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## Some Important Halides of Group 13 and Group 14 Elements

### TYPES OF HALIDES

○ **Ionic or salt-like halides :** Metals having relatively low ionisation energies, form halides which are ionic in nature. Some of the metals, in their lower oxidation states, also give essentially ionic halides. Due to high lattice energies, almost all the metallic fluorides are ionic substances.

  ◆ $AlF_3$ is essentially ionic, $AlCl_3$ dimer has intermediate character.

○ **Covalent or acidic halides :** These halides are given by non-metals, as well as by metals with high charge/size ratio. Examples are $CCl_4$, $NF_3$, $PCl_3$, etc.

○ **Complex halides :** The halides, whose central atom has vacant $p$-orbitals and/or vacant $d$-orbitals can accommodate lone pairs of electrons donated by the halide ions and can thus form complex halide ions. Examples are,
$AlF_6^{3-}$, $GaCl_4^-$, $TiBr_4^-$, $SiF_6^{2-}$, $SnCl_4^{2-}$, $PCl_6^-$, $SbF_5^{2-}$, etc. $F^-$ ion forms stable complex halide ions with smaller cations like $B^{3+}$, $Al^{3+}$, $Si^{4+}$ because of strong electrostatic force and high energies of the resulting bonds.

### HALIDES OF GROUP 13 ELEMENTS (BORON FAMILY)

○ All the elements of group-13 form trihalides ($MX_3$) (except $TlI_3$, which is not known) by direct combination with halogen.
$$2M_{(s)} + 3X_{2(g)} \xrightarrow{\Delta} 2MX_3 \quad (X = F, Cl, Br \text{ or } I)$$

○ All the trihalides of group 13 elements are known except Tl(III) iodide.

○ Due to small size and high electronegativity of boron, all boron halides are covalent in nature and act as Lewis acids. These halides exist as monomeric molecules having planar triangular geometry ($sp^2$ hybridisation).

○ All boron trihalides except $BF_3$, are hydrolysed to boric acid.
$$BX_3 \cdot 3H_2O \longrightarrow B(OH)_3 + 3HX; \quad (X = Cl, Br, I)$$
However, $BF_3$ forms an addition product with water.
$$BF_3 + H_2O \rightleftharpoons H^+[BF_3OH]^- \xrightleftharpoons{H_2O} H_3O^+[BF_3OH]^-$$

Being a Lewis acid and having less tendency for hydrolysis, $BF_3$ is used as a catalyst in organic reactions e.g., Friedel–Crafts reaction.

○ Boron atom, in $BX_3$, has six electrons in the outermost orbit and thus, it can accept a pair of electrons from a donor molecule like $NH_3$ to complete its octet. Hence, boron halides act as very efficient Lewis acids.



Ammonia (electron donor)     Boron trifluoride (electron acceptor)
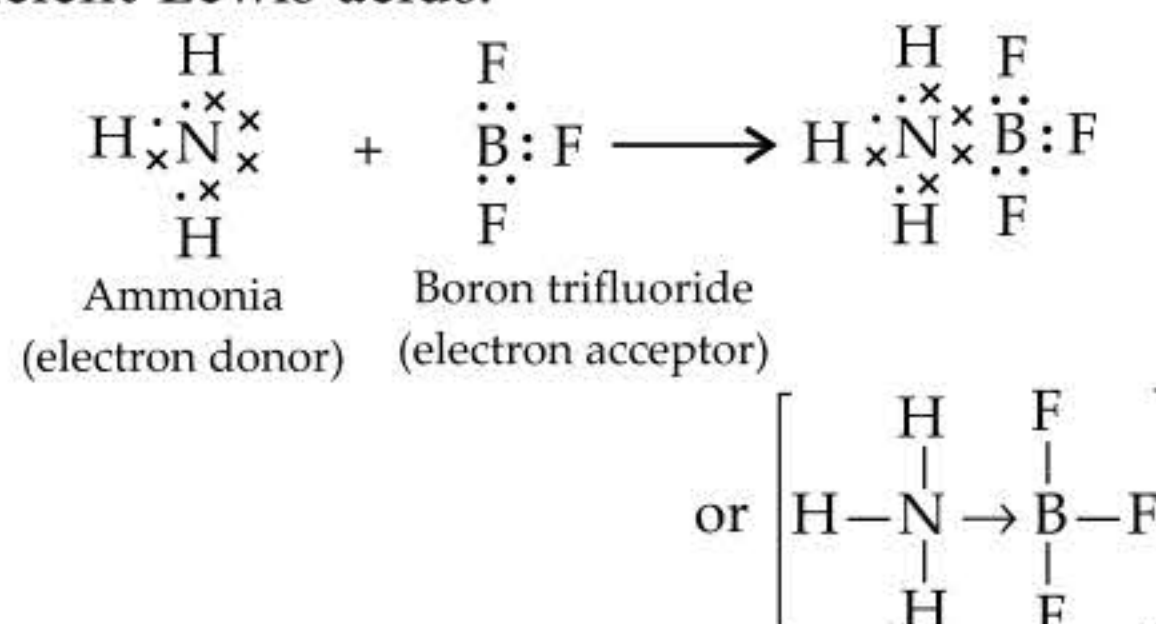
Similarly, $R_2O: + BF_3 \longrightarrow [R_2O \rightarrow BF_3]$

○ The relative Lewis acid characters of boron trihalides are found to obey the order :
$$BI_3 > BBr_3 > BCl_3 > BF_3$$

  ◆ This anomalous behaviour of $BF_3$ has been explained on the basis of the relative tendency of the halogen atom to back-donate its unutilised electrons to the vacant $p$-orbitals of boron atom. In boron trifluoride, each fluorine has completely filled unutilised $2p$-orbitals while boron has a vacant $2p$-orbital. Now since both of these orbitals belong to same energy level ($2p$), they can overlap effectively as a result of which fluorine electrons are transferred into the vacant $2p$-orbital of boron resulting in the formation of an additional $p\pi$-$p\pi$ bond. This type of bond formation is known as **back bonding** or **back donation.**

