁻ (3) (R₂SiO)_n (4) (SiO₃)_n²⁻
- Glass or silica is soluble in :
 (1) HClO₄ (2) HF (3) Aqua-regia (4) H₂SO₄
- Si₂O₇⁶⁻ anion is obtained when
 (1) no oxygen of a SiO₄⁴⁻ tetrahedron is shared with another SiO₄⁴⁻ tetrahedron
 (2) one oxygen of a SiO₄⁴⁻ tetrahedron is shared with another SiO₄⁴⁻ tetrahedron
 (3) two oxygen of a SiO₄⁴⁻ tetrahedron is shared with another SiO₄⁴⁻ tetrahedron
 (4) three or all four oxygen of a SiO₄⁴⁻ tetrahedron is shared with another SiO₄⁴⁻ tetrahedron
- Consider the following route of reactions
 $\text{R}_2\text{SiCl}_2 + \text{Water} \rightarrow (\text{A}) \xrightarrow{\text{polymerisation}} (\text{B})$
 Compound(B) in above reaction is
 (1) Dimer silicone (2) Linear chain silicone
 (3) cross linked silicone (4) polymerisation of (A) does not occur

5. $(\text{Si}_2\text{O}_5)_n^{2n-}$ 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
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
7. Different layers in graphite are held together by :
- (1) Ionic bonding
 - (2) Metallic bonding
 - (3) Covalent bonding
 - (4) Vander Waal's forces
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

BORON FAMILY (GROUP 13)

INTRODUCTION

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

GENERAL CHARACTERISTICS

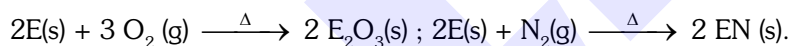
Physical properties :

- 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), could exist in liquid state during summer. Its **high boiling point (2676 K) makes it a useful material for measuring high temperatures.**

Chemical properties

Reactivity towards air

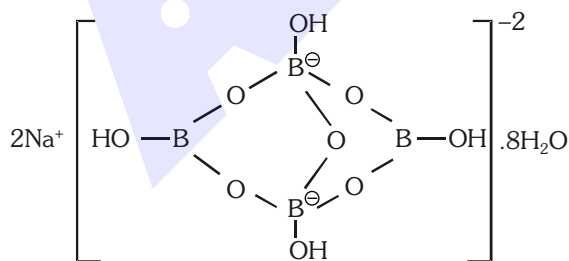
- Boron is unreactive in crystalline form.
- Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack.
- Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.



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.

COMPOUNDS OF BORON

(I) Borax ($Na_2B_4O_7 \cdot 10H_2O$) / $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$



Important points :

B-O-B linkage = 5

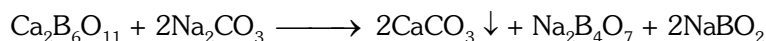
Two Boron- sp^2 hybridised

Two Boron- sp^3 hybridised

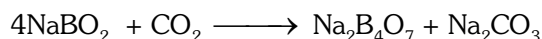
Two tetrahedral and two trigonal planar units are present

(A) Methods of Preparation**(i) From Colemanite.**

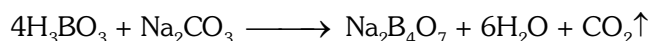
When colemanite powder is heated with Na_2CO_3 solution, the following reaction occurs with the precipitation of CaCO_3 .



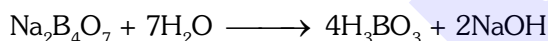
The filtrate is cooled when white crystals of borax are precipitated. The mother liquor on treatment with CO_2 converts NaBO_2 to $\text{Na}_2\text{B}_4\text{O}_7$ which precipitates out on crystallization.

**(ii) From orthoboric acid.**

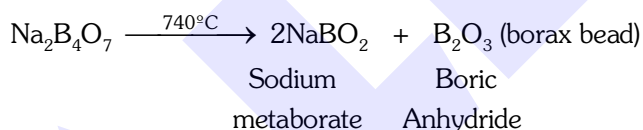
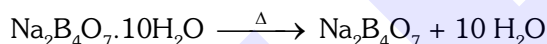
Borax is obtained by the action of Na_2CO_3 on orthoboric acid.

**(B) Properties :**

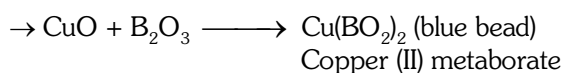
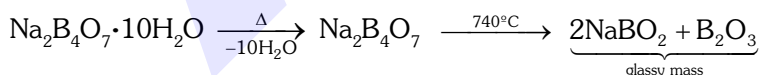
- (i) Borax is a white powder, less soluble in cold water, more soluble in hot water.
- (ii) Its aqueous solution is alkaline because of its hydrolysis to weak acid H_3BO_3 and strong alkali NaOH .

**(iii) Action of heat.**

When borax powder is heated, it first swells due to loss of water but at 740°C it converted into colourless transparent liquid, which solidifies into glass like material known as borax bead.

**(C) Borax-bead test :**

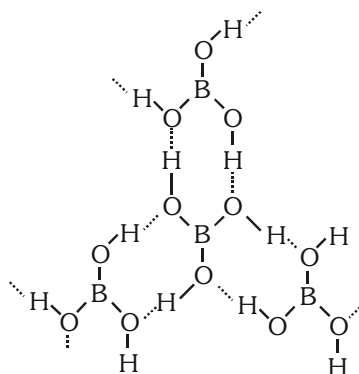
Borax reacts with certain metal salts such as, Ni^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Mn^{2+} etc. to form coloured metaborates. The colour of the metaborates can be used to identify the metallic ions (cations) in salts.

**(D) Uses :** Borax is used

1. in borax bead test
2. in purifying gold
3. as flux during welding of metals
4. in production of heat resistant glass (eg. pyrex glass)

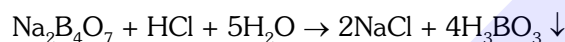
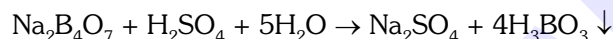
(II) ORTHO BORIC ACID [$\text{H}_3\text{BO}_3/\text{B}(\text{OH})_3$]

It has a layered structure in which planar BO_3 units are attached by hydrogen bonds as shown below and these layers are weakly held by Vander Waal's forces due to which boric acid is soft and slippery.

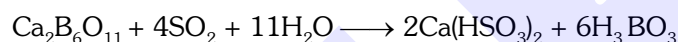


(A) Preparation :

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

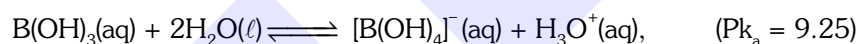


- (ii) From Colemanite: Powdered colemanite is suspended in water and excess SO_2 is passed through it. On filtering and cooling the filtrate, white crystals of H_3BO_3 are obtained.



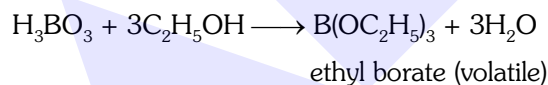
(B) Properties:

It is a weak monobasic acid. It is not a protonic acid but acts as a lewis acid by accepting electrons from OH^- ion.



(C) Test for Borate radical :

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



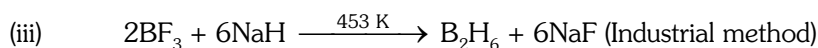
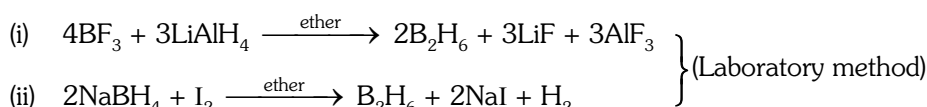
Uses :

1. It is an antiseptic and its water solution is used as an eyewash.
2. It is also used in glass, enamel and pottery industry.

(III) DIBORANE (B_2H_6)

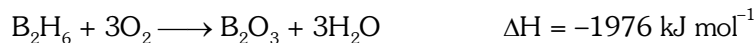
Binary compounds of boron with hydrogen are called boron hydrides or boranes.

(A) Preparation :



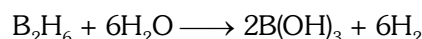
(B) Properties :

- (i) B_2H_6 is colourless gas and highly toxic (boiling point 183 K).
 (ii) It catches fire spontaneously in air and explodes with O_2 . Reaction with oxygen is extremely exothermic.



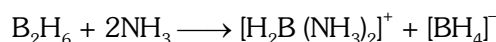
Mixtures of diborane with air or oxygen in flame spontaneously producing large amount of heat. Diborane has a higher heat of combustion per unit weight of fuel than most other fuels. It is therefore used as a rocket fuel.

