"Bringing Excellence to Students"

Handwritten Notes
On
P Block Elements

p-Block Elements (ns^2np^{1-6})

* Group 13 Elements:

13 (IIIB)
$_5B$ ($2s^2 2p^1$)
$_{13}Al$ ($3s^2 3p^1$)
$_{31}Ga$ ($4s^2 4p^1$)
$_{49}In$ ($5s^2 5p^1$)
$_{81}Tl$ ($6s^2 6p^1$)

- **Physical Properties:** a) Atomic & ionic radii - Increase from B to Al then decrease from Al to Ga & then again increase. (For Ga, additional 10 d electrons) b) Ionisation enthalpy: Less than the corresponding members of alkaline earth metals and shows no regular trend - B > Tl > Ga > Al > In. (low screening effect of d & f electrons) c) electronegativity decreases from B to Al & then increases. (discrepancy in atomic size) d) Metallic or electropositive character - increases from B to Al, then decreases. e) density - increases down the group. f) melting & boiling points - mp decreases sharply on moving down the group from B to Ga & then increase from Ga to Tl while bp decreases from B to Tl. g) reducing character - Al > Ga > In > Tl. h) physical state - Al, Ga, Tl, In are silvery white. Ga can exist in liquid state during summer (mp - 303K). Boron is non-metallic, hard & black.

- **Chemical Properties:** a) $4M + 3O_2 \rightarrow 2M_2O_3$ All react at high temperature, Tl forms some Tl_2O as well. Boron trioxide is naturally acidic, Al & Ga oxides are amphoteric; In, Tl oxides are basic.

b) $2Al + N_2 \rightarrow 2AlN$ Only Al reacts at high temperature.

c) $2M + 3X_2 \rightarrow 2MX_3$ All form trihalides. TlI_3 is unknown & $Tl^+[I_3]^-$ is formed.

d) $2M + 6HCl \rightarrow 2MCl_3 + 3H_2$ All react with dilute mineral acids except B. Al rendered passive by HNO_3 particularly when concentrated.

e) $2Al + 2NaOH + 6H_2O \rightarrow 2NaAlO_2 \cdot 2H_2O + 3H_2$ Only Al & Ga react.

f) $M + NH_3 \rightarrow MNH_2$ All form amides.

- Stability of +3 oxidation state $B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$
- Stability of +1 oxidation state $B^{+} < Al^{+} < Ga^{+} < In^{+} < Tl^{+}$
- Lewis acid character – $BX_3 > AlX_3 > GaX_3 > InX_3$

  $BF_3 < BCl_3 < BBr_3 < BI_3$.
- Basic Strength –

  $B_2O_3 < Al_2O_3 < Ga_2O_3 < In_2O_3 < Tl_2O_3$

  $B(OH)_3 < Al(OH)_3 < Ga(OH)_3 < In(OH)_3 < Ti(OH)_3$
- Anomalous behaviour of ~~Carbon~~ Boron:

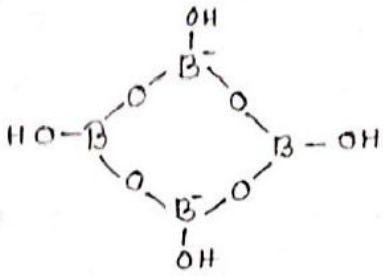
a) Boron shows anomalous behaviour due to its small size, high nuclear charge, high electronegativity & non-availability of d electrons.

b) Main differences – i) Boron is a typical non-metal whereas others are metals. ii) allotropy is exhibited alone by Boron. iii) It is a bad conductor of electricity whereas others are good conductors. iv) It forms only covalent compounds while others also form some ionic compounds. v) Hydroxides & oxides of boron are acidic in nature whereas those of others are amphoteric & basic. vi) Trihalides of boron exist as monomer whereas others exist as dimers. vii) Borates are more stable than aluminates. viii) It exhibits max. covalency of 4 while others exhibit a max covalency of 6. ix) It doesn't decompose steam while others do so. x) Concentrated HNO_3 oxidises boron to boric acid while others become passive specially Al & Ga.

