CHAPTER -02
P-BLOCK ELEMENTS

P-BLOCK ELEMENTS

Conceptual Part		Compounds of P-block	
Back Bonding	Allotropes	13 group- Borax, H_3BO_3, B_2H_6 Alum	16 group- O_2, O_3, H_2S, SO_2, H_2SO_4
Inert pair effect	Silicate / Silicones	14 group-CO, CO_2, carbides	17 group- X_2, Cl_2, HCl, $CaOCl_2$
Hydrolysis	Bleaching Agent	15 group-N_2, NH_3, oxides, HNO_3, PH_3, PCl_3, PCl_5 oxides	18 group- Xenon fluorides
Oxyacids			

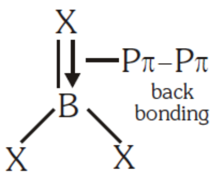
Back Bonding

Back bonding : Coordinate type bond.
If coordinate type π bond get form between central atom & bonded atom of a molecule it is known as back bonding.

Condition for formation of back bonding

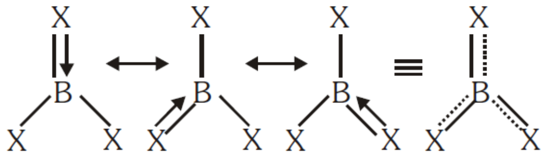
- One species must have lone pair.
- another species must have vacant orbital
- size of atom should be small.

Example 1: Back bonding in Boron Trihalide



X=F, Cl, Br, I
X → Contain lp --------donar
B → Contain vacant orbital - acceptor

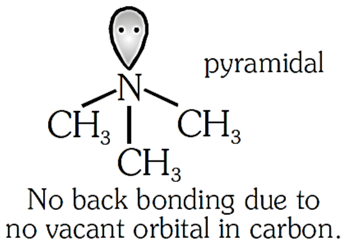
Example 2: Exhibit resonance in Back bond

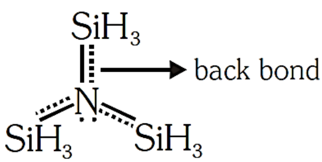


Extent of back bonding	$\underset{2p-2p}{BF_3} > \underset{2p-3p}{BCl_3} > \underset{2p-4p}{BBr_3} > \underset{2p-5p}{BI_3}$
Lewis acid strength	$BF_3 < BCl_3 < BBr_3 < BI_3$

Few more examples of back bonding

1. Shape of trimethyl amine pyramidal while shape of trisillyl amine is triangular planar.



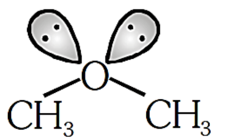


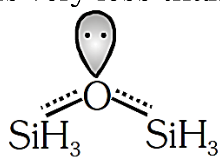
2. Lewis base strength

$$\ddot{N}(CH_3)_3 > \underline{\ddot{N}(SiH_3)_3}$$

lp involve in
back bonding

3. Bond angle of $(CH_3)_2O$ is very less than $(SiH_3)_2O$





INERT PAIR EFFECT

Some heavy metallic elements of P-block exhibit higher stability in lower oxidation state in comparisons of their group oxidation state it is due to inert pair effect.

$Tl^{+1} > Tl^{+3}$

$Pb^{+2} > Pb^{+4}$

$Bi^{+3} > Bi^{+5}$

electron pair of s-subshell of valence shell is reluctant to participate during chemical combination, it is known as inert pair & this effect is known as inert pair effect.

It is due to higher amount of energy required for this electron pair removal which is not compensated by bond formation energy.

Generally in oxide & fluorides inert pair effect becomes non-effective [due to higher bond energy]

$TlCl$ exist but not $TlCl_3$ PbI_2 exist but not PbI_4 $BiCl_3$ exist but not $BiCl_5$	Due to inert pair

Order of stability of oxidation state

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

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

$C^{2+} < Si^{2+} < Gu^{2+} < Sn^{2+} < Pb^{2+}$

HYDROLYSIS Hydro – Water lysis - break down

Break down of a molecule through water and formation of new product is known as hydrolysis.

- It is nucleophilic substitution reaction.

$$H\ddot{O}H + MX \longrightarrow H{-}\underset{\displaystyle H}{\overset{..}{O}}{-}{-}{-}M{-}X \longrightarrow M{-}OH + HX$$

molecule — Intermediate — Product

-

extent of hydrolysis ∝ covalent character.	
$BeCl_2 + 2HOH \rightarrow Be(OH)_2 + 2HCl$ $BCl_3 + 3HOH \rightarrow B(OH)_3 + 3HCl$ $AlCl_3 + 3HOH \rightarrow Al(OH)_3 + 3HCl$	$BF_3 + 3HOH \rightarrow B(OH)_3 + 3HF$ $3BF_3 + 3HF \rightarrow 3H^{+}[BF_4]^{-}$ $4BF_3 + 3H_2O \rightarrow 3H[BF_4]$ (partially hydrolysis)
$SiCl + 4HOH \rightarrow Si(OH)_4 + 4HCl$ or SiO_2 $SF_6 + H_2O \rightarrow$ No hydrolysis due to crowding $CCl_4 + HOH \xrightarrow[\text{conditions}]{\text{ordinary}}$ No hydrolysis	Similarly $SiF_4 + 4HOH \rightarrow Si(OH)_4 + 4HF$ $2SiF_4 + 4HF \rightarrow H_2^{+}\,[SiF_6]^{2-}$ hydrolysis followed by

Carbon → No vacant orbital.	Lewis acid-base reaction.

