7. THE P-BLOCK ELEMENTS

The elements in which the last electron enters in the valence p-sub shell are called the p-block elements. They include elements of the groups 13 to 18. Their general outer electronic configuration is ns^2np^{1-6} (except He which has $1s^2$ configuration).They includes metals, non-metals and metalloids.

Ammonia

Preparation: In laboratory, ammonia is obtained by treating ammonium salts with caustic soda or lime.

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$$

$(NH_4)_2 SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$

On a large scale, ammonia is manufactured by Haber's process.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

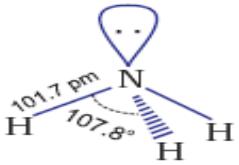
In accordance with Le Chatelier's principle, high pressure of about 200 atm, a temperature of about 700 K and the catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 are employed to increase the rate of this reaction.

Properties

Ammonia is a colourless gas with a pungent smell. It is highly soluble in water because of its ability to form inter molecular hydrogen bond with water. Liquid ammonia has high melting and boiling points because of inter molecular hydrogen.

The ammonia molecule has a *trigonal pyramidal geometry*.

It has three bond pairs and one lone pair of electrons as shown in the structure.



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

$NH_3(g) + H_2O(l) \rightarrow NH_4^+ (aq) + OH^- (aq)$

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 complex compounds which find applications in detection of metal ions such as Cu^{2+}, Ag^+:

$Cu^{2+} (aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq)$

(blue) (deep blue)

Uses: Ammonia is used to produce various nitrogenous fertilizers and in the manufacture of nitric acid. Liquid ammonia is used as a refrigerant.

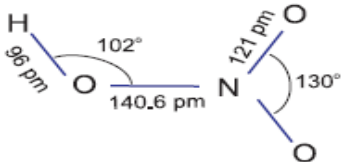
Nitric Acid: It is the most important oxoacid of Nitrogen.

Manufacture: Ostwald's process.

It involves three steps:

1. The catalytic oxidation of NH_3 by atmospheric oxygen in presence of platinum/ rhodium gauge (wire) catalyst.
   $4 NH_3(g) + 5 O_2(g) \xrightarrow{\text{Pt/Rh gauge catalyst, 500K \& 9 bar}} 4NO(g) + 6 H_2O(g)$
2. The nitric oxide is converted to NO_2
   $2NO(g) + O_2(g) \rightleftharpoons 2 NO_2 (g)$
3. Absorption of nitrogen dioxide in water to get nitric acid
   $3 NO_2(g) + H_2O(l) \longrightarrow 2 HNO_3(aq) + NO(g)$

Properties: it is a colourless liquid. In the gaseous state, HNO_3 exists as a planar molecule with the structure as shown.



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

$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^- (aq)$

Concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid, temperature

and the nature of the material undergoing oxidation.

$$3Cu + 8\ HNO_3(dilute) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$
$$Cu + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Concentrated nitric acid also oxidises non–metals and their compounds. Iodine is oxidised to iodic acid, carbon to carbon dioxide etc.

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10\ NO_2 + 4H_2O$$
$$C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO_2$$

Brown Ring Test: It is a test used for the detection of nitrates. It is carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layer indicate the presence of nitrate ion in solution.

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$$
$$[Fe\ (H_2O)_6\ ]^{2+} + NO \rightarrow [Fe\ (H_2O)_5\ (NO)]^{2+} + H_2O$$
(brown)

Uses: 1) The major use of nitric acid is in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics.
2) It is also used for the preparation of nitroglycerin, trinitrotoluene and other organic nitro compounds.
3) It is used for the *pickling of stainless steel,* etching of metals and as an oxidiser in rocket fuels.

Phosphorus Halides

Phosphorus forms two types of halides, PX_3 and PX_5

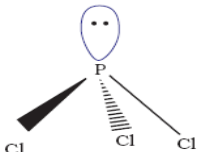
Phosphorus Trichloride (PCl_3)

Preparation: It is obtained by passing dry chlorine gas over heated white phosphorus.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

It is a colourless oily liquid. It fumes in moist air because it hydrolyses in the presence of moisture and form HCl(g). $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

Structure: It has a pyramidal shape as shown, in which phosphorus is sp^3 hybridized



Phosphorus Pentachloride (PCl_5)

Preparation

It is prepared by the reaction of white phosphorus with excess of dry chlorine.