* Some Important Compounds:

Compound- Borax ($Na_2B_4O_7 \cdot 10H_2O$)

1. Structure: $Na_2B_4O_5(OH)_4 \cdot 8H_2O$



$[B_4O_5(OH)_4]^{2-}$

2. Preparation:

From colemanite:

- $Ca_2B_6O_{11} + 2Na_2CO_3 \xrightarrow{\Delta} 2CaCO_3\downarrow + Na_2B_4O_7 + 2NaBO_2$
- $4NaBO_2 + CO_2 \longrightarrow Na_2CO_3 + Na_2B_4O_7$

3. Properties: i) Its solution is basic in nature due to hydrolysis.

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{4H_3BO_3}$$

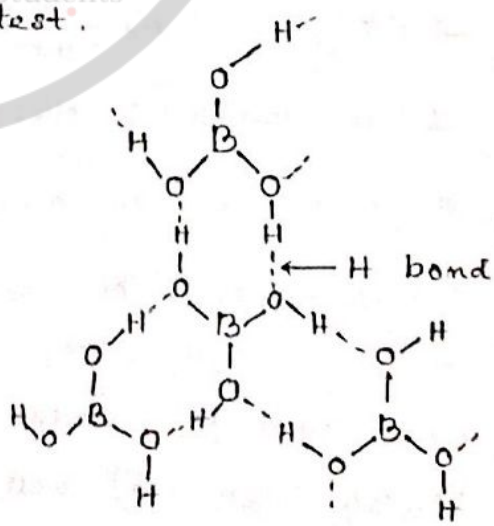
ii) action of heat:

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow[-10H_2O]{\Delta} \underset{\text{Sodium Metaborate}}{\text{Anhydrous } Na_2B_4O_7} \xrightarrow{740^\circ C} \underbrace{2NaBO_2 + \overset{\text{Boric anhydride}}{B_2O_3}}_{\text{Transparent bead}}$$

4. Uses: i) as water softener & cleaning agent.
ii) for borax bead test.

Compound- Boric acid/ Orthoboric acid (H_3BO_3)

1. Structure:



2. Preparation:

From Borax:

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + Na_2SO_4.$$

■ By hydrolysis of boron compounds:

$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$

$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$

$BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$

3. Properties: i) It is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid.

$B(OH)_3 + 2H\text{-}OH \longrightarrow [B(OH)_4]^- + H_3O^+$

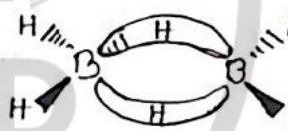
ii) Action of heat: $H_3BO_3 \xrightarrow{370K} HBO_2 + H_2O$ (Metaboric acid)

$4HBO_2 \xrightarrow[-H_2O]{410K} H_2B_4O_7 \xrightarrow{\Delta} 2B_2O_3 + H_2O$ (Tetraboric acid; Boron trioxide)

4. Uses: i) Used in the manufacture of heat resistant borosilicate glass. ii) aqueous solution of boric acid is used as a mild antiseptic especially as eye wash under the name boric lotion.

- Compound- Diborane (B_2H_6)

1. Structure: 4 2c-2e B-H terminal bonds



2 3c-2e B-H Bridge / Banana bonds.

2. Preparation:

■ $4BF_3 + 3LiAlH_4 \xrightarrow[ether]{diethyl} 2B_2H_6 + 3LiF + 3AlF_3$

■ Lab method: $2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$

■ Industrial method: $2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$.

3. Properties: i) It catches fire spontaneously upon exposure to air. $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$. ii) Boranes are readily hydrolysed by water to form boric acid. $B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$. iii) With methanol, trimethyl borate is formed. $B_2H_6 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$ iv) Diborane undergoes cleavage reactions with Lewis bases to give borane adducts. $B_2H_6 + 2NMe_3 \longrightarrow 2BH_3 \cdot NMe_3$

$B_2H_6 + 2CO \longrightarrow 2BH_3 \cdot CO$

v) Reaction with metal hydrides :

$2NaH + B_2H_6 \xrightarrow[ether]{diethyl} 2Na^+[BH_4]^-$ Sodium borohydride.

$2LiH + B_2H_6 \xrightarrow[ether]{diethyl} 2Li^+[BH_4]^-$

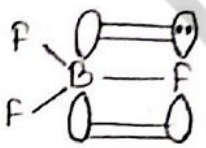
vi) Reaction with NH_3 :

$3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\Delta} \underline{2B_3N_3H_6} + 12H_2$

Inorganic benzene

4. Uses : i) for preparing a number of borohydrides such as $LiBH_4$, $NaBH_4$ etc. ii) As a reducing agent in organic reactions.