15th Group Halides
$NF_3 + HOH \xrightarrow[\text{conditions}]{\text{ordinary}}$ No hydrolysis
$NCl_3 + HOH \rightarrow NH_3 + 3HOCl$
$PCl_3 + HOH \rightarrow H_3PO_3 + 3HCl$
$AsCl_3 + HOH \rightarrow As(OH)_3 + 3HCl$
$SbCl_3 + HOH \rightarrow SbOCl + 2HCl$ (partial hydrolysis)
$BiCl_3 + HOH \rightarrow BiOCl + 2HCl$ (partial hydrolysis)
$PCl_5 + HOH \rightarrow POCl_3 \rightarrow H_3PO_4$ partial completely

Hydrolysis of higher covalent character containing salt
$Be_2C + 4HOH \rightarrow 2BE(OH)_2 + CH_4$
$Mg_2C_3 + 4HOH \rightarrow 2Mg(OH)_2 + C_3H_4$
$CaC_2 + 2HOH \rightarrow Ca(OH)_2 + C_2H_2$
$Al_4C_3 + 12HOH \rightarrow 4Al(OH)_3 + 3CH_4$
$Mg_3N_2 + 6HOH \rightarrow 3Mg(OH)_2 + 2NH_3$
$AlN + 3HOH \rightarrow Al(OH)_3 + NH_3$
$Ca_3P_2 + 6HOH \rightarrow 3Ca(OH)_2 + 2PH_3$
$LiH + HOH \rightarrow LIOH + H_2$
$CaH_2 + 2HOH \rightarrow Ca(OH)_2 + H_2$

Hydrolysis of Interhalogen Compounds	
$AX + HOH \rightarrow HX + HOA$	
$AX_3 + HOH \rightarrow 3HX + HAO_2$	HX Hydrohalic acid $HOA, HAO_2, HAO_3 HAO_4$ oxyacid of halogen
$AX_5 + HOH \rightarrow 5HX + HAO_3$	
$AX_7 + HOH \rightarrow 7HX + HAO_4$	

Some specific hydrolysis
$XeF_2 \xrightarrow{HOH} Xe + 2HF + O_2$
$6XeF_4 \xrightarrow{HOH} 4Xe + 2XeO_3 + 24HF + 3O_2$
$XeF_6 \xrightarrow{HOH} 2HF + \underset{\text{partial}}{XeOF_4} \xrightarrow{HOH} 2HF + \underset{\text{partial}}{XeO_2F_2} \xrightarrow{HOH} 2HF + \underset{\text{complete}}{XeO_3}$

Oxy-Acids

- Mainly oxy-acids are hydroxide of Non-metal oxides.
- No. of H^+ ion furnish by an oxyacid is known as their basicity. Oxyacid obtained by dissolving non-metal oxide in water.
  Eg. $CO_2 + HOH \rightarrow H_2CO_3$ or $OC(OH)_2$
  Here: $CO_2 \rightarrow$ Non metal oxide – Anhydride of carbonic acid $OC(OH)_2 \rightarrow$ Oxyacid
- NO_2 $\rightarrow$ Mixed anhydride
- it gives $\rightarrow$ HNO_2 & HNO_3

Oxide		**Acid**		
N_2O_3	$\longrightarrow$	HNO_2	–	Nitrous acid
N_2O_5	$\longrightarrow$	HNO_3	–	Nitric acid
P_4O_{10}	$\longrightarrow$	H_3PO_4	–	Phosphoric acid
SO_2	$\longrightarrow$	H_2SO_3	–	Sulphurous acid
SO_3	$\longrightarrow$	H_2SO_4	–	Sulphuric acid
Cl_2O_7	$\longrightarrow$	$HClO_4$	–	Perchloric acid

- Oxyacids of different elements

Order of acidic strength:

$H_3PO_2 > H_3PO_3 > H_3PO_4$

Reducing nature

$H_3PO_2 > H_3PO_3 > H_3PO_4$

	Element	Oxide	Oxyacid	Basicity
1	Boron	B_2O_3	$Ba(OH)_3$ boric acid	Not protonic acid monobasic Lewis acid
2	Carbon	CO_2	H_2CO_3 carbonic acid	Two
3	Nitrogen		$H_2N_2O_2$ Hyponitrous acid HNO_2 Nitrous acid HNO_3 Nitric acid HNO_4 Pernitric acid	
4	Phosphorus		H_3PO_2 Hypophosphorus acid H_3PO_3 Phosphorus acid H_3PO_4 Ortho phosphoric acid HPO_3 Meta phosphoric acid $H_4P_2O_5$ Pyrophosphorus acid $H_4P_2O_7$ Pyrophosphoric acid $H_4P_2O_6$ Hypophosphoric acid	

OXYACIDS OF SULPHUR

1. Sulphurous acid - H_2SO_3
2. Sulphuric acid - H_2SO_4
3. Thiosulphuric acid - $H_2S_2O_3$
4. Peroxymonosulphuric (Caro's acid) - H_2SO_5 (Peroxide bond)

