# TDC Part I
## Paper I, Group B
## Inorganic Chemistry

## Department of Chemistry

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## TOPIC: - Group 15, Compounds, Halides

# Halides

Two series of halides are known – the trihalides ($MX_3$) and pentahildes ($MX_5$). The trihalides are known for all the elements and can be prepared by direct combination. But if the halogen is in excess than the pentahalide is formed in addition. The trihalides are all covalent apart from $BiF_3$ that is ionic. $SbF_3$ and the other halides of bismuth have partial ionic character. The central atom is $sp^3$ hybridized and the shape is pyramidal (like $NH_3$) (fig 20).

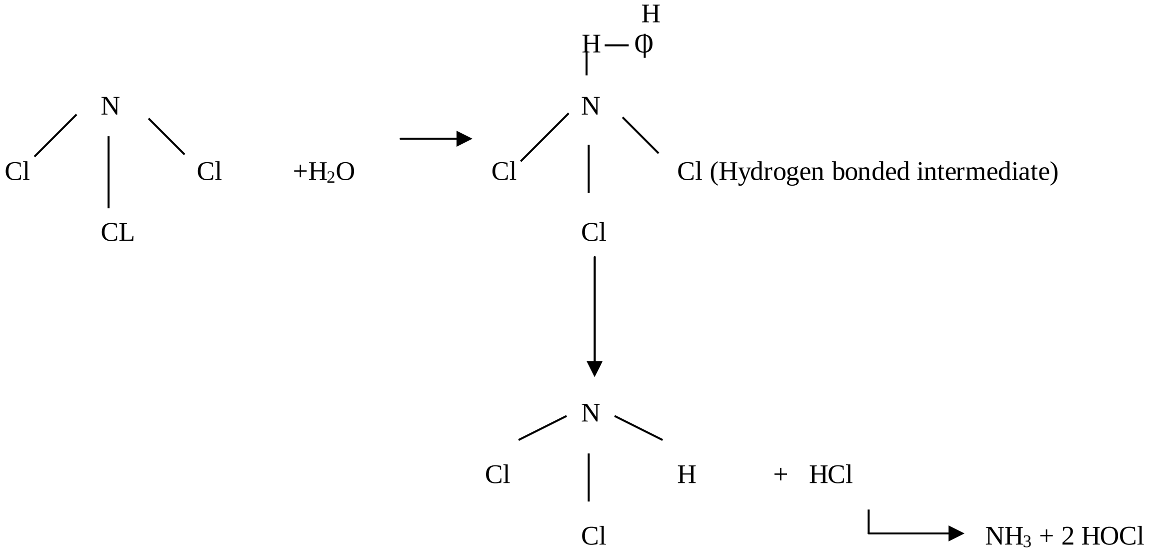
Apart from $NF_3$ that is very stable the trihalides hydrolyze but the products vary.

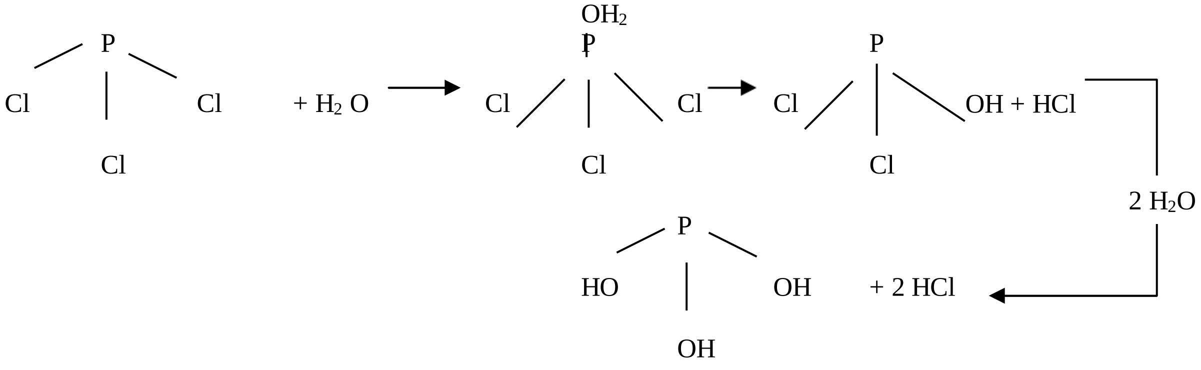
$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl$

$PCl_3 / AsCl_3 + 3H_2O \longrightarrow H_3PO_3 / H_3AsO_3 + 3HCl$

$SbCl_3 / BiCl_3 + H_2O \longrightarrow SbOCl / BiOCl + 2HCl$

The different products obtained in case of hydrolysis of $NCl_3$ and $PCl_3$ is due to a difference in mechanism, which results in formation of different intermediates.