- (iii) It readily hydrolysed by water to give boric acid.

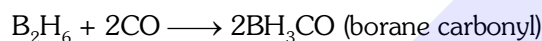
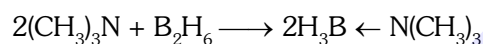


- (iv) Diborane undergoes cleavage reactions with lewis bases.

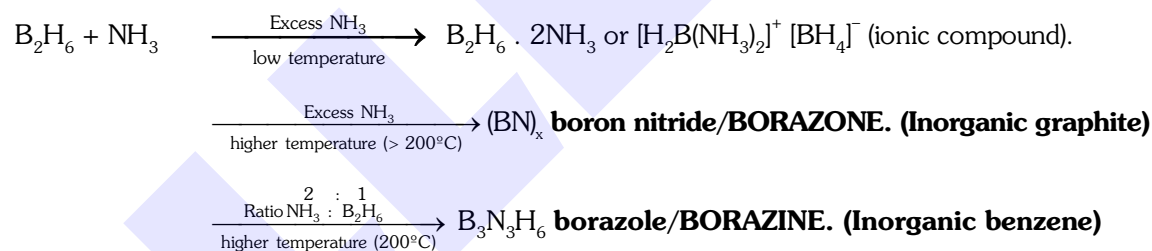
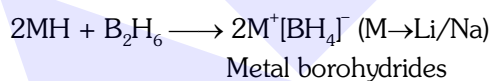
- Small amines such as NH_3 , CH_3NH_2 and $(CH_3)_2NH$ give unsymmetrical cleavage of diborane.



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



- (v) The reaction with ammonia depends on conditions.

**(vi) Reaction with LiH or NaH****(IV) ALUM**

- (a) Alums are double salt with their general formula $M_2SO_4 \cdot M'_2(SO_4)_3 \cdot 24H_2O$
 where M = monovalent radical like Na^+ , K^+ , NH_4^+ and M' = Trivalent radical like Al^{+3} , Cr^{+3} , Fe^{+3} .
 (b) The different alums are -
 (i) Potash alum - $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
 (ii) Chrome alum - $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$
 (iii) Iron alum - $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$
 (iv) Ammonium alum - $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
 (c) In alums each metal ion is surrounded by six water molecules.
 (d) Lithium does not form alum because Li ion is too small to have a coordination number of six.

Properties :

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

Uses :

- Alum is used to stop bleeding.
- It is used for purification of water.
- It is used as a mordant in dyeing industry.
- Alum is used for tanning of leather.

BEGINNER'S BOX-5

- Which of the following can be detected by the borax-bead test ?
 (1) Ni^{2+} (2) Co^{2+} (3) Pb^{+2} (4) Both (1) & (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
- The hydrolysis of borax produces –
 (1) An acidic medium (2) A basic medium
 (3) A neutral medium (4) An acidic or an neutral medium
- In alums, each metal ion is surrounded by–
 (1) Two water molecules (2) Four water molecules
 (3) Six water molecules (4) Eight water molecules
- 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
- Inorganic graphite is :-
 (1) $\text{B}_3\text{N}_3\text{H}_6$ (2) B_2H_6 (3) BN (4) BF_3
- 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
- Which is correct about diborane-
 (1) highly toxic liquid (2) Inflammable in air
 (3) have 4 bridge bond (4) has $4\text{C}-3\text{e}^-$ bond.
- Nature of boric acid H_3BO_3 is-
 (1) Weak acid (2) amphoteric (3) strong base (4) None
- Borax bead is -
 (1) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (2) $\text{NaBO}_2 + \text{B}_2\text{O}_3$ (3) $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ (4) All

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 O₂

- All elements when heated with O₂ form two types of oxide (MO and MO₂)
- SiO only exist at high temperature.

Reactivity towards H₂O

- C, Si and Ge do not react with H₂O
- Sn decomposes steam to form dioxide and H₂ gas

$$\text{Sn} + 2\text{H}_2\text{O}(\text{steam}) \longrightarrow \text{SnO}_2 + 2\text{H}_2$$
- Pb is unaffected by H₂O due to formation of protective layer of oxide.

Catenation property

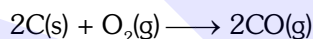
- C has maximum tendency due to formation of strong C-C bond.
- On moving down the group tendency of catenation decreases due to increase in size.
- Lead does not show catenation.

COMPOUNDS OF CARBON

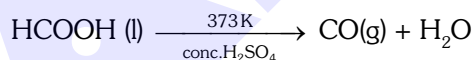
(A) Carbon Monoxide (CO)

(I) Preparation of CO

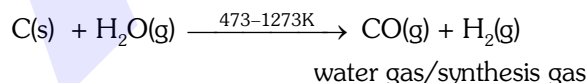
- It is obtained by direct oxidation of C in limited supply of O₂/air.



- In the laboratory it can be prepared by dehydrating formic acid with concentrated sulphuric acid.



- On commercial scale it is prepared by passing steam over hot coke.



When air is used instead of steam a mixture of CO and N₂ is obtained which is known as producer gas. Both water gas and producer gas are very important fuels.

(II) Physical Properties

- Carbon monoxide is a colourless, odourless gas which burns in air with a blue flame, forming CO₂.
- It is almost water insoluble.
- 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.
- It acts as good reducing agent and used in extraction of many metals from their oxides ores.

(B) CARBON DIOXIDE (CO₂)
Preparation :

- (i) Complete combustion of carbon containing compounds.

$$\text{CH}_4 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$$
- (ii) In the laboratory it can be conveniently made by the action of dilute hydrochloric acid on calcium carbonate:

$$\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell)$$
- (iii) Industrially it is produced as a by-product during the manufacture of quicklime from lime stone :

$$\text{CaCO}_3(\text{s}) \xrightarrow{\Delta} \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$

Properties :

- (i) It is a colourless, odourless gas.
- (ii) Carbon dioxide is the acid anhydride of carbonic acid, which is a weak dibasic acid and ionises in two steps as follows :

$$\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

$$\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{CO}_3^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

$\text{H}_2\text{CO}_3 / \text{HCO}_3^-$ buffer system helps to maintain pH of blood between 7.26 to 7.42.
- (iii) Carbon dioxide readily reacts with alkalis forming the carbonate and, if CO₂ is in excess, the hydrogen carbonate is formed. This is the basis of the lime-water test for CO₂ gas.

$$\text{Ca}(\text{OH})_2(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{liq}) ; \quad \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{liq}) + \text{CO}_2(\text{g}) \rightarrow \text{Ca}(\text{HCO}_3)_2(\text{aq})$$
- (iv) Gaseous CO₂ is extensively used to carbonate soft drinks. Being heavy and non-supporter of combustion it is used as fire extinguisher. A substantial amount of CO₂ is used to manufacture urea.
- (v) CO₂ can be obtained as a solid in form of dry ice by allowing liquid CO₂ to expand rapidly. Dry ice is used as a refrigerant for ice cream and frozen food.

(C) Carbides :

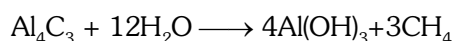
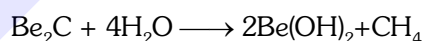
On the basis of type of bonding carbides are of three types :-

- (i) Salt like carbides (ionic carbides)
- (ii) Covalent carbides (giant molecular carbides)
- (iii) Interstitial carbides.

(I) Salt like carbides (ionic carbides) :

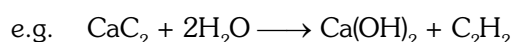
- (a) These are formed by strong electropositive elements of groups 1, 2 and 13
- (b) These are transparent crystalline substances and do not conduct electric current in the solid state.
- (c) These are easily hydrolysed by water or dilute acids to give aliphatic hydrocarbons,
- (i) **Methanides (Methides)** – Methanides are the carbides which give methane on hydrolysis.

They contain C⁴⁻ ions.



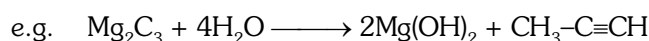
- (ii) **Acetylides** – These are the carbides which yield acetylene on hydrolysis.

They contain C₂²⁻ ions.



- (iii) **Alkylides** – These carbides give propyne (CH₃-C≡CH) on hydrolysis.

They contain C₃⁴⁻ ions.



(II) Covalent carbides (giant molecular carbides)

- (a) Covalent carbides are the compounds of carbon with elements having similar electronegativity.
- (b) These are covalent, polymeric, thermally stable, extremely hard, having high melting point and chemically inert solid.
- (c) B_4C and SiC are two main covalent carbides.

