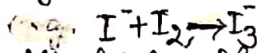


⇒ What are Polyhalides?

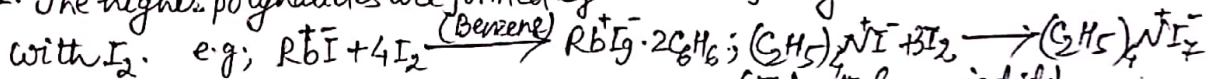
Salts containing mononegative anions consisting of a central halogen joined to other halogen atoms are known as Polyhalides. Polyhalide anions of the types  $X_n^-$ ,  $XX_n^-$  &  $XX'_n^-$  have been characterized and the majority of the compounds have I (Iodine) as the central atom. The first type ( $X_n^-$ ) includes  $Cl_3^-$ ,  $Br_3^-$ ,  $I_3^-$ ,  $I_5^-$ ,  $I_7^-$  &  $I_9^-$ ; of these  $I_3^-$  is by far the most common and stable anion. The  $Br_3^-$  ion is much less stable than  $I_3^-$  and only a few unstable  $Cl_3^-$  compounds are known.  $NOF_3^-$  compounds are known presumably because F has no available d-orbitals and therefore cannot expand its octet. Polyhalides of second type ( $XX_n^-$ ) includes  $ICl_2^-$ ,  $IBr_2^-$ ,  $ClBr_2^-$ ,  $ICl_4^-$ ,  $BrF_4^-$ ,  $IF_6^-$  etc. and majority of  $XX_n^-$  anions have a central iodine atom. The second only known polyhalides of the third type ( $XX'_n^-$ ) are  $FIBr^-$ ,  $ClIBr^-$  &  $FICl_3^-$ .

\* Preparation: Polyhalides are prepared by a number of methods:

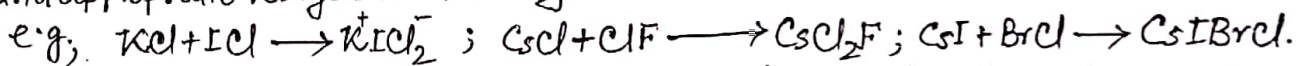
1. By the reaction of  $I^-$  (iodide) and requisite amount of  $I_2$  (iodine) with/without a solvent.



2. The higher polyhalides are formed by reaction of larger cation such as  $R_6^+$ ,  $NR_4^+$  etc.



3. Polyhalides containing different halogens are prepared by reaction between metal halide and appropriate halogen or interhalogen in absence of a solvent.



\* Properties: 1. Most polyhalides are low melting coloured solids, the colour varies from yellow to black

2. They are soluble in solvents of high dielectric constant, e.g. water

3. They are typically ionic compounds, so dissociate in solution or on heating into a simple halide and a halogen or interhalogen: e.g,  $KI_3 \xrightarrow{\Delta} KI + I_2$ ;  $KBrCl \xrightarrow{\Delta} KCl + IBr$ .

4. A more electronegative halogen may replace a less electronegative/less reactive one in a polyhalide. e.g;  $KIBr_2 + Cl_2 \rightarrow KICl_2 + Br_2$

5. A more electropositive halogen may replace a less electropositive one in a polyhalide e.g;  $MBr_3 + I_2 \rightarrow MI_2 + IBr$ .

6. A halogen may be added directly to a polyhalide e.g;  $KICl_2 + Cl_2 \rightarrow KICl_4$

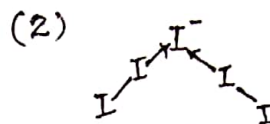
7. Polyhalides may dissolve in liquid halogen or interhalogen to yield solutions, from which the original polyhalide may be crystallized on evaporation. The polyhalides  $KIBr_2$ ,  $NH_4IBr_2$  &  $RbIBr_2$  form such solutions in bromine ( $Br_2$ ).

\* Structure & Bonding: The structures of polyhalides are known. In the polyhalides, the heaviest (high atomic mass) halogen acts as the central atom and the other halogen atoms are symmetrically arranged around it. Generally, the central halogen utilizes d-orbitals in its valency shell to form covalent ( $\sigma$ ) bonds with the other halogens in the polyhalide ion.

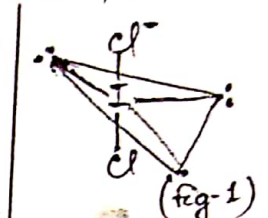
The  $I_3^-$  has the linear structure ( $I \cdots I - I$ ).  $I_5^-$ ,  $I_7^-$ ,  $I_8^-$  &  $I_9^-$  are loose aggregates  $I_5^-$  is believed to consist of two iodine molecules weakly coordinated to  $I^-$  ion.