In a case of $SbCl_3$ and $BiCl_3$ the hydrolysis is incomplete and may be repressed on adding HCl.

Nitrogen does not form pentahalides due to non – availability of d orbitals. Due to inert pair effect pentahalides of bismuth are less stable and only $BiF_5$ is known. The pentahalides of phosphorous are well characterized. In the gaseous phase they have trigonal bipyramidal structure (fig 21)

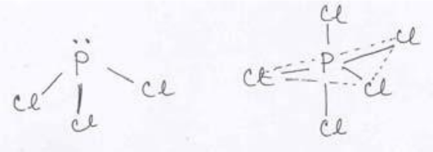


Fig.21: Structures of $PCl_3$ and $PCl_5$

This structure is retained in the solid state for $PF_5$ but $PCl_5$ dimerises in the solid state and exists as $[PCl_4]^+[PCl_6]^-$

Phosphorous pentachloride is the most important pentahalide and is obtained by treating phosphorous trichloride with chlorine.

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

It hydrolyses readily.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2\,HCl$$

$$POCl_3 + 3H_2O \longrightarrow \underset{\text{Phosphoric acid}}{H_3PO_4} + 3HCl$$

It is widely used in organic synthesis as a halogenating agent.

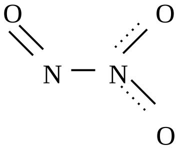
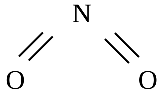
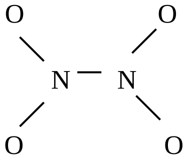
$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

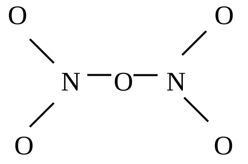
$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

**Nitrogen oxides and oxo acids**

The common oxides and oxoacids of nitrogen are summarized in Table 14 and their structures are also depicted there.

**Table 14: Oxides of Nitrogen**

| Formula | Name | Structure | Remarks |
|---|---|---|---|
| $N_2O$ | Nitrous Oxide | $N=N=O$ | Oxidn.state + 1<br>( O.S.) |
| NO | Nitric Oxide |  | O. S + 2<br>Bond order 2.5 Paramagnetic |
| $N_2O_3$ | Nitrogen Sesquioxide |  | O.S + 3<br>Dissociates readily to NO & $NO_2$ |
| $NO_2$ | Nitrogen Dioxide |  | O.S + 4<br>Paramagnetic<br>Following equilibrium presents<br>$2NO_2 = N_2O_4$ |
| $N_2O_4$ | Dinitrogen Tetraoxide |  | O.S + 4<br>Dissociates to $NO_2$ |

|  |  |  |  |
|---|---|---|---|
| $N_2O_5$ | Dinitrogen Pentoxide |  | O.S + 5<br>N-O-N may be bent. Exists as $NO_2^+NO_3^-$ in solid state |

They all exhibit pл-pл multiple bonding between nitrogen and oxygen atoms. The other elements of Group 15 cannot form such bonds and consequently nitrogen forms a number of compounds for which P, As, Sb or Bi analogues are not known. Oxides in lower oxidation state are neutral while those in higher oxidation states are acidic.

Nitrous oxide, $N_2O$, is obtained by the thermal decomposition of ammonium nitrate

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

It is used as a mild dental anaesthetic and propellant for aerosols. On atmospheric decomposition it releases nitrogen and oxygen that are environment friendly (unlike CFCS) However $N_2O$ contributes to green house effect.

Nitric oxide is obtained by the action of dilute nitric acid on copper.

$$3Cu + 8HNO_3 \longrightarrow 3Cu\,(NO_3)_2 + 2NO + 4H_2O$$

It is released during combustion of fossil fuels and is present in exhausts of automobiles and power plants. It is also obtained by action of lightning on atmosphere nitrogen and oxygen. The NO is slowly oxidized to $NO_2$, these two gases are collectively referred to as $NO_x$ and contribute to the problem of acid rain and destruction of ozone layer. It is a neutral oxide and is an important intermediate for manufacture of nitric acid by catalytic oxidation of ammonia. It is an odd electron molecule and forms coordination complexes with metal ions. One such complex $[Fe(H_2O)_5NO]^{2+}$ is responsible for the colour in the “brown ring” test for nitrates. Nitrogen dioxide, $NO_2$ is a toxic gas obtained by thermal decomposition of lead nitrate.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