Completely filled 2p-orbital of fluorine     Vacant 2p-orbital of boron



Back bonding in $BF_3$ molecule
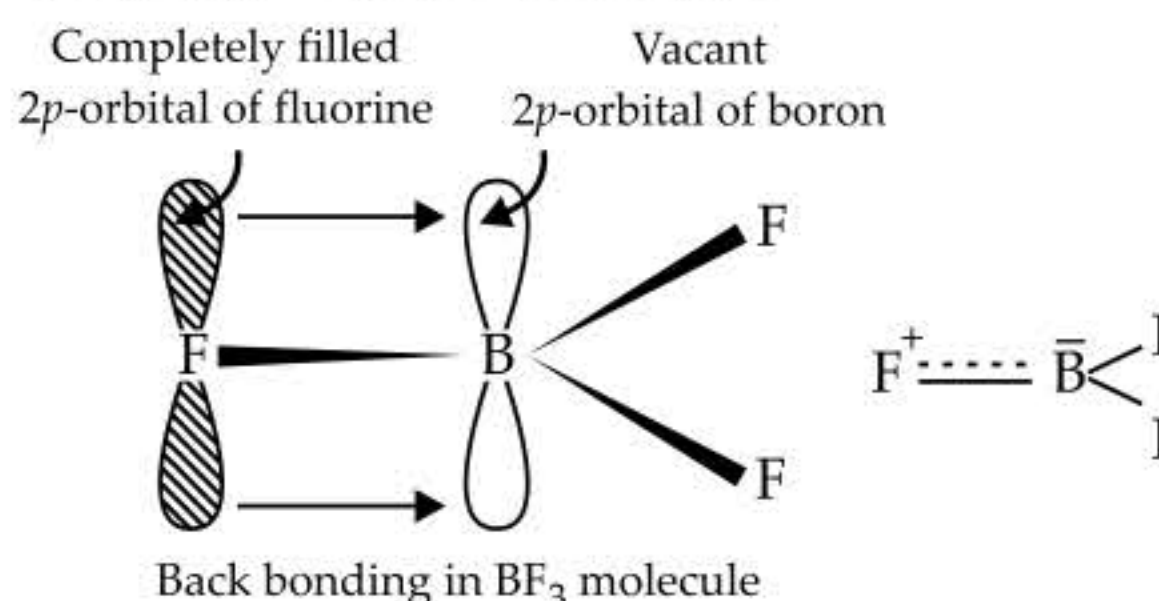
- Thus the B—F bond has some double bond character. Back bonding may take place between boron and any of the three fluorine atoms and thus boron trifluoride is regarded as a resonance hybrid of the following structures :
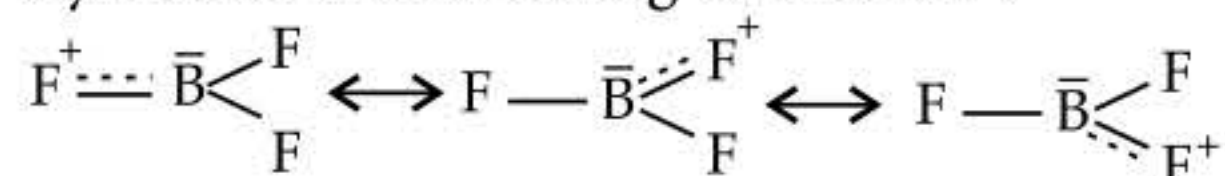


- As a result of back bonding, the electron deficiency of boron is reduced and hence Lewis acidic nature is decreased. The tendency for the formation of back bonding ($p\pi$-$p\pi$ bond) is maximum in $BF_3$ and decreases very rapidly from $BF_3$ to $BI_3$. Thus, $BI_3$, $BBr_3$ and $BCl_3$ are stronger Lewis acids than $BF_3$.

○ Lewis acid character of halides of the group 13 elements decreases in the order :

$$B > Al > Ga > In$$

○ Boron halides form complex halides of the type, $[BF_4^-]$, in which boron atom extends its coordination number to four by utilising empty $p$-orbital. It cannot extend its coordination number beyond four due to non-availability of $d$-orbitals. However, the other trihalides of this group form complex halides of the type $(AlF_6)^{3-}$, $(GaCl_6)^{3-}$ and $(InCl_6)^{3-}$ etc., where the central atom extends its coordination number to six by the use of $d$-orbitals.

○ The fluorides of Al, Ga, In and Tl are ionic and have high melting points.

○ Other halides of Al, Ga, In and Tl are largely covalent in anhydrous state and possess low melting points. These halides do not show backbonding because of increase in the size of the element. However, they make use of vacant $p$-orbitals by coordinate bond i.e., metal atoms complete their octet by forming dimers. Thus, aluminium chloride, aluminium bromide and indium iodide exist as dimers both in the vapour state and in the non-polar solvents.