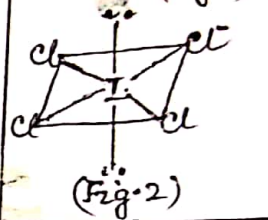
It is planar and V-shaped.



The trihalides (e.g.,  $KI_3$ ,  $KICl_2$ ,  $CsIBrF$ ) all contain a linear trihalide ion with the iodine acting as the central atom. Iodine is believed to be  $sp^3d$  hybridised in these ions. Cl & Br atoms lie at the two apexes of a trigonal bipyramid and three lone pairs of electrons in the equatorial plane. (Fig. 1)



Polyhalide ions, e.g.,  $ICl_4^-$ ,  $BrF_4^-$  etc. containing five halogen atoms are all square planar, except  $IF_4^-$ , which appears to have cis configuration for the two unpaired electrons. Thus,  $ICl_4^-$  is planar, the central I-atom being  $sp^3d^2$  hybridised.  $I_{53}$ :  $5s^2 5p_x^2 5p_y^1 5p_z^1 5d_{x^2-y^2}^1 5d_{z^2}^0$



In  $6 sp^3d^2$  hybrid orbitals, two have paired electrons (as lone pairs), three have unpaired electron overlap with  $2p_z$  orbital of Cl-atom forming  $\sigma$ -bond (I-Cl) and one  $sp^3d^2$  hybrid orbital vacant overlap with filled  $2p_z$  orbital of  $Cl^-$  to form  $I^{\ominus}-Cl^{\ominus}$  bond (Fig. 2).

⇒ What are Pseudo halogens?

A group of electronegative anions containing two or more electronegative atoms which in the free state show similarity to the halogens are called Pseudohalogens. They are also called halogenoids. The more important pseudohalogens are Cyanogen,  $(CN)_2$ ; thiocyanogen,  $(SCN)_2$ ; selenocyanogen,  $(SeCN)_2$  & Azidocarbonyl sulphide,  $(SCSN_3)_2$ . The best known example is Cyanogen,  $(CN)_2$ .

\* Resemblances of Pseudohalogens with halogens:

The pseudohalogens resemble halogens in the following respects:

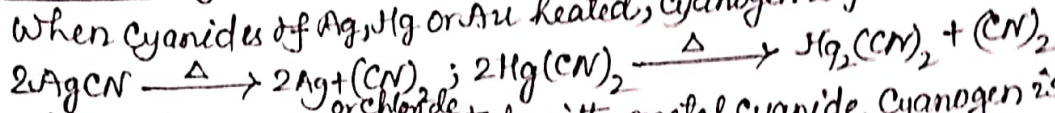
1. Pseudohalogens like halogens are dimeric and fairly volatile in the free state.
2. They combine like halogens with hydrogen to form monobasic acids, which are generally strong acid in aqueous solutions. e.g.,  $(CN)_2 + H_2 \rightarrow 2HCN$  (Cyanogen) (Hydrogen cyanide) (Hydrocyanic acid);  $Cl_2 + H_2 \rightarrow 2HCl$  (Chlorine) (Hydrogen chloride) (Hydrochloric acid)
3. They form insoluble salts with  $Ag^+$ ,  $Pb^{2+}$  &  $Hg_2^{2+}$ . Hydrocyanic acid
4. They form a large number of complexes similar to halide complexes. e.g.,  $[Cu(CN)_4]^{2-}$  &  $[CuCl_4]^{2-}$ ;  $[Co(CN)_6]^{3-}$  &  $[CoCl_6]^{3-}$ .
5. They react with alkalis just like the halogens. e.g.,  $(CN)_2 + 2KOH \xrightarrow{\text{Cold, Dilute}} KCN + KOCN + H_2O$  (Pot. cyanide) (Pot. hypocyanide);  $Cl_2 + 2KOH \xrightarrow{\text{Cold, Dilute}} KCl + KOCl + H_2O$  (Potassium hypochlorite)
6. Some pseudohalogens, like halogens add to an ethylenic bond to form addition compd. e.g.,  $H_2C=CH_2 + (SCN)_2 \rightarrow H_2C(SCN)-CH_2(SCN)$ ;  $H_2C=CH_2 + Br_2 \rightarrow H_2C(Br)-CH_2(Br)$ .
7. Pseudohalogens, like halogens are oxidising agents. The oxidising power of the halogens and pseudohalogens decrease in the following order:  $F_2 > Cl_2 > Br_2 > (CN)_2 > (SCN)_2 > I_2 > (SeCN_3)_2 > (SeCN)_2 \dots$
8. They can form inter halogenoid compounds, e.g.  $CNSeCN$ ,  $CNSeCN$ ,  $CNSeCN_3$  etc. and mixed halogen pseudo halogen compounds, e.g.  $CNCl$ ,  $CNBr$ ,  $ClN_3$ ,  $SCNCl_2$  etc.
9. They combine with various metals like halogens to give salts containing pseudohalide anion.
10. Pseudohalogens, unlike halogens undergo polymerization. e.g.  $x(CN)_2 \xrightarrow{500^\circ C} 2(CN)_x$ ;  $x(SCN)_2 \rightarrow 2(SCN)_x$