- Compound- BF_3

1. Structure:  $p\pi$-$p\pi$ back bonding.

2. Preparation: $B_2O_3 + 6HF \rightarrow 2BF_3 + 3H_2O$.

3. Properties : i) It undergoes rapid halide exchange reactions. $BF_3 + BCl_3 \rightarrow BF_2Cl + BCl_2F$.

ii) It is electron deficient, hence acts as Lewis acid that forms adducts with lewis bases.

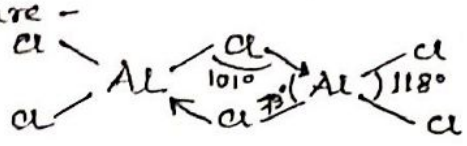
$BF_3 + (C_2H_5)_2O \rightarrow BF_3 \cdot O(C_2H_5)_2$ iii) It reacts with water to give boric acid and fluoroboric acid.

$4BF_3 + 3H_2O \rightarrow 3HBF_4 + B(OH)_3$

- 4 Uses : i) acts as a catalyst in organic reaction.
ii) used as an important reagent in organic chemistry as a Lewis acid.

- Compound- $AlCl_3$.

1. Structure -



2. Preparation: $2Al + 3Cl_2 \longrightarrow 2AlCl_3$

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

$Al_2O_3 + 3C + 3Cl_2 \xrightarrow{100^\circ C} 2AlCl_3 + 3CO$

3. Properties: i) Anhydrous $AlCl_3$ fumes in moist air due to hydrolysis & the resulting solution is acidic. ii) $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$

iii) $AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3\downarrow + 3NH_4Cl$

Gelatinous ppt.
Insoluble in NH_4OH

iv) $AlCl_3 + 3NaOH \longrightarrow Al(OH)_3\downarrow + 3NaCl$

Soluble in excess NaOH

v) $AlCl_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$.

Soluble metaaluminate.

4. Uses: Anhydrous $AlCl_3$ is used as a catalyst in Friedel-Crafts reaction & in cracking of petroleum.

- Alums: Alums are double sulphates of the type $M_2SO_4 \cdot M'_2(SO_4)_3 \cdot 24H_2O$ where M is a univalent cation like Na^+, K^+ & NH_4^+ and M' is a trivalent cation like Al^{3+} Fe^{3+}, Cr^{3+}.

Potash alum - $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

Sodium alum - $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

- Uses: Potash alum is used for purification of water, as styptic, in fire extinguishers, as mordant for dyeing & for tanning of leather.

Group 14 Elements:

14 (IVB).
C ($2s^2 2p^2$)
Si ($3s^2 3p^2$)
Ge ($4s^2 4p^2$)
Sn ($5s^2 5p^2$)
Pb ($6s^2 6p^2$).

- **Physical Properties:** a) atomic & ionic radii / covalent radii - C < Si < Ge < Sn < Pb b) ionisation energy - C > Si > Ge > Sn > Pb. c) electronegativity - C > Si ≃ Ge ≃ Sn < Pb. d) oxidation state - Stability of +4 oxidation state decreases down the group while that of +2 increases. e) Melting & boiling points - decrease from C to Pb. f) density - increases regularly from C to Pb. g) allotropy - all elements show allotropy.

- **Chemical Properties:**

Group 14 Elements
- Action of air → MO, MO_2
- Reaction with H_2O → $SnO_2 + H_2$
- Reaction with acid → $GeHCl_3$ (with hot HCl gas); $SnCl_2$ & H_2PbCl_4 (with conc. HCl)
- Reaction with alkalies → Na_2SiO_3, Na_2SnO_3
- Reaction with halogens → MX_4 & MX_2

- Pb does not decompose steam because of the protective layer of oxide.
- $PbBr_4$ & PbI_4 do not exist due to the fact that Pb^{4+} is a strong oxidising agent while Br^- & I^- are strong reducing agents, hence Pb^{4+} can't survive in presence of Br^- & I^- ions.
- Catenation tendency - C >> Si > Ge ≃ Sn >> Pb
- Acidic strength - $\underbrace{CO_2 > SiO_2}_{\text{acidic}} > \underbrace{GeO_2}_{\text{less acidic}} > \underbrace{SnO_2 > PbO_2}_{\text{amphoteric}}$