Dimer structure of $AlCl_3$
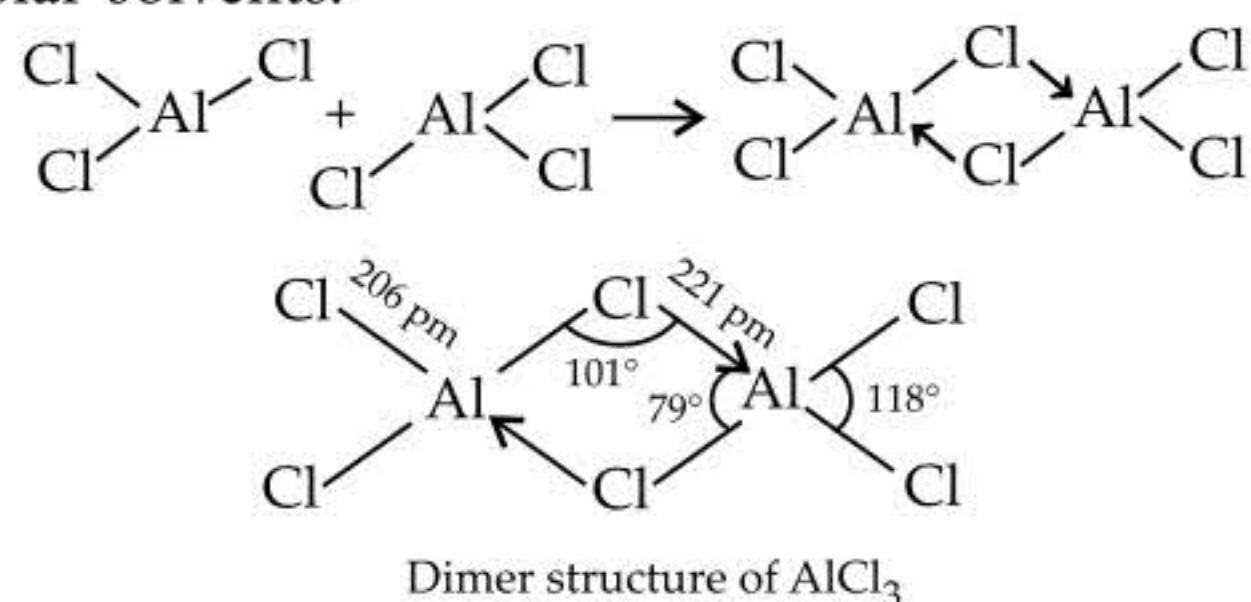
○ The dimer structure for $Al_2Cl_6$ is supported by the following facts :
- Vapour density of aluminium chloride measured at 400°C corresponds to the formula $Al_2Cl_6$.

- Bond distance between Al—Cl bond forming bridge is greater (2.21 Å) than the distance between Al—Cl bond present in the end (2.06 Å).

- The dimeric structure disappears when the halides are dissolved in water. This is due to high heat of hydration which splits the dimeric structure into $[M(H_2O)_6]^{3+}$ and $X^-$ ions and the solution becomes good conductor of electricity.

$$Al_2Cl_6 + 12H_2O \longrightarrow 2[Al(H_2O)_6]^{3+} + 6Cl^-$$

Therefore, $Al_2Cl_6$ is ionic in water.

○ In addition to trihalides, these elements form divalent as well as monovalent halides. Boron also forms $B_2X_4$ which is planar in solid state and non-eclipsed in liquid or vapour state.



(Planar structure)  (Non-eclipsed structure)
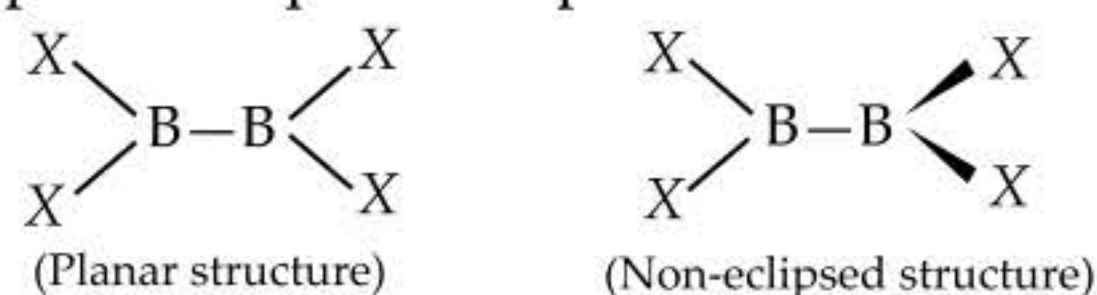
○ Monohalides ($MX$) are formed in gaseous state and they are very unstable halides. They are covalent in nature and covalent character decreases from B to Tl, and thallium halides are ionic in nature.

## BORON HALIDES

○ Boron forms all the trihalides ($BX_3$), where $X$ = F, Cl, Br or I.

**Preparation**

○ By direct combination : Under suitable conditions, boron reacts with halogens to form trihalides ($BX_3$).

$$2B + 3X_2 \longrightarrow 2BX_3$$

○ $BF_3$, an industrial catalyst may be prepared as follows :

$$3CaF_2 + B_2O_3 + 3H_2SO_4 \longrightarrow 2BF_3 + 3CaSO_4 + 3H_2O$$

○ Other boron trihalides (except $BF_3$) are prepared by following reaction :

$$B_2O_3 + 3C + 3X_2 \longrightarrow 2BX_3 + 3CO \ (X_2 = Cl_2, Br_2, I_2)$$

**Properties**

○ Due to small size of $B^{3+}$, these halides are covalent. They are non-electrolytes and do not conduct electricity in liquid state.

○ $BF_3$ is a colourless gas, $BCl_3$ is a colourless fuming liquid (b.pt. = 13°C), while $BI_3$ is a white fusible solid (m.pt. = 310°C).

○ Melting and boiling points of halides of boron ($BX_3$) decrease in the order :

$$BI_3 > BBr_3 > BCl_3 > BF_3$$

○ Boron halides (except $BF_3$) are readily hydrolysed in water.