5. Peroxydisulphuric acid (Marshal's acid) - $H_2S_2O_8$ (Peroxide bond)
6. Pyrosulphurous acid - $H_2S_2O_5$ - (S-S linkage)
7. Pyrosulphuric acid - $H_2S_2O_7$ (S-O-S linkage)
8. Thionus acid - $H_2S_2O_4$
9. Thionic acid - $H_2S_2O_6$
10. Polythionus acid - $H_2(S)_nO_4$ (S-S linkage)
11. Polythionic acid - $H_2(S)_nO_6$ (S-S linkage)

OXYACIDS OF HALOGEN (Cl)

1. Hypochlorous acid- $HClO$
2. Chlorous acid - $HClO_2$
3. Chloric acid - $HClO_3$
4. Perchloric acid - $HClO_4$

Order of acidic strength

$HClO < HClO_2 < HClO_3 < HClO_4$

Oxidising nature

$HClO > HClO_2 > HClO_4 > HClO_4$

ALLOTROPY

- Those substance which are made up of same elements but having different bonding arrangement are known as allotropes & this phenomenon known as allotropy.
- Those elements which exhibit higher tendency of catenation exhibit higher tendency of allotropy.
- Therefore carbon, phosphorus & sulphur exhibit maximum allotropy.

ALLOTROPES OF CARBON

Diamond	Graphite	Fullerene
C-sp^3, tetrahedral structure C-C bond length 1.54 Å Compact 3 dimensional structure Hardest substance Very high mp ($\sim 3400°C$) Very high density Exhibit total internal reflection Shines brighty in light	**Hexagonal layer structure** All sp^2 hybrid carbon Unhybrid orbital electron form π-bond. This π-bond exhibit resonance and due to resonance there is mobility of electrons and it becomes conductor of electricity.	**Latest discovered allotrope of carbon it is found in chimney sooty particle.** It contain C_{60}-$C_{320;}$ C : sp^2 hybrid Contain pentagon & hexagonal structure C_{60}: Buckminster fullerene soccer ball (football) or bucky ball. C_{60}: 20 hexagon rings 12 pentagon rings Purest form of carbon No dangling bond

ALLOTROPES OF PHOSPHOROUS

(a) white phosphorous (b) Red phosphorous
(c) Black phosphorous

White phosphorous	Red Phosphorous
Waxy solid	Brittle powder
Poisonous	Non poisonous
Soluble in CS_2, Insoluble in water	Insoluble in water & CS_2
Monomer of P_4	Polymer of P_4
Highly reactive due to bond angle strain	More stable than white phosphorous
It glows in dark due to slow oxidation (phosphorescence)	It does not glow in dark
It gives phosphine (PH_3) on reaction with $NaOH$	It gives hypo phosphoric acid on reaction with $NaOH$

Order of stability or MP or density → white < red < black

$$\text{Red Phosphorous} \xrightarrow[\text{high P}]{803K} \alpha\text{-Black Phosphorous}$$

$$\text{White Phosphorous} \xrightarrow[\text{inert medium}]{573K} \text{Red Phosphorous}$$

$$\text{White Phosphorous} \xrightarrow[\text{high P}]{473K} \beta\text{-Black Phosphorous}$$

ALLOTROPES OF SULPHUR

S	
Crystalline	**Amorphous**
Rhombic sulphur (α-S) most stable form	Milk of sulphur Plastic sulphur (γ-S)
Monoclinic sulphur (β-S)	Colloidal sulphur
$\alpha\text{-S} \underset{<95°,6°C}{\overset{>95.6°C}{\rightleftharpoons}} \beta\text{-S}$	$\underset{RA}{H_2S} + \underset{OA}{2HNO_3} \xrightarrow[\text{Redox}]{} S + 2NO_2 + 2H_2O$
both are soluble in CS_2 but insoluble in water	

(a) density of $\alpha S > S$

(b) Both are puckered crown shape having S_8 units

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

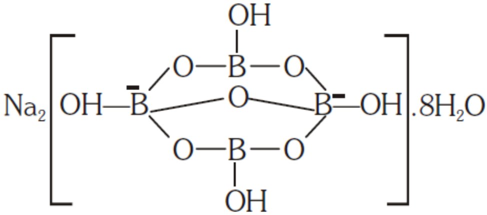
(d) S_6 is chair form of S

COMPOUNDS OF P-BLOCK

13th GROUP : BORON FAMILY

BORAX ($\boldsymbol{Na_2B_4O_7\,.10H_2O}$)

$Na_2[B_4O_5(OH)_4].8H_2O$



Cr Green	Mn pink	Fe Green	Co Blue	Ni Brown	Cu Blue

BORAX

Hydrolysis of borax

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

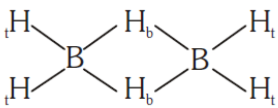
alkaline solution

Borax bead test for transition metal cations form colored transition metal meta borate

$$\underset{}{Na_2B_7O_7.10H_2O} \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{740°C} \underset{\text{Transparent borax glassy mass}}{NaBO_2 + B_2O_3}$$

$$NaBO_2 + B_2O_3 + \underset{\substack{\text{Transition}\\\text{metal cation}}}{Cu^{+2}} \longrightarrow \underset{\substack{\text{Copper meta}\\\text{borate blue color}}}{Cu(BO_2)_2}$$

DIBORANE (B_2H_6)