It is an odd electron molecule and dimerizes to give $N_2O_4$. At ordinary temperature and pressure, both exist in significant amounts in equilibrium:

$$N_2O_4\,(g) \rightleftharpoons 2NO_2(g)$$

Colourless, diamagnetic $N_2O_4$ has a weak N-N bond that can readily dissociate on warming to give the brown, paramagnetic $NO_2$. $N_2O_4$ is an acidic oxide and dissolves in water to give a mixture of nitrous and nitric acids.

$$N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$$

The two important oxo acids of nitrogen are nitrous acid, $HNO_2$ and nitric acid, $HNO_3$. Nitrous acid is a weak acid and is obtained by acidifying a nitrite or by passing an equimolar mixture of NO and $NO_2$ into water.

$$Ba(NO_2)_2 + H_2SO_4 \longrightarrow 2HNO_2 + BaSO_4(s)$$

$$NO + NO_2 + H_2O \longrightarrow 2HNO_2$$

The acid disproportionates on heating

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

Nitrous acid and nitrites are good oxidizing agents and oxidize iodide to iodine, Fe (II) to Fe (III) and Sn (II) to Sn (IV), e.g.

$$2KI + 2HNO_2 + 2HCl \longrightarrow 2H_2O + 2NO + 2KCl + I_2$$

However, strong oxidizing agents like $KMnO_4$ oxidize nitrites to nitrates.

$$2KMnO_4 + 5\ KNO_2 + 6HCl \longrightarrow 2MnCl_2 + 5KNO_3 + 3H_2O + 2KCl$$

The nitrite ion forms complexes with metals. Coordination to metal ions occurs either through nitrogen or oxygen.

Nitric acid is of immense industrial importance. It is synthesized by the Ostwald (Nobel Prize 1909) process through the following set of reactions.

$$4NH_3 + 5O_2 \xrightarrow[1000^0c]{} 4NO + 6H_2O \text{ (Pt-Rh catalyst)}$$

$$2\ NO + O_2 \longrightarrow 2NO_2$$

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

In the first step, a catalyst specific for NO formation is taken; other wise $NH_3$ is oxidized to $N_2$

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$

$HNO_3$ is a strong acid undergoing complete dissociation in dilute aqueous solution.

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$

It is an excellent oxidizing agent particularly when hot and concentrated. A mixture of concentrated $HNO_3$ and concentrated HCl in 1:3 ratios is called aqua regia and noble metals like gold and platinum dissolve in it. The reactions of $HNO_3$ with some metals and non-metals are summarized in table 15.

**Table 15: Some Reactions of Nitric Acid**

| **Reactant** | **Reaction** | **Remarks** |
|---|---|---|
| M = Mg, Mn | $M + 2HNO_3 \longrightarrow M(NO_3)_2 + H_2$ | Very Dilute Acid |
| M = Zn, Fe, Sn | $4M + 10HNO_3 \longrightarrow 4M(NO_3)_2 + 5H_2O + N_2O$<br>$5M + 12HNO_3 \longrightarrow 5M(NO_3)_2 + N_2 + 6H_2O$<br>$4M + 10HNO_3 \longrightarrow 4M(NO_3)_2 + NH_4NO_3 + 3H_2O$ | Dilute acid<br>(Oxidizing agent)<br>Very dilute acid |
| M = Cu, Bi, Hg, Ag | $3M + 8HNO_3 \longrightarrow 3M(NO_3)_2 + 2NO + 4H_2O$<br>$M + 4HNO_3 \longrightarrow M(NO_3)_2 + 2NO_2 + H_2O$ | Dilute acid<br>Conc. Acid |
| P | $P_4 + 2OHNO_3 \longrightarrow 4H_3PO_4 + 2ONO_2 + 4H_2O$ | Conc. Acid |
| $C_6H_6$ | $C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$ | Conc. Acid<br>Reaction assisted by adding conc. $H_2SO_4$ |

A mixture of concentrated nitric acid and sulphuric acid contains the nitronium ion $NO_2^+$ and is used to nitrate organic compounds.

The major use of nitric acid (~ 75%) is in the manufacture of ammonium nitrate, most of which is used as a fertilizer. Other uses include manufacture of caprolactam (one of the starting materials for synthesis of Nylon), manufacture of industrially useful organic nitro compounds (nitroglycerine, nitrocellulose etc) and manufacture of nitrates for use in explosives, pyrotechnics etc.