○ Aqueous non-oxidising acids like HF, HCl and HI do not react even with colloidal boron but anhydrous HF reacts exothermically and forms $BF_3$.
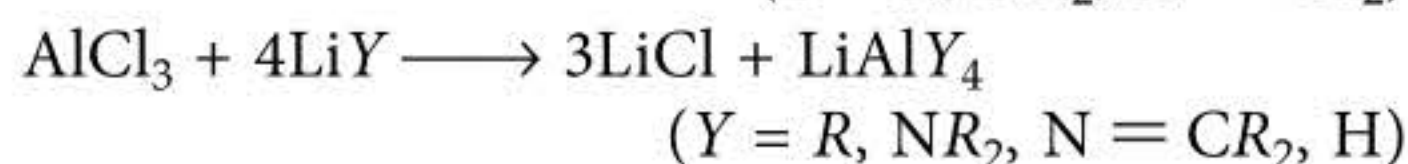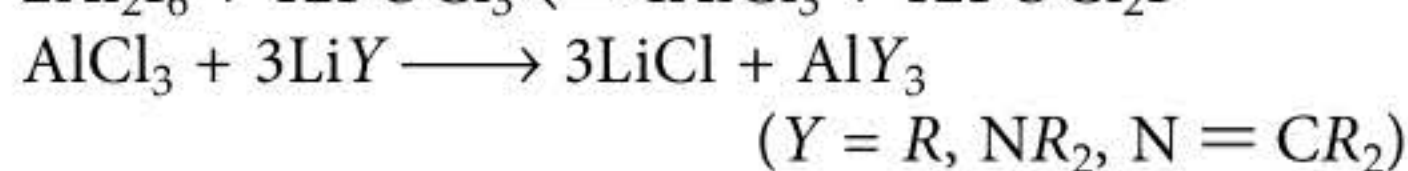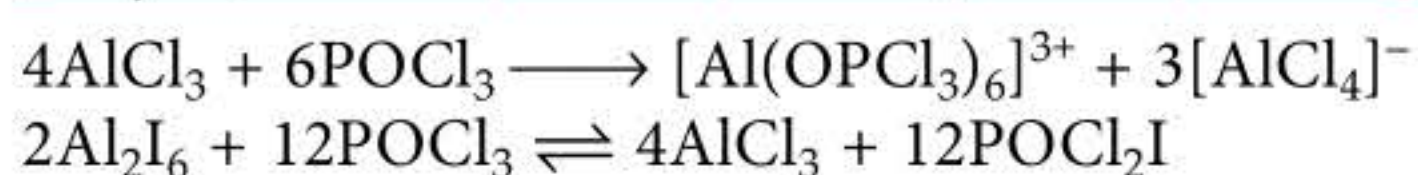
## ALUMINIUM TRIHALIDES

### Preparation

○ $AlF_3$ is made by treating $Al_2O_3$ with HF gas at 700°C and the other trihalides are made by the direct exothermic combination of the elements.

### Properties of crystalline $AlX_3$

○ $AlF_3$ differs from the other trihalides of Al in being non-volatile, insoluble, and in having a much greater heat of formation.

| Property | $AlF_3$ | $AlCl_3$ | $AlBr_3$ | $AlI_3$ |
|----------|---------|----------|----------|---------|
| m.pt./°C | 1290 | 192.4 | 97.8 | 189.4 |
| Sublimation pt. (1 atm)/°C | 1272 | 180 | 256 | 382 |
| $\Delta H_f^\circ$/kJ mol$^{-1}$ | 1498 | 707 | 527 | 310 |

$4AlCl_3 + 6POCl_3 \longrightarrow [Al(OPCl_3)_6]^{3+} + 3[AlCl_4]^-$

$2Al_2I_6 + 12POCl_3 \rightleftharpoons 4AlCl_3 + 12POCl_2I$

$AlCl_3 + 3LiY \longrightarrow 3LiCl + AlY_3$
$$(Y = R, NR_2, N = CR_2)$$

$AlCl_3 + 4LiY \longrightarrow 3LiCl + LiAlY_4$
$$(Y = R, NR_2, N = CR_2, H)$$

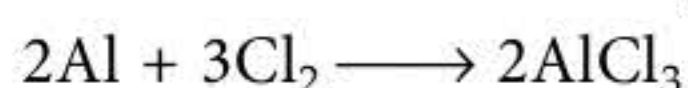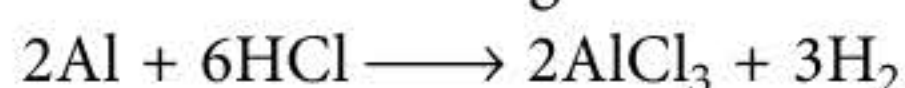Similarly, NaOR reacts to give $Al(OR)_3$ and $NaAl(OR)_4$. $AlCl_3$ also converts non-metal fluorides into the corresponding chlorides, e.g.,

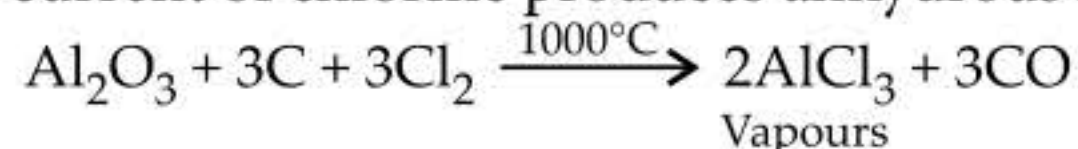$BF_3 + AlCl_3 \longrightarrow AlF_3 + BCl_3$

## ALUMINIUM CHLORIDE, $AlCl_3$

### Preparation

○ **Anhydrous aluminium chloride :** It is prepared by passing dry HCl gas or chlorine gas over heated aluminium turnings in the absence of air.

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

$2Al + 3Cl_2 \longrightarrow 2AlCl_3$

◆ A mixture of alumina and carbon on heating in a current of chlorine produces anhydrous $AlCl_3$.

$Al_2O_3 + 3C + 3Cl_2 \xrightarrow{1000°C} 2AlCl_3 + 3CO$
Vapours
$\downarrow$ cooled
Solid anhydrous aluminium chloride

○ **Hydrated aluminium chloride :** $AlCl_3 \cdot 6H_2O$ is ionic and formed when aluminium metal or aluminium hydroxide is dissolved in dilute hydrochloric acid.