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

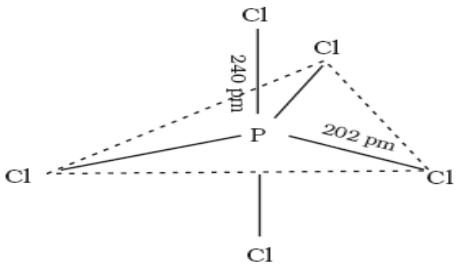
Properties

PCl_5 is an yellowish white powder. It also fumes in moist air because it hydrolyses in the presence of moisture and form HCl(g).

$$PCl_5 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

Structure:

In gaseous and liquid phases, it has a trigonal bipyramidal structure. The three equatorial P–Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs.



Sulphuric Acid: It is the most important oxoacid of sulphur.

Manufacture: Contact Process

It involves three steps:

(i) Burning of sulphur or sulphide ores in air to generate SO_2.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

(ii) Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5)

$$2\ SO_2 + O_2 \rightarrow 2\ SO_3$$

(iii) Absorption of SO_3 in H_2SO_4 to give *Oleum* ($H_2S_2O_7$). Dilution of oleum with water gives H_2SO_4 of the desired concentration.

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

Properties

Sulphuric acid is a colourless, dense, oily liquid. It dissolves in water with the evolution of a large quantity of heat. Hence, for diluting the acid, the concentrated acid must be added slowly into water with constant stirring.

The chemical reactions 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.

It is dibasic acid and forms two series of salts- normal sulphates and acid sulphates

Because of its low volatility sulphuric acid can be used for the manufacture of more volatile acids from their corresponding salts.

$$2\ MX + H_2SO_4 \rightarrow 2\ HX + M_2SO_4$$ (where X = F, Cl, NO_3 etc. and M is a metal)

Concentrated sulphuric acid is a strong dehydrating agent and drying agent. Many wet gases can be dried by passing them through sulphuric acid. Sulphuric acid removes water from organic compounds

e.g.: $C_{12}H_{22}O_{11} + H_2SO_4 \rightarrow 12C + 11H_2O$

Hot concentrated sulphuric acid is a moderately strong oxidising agent. It oxidises both metals and non-metals and the acid itself reduces to SO_2.

$$Cu + 2\ H_2SO_4(conc.) \rightarrow CuSO_4 + SO_2 + 2H_2O$$

$$3S + 2H_2SO_4(conc.) \rightarrow 3SO_2 + 2H_2O$$

Uses: The important uses of Sulphuric acid are:

1) In the manufacture of fertilizers 2) in petroleum refining 3) in the manufacture of pigments, paints and dyestuff intermediates 4) in detergent industry 5) in metallurgical applications 6) as electrolyte in storage batteries 7) in the manufacture of nitrocellulose products and 8) as a laboratory reagent.

Interhalogen Compounds

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as AX, AX_3, AX_5 and AX_7, where both A and X are halogens. A is larger and more electropositive than X. As the size of the central atom (A) increases, the stability of the compound also increases.

Preparation

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds.

$Cl_2 + F_2 \xrightarrow{437K} 2ClF$ (equal volume)

$I_2 + 3Cl_2 \longrightarrow 2ICl_3$ (excess)

Properties

These are all covalent molecules and are diamagnetic in nature. They are volatile solids or liquids except ClF which is a gas at 298 K. Their physical properties are intermediate between those of constituent halogens. The interhalogen compounds are more reactive than halogens (except fluorine).

This is because A–X bond in interhalogens is weaker than X–X bond in halogens except F–F bond.

The types of inter halogen compounds and their structures are as follows:

Type	Examples	Structure
AX	ClF, BrF, IF, BrCl, BrI	Linear
AX_3	ClF_3, BrF_3, IF_3, ICl_3, IBr_3 etc.	Bent T-shaped
AX_5	ClF_5, BrF_5, IF_5	Square pyramidal
AX_7	IF_7	Pentagonal bipyramidal

Uses: 1) These compounds can be used as non aqueous solvents.

2) Interhalogen compounds are very useful fluorinating agents.