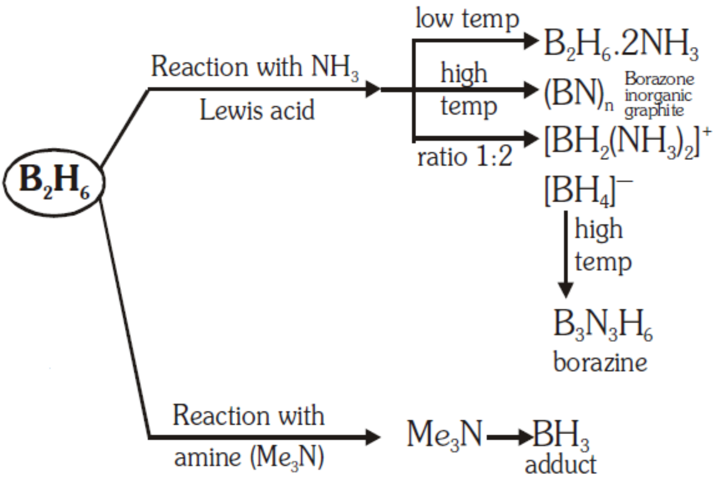
dimer due to formation of
3 centre-2e-bond

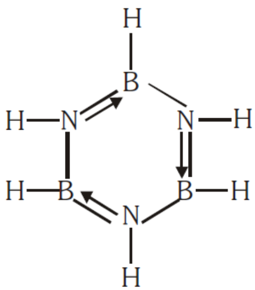
(i) $3Mg + 2B \rightarrow Mg_3B_2 \xrightarrow{H_3PO_4} B_2H_6$

(ii) $B_2O_3 + 3H_2 + 2Al \xrightarrow[B_2H_6 + Al_2O_3]{150°C\ (MOP)}$

(iii) $2BF_3 + 6NaH \xrightarrow{180°C} B_2H_6 + 6NaF$

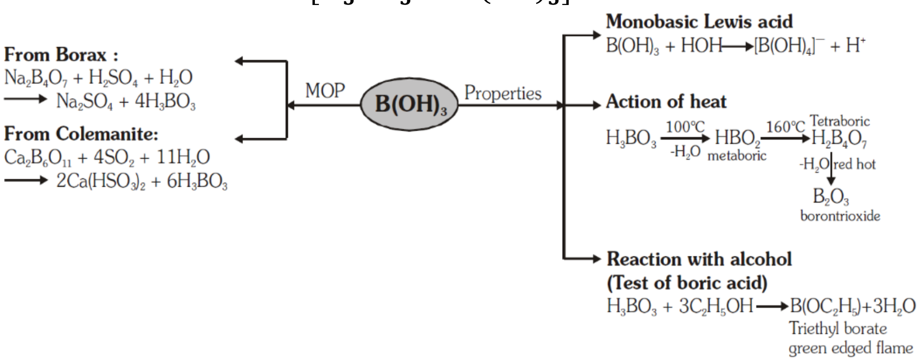
(iv) $NaBH_4 + I_2 \xrightarrow{\text{ether}} B_2H_6 + 2NaI + H_2$





Isoelectronic & Isostructural with benzene
∴ It is called as Inorganic Benzene

ORTHOBORIC ACID $[H_3BO_3 \text{ or } B(OH)_3]$



13^{th} GROUP : BORON FAMILY

ALUMS $[M_2SO_4.M'_2(SO_4)_3.24H_2O]$

Alums are the double salts of Type $[M_2SO_4.M'_2(SO_4)_3.24H_2O]$
M : Monovalent Cation: $Na^+, K^+, Rb^+, Cs^+, NH_4^+$
M' : Trivalent cation : $Al^{3+}, Fe^{3+} \& Cr^{3+}$

Soda alum

$Na_2SO_4.Al_2(SO_4)_3.24H_2O$

Potash alum

$K_2SO_4.Al_2(SO_4)_3.24H_2O \xleftarrow{\text{example}}$ Alum $\xrightarrow{\text{properties}}$

- aq. Solution acidic
- Coagulant
- Mordant for dyeing
- Tanning of leather

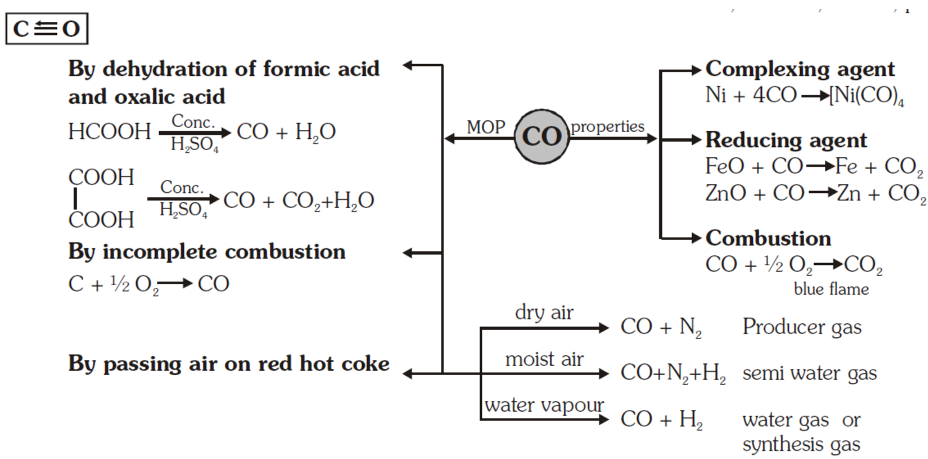
Ammonium alum

$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$

14^{th} GROUP : CARBON FAMILY

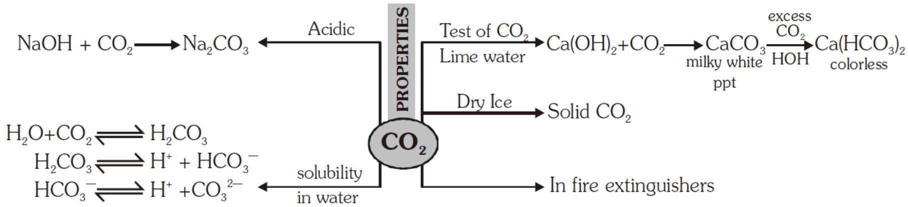
CARBON MONOXIDE [CO]