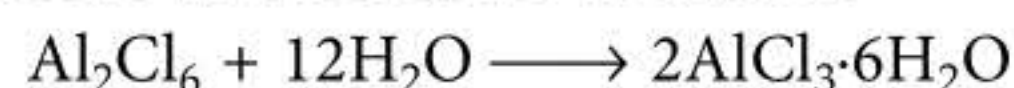$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$

$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$
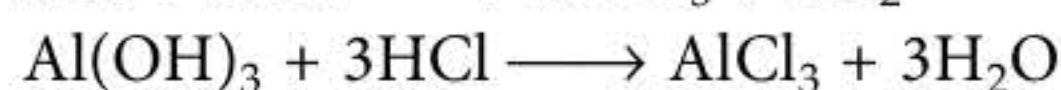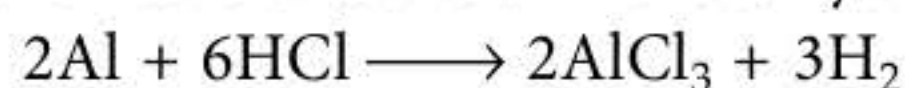
### Chemical nature

○ Anhydrous aluminium chloride fumes in moist air due to the evolution of HCl.

$Al_2Cl_6 + 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl$
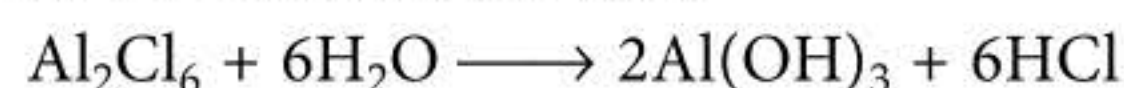
In water, it converts into hydrated aluminium chloride which is ionic in nature.

$Al_2Cl_6 + 12H_2O \longrightarrow 2AlCl_3 \cdot 6H_2O$

○ Anhydrous aluminium chloride forms an addition product with ammonia gas.

$Al_2Cl_6 + 12NH_3 \longrightarrow 2[AlCl_3 \cdot 6NH_3]$

○ When ammonium hydroxide $NH_4OH$ is added to the solution of aluminium chloride, a gelatinous precipitate of aluminium hydroxide appears which does not dissolve in excess of $NH_4OH$.

$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3\downarrow + 3NH_4Cl$
gelatinous ppt.
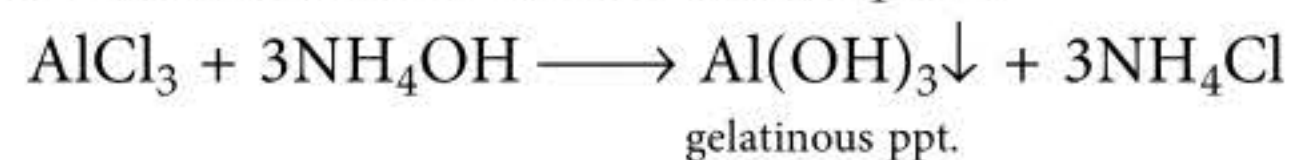
○ When sodium hydroxide (NaOH) is added to the solution of aluminium chloride drop by drop, a white gelatinous precipitate forms which dissolves in excess of sodium hydroxide forming sodium meta aluminate.

$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3\downarrow + 3NaCl$
gelatinous ppt.

$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$
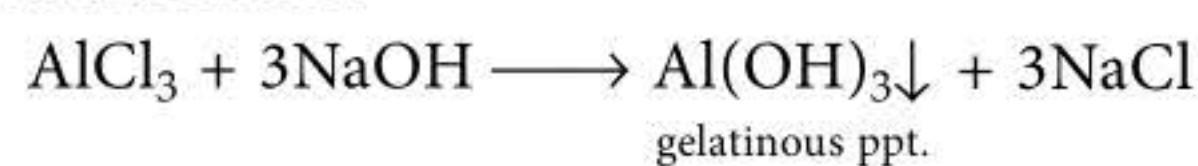
## HALIDES OF GROUP 14 ELEMENTS (CARBON FAMILY)

○ Group-14 elements form covalent tetrahalides of the type $MX_4$ having tetrahedral nature, except $PbBr_4$ and $PbI_4$. The non-existence of $PbBr_4$ and $PbI_4$ is due to the fact that $Pb^{4+}$ ion is a strong oxidising agent while $Br^-$ and $I^-$ ions are strongly reducing agents. Thus, $Pb^{4+}$ ion cannot survive in presence of $Br^-$ or $I^-$ ion and is reduced to $Pb^{2+}$ ion.

$Pb^{4+} + 2Br^- \longrightarrow Pb^{2+} + Br_2$

○ Except carbon, all other elements of group-14 also form dihalides such as $MX_2$. The stability of divalent halides increases down the group in accordance with inert pair effect.

○ The order of thermal stability of tetrahalides is :
$CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$

◆ The thermal stability and volatility of tetrahalides with a common central atom decreases with the increase in molecular weight of the tetrahalides i.e.,

$MF_4 > MCl_4 > MBr_4 > MI_4$

i.e., $CF_4 > CCl_4 > CBr_4 > CI_4$
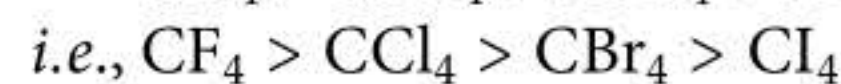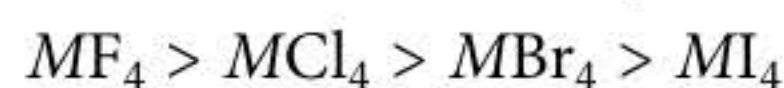
This is due to the decrease in the C — X bond energies from C — F to C — I.

- The tetrahalides (except carbon halides) are readily hydrolysed by water. The trend towards hydrolysis decreases down the group. Thus, silicon tetrachloride $SiCl_4$, fumes in moist air liberating hydrogen chloride.