(3)

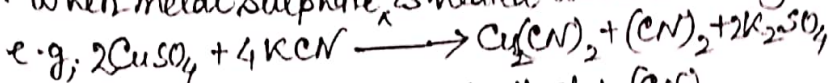
⇒ Cyanogen, (CN)<sub>2</sub>: It is best known pseudohalogen.

\* Preparation: Cyanogen may be prepared by different methods as given below:

1. When cyanides of Ag, Hg or Au heated, cyanogen is formed.



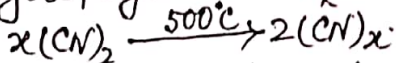
2. When metal sulphate or chloride is heated with metal cyanide, cyanogen is formed.



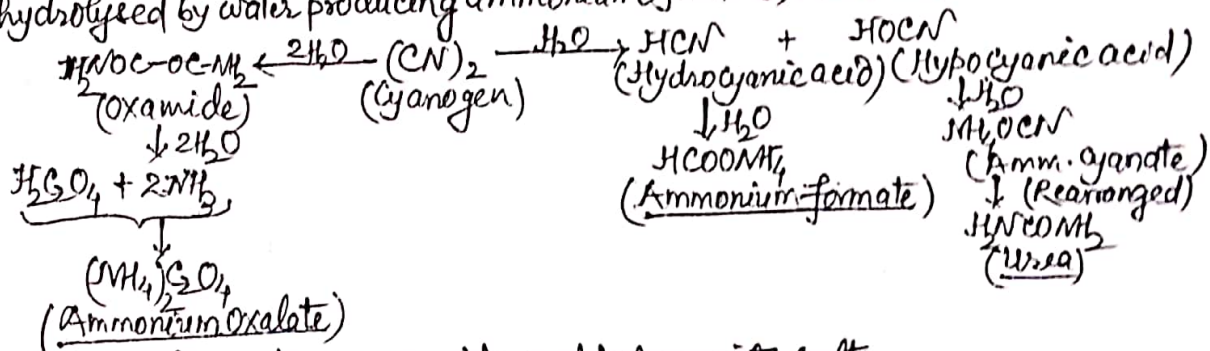
\* Properties: 1. It is a colourless poisonous gas, soluble in water.

2. It readily condenses to a liquid (boiling point = -21.2°C) and freezes to a solid (melting point = -27.9°C)

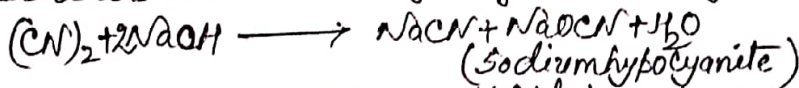
3. It undergoes polymerization at 500°C to insoluble paracyanogen, (CN)<sub>x</sub>.



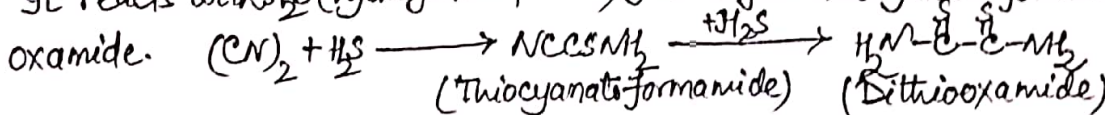
4. It get hydrolysed by water producing ammonium formate, urea and amm. oxalate.



5. It reacts with alkalis to give cyanide and hypocyanite salts.



6. It reacts with H<sub>2</sub>S (hydrogen sulphide) gas to give thiocyanato formamide and dithio oxamide.



\* Structure: Brockway (1933) from electron diffraction studies shown that cyanogen, (CN)<sub>2</sub> has a resonance structure. The most important and stable cononical form being N≡C-C≡N. This structure is in agreement with the parachor measurements and low value of the dipolement of it.