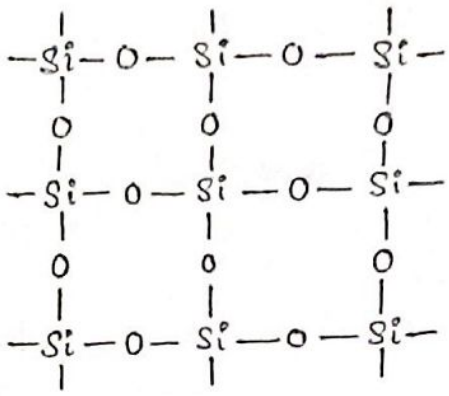
- Anomalous behaviour of Carbon: a) Carbon differs from rest of the members of group 14 because of its small size, high electronegativity, property of catenation & absence of d- orbitals. b) Main differences – i) The melting & boiling points, ionisation energy & electronegativity of C are very high as compared to the rest of the members. ii) It has max. tendency to show catenation as compared to other members of the family. iii) It has high tendency to form $p\pi - p\pi$ multiple bonds while others form $p\pi - d\pi$ bonds & that also to a lesser extent. iv) CO_2 is a gas while the dioxides of other members are solids.

- Oxides of Carbon :

Oxide	Preparation	Properties & Uses
CO	1. $2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$ 2. $HCOOH \xrightarrow[\text{Conc. } H_2SO_4]{373K} H_2O + CO$ 3. $C(s) + H_2O(g) \xrightarrow{473-1273K} \underbrace{CO(g) + H_2(g)}_{\text{Water gas}}$ 4. $2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273K} \underbrace{2CO(g) + 4N_2(g)}_{\text{Producer gas.}}$	1. powerful reducing agent & reduces many metal oxides to the metal. 2. CO molecule acts as a donor & reacts with metals to form metal carbonyls. 3. It is an important fuel as it is a component of water gas; producer gas & coal gas. 4. It's toxic because it forms a complex with haemoglobin in the blood, and this complex is more stable than oxy-haemoglobin.
CO_2	1. $C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$ 2. $CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$ 3. $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$ (limestone) 4. $CaCO_3(s) + 2HCl(aq.) \rightarrow CaCl_2(aq.) + CO_2(g) + H_2O(l)$	1. an acidic oxide, reacts with bases to form salts. 2. Solid CO_2 is called dry ice & is used to freeze foods & ice cream. 3. It's not poisonous but in excess may lead to increase in greenhouse effect.

* Some Important Compounds :

• Silicon dioxide / Silica (SiO_2) :

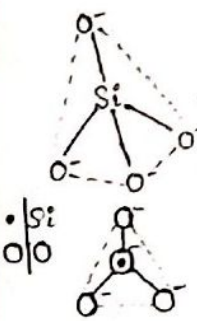


1. Structure : Has a 3D network structure in which each silicon is bonded to 4 O atoms which are tetrahedrally disposed around Silicon.

2. Properties : i) Occurs in several crystallographic forms (Quartz, cristobalite, tridymite). ii) non-reactive because of very high Si-O bond enthalpy. iii) $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$ iv) $SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$.

3. Uses : i) extensively used as piezoelectric material, made possible to develop extremely accurate clocks, modern radio & television. ii) Silica is used in the manufacture of glass & lenses for optical instruments. iii) Powdered quartz is used to manufacture silica bricks. iv) Silica gel ($SiO_2 \cdot xH_2O$) is used in chromatography & also for adsorbing moisture.

• Silicates : The basic building unit of all silicates is tetrahedral SiO_4^{4-} ion. Depending upon the linkages of SiO_4^{4-}. Depending upon the linkages of SiO_4^{4-} units, different types of structural arrangements are possible for silicates such as linear chains, cyclic chains, sheets etc.



• Zeolites : These are a class of 3D aluminosilicates. Their general formula is

$M_{x/n}[AlO_2]_x[SiO_2]_y \cdot mH_2O$, where $M = Na^+, K^+$ or Ca^{2+}, n = charge on the simple cation, m = no. of molecules of water of hydration.

- **Silicones:** Silicones are organo-silicon polymeric compounds containing Si–O–Si linkages.

1. **Preparation:** $2RCl + Si \xrightarrow[570K]{Cu\ Powder} R_2SiCl_2$ (Dialkyl dichloro silane)

$R_2SiCl_2 \xrightarrow[-HCl]{+H_2O} R_2Si(OH)_2$ (Dialkyl dihydro silane) $\xrightarrow{-H_2O}$ $\left[-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\right]_n$ Silicone

$HO-\underset{R}{\overset{R}{Si}}-OH + HO-\underset{R}{\overset{R}{Si}}-OH + HO-\underset{R}{\overset{R}{Si}}-OH \xrightarrow{-H_2O}$ Polymerisation $-O-\left(\underset{R}{\overset{R}{Si}}-O\right)_n-\underset{R}{\overset{R}{Si}}$ Silicone.