(III) Interstitial carbides.

Transition metals like Ti, Zr, Hf, V, Nb, Ta and Mo form these carbides. The metals retain their **close packed lattice** and carbons are incorporated in their interstitial spaces. These carbides are extremely hard and have very high melting points. The carbides of V and Ta are very hard hence they are used for manufacture of high speed cutting tools.

GLASS

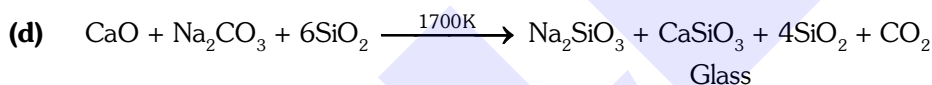
- (a) Glass is a hard, brittle transparent, amorphous solid or supercooled liquid made up of silicates of Na, Ca and other metals like Pb, Zn etc.
- (b) Being amorphous solid (not a true solid) it has no sharp melting and melts at high temperature.
- (c) Glass has no definite chemical formula, however it may be represented as :



where M = monovalent metals (eg : Na, K)

M' = bivalent metals Ca, Pb, Zn etc.

x and y are integers.

**Different Types of Glass**

- (i) **Soda or Soft glass or Sodalime glass** : It is common glass. Contains Na & Ca metal silicate. Used for formation of tube, window.
- (ii) **Potash or Hard glass** : It is a mixture of potassium and calcium silicates. It fuses with difficulty. It is used for making hard glass apparatus.
- (iii) **Flint glass** : It is mixture of potassium and lead silicates. It has a very high refractive index and is used for making electric bulbs and optical instruments.
- (iv) **Crooke's glass** : It is an optical glass containing CeO_2 which prevents the entry of UV rays.
- (v) **Pyrex glass or borasil or borosilicate glass** : It is used to make lab appliances as it is resistant to heat, shock and common reagents. It is a mixture of zinc and barium borosilicates and alumina silicate.

Small part of SiO_2 is replaced by boric oxide/borax.

Low thermal expansion coefficient, can withstand sudden change in temperature so used for making lab glass wares.

SOME GASEOUS FUELS

- (a) Water gas or syn gas = $CO + H_2$
- (b) Producer gas = $CO + N_2$
- (c) Semi water gas = $CO + N_2 + H_2$
- (d) Natural gas = CH_4
- (e) Coal gas = $[CO_2 + CO + H_2 + CH_4]$

BEGINNER'S BOX-6

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

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

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

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

NITROGEN FAMILY (GROUP 15)

INTRODUCTION

Group 15 includes nitrogen phosphorus, arsenic, antimony and bismuth.

Nitrogen and phosphorus are non metals, arsenic and antimony are metalloids and bismuth is a typical metal.

PHYSICAL PROPERTIES:

- Dinitrogen is a diatomic gas while all others are solids.
- Except nitrogen, all the elements show allotropy.

CHEMICAL PROPERTIES

Oxidation States and trends in a chemical reactivity :

- The common oxidation states of these elements are -3, +3 and +5. The tendency to exhibit -3 oxidation state decreases down the group, bismuth hardly forms any compound in -3 oxidation state.
- Nitrogen also exhibits +1, +2, +4 oxidation states when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxyacids.
- In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution.

For example, $3 \text{HNO}_2 \longrightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2 \text{NO}$

- Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and -3 both in alkali and acid. However +3 oxidation state in case of arsenic, antimony and bismuth become increasingly stable with respect to disproportionation.

Reactivity towards hydrogen :

- All the elements of Group 15 form hydrides of the type EH_3 where $\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}$ or Bi .
- The stability of hydrides decreases from NH_3 to BiH_3 . Which can be determined by bond dissociation enthalpy. Consequently the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides.

Reactivity towards oxygen :

- All these elements form two types of oxides : E_2O_3 and E_2O_5 . On moving down the group acidic nature decreases. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth is predominantly basic.

Reactivity towards halogens :

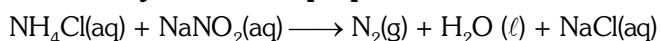
- These elements react to form two series of halides : EX_3 and EX_5 .
- All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only NF_3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.

COMPOUND OF NITROGEN

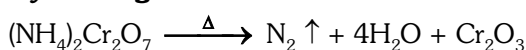
1. NITROGEN GAS (N_2) :

(a) Preparation :

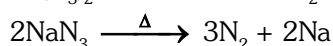
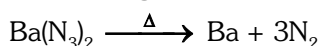
(i) Laboratory method of preparation :



(ii) By heating ammonium dichromate :



(iii) Very pure nitrogen can be obtained by heating sodium or barium azide.

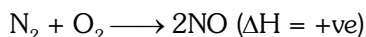


(iv) **Industrial methods of preparation :**

From liquified air by fractional distillation : The boiling point of N_2 is -196°C and that of oxygen is -183°C and hence they can be separated by fractional distillation of air.

 (b) **Properties :**

- (i) N_2 is a colourless, odourless gas and very less soluble in water.
- (ii) N_2 is rather inert at room temperature due to high bond enthalpy of $N\equiv N$ bond.
- (iii) **Reaction with oxygen:** Dinitrogen combines with dioxygen only at very high temperature (at about 2000K) to form nitric oxide.

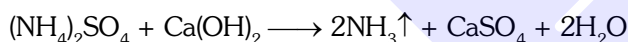
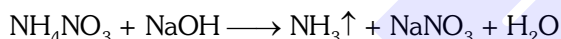

 (c) **Uses :**

- (i) For providing an inert atmosphere during many industrial processes. (eg. in iron and steel industry)
- (ii) For manufacture of NH_3 by the Haber's process.
- (iii) Liquid dinitrogen is used as a refrigerent to preserve biological materials, food items & in cryosurgery.

2. AMMONIA (NH_3)

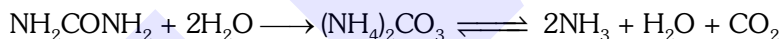
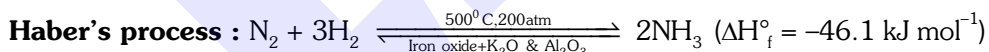
 (a) **Preparation :**

- (i) By the action of any base or alkali on any ammonium salt :



This is a general method and is used as a test for ammonium salts.

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

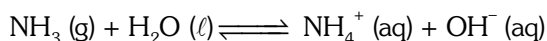

 (ii) **Industrial methods of preparation :**


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 $200 \times 10^5 \text{ Pa}$ (about 200 atm), a temperature of $\sim 700 \text{ K}$ 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.

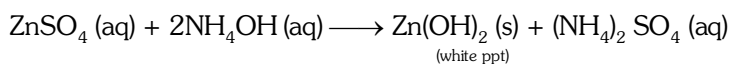
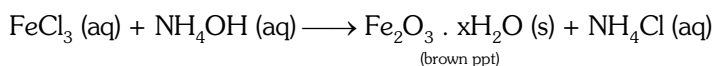
- (b) **Physical properties :** Ammonia is a colourless gas with a pungent odour.
Highly soluble in H_2O

 (c) **Chemical properties :**

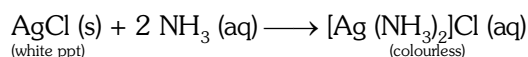
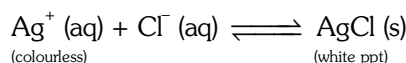
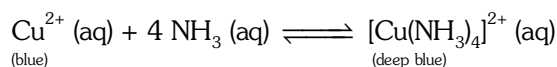
- (i) Its aqueous solution is weakly basic due to the formation of OH^- ions.



- (ii) It forms ammonium salts with acids, e.g., NH_4Cl , $(NH_4)_2SO_4$ etc. As a weak base, it precipitates the hydroxides of many metals from their salt solutions. For example ,



- (iii) The presence of lone pair of electrons on the nitrogen atoms of the ammonia molecule makes it a Lewis base. It donates the electrons pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of metal ions such as Cu^{2+} , Ag^+

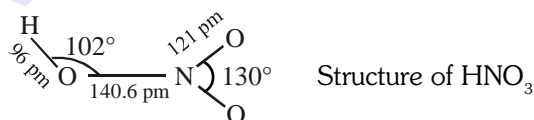


3. OXIDES OF NITROGEN :

Nitrogen forms a number of oxides, N_2O , NO , N_2O_3 , NO_2 or N_2O_4 and N_2O_5 . All these oxides of nitrogen exhibit $\text{p}\pi\text{-p}\pi$ multiple bonding between nitrogen and oxygen.

