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^2np^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.:- $3HNO_2 \longrightarrow H_2O + 2NO + HNO_3$

  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 pπ-pπ multiple bonds whereas the heavier members of this group do not form pπ –pπ because there 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 dπ-pπ due to the non availibility of d-orbitals whereas other elements can.

Trends In Properties:-

Thermal Stability(decresing order) - $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Bond(E-H) Dissociation Enthalpy(decreasing order)- $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Reducing character(decreasing order) - $BiH_3 > SbH_3>AsH_3> PH_3 > NH_3$

Basic character(decreasing order)- $NH_3>PH_3>AsH_3>SbH_3>BiH_3$

Acidic character(decreasing order)- $N_2O_3>P_2O_3>As_2O_3>Sb_2O_3>Bi_2O_3$

Boiling points(decreasing order)- $BiH_3>SbH_3>NH_3>AsH_3>PH_3$

Acidic Character(decreasing order)- $N_2O_5>N_2O_4> N_2O_3$

Dinitrogen:-

Preparation

- Commercial preparation – By the liquification& fractional distillation of air.
- Laboratory preparation – By treating an aqueous solution NH_4Cl with sodium nitrate .
  $NH_4Cl + NaNO_2 \rightarrow N_2 + 2H_2O + NaCl$
- Thermal decomposition of ammonium dichromate also give N_2.

$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3$

- 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.
  $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$
- In large scale it is manufactured by Haber 'process
  $N_2 + 3H_2 = 2NH_3$
  $\Delta H^0 = -46.1 kJ/mol$
  Acc.to Lechatelier's principle the favourable conditions for the manufacture of NH_3 are:-
  Optimum temperature : 700 K
  High pressure : 200 atm

Catalytst: 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 .

$ZnSO_4 + 2NH_4OH \rightarrow Zn(OH)_2 + (NH_4)_2SO_4$

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

$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$

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_4or NO_2	+4	Acidic
Dinitrogenpentaoxide	N_2O_5	+5	Acidic

NITRIC ACID

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

$$4NH_3 + 5O_2 \xrightarrow[\Delta]{Rh-Pt\ guage} 4NO + 6H_2O$$

$$2NO + O_2 \Rightarrow 2NO_2$$

$$3NO_2 + H_2O \Rightarrow 2HNO_3 + NO$$

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 [$P_4+3NaOH+3H_2O \rightarrow PH_3+3NaH_2PO_2$]

Other methods: $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$

Phosphorous halides

Phosphorous forms two types of halides PX_3& PX_5 (X=F,I,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.

  $4H_3PO_3 \rightarrow 3H_3PO_4+PH_3$

- Acids which contains P-H bond have strong reducing properties.EX:-H_3PO_2
- Hydrogen atom which are attached with oxygen in P-OH bond are ionisable and account for the basicity.