Colorless odourless, tasteless, neutral, poisionous gas



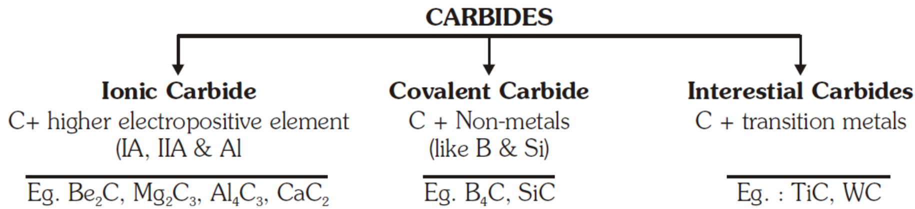
CARBON DI-OXIDE $[O = C = O]$

sp hybridised, acidic, green house gas partially soluble in water



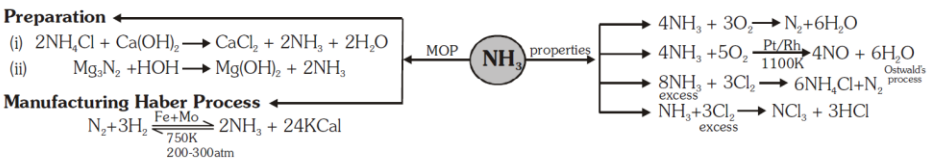
CARBIDES

Binary compounds of carbon with other elements (except hydrogen) are known as carbides



COMPOUNDS OF NITROGEN FAMILY

AMMONIA (NH_3)



NITRIC ACID (HNO_3)

HNO_3, nitric acid was earlier called as aqua fortis (meaning strong water). It usually acquires yellow colour. due to its decomposition by sunlight into NO_2.

Method of preparation

Ostwald process :

$$4NH_{3(g)} + 5O_{2(g)} \frac{Pt/Rh}{500L, 9bar} 4HO + 6H_2O$$

$2NO + O_2 \rightleftharpoons 2NO_2$

$3NO_2 + H_2O \rightarrow \underset{(aq.)}{2HNO_3} + \underset{\text{recycled}}{\underset{\downarrow}{NO_{(g)}}}$

Concentration of nitric acid	Metal	Main products
Very Dilute HNO_3	Mg, Mn	H_2 + metal nitrate
	Fe, Zn, Sn	NH_4NO_3 + metal nitrate
	Cu, Ag, Hg	No reaction
Dilute HNO_3	Fe, Zn	N_2O +
	Zn, Fe, Pb, Cu, Ag	NO +
Conc. HNO_3	Sn	$NO_2 + H_2SNO_3$ (Metastannic acid)
Conc. HNO_3	Fe, Co, Ni, Cr, Al	rendered passive

PHOSPHINE (PH_3)

Preparation :

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

(ii) $PH_4I + NaOH \longrightarrow NaI + H_2O + PH_3$

Laboratory preparation :

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

Physical properties :

Colourless gas having smell of garlic or rotten fish, slightly soluble in water and slightly heavier than air.

Chemical properties :

(i) $2PH_3 + 4O_2 \longrightarrow P_2O_3 + 3H_2O$

(ii) $4PH_3 \xrightarrow{713K} P_4 + 6H_2$

(iii) $PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$

PHOSPHORUS HALIDES

Phosphorus form two types of halides, phosphorus trihalides, PX and phosphorus pentahalides, $PX_5 (X = F, Cl, Br)$.

PCl_3

Preparation :

$P_4 + 6Cl_2 \longrightarrow 4PCl_3$

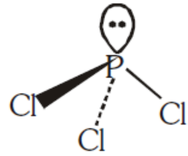
Properties :

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

$2PCl_3 + O_2 \longrightarrow 2POCl_3$

$PCl_3 + Cl_2 \longrightarrow PCl_5$

Structure:



PCl_5

Preparation :

$P_4 + 10Cl_{2(g)} \longrightarrow 4PCl_{5(s)}$

$PCl_3 + Cl_{2(g)} \longrightarrow 4PCl_{5(s)}$

$P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_3 + 10SO_2$

Properties :

Pale yellow crystalline solid.

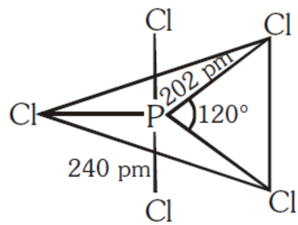
In solid state it exists as $[PCl_4]^+[PCl_6]^-$.

It sublimes on heating.