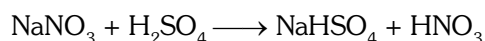
Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$\text{NH}_4\text{NO}_3 \xrightarrow{\text{Heat}} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	colourless gas, neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$	colourless gas, neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{K}} 2\text{N}_2\text{O}_3$	blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{K}} 4\text{NO}_2 + 2\text{PbO} + \text{O}_2$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2\text{NO}_2 \xrightleftharpoons[\text{Heat}]{\text{cool}} \text{N}_2\text{O}_4$	colourless solid/liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N_2O_5	+ 5	$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	colourless solid, acidic

4. NITRIC ACID (HNO_3)



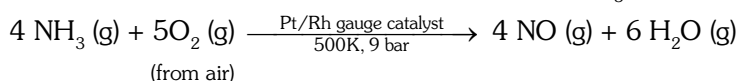
(A) Preparation :

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

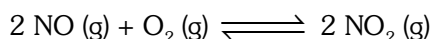


On a large scale it is prepared mainly by **Ostwald's process**.

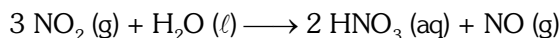
This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.



Nitric oxide thus formed combines with oxygen giving NO_2 .



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



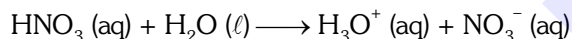
NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto $\sim 68\%$ by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4 .

(B) Physical properties :

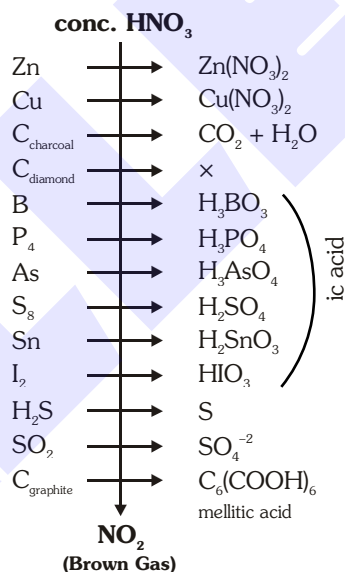
- (i) It is a colourless liquid. Freezing point is 231.4 K and boiling point is 355.6 K . Laboratory grade nitric acid contains $\sim 68\%$ of the HNO_3 by mass and has a specific gravity of 1.504 .
- (ii) In the gaseous state, HNO_3 exists as a planar molecule.

(C) Chemical properties

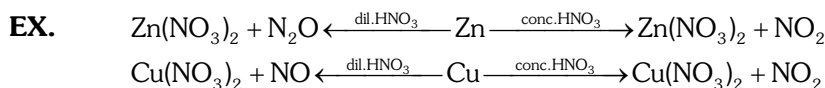
- (i) In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.



- (ii) Concentrate nitric acid is a strong oxidising agent and attacks most metals except Noble metal like Au & Pt . The product of oxidation depend upon the concentration of the acid, temperature and nature of metal.
- (iii) Concentrate HNO_3 also oxidises non-metals into their ic acids.

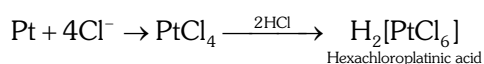
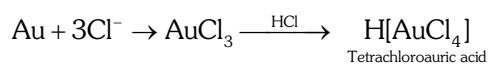


Types of Metal	conc. HNO_3	dil. HNO_3	very dil. HNO_3
negative SRP metal	Metal nitrate + NO_2	Metal nitrate + N_2O	Metal nitrate + $\text{NH}_4\text{NO}_3/(\text{NH}_3)$
positive SRP metal & Pb	Metal nitrate + NO_2	Metal nitrate + NO	\times
Metalloids, Non-metals & Sn	ic-acid + NO_2	\times	\times



Some important points

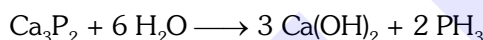
- **Mg and Mn form H₂ gas on reaction with very dilute HNO₃**
- **Be, Al, Fe, Cr do not react with conc. HNO₃ due to formation of protective oxide layer.**
- **Au and Pt (Noble metals) do not react with conc. HNO₃**
- **Sn reacts with conc. HNO₃ and forms H₂SnO₃ (metastannic acid)**
- **Au and Pt react only with aqua regia (3 part of conc. HCl and 1 part of conc. HNO₃)**

**(D) Uses :-**

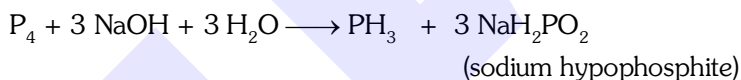
The major use of nitric acid is in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds. Other major uses are in the pickling of stainless steel, etching of metals and as an oxidiser in rocket fuels.

COMPOUNDS OF PHOSPHORUS :**1. Phosphine (PH₃) :****(a) Preparation :**

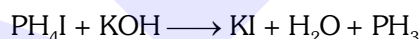
- (i) Phosphine is prepared by the reaction of calcium phosphide with water.



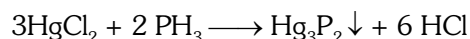
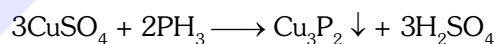
- (ii) In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO₂.



- (iii) When pure, it is non inflammable but becomes inflammable owing to the presence of P₂H₄ or P₄ vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH₄I) which on treating with KOH gives off phosphine.

**(b) Properties :**

- (i) It is a colourless gas with rotten fish smell and is highly poisonous. It is slightly soluble in water. The solution of PH₃ in water decomposes in presence of light giving red phosphorus and H₂.
- (ii) When absorbed in copper sulphate or mercuric chloride, the corresponding phosphides are obtained.



- (iii) Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids



- **Uses :** The spontaneous combustion of phosphine is technically used in **Holme's signals**. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.
- It is also used in the production of smoke screens. Calcium phosphide reacts with water producing phosphine which burns in air to give clouds of phosphorus pentoxide and that acts as smoke screens.

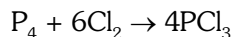
2. PHOSPHOROUS HALIDES

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

Phosphorous Trichloride (PCl_3)

(a) Method of preparation

(i) It is obtained by passing dry chlorine over heated white phosphorus.

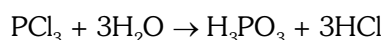


(ii) It is also obtained by the action of thionyl chloride with white phosphorus.

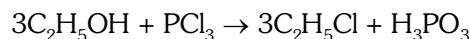
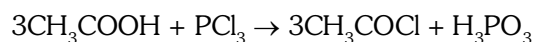


(b) Properties

(i) It is a colourless oily liquid and hydrolyses in the presence of moisture.



(ii) It reacts with organic compounds containing $-OH$ group such as CH_3COOH , C_2H_5OH .



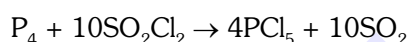
PHOSPHORUS PENTACHLORIDE (PCl_5)

(a) Method of preparation

(i) Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

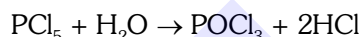


(ii) It can also be prepared by the action of SO_2Cl_2 on phosphorus.

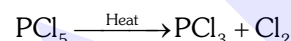


(b) Properties

(i) PCl_5 is a yellowish white powder and in moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.



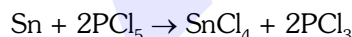
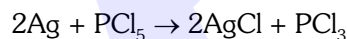
(ii) When heated, it sublimes but decomposes on stronger heating.



(iii) It reacts with organic compounds containing $-OH$ group converting them to chloro derivatives.



(iv) Finally divided metals on heating with PCl_5 give corresponding chlorides.



NCERT QUESTIONS (REASONING)

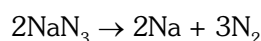
Q.1 Why BiH_3 is the strongest reducing agent amongst all the hydrides of Group 15 elements ?

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.



Q.3 Why N₂ is less reactive at room temperature?

Ans. N₂ is less reactive at room temperature because of the high bond enthalpy of N≡N bond.

Q.4 Why does R₃P = O exist but R₃N = 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?

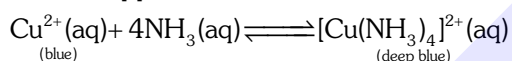
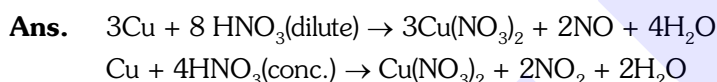
Ans. N–N bond is weaker than the single P–P bond due to high interelectronic repulsion of non-bonding electrons as a result the catenation tendency is weaker in nitrogen.

