

p-Block Elements

Points to remember:-

The general valence shell electronic configuration of p-block elements $ns^2 np^{1-6}$

GROUP 15 ELEMENTS:-

Group 15 elements ; N, P, As, Sb & Bi

General outer electronic configuration: $ns^2 np^3$

Physical Properties:-

- Dinitrogen is a diatomic gas while all others are solids.
- N & P are non-metals. As & Sb metalloids & Bi is a metals .this is due to decrease in ionization enthalpy & increase in atomic size .
- Electro negativity decreases down the group .

Chemical properties:-

- Common oxidation states : -3, +3 & +5.
- Due to inert pair effect, the stability of +5 state decreases down the group & stability of +3 state increases .
- In the case of Nitrogen all Oxidation states from +1 to +4 tend to disproportionate in acid solution , e.g.:-
 $3\text{HNO}_2 \longrightarrow \text{H}_2\text{O} + 2\text{NO} + \text{HNO}_3$
Anomalous behavior of Nitrogen :- due to its small size, high electronegativity, high ionization enthalpy and absence of d-orbital.

N_2 has unique ability to form $\pi-\pi$ multiple bonds whereas the heavier members of this group do not form $\pi-\pi$ because their atomic orbitals are so large & diffuse that they cannot have effective overlapping.

Nitrogen exists as diatomic molecule with triple bond between the two atoms whereas other elements form single bonds in elemental state.

N cannot form $d\pi-\pi$ due to the non availability of d-orbitals whereas other elements can.

Trends In Properties:-

Thermal Stability(decreasing order) - $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$

Bond(E-H) Dissociation Enthalpy(decreasing order)- $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$

Reducing character(decreasing order) - $\text{BiH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$

Basic character(decreasing order)- $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3 > \text{BiH}_3$

Acidic character(decreasing order)- $\text{N}_2\text{O}_3 > \text{P}_2\text{O}_3 > \text{As}_2\text{O}_3 > \text{Sb}_2\text{O}_3 > \text{Bi}_2\text{O}_3$

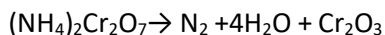
Boiling points(decreasing order)- $\text{BiH}_3 > \text{SbH}_3 > \text{NH}_3 > \text{AsH}_3 > \text{PH}_3$

Acidic Character(decreasing order)- $\text{N}_2\text{O}_5 > \text{N}_2\text{O}_4 > \text{N}_2\text{O}_3$

Dinitrogen:-

Preparation

- Commercial preparation – By the liquification & fractional distillation of air.
- Laboratory preparation – By treating an aqueous solution NH_4Cl with sodium nitrate .
 $\text{NH}_4\text{Cl} + \text{NaNO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} + \text{NaCl}$
- Thermal decomposition of ammonium dichromate also give N_2 .



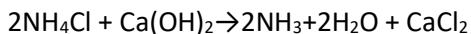
- Thermal decomposition of Barium or Sodium azide gives very pure N_2 .

PROPERTIES

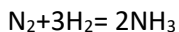
At high temperature nitrogen combines with metals to form ionic nitride (Mg_3N_2) & with non-metals, covalent nitride.

AMMONIA PREPARATION

- In laboratory it is prepared by heating ammonium salt with NaOH or lime.



- In large scale it is manufactured by Haber 'process



$$\Delta H^0 = -46.1 \text{ kJ/mol}$$

Acc.to Lechatelier's principle the favourable conditions for the manufacture of NH_3 are:-

Optimum temperature : 700 K

High pressure : 200 atm

Catalyst: Iron Oxides

Promoter : K_2O & Al_2O_3

PROPERTIES

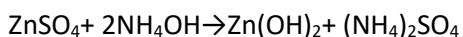
Ammonia is a colorless gas with pungent odour.

Highly soluble in water.

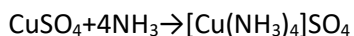
In solids & liquid states it exists as an associated molecule due to hydrogen bonding which accounts for high melting & boiling points of NH_3

Trigonal Pyramidal shape NH_3 molecule.

Aqueous solution of ammonia is weakly basic due to the formation of OH^- ion .



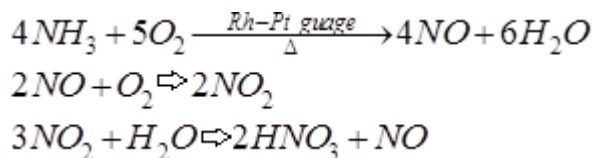
Ammonia can form coordinate bonds by donating its lone on nitrogen, ammonia forms complexes.



Name	Formula	Oxidation state	Chemical nature
Nitrous oxide or Laughing gas	N_2O	+1	Neutral
Nitric oxide	NO	+2	Neutral
Dinitrogen trioxide	N_2O_3	+3	Acidic
Dinitrogen tetra oxide	N_2O_4 or NO_2	+4	Acidic
Dinitrogenpentaoxide	N_2O_5	+5	Acidic

NITRIC ACID

Industrial preparation: Ostwald's process – it is based upon catalytic oxidation of ammonia by atmospheric oxygen. The main steps are



PROPERTIES:-

- (i) conc. HNO_3 is a strong oxidizing agent & attacks most metals gold & Pt.
- (ii) Cr & Al do not dissolve HNO_3 because of the formation of a protective film of oxide on the surface.
- (iii) It oxidises non metals like I_2 to HNO_3 , C to CO_2 , S to H_2SO_4
- (iv) Brown ring test is used to detect (Nitrate) NO_3^- .

PHOSPHOROUS:-

ALLOTROPIC FORMS: White, red α -black & β -black.

White phosphorous is more reactive than red phosphorous because white P exists as discrete P_4 molecules and red P possess several P_4 molecules linked together.

PHOSPHINE

Preparation: It is prepared in laboratory by heating white P with concentrated NaOH solution in an

Inert atmosphere of CO_2 [$\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$]

Other methods: $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$



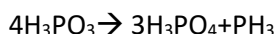
Phosphorous halides

Phosphorous forms two types of halides PX_3 & PX_5 ($\text{X}=\text{F}, \text{I}, \text{Br}$)

Trihalides have pyramidal shape and pentahalides have trigonalbipyramidal structure.

OXOACIDS OF PHOSPHOROUS

- The acids in +3 oxidation state disproportionate to higher & lower oxidation state.



- Acids which contain P-H bond have strong reducing properties. EX: $-\text{H}_3\text{PO}_2$
- Hydrogen atoms which are attached with oxygen in P-OH bond are ionisable and account for the basicity.