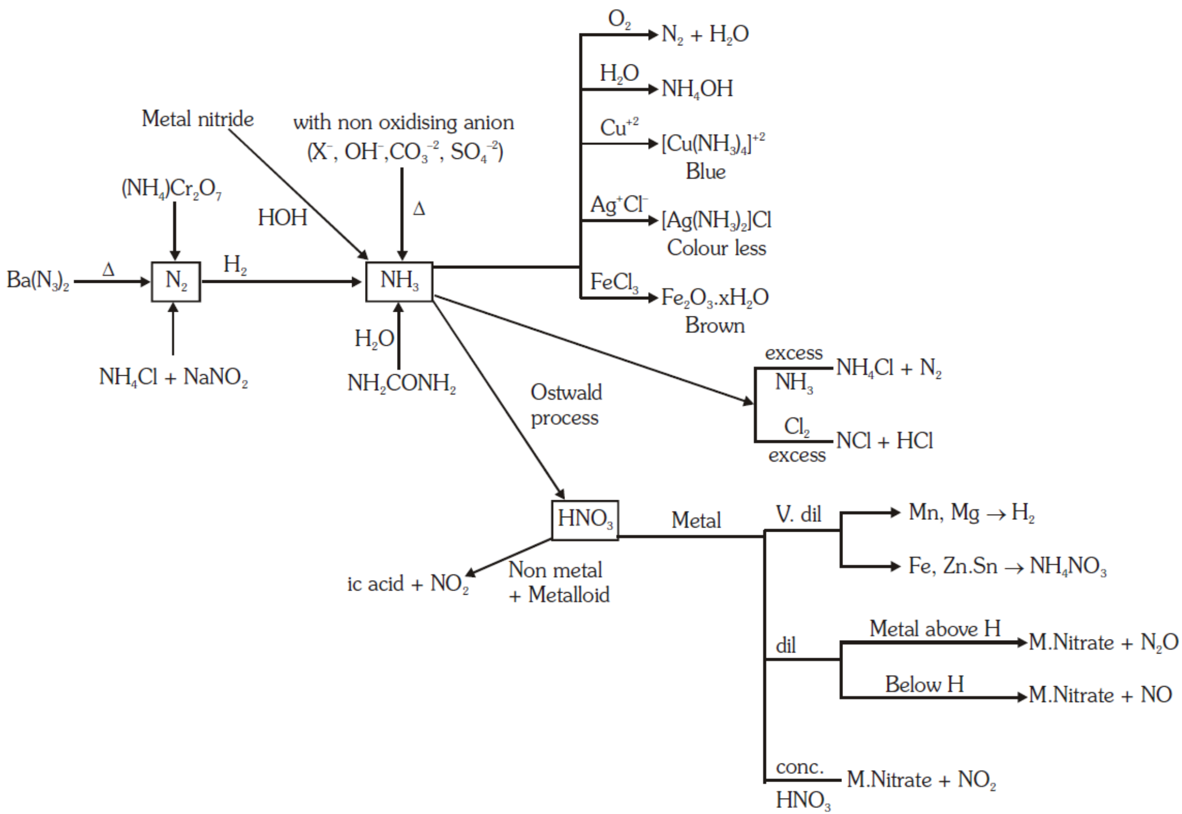
$PCl_5 \overset{\text{heat}}{\rightleftharpoons} PCl_3 + Cl_2$

$PCl_5 + H_6O \overset{\text{partial hydrolysis}}{\rightleftharpoons} POCl_3 + 2HCl \xrightarrow{H_2O} H_3PO_4 + 5HCl$

Structure:

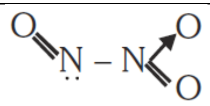
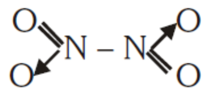
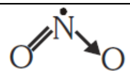
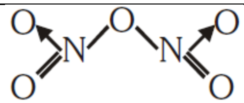


Reaction of N & its compounds

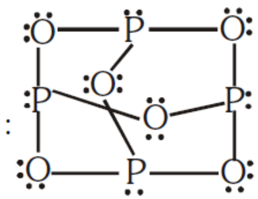


STRUCTURE OF OXIDES OF NITROGEN AND PHOSPHORUS

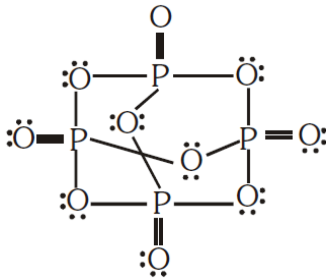
NITROGEN

Oxide of Nitrogen	Oxid. state	Physical appearance	Structure
N_2O nitrous oxide	+1	Colourless gas	$N \equiv N \rightarrow O$
NO Nitric oxide	+2	Colourless gas	$N = 0$
N_2O_3 Dinitrogen trioxide	+3	Blue colour solid	
N_2O_4 Dinitrogen tetraoxide	+4	Colourless solid	
NO_2 Nitrogen dioxide	+4	Brown gas	
N_2O_5 Dinitrogen pentaoxide	+5	Colourless solid	

Structure of phosphorus trioxide (P_4O_6)



Structure of phosphorus pentaoxide (P_4O_{10})



GROUP 16 ELEMENTS

HYDRIDES

All these elements form stable hydrides of the type H_2M

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

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

$$Na_2Se + H_2SO_4 \longrightarrow H_2Se + Na_2SO_4$$

- H_2O is a liquid due to hydrogen bonding. Others are colourless gases with unpleasant smell.
- Compound: H_2O > H_2S > H_2Se > H_2Te
  Bond angle: 104.5° 92.5° 91° 90°
  (all sp^3 hybridised)