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

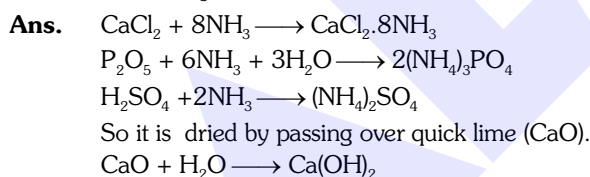
Ans. In accordance with Le Chatelier's principle, high pressure would favour the formation of ammonia. The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200 atm), a temperature of ~ 700 K and the use of a catalyst such as iron oxide with small amounts of K₂O and Al₂O₃ to increase the rate of attainment of equilibrium.

Q.7 How does ammonia react with a solution of Cu²⁺?

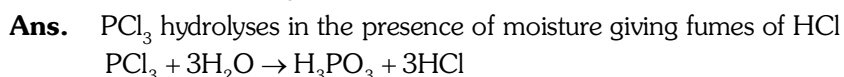
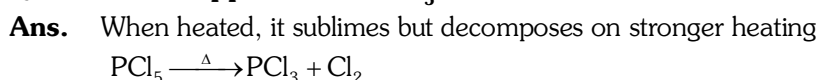
Ans. The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule makes it a Lewis base. It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of Cu²⁺.

**Q.8 Illustrate how copper metal can give different products on reaction with HNO₃.****Q.9 Why is nitrogen di-oxide paramagnetic in gaseous state but the solid obtained on cooling it is diamagnetic.**

Ans. NO₂ contains odd number of electrons in its valence shell. On cooling it forms dimer and converted to stable N₂O₄ which is a colourless solid and diamagnetic in nature.

Q.10 Why NH₃ gas cannot be dried by passing over P₂O₅, CaCl₂ and H₂SO₄?**Q.11 Why inert atmosphere of CO₂ is taken in the formation of PH₃ by the reaction of white phosphorous with conc. NaOH solution.**

Ans. To decrease the partial pressure of O₂ in atmosphere.

Q.12 Why does PCl₃ fumes in moisture?**Q.13 What happens when PCl₅ is heated?****Q.14 Can PCl₅ 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

- Which of the following halide of nitrogen is stable?
 (1) NF_3 (2) NCl_3 (3) NBr_3 (4) NI_3
- 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
- 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 $[\text{N} \rightarrow \text{O}]$ bond
- Which of the following process is not involved in Ostwald's process for the manufacture of HNO_3 ?
 (1) $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \xrightarrow[500\text{K}, 9\text{bar}]{\text{Pt}} 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
 (2) $2\text{NO}(\text{g}) + \text{O}_2 \rightleftharpoons 2\text{NO}_2(\text{g})$
 (3) $3\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HNO}_3(\text{aq}) + \text{NO}(\text{g})$
 (4) $\text{NO}_2 \xrightarrow{\text{low temp.}} \text{N}_2\text{O}_4$
- Which of the following salts give NH_3 in alkaline medium?
 (1) $(\text{NH}_4)_2\text{CO}_3$ (2) $(\text{NH}_4)_2\text{SO}_4$
 (3) NH_4Cl (4) All of the above
- Which of the following reaction is suitable for obtaining very pure nitrogen?
 (1) $\text{NH}_4\text{Cl}(\text{aq}) + \text{NaNO}_2(\text{aq}) \longrightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + \text{NaCl}(\text{aq})$
 (2) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\Delta} \text{N}_2 + 4\text{H}_2\text{O} + \text{Cr}_2\text{O}_3$
 (3) $\text{Ba}(\text{N}_3)_2 \xrightarrow{\Delta} \text{Ba} + 3\text{N}_2$
 (4) All of the above
- 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
- 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
- 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
- Which paramagnetic gas is evolved if lead nitrate is heated.
 (1) O_2 (2) NO (3) Both (4) None

OXYGEN FAMILY (GROUP 16)

INTRODUCTION

Oxygen, sulphur, selenium, tellurium and polonium constitute group 16 of the periodic table. This is sometimes known as group of chalcogens (ore forming elements) because a large number of metals ores are oxides or sulphides.

Oxygen and sulphur are non-metal, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 138.4 days).

Physical Properties :

- Oxygen is a gaseous diatomic molecule while other elements are solid.
- The melting and boiling points increase with an increase in atomic number down the group. The larger difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exist as diatomic molecules (O_2) whereas sulphur exists as polyatomic molecule (S_8).

Chemical Properties

• Oxidation states and trends in chemical reactivity :

The elements of group 16 exhibit a number of oxidation states. The stability of -2 oxidation state decreases down the group. Except oxygen other elements of the group exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common. Sulphur, selenium and tellurium usually show + 4 oxidation in their compounds with oxygen and +6 oxidations state with fluorine. The stability of +6 oxidation state decreases down the group and stability of + 4 oxidation state increases (inert pair effect). Bonding in + 4 and + 6 oxidation states are primarily covalent.

• Reactivity with hydrogen :

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

- **Reactivity with oxygen :** All these elements form oxides of the EO_2 and EO_3 types where $E = S, Se, Te$ or Po . Ozone (O_3) and sulphur dioxide (SO_2) are gases while selenium dioxide (SeO_2) is solid. Reducing property of dioxide decreases from SO_2 to TeO_2 ; SO_2 is reducing while TeO_2 is an oxidising agent. Besides EO_2 type sulphur, selenium and tellurium also form EO_3 type oxides (SO_3, SeO_3, TeO_3). Both types of oxides are acidic in nature.

- **Reactivity toward the halogens :** Elements of group 16 form a larger number of halides of the type EX_6, EX_4 and EX_2 where E is an element of the group 16 and X is a halogen. The stabilities of the halides decrease in the order $F > Cl > Br > I$. Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride SF_6 is exceptionally stable for steric reasons.

Amongst tetrafluorides, SF_4 is a gas, SeF_4 liquid and TeF_4 a solid

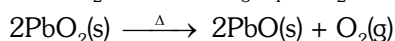
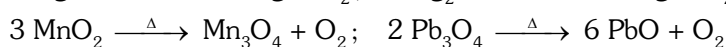
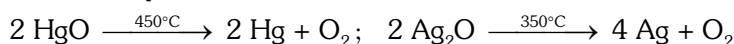
All elements except oxygen form dichlorides and dibromides. The well known monohalides are dimeric in nature, examples are $S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2$ and Se_2Br_2 . These dimeric halides undergo disproportionation as given $2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$.

COMPOUNDS OF OXYGEN

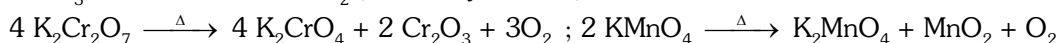
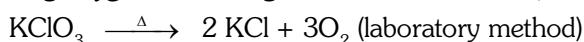
1. DIOXYGEN (O_2)

(a) Preparation :

By thermal decomposition of oxides of metals.



By heating oxygen containing salts such as chlorates, dichromates and permanganates.

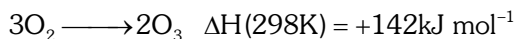


Properties:

- Dioxygen is a colourless and odourless gas and tasteless gas.
- Oxygen atom has three stable isotopes: ^{16}O , ^{17}O and ^{18}O . Molecular oxygen.
- O_2 is paramagnetic (by MOT)
- Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases.

2. OZONE (O_3) :

- (a) **Preparation :** It is prepared by passing pure and dry oxygen through a silent electric discharge.



Mixture obtained contains 5-10% ozone by volume and this mixture is called ozonised oxygen.

Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition. If concentrations of ozone greater than 10 per cent are required, a battery of ozonisers can be used, and pure ozone (b.p. 385 K) can be condensed in a vessel surrounded by liquid oxygen.

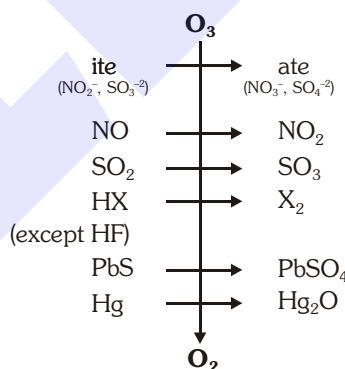
- (b) **Physical properties :**

- Pure ozone is a pale blue gas, dark blue liquid and violet-black solid.
- Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen. Therefore, high concentrations of ozone can be dangerously explosive.

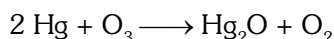
- (c) **Chemical properties :**

Oxidising behaviour of ozone :

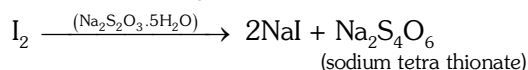
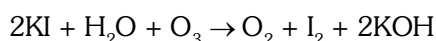
Due to the ease with which it liberates atoms of nascent oxygen ($\text{O}_3 \rightarrow \text{O}_2 + \text{O}$), it acts as a powerful oxidising agent.