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{Silicic acid}}{Si(OH)_4} + 4HCl$$
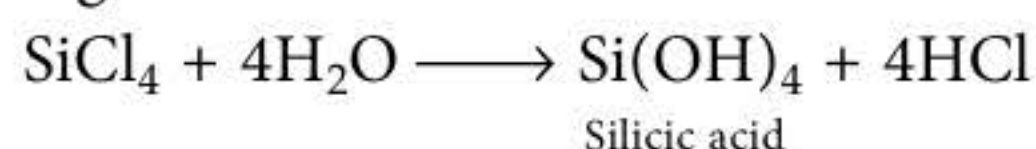
- Since carbon has no $d$-orbital, it cannot extend its coordination number beyond four, so its halides are not attacked (hydrolysed) by water. On the other hand, silicon and other elements of this group have vacant $d$-orbitals to which water molecules can coordinate and hence, their halides are hydrolysed by water.

- Due to the presence of vacant $d$-orbitals Si, Ge, Sn and Pb also form hexahaloanions of type $[MX_6]^{2-}$, in which atom is hexacoordinated ($M$ = Si, Ge, Sn or Pb).

- The tetrahalides of carbon, on the other hand, do not form any complex ion because carbon has no $d$-orbital to accommodate any more electrons from the ligand (donor) like $X^-$.

## HALIDES OF TIN

- **Stannous fluoride, $SnF_2$** : It is obtained by reacting SnO with HF.

$$SnO + 2HF \longrightarrow SnF_2 + H_2O$$

- **Stannic fluoride, $SnF_4$** : It can be prepared by gently heating $SnCl_4$ with excess of HF, until no more HCl is liberated.

$$SnCl_4 + 4HF \longrightarrow SnF_4 + 4HCl$$

## STANNOUS CHLORIDE, $SnCl_2$

### Preparation

- Tin reacts with hot concentrated HCl to give hydrated $SnCl_2 \cdot 2H_2O$.

- Anhydrous $SnCl_2$ is formed when dry HCl gas is heated over tin or by heating a mixture of Sn and calculated quantity of mercuric chloride.

$$Sn + 2HCl_{(gas)} \longrightarrow SnCl_2 + H_2$$
$$Sn + HgCl_2 \longrightarrow SnCl_2 + Hg$$
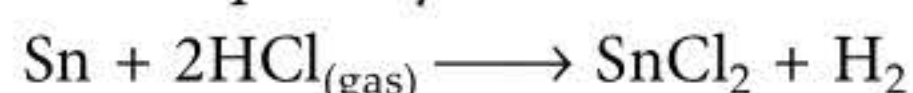
- Anhydrous salt cannot be obtained by heating the hydrated salts. On heating hydrolysis is noticed with the formation of a white solid (tin hydroxy chloride).
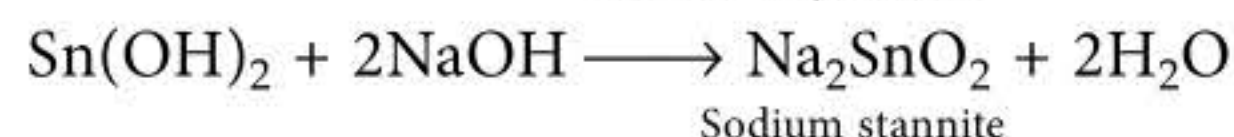
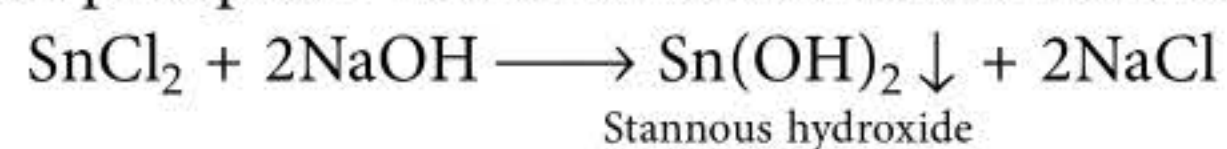$$SnCl_2 \cdot 2H_2O \longrightarrow Sn(OH)Cl + H_2O + HCl$$
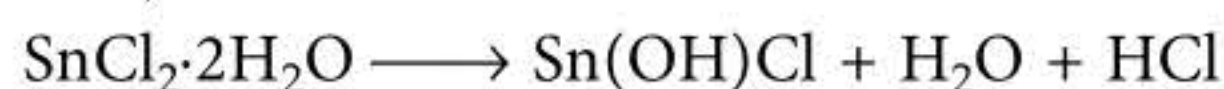
### Physical properties

- It is a white crystalline solid, soluble in water, alcohol and ether.

- In water, it is hydrolysed readily. But, in presence of HCl, hydrolysis is reversed.

### Chemical properties

- Reaction with alkalies : It reacts with NaOH, forms a white precipitate which dissolves in excess of alkali.

$$SnCl_2 + 2NaOH \longrightarrow \underset{\text{Stannous hydroxide}}{Sn(OH)_2\downarrow} + 2NaCl$$
$$Sn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sodium stannite}}{Na_2SnO_2} + 2H_2O$$

- Reaction with $H_2S$ : It reacts with $H_2S$ to give a dark brown ppt. of SnS. This precipitate is soluble in yellow ammonium sulphide, $(NH_4)_2S_2$, due to the formation of ammonium thiostannate $(NH_4)_2[SnS_3]$.