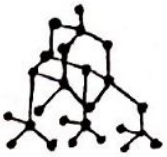
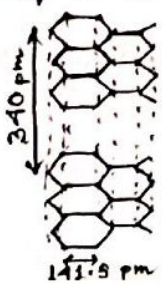
■ Chain length of polymer can be controlled by adding R_3SiCl which blocks the ends as shown below.

$n\ HO-\underset{CH_3}{\overset{CH_3}{Si}}-OH + HO-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3 \xrightarrow{-H_2O}$ Polymerisation $\left(O-\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_n-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$

2. **Properties:** Being surrounded by non-polar alkyl groups, water repelling in nature. Have high thermal stability, high dielectric strength, resistance to oxidation & chemicals.

3. **Uses:** Used as sealant, greases, water proofing fabrics, lubricants.

- **Allotropes of Carbon:** Carbon

Natural Crystalline		Artificial Crystalline	Amorphous
Diamond (sp^3 hybridisation, hardest substance) 	Graphite (sp^2 hybridisation, soft to touch) 	Fullerenes, eg. C_{60} also known as bucky ball, has 12 five membered & 20 six membered rings & C is sp^2 hybridised.	Wood charcoal, sugar charcoal, lamp black etc.

* Group 15 Elements : Collectively called pnictogens.

15 (VB)
N ($2s^2 2p^3$)
P ($3s^2 3p^3$)
As ($4s^2 4p^3$)
Sb ($5s^2 5p^3$)
Bi ($6s^2 6p^3$)

• Occurrence: Molecular N_2 comprises 78% by volume of the atmosphere. In the Earth's crust, it occurs as sodium nitrate, $NaNO_3$ (Chile saltpetre) & KNO_3 (Indian Saltpetre). It is found in the form of proteins in plants & animals. P occurs in minerals of the apatite family, $Ca_9(PO_4)_6 \cdot CaX_2$ (X = F, Cl or OH) (eg fluorapatite, $Ca_9(PO_4)_6 \cdot CaF_2$) which are the main components of phosphate rocks. P is present in bones as well as in living cells. Phosphoproteins are present in milk and eggs. As, Sb, Bi are found mainly as sulphide minerals.

• General Characteristics: a) Electronic config - ns^2np^3.
b) Physical state and metallic character - N_2 (unreactive gas), P_4 (solid non metal), As_4 & Sb_4 (solid metalloids), Bi (metal). c) atomic radii - Increase down the group, smaller than that of group 14 elements due to increased nuclear charge. d) Melting & boiling points - M.Pt. increases from N to As and then decreases whereas B.Pt. increases from N to Sb and decreases very slightly then. e) Ionisation enthalpy - decreases regularly down the group due to increase in size. f) electronegativity - decreases down the group. g) Allotropy - Nitrogen (α & β nitrogen), phosphorus (white, red, scarlet, violet, α-black, β-black), arsenic (grey, yellow, black), antimony (metallic, yellow, explosive).

• Chemical Properties: a) Stability of +3 oxidation state increases and that +5 decreases down the group due to inert pair effect.

b) Halides: All elements form trihalides of the type NX_3 & except nitrogen, all form pentahalides (NX_5).

b)i) stability: $NF_3 > NCl_3 > NBr_3$ b)ii) Lewis acid strength- $PCl_3 > AsCl_3 > SbCl_3$ & $PF_3 > PBr_3 > PI_3$. b)iii) Lewis base strength - $NI_3 > NBr_3 > NCl_3 > NF_3$. b)iv) Bond angle - $PF_3 < PCl_3 < PBr_3 < PI_3$ (increasing bp-bp repulsions).

c) Hydrides: All elements form hydrides of type MH_3 which are covalent & pyramidal in shape.

Ease of Formation ; Stability ; Basic Character ; Solubility ; Bond angle ; Strength of H-H bond ; Dipole moment ; Decomposition temperature.

→ Max

BiH_3 SbH_3 AsH_3 PH_3 NH_3

Max ←

Rate of Combustion ; Poisonous nature ; Covalent Character ; Reducing Character

d) Oxides: All form oxides (X_2O_3, X_2O_4, X_2O_5).