Tests for Ozone

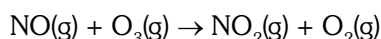
- (i) **Tailing of mercury :** Pure mercury is a mobile liquid but when brought in contact with O_3 its mobility decreases and it starts sticking to glass surface forming a type of tail due to the dissolution of Hg_2O in Hg.



- (ii) **Estimation of Ozone :** 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.



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



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

- (e) **Uses :-**

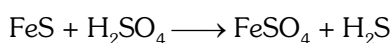
Used as a germicide, disinfectant and for sterilising water.

Used as a bleaching agent for oils, ivory, starch etc.

COMPOUNDS OF SULPHUR :

1. Hydrogen Sulphide (H₂S)

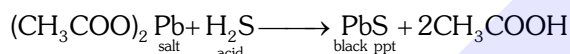
- (a) **Preparation :**



It is prepared in kipp's apparatus

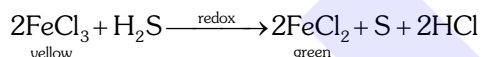
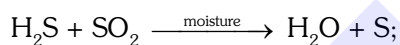
- (b) **Properties :**

- Colourless gas with rotten egg smell .
- Moderately soluble in water but solubility decreases with increasing temperature.
- It gives black ppt with lead acetate



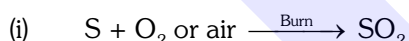
Reducing behaviour :

Acts as a strong reducing agent as it decomposes evolving hydrogen.

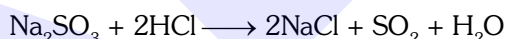


2. SO₂ (Sulphur Dioxide)

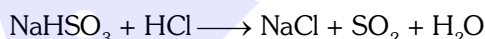
- (a) **Preparation :**



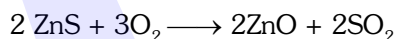
- (ii) By reaction of metal sulphites with dilute HCl (Laboratory method)



Similarly bisulphites also give SO₂ with dilute HCl



- (iii) By heating sulphides (metal sulphide ores) in excess of air.



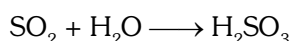
By this method SO₂ is obtained in large scale

- (b) **Physical Properties :**

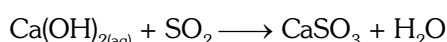
- Colourless gas with pungent smell.
- It is heavier than air and is highly soluble in water.

- (c) **Chemical Properties :**

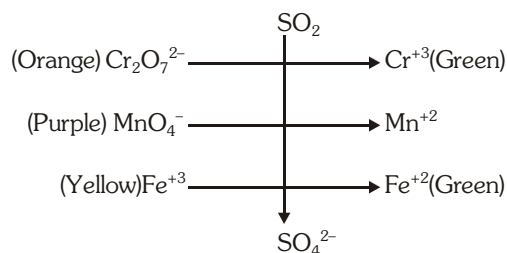
- (i) It is an acidic oxide and thus dissolve in water forming sulphurous acid.



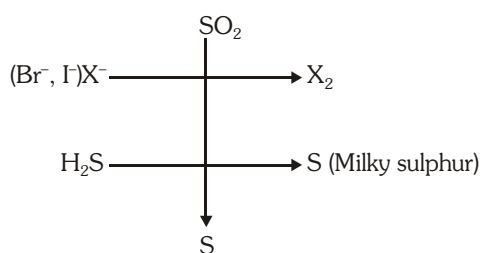
- (ii) It turns lime water milky due to formation of CaSO₃.



- (iii) SO₂ act as an oxidising as well as reducing agent.

Reducing nature :


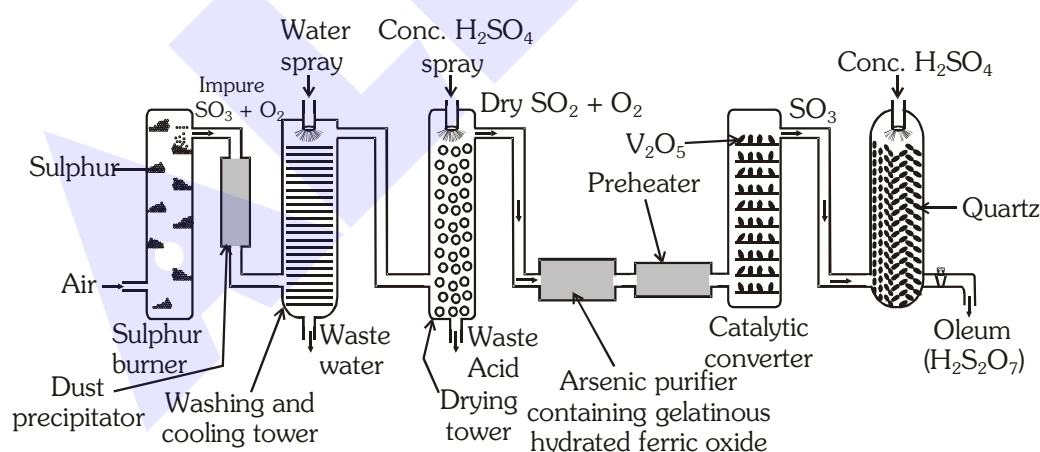
The above reactions are not given by CO_2 , so they are used to distinguish between SO_2 and CO_2

Oxidising nature :

(d) Uses :-

In refining of petrol and sugar.

In bleaching of wool and silk.

As an antichlor, disinfectant and preservative.

3. SULPHURIC ACID (H_2SO_4) :
(a) Preparation (Contact process) :


Flow diagram for the manufacture of sulphuric acid

Sulphuric acid is one of the most important industrial chemicals worldwide.

Sulphuric acid is manufactured by the contact process which involves three steps :

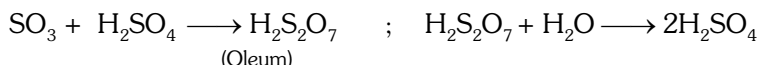
- (i) burning of sulphur or sulphide ores in air to generate SO_2
- (ii) Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5), and
- (iii) Absorption of SO_3 in H_2SO_4 to give Oleum ($\text{H}_2\text{S}_2\text{O}_7$)

The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).



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.

Dilution of oleum with water gives H_2SO_4 of the desired concentration. In the industry two steps are carried out simultaneously to make the process a continuous one and also to reduce the cost.



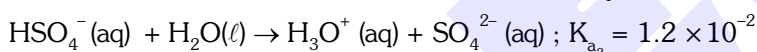
The sulphuric acid obtained by Contact process is 96-98% pure.

(b) Physical properties : Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K. The acid freezes at 283 K and boils at 611 K. It dissolves in water with the evolution of a larger quantity of heat.

(c) Chemical properties :

The chemical reaction of sulphuric acid are as a result of the following characteristics : (a) low volatility (b) strong acidic character (c) strong affinity for water and (d) ability to act as an oxidising agent in aqueous solution.

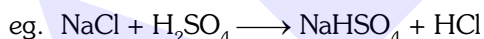
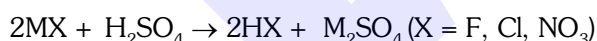
Sulphuric acid ionises in two steps.



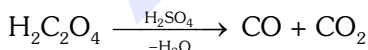
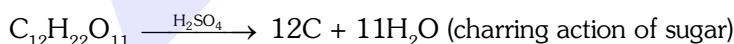
The larger value of K_{a_1} ($K_{a_1} > 10$) means that H_2SO_4 is largely dissociated into H^+ and HSO_4^- . Greater the value of dissociation constant (K_a) the stronger is the acid.

The acid forms two series of salts : Normal sulphates (such as sodium sulphate and copper sulphate and acid sulphate (e.g., sodium hydrogen sulphate)

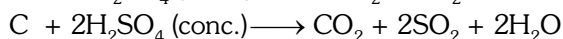
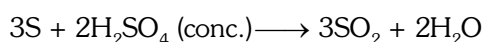
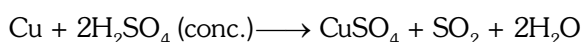
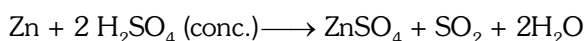
Sulphuric acid, because of its low volatility can be used to manufacture more volatile acid from their corresponding salts.



Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compound; it is evident by its charring action on carbohydrates.



Hot concentrated sulphuric acid is moderately strong oxidising agent. In this respect it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2 .