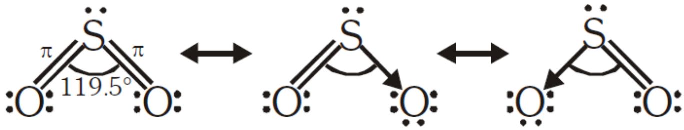
- The weakening of M–H bond with the increase in the size of M (not the electronegativity) explains the increasing acidic character of hydrides down the group.
- **Halides:** All these elements form a number of halides. The halides of oxygen are not very stable. Selenium does not form dihalides
  e.g. OF_2, Cl_2O_6, I_2O_5, etc.
- **Oxides :** Oxides of other elements are as follows :

Element	Monoxide	Dioxide	Trioxide
S	SO	SO_2	SO_3
Se	–	SeO_2	SeO_3
Te	TeO	TeO_2	TeO_3

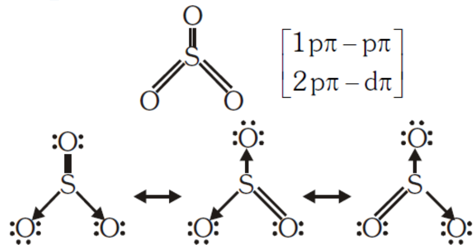
Po	PoO	PoO_2	$-$

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

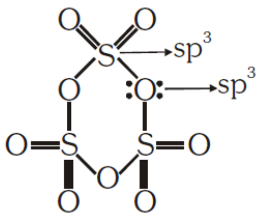
$\begin{bmatrix} 1p\pi - p\pi \\ 1p\pi - d\pi \end{bmatrix}$



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



- In solid state it exists as a cyclic trimer $(SO_3)_3$, α-form or as linear cross-linked sheets, β-form.



$S = O$ bond $\Rightarrow 6$

$S - O - S$ bond $\Rightarrow 3$

α-form

OXYGEN (O_2)

- ***Preparation :*** By action of heat on oxygen rich compounds :
  - **From oxides :**

    $2Hg\,O \xrightarrow{\Delta} 2Hg + O_2$
  - **From peroxides :**

    $2Na_2O_2 + 2H_2O \longrightarrow O_2 + 4NaOH$

    $2BaO_2 \xrightarrow{\Delta} 2BaO + O_2$

- **From decomposition of certain compounds**

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

  $$2KNO_3 \longrightarrow 2KNO_2 + 3O_2$$

- **Chemical properties :** On heating it combines directly with metals and non-metals, causing oxidation.

  $$C + O_2 \longrightarrow CO_2$$

  $$S + O_2 \longrightarrow SO_2$$

  $$Pb + O_2 \longrightarrow PbO_2$$

  $$2CH_3OH + O_2 \longrightarrow 2HCHO + 2H_2O$$

- **Uses:**
  - When mixed with He or CO_2, it is used for artificial respiration.
  - In welding and cutting.
  - As a fuel in rockets.

OZONE (O_3)

- **Preparation :**
  - **Lab method :**

    $$3O_2 \overset{\text{Electric discharge}}{\rightleftharpoons} 2O_3 (\Delta H = +ve)$$

- **Properties :** Pale blue gas with characteristic strong smell, slightly soluble in water but more soluble in turpentine oil or glacial acetic acid.
  - Decomposition:

    $$2O_3 \xrightarrow{573K} 3O_2 + 68kcal$$

  - Oxidising action:

    $$O_3 \longrightarrow O_2 + O$$

    $$PbS + 4O \longrightarrow PbSO_4$$

  - Reducing action:

    $$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

$BaO_2 + O_3 \longrightarrow BaO + 2O_2$

- **Ozone reaction:**
  (i) Tailing of Mercury : $2Hg + O_2 \longrightarrow Hg_2O + O_2$
  (ii) Estimation of Ozone : $2KI + H_2O + O_3 \longrightarrow O_2 + I_2 + KOH$
  $I_2 \xrightarrow{(Na_2S_2O_3.5H_2O)} 2NaI + Na_2S_4O_6$

- **Uses :**
  - Bleaching ivory, flower, delicate fabrics, etc.
  - As germicide and disinfectant, for sterilising water.
  - Manufacture of $KMnO_4$ and artificial silk.

SULPHUR DIOXIDE (SO_2)

- **Preparation :**
  - By heating sulphur in air. $S + O_2 \xrightarrow{\Delta} SO_2$
  - **Lab method:**
    By heating Cu with conc. H_2SO_4.
    $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

- **Properties:**
  - **As reducing agent:**
    $SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$
    $2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$
  - **As oxidising agent :**
    $2H_2S + SO_2 \longrightarrow 2H_2O + 3S \downarrow$
  - **Bleaching action :**
    Its bleaching action is due to reduction.
    $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$
    Coloured matter + H $\longrightarrow$ Colourless matter.
    2(Nascent hydrogen)

- **Uses:**
  - In the manufacture of sulphuric acid, sulphites and hydrogen sulphide.

- As a disinfectant and fumigate.
- For bleaching delicate articles.

SULPHURIC ACID (H_2SO_4)

It is also known as oil of vitriol and king of chemicals.