N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3
N_2O_4	P_2O_4	As_2O_4	Sb_2O_4	Bi_2O_4
N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5

↓ acidic nature increases

→ acidic nature decreases.

• Anomalous properties of nitrogen: a) N_2 differs from the rest of the members due to small size, high electronegativity, high ionisation enthalpy & non-availability of d orbitals. b) N_2 has unique ability to form $p\pi$-$p\pi$ multiple bonds with itself and other elements having small size and high electronegativity. c) N_2 bond enthalpy of $N \equiv N$ is very high. d) Nitrogen cannot form $d\pi$-$p\pi$ bond.

• Allotropes of Phosphorus:

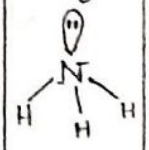
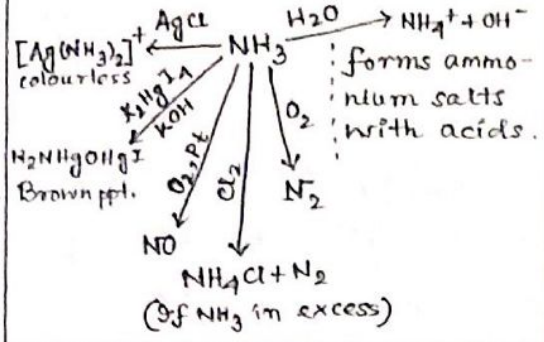
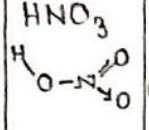
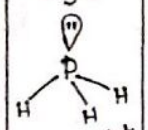
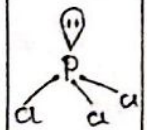
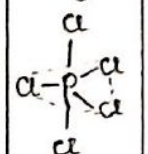
■ White Phosphorus: A translucent, white waxy solid; poisonous, insoluble in water, soluble in carbon disulphide & glows in dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3. $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + NaH_2PO_2$. White phosphorus is less stable and therefore more reactive than the other solid phases under normal conditions because of angular strain under the effect of small angle, 60°, in the P_4 molecule. It readily catches fire in air to give dense white fumes of P_4O_{10}. $P_4 + 5O_2 \rightarrow P_4O_{10}$.

■ Red Phosphorus: Obtained by heating white P at 573 K in an inert atmosphere for several days. It is odourless, non-poisonous and insoluble in water as well as in carbon disulphide. Chemically less reactive than white Phosphorus. It is polymeric, consisting of chains of P_4.

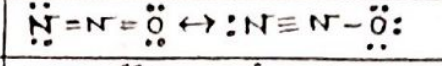
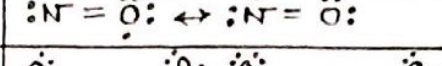
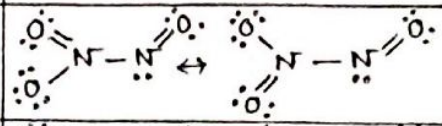
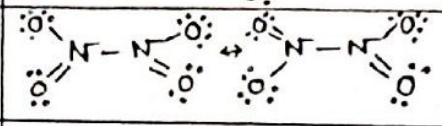
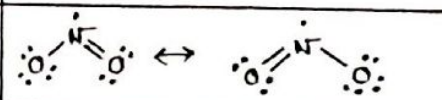
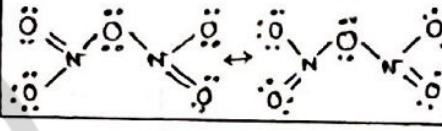
■ Black Phosphorus: Has two forms α-black, β-black. α-black P is formed when red P is heated in a sealed tube at 803 K. It can be sublimed in air, has opaque monoclinic or rhombohedral crystals. β-black P is formed by heating white P at 473 K under high pressure.