(d) Uses :

- In the manufacture of fertilisers (ammonium sulphate, superphosphate)
- In petroleum refining
- Metallurgical applications
- As a laboratory reagent

NCERT QUESTIONS (REASONING)

Q.1 H₂S is less acidic than H₂Te. Why?

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

Q.2 Why is H₂O a liquid and H₂S a gas?

Ans. Hydrogen bonds are present between H₂O molecules while between H₂S molecules, vander Waal's forces are present.

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

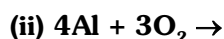
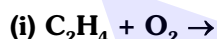
Ans. Oxygen exist as a O₂ molecule while sulphur exist as a S₈ molecule and due to more molecular mass sulphur is solid.

Q.4 Knowing the electron gain enthalpy values for O → O⁻ and O → O²⁻ as -141 and 702 kJ mol⁻¹ respectively, how can you account for the formation of a large number of oxides having O²⁻ 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:


Ans. (i) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

(ii) $4Al + 3O_2 \rightarrow 2Al_2O_3$

Q.7 How is O₃ 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 O₃ 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 SO₂ detected?

Ans. It has colourless gas with pungent smell and decolourise acidified KMnO₄ 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 $K_{a_2} \ll K_{a_1}$ for H_2SO_4 in water?

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

BEGINNER'S BOX-8

- Which of the following is not oxidised by O_3 ?
(1) KI (2) FeSO_4 (3) KMnO_4 (4) K_2MnO_4
- In which of the following reaction conc. H_2SO_4 is not used as an oxidising agent?
(1) $\text{Cu} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$ (2) $2\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$
(3) $\text{CaF}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + 2\text{HF}$ (4) None
- 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
- HCOOH reacts with conc. H_2SO_4 to produce
(1) CO (2) CO_2 (3) NO (4) NO_2
- Regarding O_3 incorrect statement is-
(1) ozone is an 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
- What happens when SO_3 is passed through water-
(1) H_2SO_4 (2) $\text{H}_2\text{O} + \text{S}$ (3) $\text{H}_2\text{S} + \text{O}_2$ (4) None

HALOGEN FAMILY (GROUP-17)

(A) INTRODUCTION

F, Cl, Br, I and At are members of group 17. These are known as halogens (Salt producers). They are highly reactive non metallic elements. At is a radioactive element.

(B) PHYSICAL PROPERTIES

- (i) Fluorine and chlorine are gases, bromine is a liquid whereas iodine is a solid.
- (ii) Their melting and boiling points steadily increase with atomic number.
- (iii) All halogens are coloured. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours.

For example, F_2 has yellow, Cl_2 has greenish yellow, Br_2 has red and I_2 has violet colour.

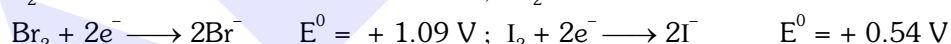
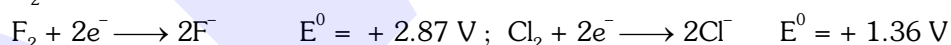
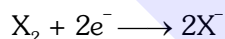
- (iv) Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water. But are soluble in organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.
- (v) The X-X bond disassociation enthalpies from chlorine onwards show the expected trend : $Cl - Cl > Br - Br > F - F > I - I$. The reason for the smaller enthalpy of dissociation of F_2 is the relatively larger electrons-electrons repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2 .

(C) CHEMICAL PROPERTIES

(i) Oxidation states and trends in chemical reactivity

- All the halogens exhibit -1 oxidation state. However, chlorine, bromine and iodine exhibit +1, +3, +5 and +7 oxidation states also. The higher oxidation states of chlorine, bromine and iodine are realised mainly when they are in combination with the small and highly electronegative fluorine and oxygen atoms e.g., in interhalogens, oxides and oxoacids.
- The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only -1 oxidation state.
- All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

Standard Reduction Potential (SRP)



More the value of the SRP, more powerful is the oxidising agent.

Hence the order of oxidising power is $F_2 > Cl_2 > Br_2 > I_2$

Order of reducing behaviour is $I^- > Br^- > Cl^- > F^-$

(ii) Reactivity towards oxygen :

- Fluorine forms two oxides OF_2 and O_2F_2 . However, only OF_2 is the thermally stable at 298 K. These oxide are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents.
- O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from nuclear fuel.
- Chlorine, bromine and iodine form oxides in which the oxidation states of these halogen vary from +1 to +7. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, $I > Cl > Br$. The higher oxides of halogens tend to be more stable than the lower ones. This is called middle row anomaly.
- Chlorine oxides, Cl_2O , ClO_2 , Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.
- The bromine oxides, Br_2O , BrO_2 , BrO_3 are the least stable halogen oxides (Middle row anomaly) and exist only at low temperature. They are very powerful oxidising agents.

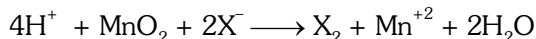
- The iodine oxides, I_2O_4 , I_2O_5 , I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is very good oxidising agent and is used in the estimation of carbon monoxide.

COMPOUNDS OF HALOGEN

1. CHLORINE GAS (Cl_2)

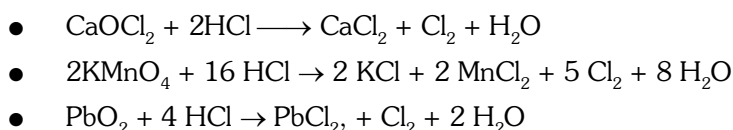
(a) Preparation :

- (i) By heating chloride with concentrated H_2SO_4 in presence of MnO_2 .



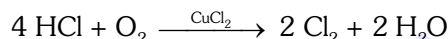
Bromides and iodides also liberate Br_2 and I_2 respectively with concentrated H_2SO_4 and MnO_2 .

- (ii) By the action of HCl on $KMnO_4$ / $CaOCl_2$ / PbO_2 .

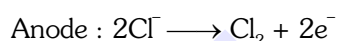


- (iii) **Commercial preparation :**

- Deacon's process :** By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.



- Electrolytic process :** Chlorine is obtained by the electrolysis of brine (concentrated $NaCl$ solution). Chlorine is liberated at anode. It is obtained as a by-product in many chemical industries e.g.; in manufacturing of sodium hydroxide.

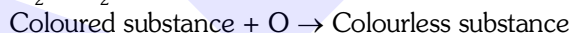


(b) Physical properties :

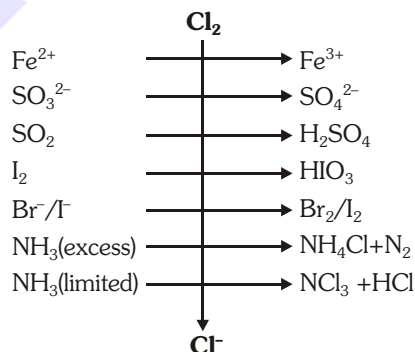
It is a greenish-yellow gas with pungent and suffocating odour. It is about 2–5 times heavier than air. It can be liquefied into greenish-yellow liquid which boils at 239 K. It is soluble in water.

(c) Chemical properties :

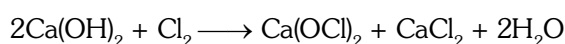
Oxidising & bleaching properties : Chlorine dissolves in water giving HCl and $HOCl$. Hypochlorous acid ($HOCl$) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.



Oxidising behaviour of Cl_2



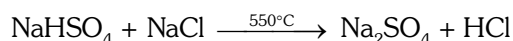
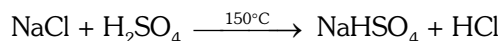
With dry slaked lime it gives bleaching powder



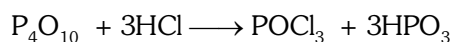
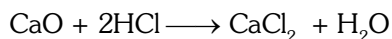
bleaching powder

(d) Uses :

- For bleaching wood pulp, cotton textiles.
- In the extraction of Au & Pt.
- In sterilising drinking water.
- In the preparation of phosgene (COCl_2), tear gas (CCl_3NO_2)

2. HALOGEN ACIDS (HCl)
(a) Preparation :
(i) By heating a halide with concentrated acid :


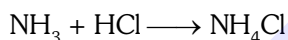
- HCl cannot be dried over P_2O_5 (P_4O_{10}) or quick lime since they react with HCl gas chemically.



- HCl is, hence dried by passing through concentrated H_2SO_4 .

(b) Properties :

- This is colourless, pungent smelling gas with acidic taste.
- Its aqueous solution is called hydrochloric acid.
- It reacts with NH_3 & gives white fumes of NH_4Cl .