- **Manufacture of sulphuric acid :**
  - Lead chamber process :
    The various steps involved are :
  - **Contact process :**
    Step involved
    (a) Production of SO_2
    $S + O_2 \longrightarrow SO_2$
    M.Sulphide $+O_2 \longrightarrow SO_2$
    (b) Conversion of SO2 to SO3
    $SO_2O_2 \overset{V_2O_5}{\rightleftharpoons} SO_3$
    (c) $SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$ oleum
    $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$
- **Properties :** Its specific gravity is 1.8 and it is 98% by weight.
  - It is strong dibasic acid.
    $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$
  - It acts as an oxidising agent.
    $H_2SO_4 \longrightarrow H_2O + SO_2 + O$
  - Non metals are oxidised to their oxides and metals to the corresponding sulphates.
    $C + 2O \longrightarrow CO_2$
  - Dehydrating agent : It is strongly dehydrating in nature.
    $C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$
    (Charring of sugar)

- **Uses:**
  - In lead storage batteries.
  - In manufacture of paints and pigments.
  - In metallurgy for electrolytic refining of metals.

GROUP 17 ELEMENTS

- **Reactivity :** All halogens are chemically very reactive elements. This is due to their low dissociation energy and high EN. Fluorine is the most reactive and iodine is the least reactive halogen.
- **Oxidising power :** F is the most oxidising element due to high hydration enthalpy.
  $F_2 > Cl_2 > Br_2 > I_2$

HYDROGEN HALIDES

Bond strength, bond length and thermal stability :

- Since size of halogen atom increases from F to I down the group, bond length of $H - X$ bond increases down the group.
  ∴ reactivity and acidic character ↑.
  $HF < HCl < HBr < HI$
- Bond strength order
  $HF > HCl > HBr > HI.$
- Bond energy order
  $HF > HCl > HBr > HI.$

REDUCING CHARACTER :

The reducing character of hydrogen halides increases down the group as

$$HF < HCl < HBr < HI$$

$$2HX \longrightarrow H_2 + X_2$$

A less thermally stable compound has more tendency to release hydrogen easily and show greater reducing property.

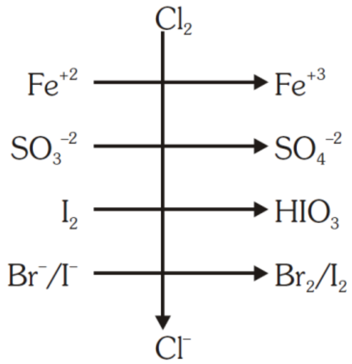
OXIDES :
$F \longrightarrow O_2F_2, OF_2$
$Cl \longrightarrow Cl_2O, Cl_2O_3, Cl_2O_5, Cl_2O_7, Cl_2O_2, ClO_3$
$Br \longrightarrow Br_2O, Br_2O_7, Br_2O_5$
$I \longrightarrow I_2O, I_2O_7, I_2O_5, I_4O_9$ (Ionic)

Stability :
$I > Cl > Br$ (Middle row anormaly)

CHLORINE (Cl_2)

- **Preparation :** By oxidation of conc. HCl.
  $PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$
  $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$
- **Manufacture :**
  Weldon's process : By heating pyrolusite with conc. HCl.
  $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$
- **Properties :** It is a yellowish green gas, poisonous in nature, soluble in water. Its aqueous solution is known as chlorine water which on careful cooling gives chlorine hydrate $Cl_2.8H_2O$.
  Bleaching action and oxidising property
  (i) $Cl_2 + H_2O \longrightarrow HOCl + HCl$
  $HOCl \longrightarrow HCl + [O]$
  Coloured matter + nascent $[O]$ → Colourless matter
  The bleaching action of chlorine is permanent and is due to its oxidising nature.
  (ii) $SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$

Oxidising behaviour of Cl_2



- **Addition reactions :**
  $SO_2 + Cl_2 \longrightarrow SO_2Cl_2$
  $CO + Cl_2 \longrightarrow COCl_2$

■ **Uses:**

- It is used as a
  (i) bleaching agent
  (ii) disinfectant
  (iii) in the manufacture of $CHCl_3, CCl_4, DDT$, bleaching powder, poisonous gas phosgene ($COCl_2$), tear gas (CCl_3NO_2) and mustard gas ($ClC_2H_4SC_2H_4Cl$).

HYDROCHLORIC ACID, (HCl)

■ **Preparation :** By dissolving hydrogen chloride gas in water. Hydrogen chloride gas required in turn can be prepared by the following methods:

- By the direct combination of hydrogen and chlorine.

  $H_{2(g)} + Cl_{2(g)} \xrightarrow{\text{Sunlight}} 2HCl_{(g)}$
- Hydrogen chloride gas can also be obtained by burning hydrogen in chlorine.
- **By heating halid with conc. H_2SO_4**

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$
$$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$$

Imp. Points :

- HCl cannot be dried by P_2O_5 or quick lime.
  $CaO + 2HCl \longrightarrow CaCl_2 + H_2$
  $P_4O_{10} + 3HCl \longrightarrow POCl_3 + 3HPO_3$
- **Reducing property :**
  HCl is a strong reducing agent.
  $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

- **Uses:**
  - In the production of dyes, paints, photographic chemicals, etc.
  - Used in the preparation of chlorides, chlorine, aquaregia, etc.
  - Used as a laboratory reagent.

INTERHALOGEN COMPOUNDS

- These compounds are regarded as halides of more electropositive (i.e. less elecronegative) halogens.
- Types of interhalogen compound :
  AB type : $ClF, BrF, BrCl, ICl, IBr$
  AB_3 type : ClF_3, BrF_3, ICl_3
  AB_5 type : BrF_5, IF_5
  AB_7 type : IF_7

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.