* Some Important Compounds:

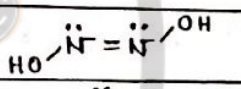
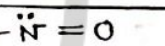
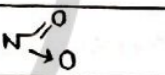
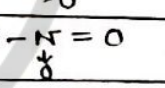
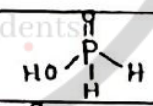
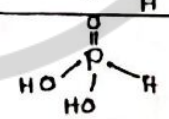
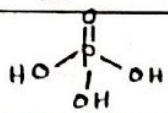
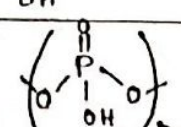
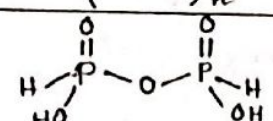
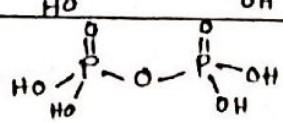
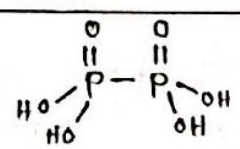
Cmpd	Preparation	Properties	Uses
N_2 $N \equiv N$ Isotopes N_7^{14}, N_7^{15}	$NH_4Cl + NaNO_2 \rightarrow N_2\uparrow + 2H_2O + NaCl$ $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2\uparrow + 4H_2O + Cr_2O_3$ $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2\uparrow$	$N_2 \xrightarrow{O_2, 2000K} NO$ $N_2 \xrightarrow{H_2, 773K, 200 atm, Haber's process} NH_3$ $N_2 \xrightarrow{M} M_3N$ $N_2 \xrightarrow{B} BN$ $N_2 \xrightarrow{Si} Si_3N_4$ $N_2 \xrightarrow{CaC_2} CaCN_2 + C$ $N_2 \xrightarrow{Al_2O_3 + C} AlN + CO$	Used in manufacture of HNO_3, NH_3, $Ca(CN)_2$.

cmpd	Preparation	Properties	Uses
NH_3 	$N_2(g) + 3H_2(g)$ $2NH_3$ 200 atm P, 773 K, catalyst, Haber's Process $\Delta H_f^\circ = -46$ KJ/mol		Used in refrigerator manufacturing of rayon, HNO_3, $NaHCO_3$, urea, ammonium phosphate, ammonium sulphate.
HNO_3 	$2KNO_3 + H_2SO_4 \rightarrow 2HNO_3 + K_2SO_4$ Ostwald's Process - $4NH_3(g) + 5O_2(g)$ 500K, 9 bar, Pt, Rh gauze catalyst $4NO + 6H_2O$ $2NO + O_2 \rightleftharpoons 2NO_2$ $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$	$H_2SO_4 + NO_2$ SO_2 HNO_3 $C_{12}H_{22}O_{11}$ $-H_2O$ $(COOH)_2$ Sn H_2SnO_3 HCl $H_2O + NOCl + 2[Cl]$ **Brown Ring Test :** $NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$ $[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$ brown	Used as fertilizers, explosives, perfumes & dyes, pickling of stainless steel.
PH_3  rotten fish smell	$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$ Lab method - P_4 (White) $+ 3NaOH + 3H_2O \rightarrow PH_3 + NaH_2PO_2$	$NH_4^+PH_2^-$ NH_3 PH_3 HBr PH_4Br HCl $PH_4^+Cl^-$ O_2 $CuSO_4$ Δ $P_4 + H_2$ $Cu + H_3PO_4$ H_3PO_4 Ag^+ $Ag + H_3PO_3$	Used as dehydrating agent. Used in Holme's signal.
PCl_3 	$P_4 + 6Cl_2 \rightarrow 4PCl_3$ $P_4 + 8SOCl_2 \downarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$	H_3PO_3 H_2O PCl_3 CH_3COOH H_3PO_3 C_2H_5OH H_3PO_3 SO_2 NH_3 S $POCl_3$ $P(NH_2)_3$ $PSCl_3$	Used as reagent in organic synthesis & as a precursor of PCl_5, $POCl_3$, $PSCl_3$.
PCl_5 	$P_4 + 10Cl_2 \rightarrow 4PCl_5$ $P_4 + 10SO_2Cl_2 \downarrow 4PCl_5 + 10SO_2$ N.B. In solid state it exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral & anion is octahedral.	$H_3PO_4 + HCl$ H_2O in excess PCl_5 P_4O_{10} $POCl_3$ SO_2 $SOCl_2 + POCl_3$ Δ P_4O_{10} $PCl_3 + Cl_2$ $PSCl_3$ C_2H_5OH $POCl_3 + HCl$ CH_3COOH $POCl_3 + HCl$ Ag finely divided on heating $PCl_3 + AgCl$	Used as chlorinating & dehydrating agent.