$$SnCl_2 + H_2S \longrightarrow \underset{\text{dark brown ppt.}}{SnS\downarrow} + 2HCl$$
$$SnS + \underset{\substack{\text{Yellow ammonium}\\\text{sulphide}}}{(NH_4)_2S_2} \longrightarrow \underset{\substack{\text{Ammonium}\\\text{thiostannate}}}{(NH_4)_2SnS_3}$$
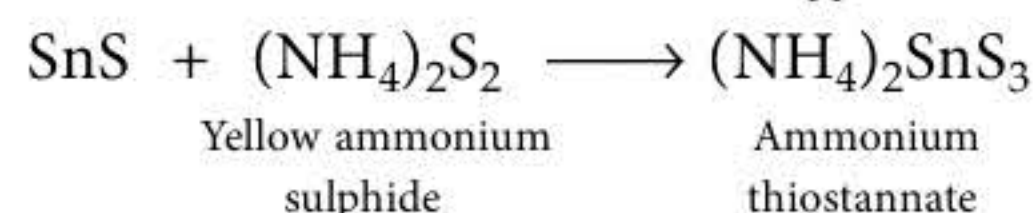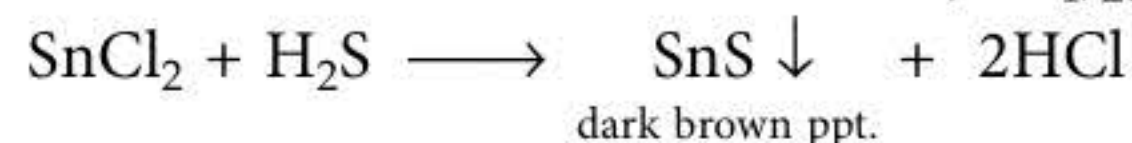
- Reducing properties : $SnCl_2$ acts as a strong reducing agent.

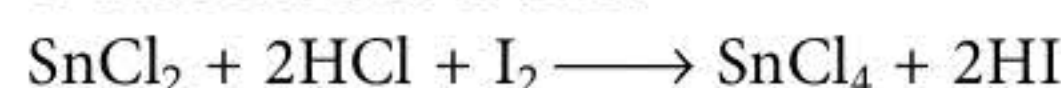  ◆ $SnCl_2$ reduces $HgCl_2$ to $Hg_2Cl_2$ (white ppt.) and finally to metallic Hg.

$$2Hg^{2+} + Sn^{2+} \longrightarrow Hg_2^{2+} + Sn^{4+}$$
$$Hg_2^{2+} + Sn^{2+} \longrightarrow 2Hg\downarrow + Sn^{4+}$$

  ◆ It reduces ferric salts to ferrous salts and cupric salts to cuprous salts.

$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$
$$2Cu^{2+} + Sn^{2+} \longrightarrow 2Cu^+ + Sn^{4+}$$

  ◆ It reduces —$NO_2$ group is to —$NH_2$ group.

$$3SnCl_2 + \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6HCl \longrightarrow$$
$$3SnCl_4 + \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$
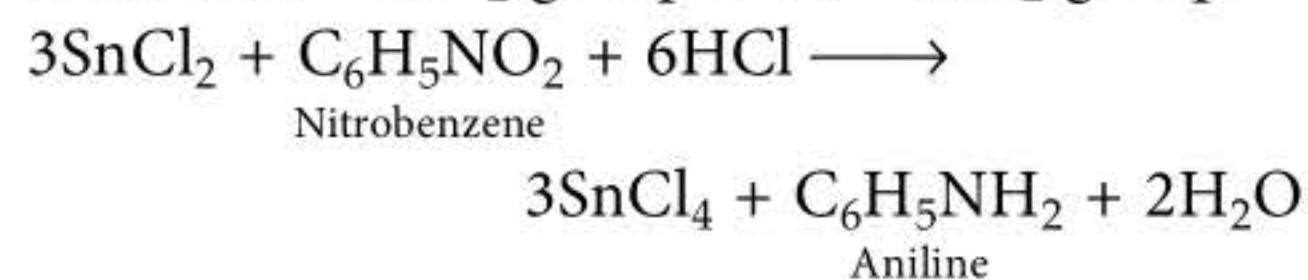
  ◆ It decolourises iodine.

$$SnCl_2 + 2HCl + I_2 \longrightarrow SnCl_4 + 2HI$$

  ◆ It reduces gold chloride to metallic gold sol (Purple of Cassius).

$$3SnCl_2 + 2AuCl_3 \longrightarrow \underset{\text{Colloidal gold}}{2Au} + 3SnCl_4$$
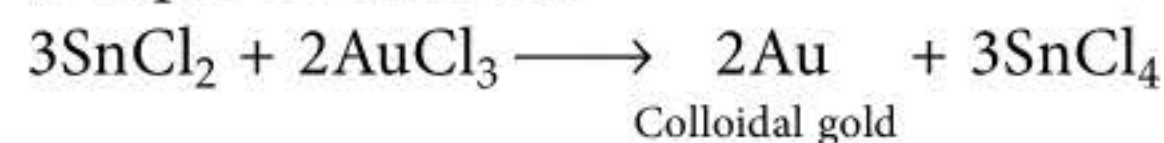
| EXAM DATES 2017 | |
|---|---|
| Karnataka CET | 2nd May (Biology & Mathematics) |
| | 3rd May (Physics & Chemistry) |
| NEET | 7th May |
| MHT CET | 11th May |
| COMEDK (Engg.) | 14th May |
| BITSAT | 16th May to 30th May (Online) |
| JEE Advanced | 21st May |
| J & K CET | 27th May to 28th May |
| AIIMS | 28th May |
| JIPMER | 4th June |

## STANNIC CHLORIDE, SnCl$_4$

○ SnCl$_4$·5H$_2$O, is known as "butter of tin" or "oxymuriate of tin".