3. Pseudo halogens and pseudo halides : Some inorganic compounds consisting of two or more atoms of which at least one is N have been found to behave like halogens & they are known as pseudo halogen solids,

Pseudo halogens	Pseudo halides
(i) $(\text{CN})_2$ cyanogen	(i) (CN^-) cyanide
(ii) $(\text{SCN})_2$ thiocyanogen	(ii) (SCN^-) thiocyanate ion
(iii) $(\text{SeCN})_2$ selenocyanogen	(iii) (SeCN^-) selenocyanate ion
(iv) $(\text{SCSN}_3)_2$ azidocarbonyl disulphide	(iv) (OCN^-) cyanate ion
	(v) $(\text{NCN})^{2-}$ cyanamide ion

4. INTERHALOGEN COMPOUNDS :

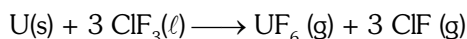
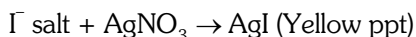
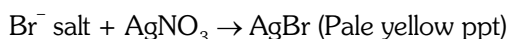
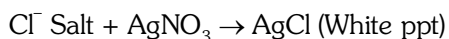
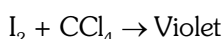
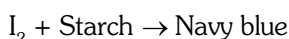
We know that halogen atoms have different electronegativity. Due to this difference in electronegativity the halogen atoms combine with each other and give rise to the formation of binary covalent compounds, which are called interhalogen compounds. These are of four types.

AB	AB_3	AB_5	AB_7^*
ClF	ClF_3	ClF_5	IF_7
BrF	BrF_3	BrF_5	
ICl	ICl_3	IF_5	
IF	IF_3		

* Where A - halogen of larger size and B is of small size.

(a) Properties :

- (i) These compounds may be gases, liquids or solids.
 Gases : ClF , BrF , ClF_3 , IF_7 ; Liquids : BrF_3 , BrF_5 ; Solids : ICl , IBr , IF_3 , ICl_3 .
- (ii) Interhalogens containing fluorine are generally colourless but inter halogens consisting of heavier halogens are coloured. The intensity of colour increases with increase in the molecular weight of the compounds.
- (iii) All interhalogens are covalent molecules and are diamagnetic in nature since all the valence electrons present as bonding or non-bonding electrons are paired.
- (iv) Interhalogen compounds are more reactive than the parent halogens but less reactive than F_2 .
- (v) These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents. ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U .

**TEST OF HALOGENS****1. F^- = Itching of glass****2. AgNO_3 test (Cl^- , Br^- , I^-)****3. Test of I_2** **4. Layer test (Br^- , I^-)**

(Note : In case of I^- violet colour is obtained.)

NCERT QUESTIONS (REASONING)

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 $\ell.p - \ell.p$ 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. $\text{Fe} + 2 \text{HCl} \longrightarrow \text{FeCl}_2 + \text{H}_2$.

Liberation of hydrogen prevents the formation of ferric chloride.

(b) Blue litmus change into red due to acidic nature ($\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$) but it is bleaching agent, therefore, it decolourises the red litmus.

ZERO GROUP (GROUP-18)

INTRODUCTION

Group 18 consists of six elements: helium, neon, argon, krypton, xenon and radon. All these are gases and chemically unreactive. They form very few compounds. Because of this they are termed noble gases.

(A) PHYSICAL PROPERTIES

- (i) All the noble gases are mono-atomic.
- (ii) They are colourless, and tasteless. They are sparingly soluble in water.
- (iii) They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces.
- (iv) Helium has the lowest boiling point (4.2K) of any known substance. It has a unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

(B) CHEMICAL PROPERTIES

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

- (i) The noble gases except helium ($1s^2$) have completely filled $ns^2 np^6$ electronic configuration in their valence shell.
- (ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

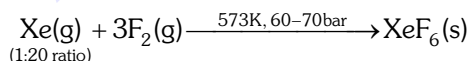
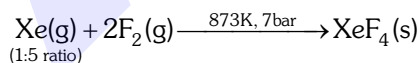
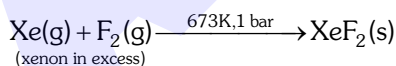
Neil Bartlett, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2^+ [PtF_6]^-$. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ mol^{-1}) was almost identical with that xenon (1170 kJ mol^{-1}). He made efforts to prepare same type of compound with Xe and was successful in preparing another red coloured compound. $Xe^+ [PtF_6]^-$ by mixing PtF_6 and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

The compounds of krypton are fewer. Only the difluoride (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g., RnF_2) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

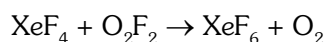
COMPOUNDS OF XENON

Xenon-fluorine compounds

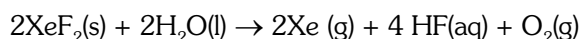
Xenon forms three binary fluorides, XeF_2 , XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.



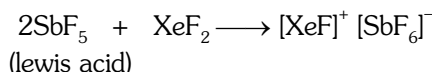
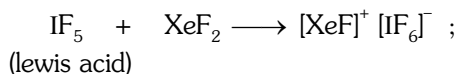
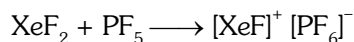
XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143K.



XeF_2 , XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K. They are powerful fluorinating agents. They are readily hydrolysed even by traces of water. For example, XeF_2 is hydrolysed to give Xe, HF and O_2 .



Formation of addition compounds : Xenon fluorides reacts with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.



[With s-block fluorides and alkyl fluorides it is F^- acceptor with others it is F^- donor]

USES OF INERT GASES :

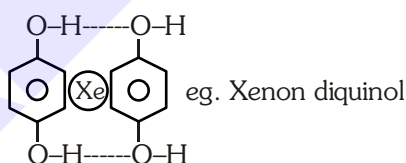
- (1) He is non-inflammable and light gas, so it is used in filling balloons for meteorological observations.
- (2) He is used in gas cooled nuclear reactors.
- (3) Liquid He is used as cryogenic agent.
- (4) He is used to produce powerful superconducting magnets.
- (5) Ne is used in discharge tubes.
- (6) Ar is used as inert atmosphere in metallurgical process.
- (7) Xenon and Krypton are used in light bulbs designed for special purposes.
- (8) He is used as a diluent for oxygen in modern diving apparatus due to its very low solubility in blood.

IMPORTANT ORDER :

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|--|------------------------------------|
| (1) $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$ | Atomic radius |
| (2) $\text{He} > \text{Ne} > \text{Ar} > \text{Kr} > \text{Xe}$ | Ionisation energy |
| (3) $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$ | Density |
| (4) $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$ | Boiling point/Melting point |
| [Atomic mass / size / polarisability / London force] \uparrow | |
| (5) $\text{He} < \text{Ne} < \text{Ar} < \text{Xe} < \text{Rn}$ [solubility in water because of dipole-induced dipole attraction] | |

Clathrate Compounds : Larger inert gas atoms are trapped into cavity or crystal structure of some organic compounds and form clathrate compounds.

- Force of attraction between noble gas and organic compound is **dipole-induced dipole** attraction.



He, Ne do not form clathrate compounds due to smaller size

BEGINNER'S BOX-9

1. Which is correct

(1) $\text{NaCl} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{yellow green gas}$	(2) $\text{NaBr} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{red brown vapour}$
(3) $\text{NaF} + \text{Cl}_2 \longrightarrow \text{NaCl} + \text{F}_2$	(4) All
2. True statement about I^- will be

(1) weak base	(2) strong nucleophile	(3) strong reducing agent	(4) all
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3. Which of the following is strong oxidising agent

(1) F_2	(2) Cl_2	(3) Br_2	(4) I_2
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4. The ion that cannot undergo disproportionation is
 (1) ClO_4^- (2) ClO_3^- (3) ClO_2^- (4) ClO^-
5. In the clathrates 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
6. XeF_2 reacts with PF_5 to give :
 (1) XeF_6 (2) $[\text{XeF}]^+ [\text{PF}_6]^-$ (3) XeF_4 (4) $[\text{PF}_4]^+ [\text{XeF}_3]^-$
7. The first compound of noble gases prepared by Neil-Bartlett was :-
 (1) $\text{Xe}^+ [\text{PtF}_6]^-$ (2) XeF_4 (3) XeF_6 (4) XeOF_4
8. Colour of F_2 is -
 (1) greenish - yellow (2) light blue (3) pink (4) pale yellow
9. IF_7 is a -
 (1) colorless gas (2) coloured gas (3) coloured solid (4) coloured liquid
10. Basis of formation of Bartlett compound is-
 (1) Ionisation enthalpy (2) Solubility (3) Boiling point (4) Color property

ANSWER'S 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	10
	Ans.	2	4	1	1	4	2	1	4	1	1