• Oxides of Nitrogen:

Oxide	Physical appearance & chemical nature	Structure.
Nitrous oxide (N_2O)	colourless gas, neutral.	
Nitric Oxide (NO)	colourless gas, neutral.	
Dinitrogen trioxide (N_2O_3)	blue solid, acidic	
Dinitrogen tetra-oxide (N_2O_4)	colourless solid, or liquid, acidic	
Nitrogen dioxide (NO_2)	brown gas, acidic	
Dinitrogen pentoxide (N_2O_5)	colourless solid, acidic	

• Oxoacids of nitrogen & phosphorus:

Oxoacid	Properties	Structure.
Hyponitrous acid ($H_2N_2O_2$)	Weak acid	
Nitrous acid (HNO_2)	Weak, unstable acid	
Nitric acid (HNO_3)	Strong, stable acid	
Peroxynitric acid (HNO_4) Pernitric acid	unstable, explosive	
Phosphinic acid, H_3PO_2 Hypophosphorous acid	monobasic, strong, reducing agent	 Basicity = 1 Oxidation state of P = +1
Phosphonic acid (Orthophosphorous acid) H_3PO_3	dibasic, reducing agent	 Basicity = 2 OS of P = +3
Phosphoric acid, H_3PO_4 Orthophosphoric acid	non-reducing, tribasic	 Basicity = 3 OS of P = +5
Metaphosphoric acid (glacial phosphoric acid) $(HPO_3)_n$	monobasic	 Basicity = 1 OS of P = +5
Pyrophosphorous acid $H_4P_2O_5$	dibasic	 Basicity = 2 OS of P = +3.
Pyrophosphoric acid $H_4P_2O_7$	Tetrabasic	 Basicity = 4 OS of P = +5
Hypophosphoric acid, $H_4P_2O_6$	Tetrabasic	 Basicity = 4 OS of P = +4

• Nitrogen may show +5 oxidation state but it is never pentavalent.

⁂ Quicklime is used for drying NH_3 as it reacts with other dehydrating agents.

⁂ In liquid or solid state, NO forms a loose dimer (N_2O_2) which is diamagnetic in nature.

⁂ Phosphine in combination with acetylene is used in preparing Holme's signals.

⁂ H_3PO_4 is used in the soft drinks.

⁂ N_2O_5 & P_2O_5 are covalent in vapor state, but ionic in solid state.

* Group 16 Elements : Group of chalcogens.

16 (VIB)
O ($2s^2 2p^4$)
S ($3s^2 3p^4$)
Se ($4s^2 4p^4$)
Te ($5s^2 5p^4$)
Po ($6s^2 6p^4$)

• General Properties : a) Physical state & metallic character: O_2 (gas), S_8 (solid non-metal), Se & Te (solid metalloid), Po (radioactive). b) atomic radii - increase down the group. c) Ionisation enthalpy - decrease down the group. d) Electronegativity - decrease down the group. e) Electron gain enthalpy - Increases from oxygen to sulphur & then decreases. f) melting & boiling points - Increase down the group upto Te & then decrease. g) allotropy - all show.

• Allotropes of Sulphur: Yellow rhombic (α-sulphur) & monoclinic (β sulphur)

The stable form at room temp is rhombic sulphur, which transforms to β-sulphur, when heated above 369 K. At 369 K, both forms are stable; this temp. is called transition temp.

- Chemical Properties: a) Stability of -2 oxidation state decreases down the group, of +4 os increases & of +6 os decreases down the group, due to inert pair effect. b) hydrides - all elements form stable hydrides of the type H_2M. c) general trend of hydrides – B.pt. $H_2O > H_2Te > H_2Se > H_2S$; Volatility. $H_2S > H_2Se > H_2Te > H_2O$; bond angle - $H_2O > H_2S > H_2Se > H_2Te$; acidic character - $H_2O < H_2S < H_2Se < H_2Te$; reducing power – $H_2Te > H_2Se > H_2S > H_2O$. d) Halides: All elements form halides of the type EX_6, EX_4, EX_2. e) Simple oxide - MgO, Al_2O_3; Mixed oxide - Pb_3O_4, Fe_3O_4 ; Acidic oxide - SO_2, Cl_2O_7, CO_2, N_2O_5 ; Basic oxide - Na_2O, CaO, BaO ; Amphoteric oxide – Al_2O_3 ; Neutral oxide - CO, NO, N_2O. f) anomalous behaviour of oxygen - Strong hydrogen bond is present in H_2O, not in H_2S, due to small size & high electronegativity.

- Dioxygen: ◪ Preparation: $2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$

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

◪ Properties: $O_2 + 2Mg = 2MgO$