SnCl$_4$ is obtained by :

◆ Hydrolysis :

$$SnCl_4 + 4H_2O \longrightarrow \underset{\text{Stannic hydroxide}}{Sn(OH)_4} + 4HCl$$

◆ Reaction with conc. HCl :

$$SnCl_4 + 2HCl \longrightarrow \underset{\text{Chlorostannic acid}}{H_2SnCl_6}$$

◆ **Reaction with NH$_4$Cl :**

$$SnCl_4 + 2NH_4Cl \longrightarrow (NH_4)_2SnCl_6$$
Ammonium chlorostannate
(pink, used as mordant in
dyeing under the name pink salt)
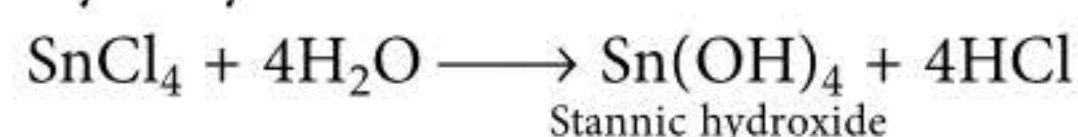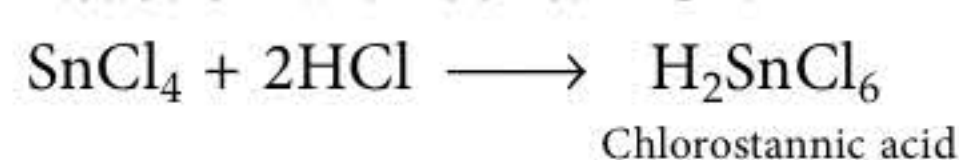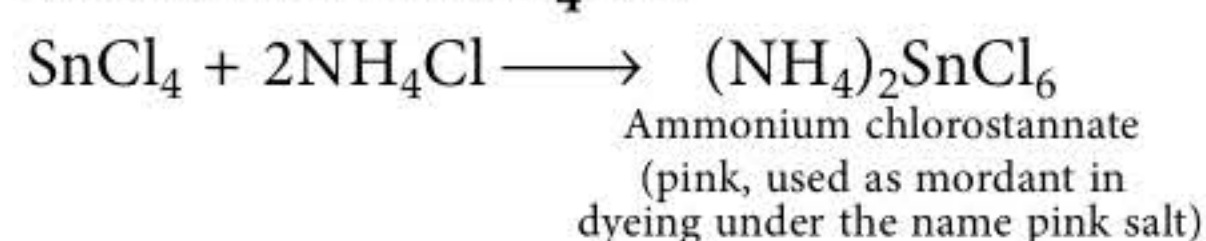
## HALIDES OF LEAD

### LEAD DIFLUORIDE, PbF$_2$

**Preparation**

○ It is formed :

◆ as a white ppt. when a soluble fluoride is added to a lead salt solution.

◆ by the action of HF on PbO or Pb(CO$_3$)$_2$.

**Properties**

○ It is a white powder with melting point 818°C.

### LEAD TETRAFLUORIDE, PbF$_4$

**Preparation**

○ Passing F$_2$ over PbF$_2$ above 250°C.

$$PbF_2 + F_2 \xrightarrow{250°C} PbF_4$$

○ By dissolving red lead or freshly prepared PbO$_2$ in BrF$_3$.

$$3PbO_2 + 4BrF_3 \longrightarrow 3PbF_4 + 2Br_2 + 3O_2$$

### LEAD CHLORIDE OR PLUMBOUS CHLORIDE, PbCl$_2$

**Preparation**

○ By adding HCl to aqueous solution of lead nitrate.

$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2\downarrow + 2HNO_3$$

**Properties**

○ It is a white crystalline solid, slightly soluble in cold water but completely soluble in hot water.

○ It is fairly soluble in concentrated hydrochloric acid forming chloroplumbic acid.

$$PbCl_2 + 2HCl \longrightarrow H_2PbCl_4$$
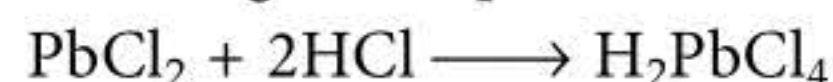
### LEAD TETRACHLORIDE OR PLUMBIC CHLORIDE, PbCl$_4$

**Preparation**

○ It is prepared by dissolving lead dioxide in a well-cooled hydrochloric acid.

$$PbO_2 + 4HCl \rightleftharpoons PbCl_4 + 2H_2O$$
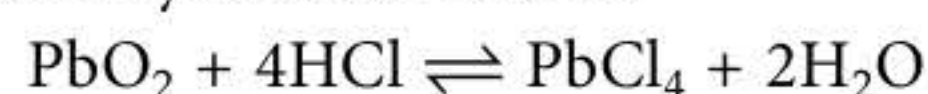
**Properties**

○ It is only slightly stable.

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

○ It is decomposed by excess of water.

○ It forms a double chloride with ammonium chloride known as ammoniumplumbichloride or ammoniumchloroplumbate, (NH$_4$)$_2$PbCl$_6$. Although the later compound is fairly stable, when treated with sulphuric acid it decomposes back to lead tetrachloride.

$$[(NH_4)_2PbCl_6] + H_2SO_4 \longrightarrow$$
$$(NH_4)_2SO_4 + PbCl_4 + 2HCl$$
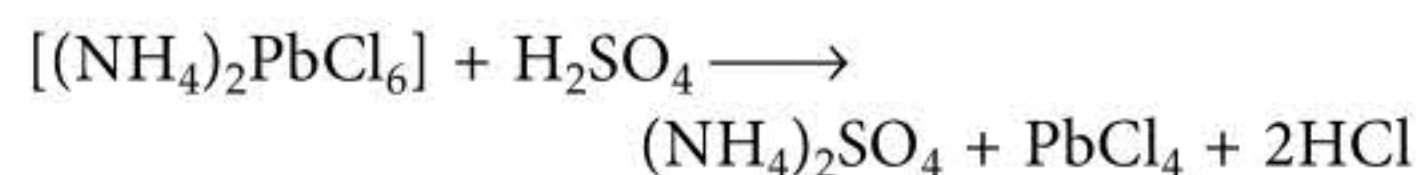
### LEAD DIIODIDE, PbI$_2$

○ It is formed :

◆ by dissolving lead, its oxide or carbonate in HI.

◆ by adding a soluble iodide to a lead salt solution. It forms golden-yellow crystals with melting point 402°C and boiling point 872°C. On heating it first turns brick red and then brown red but regains its original colour on cooling. It dissolves in a large excess of KI forming K[PbI$_3$] which is decomposed on dilution with water depositing PbI$_2$ again.

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