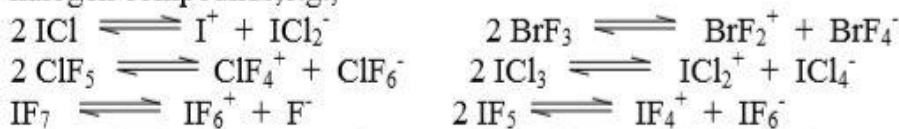


Polyhalides:

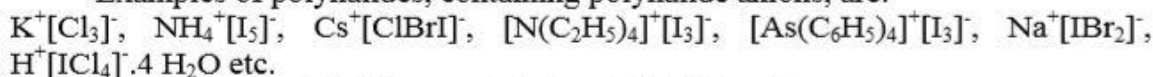
The ions (cations or anions) composed of similar halogen atoms (e.g., Cl_2^+ , Br_2^+ , I_5^+ etc.) or dissimilar halogen atoms (e.g., ICl_2^+ , IBrCl^- etc.) are called polyhalide ions. These ions may be regarded as positively or negatively charged inter-halogen ions.

The ionic compounds containing either polyhalide cations or polyhalide anions are called Polyhalides.

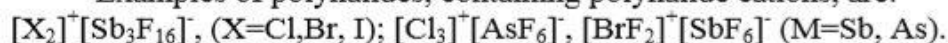
The formation of these ions observed during self-ionization of some inter-halogen compounds, e.g.,



Examples of polyhalides, containing polyhalide anions, are:



Examples of polyhalides, containing polyhalide cations, are:



Iodine has maximum tendency to form polyhalide ions. Cl, Br and I-atoms can form triatomic anions, while F-atom is not able to form F_3^- ion.

Preparation:

- i. By direct action of halogen on metallic halides or on other polyhalide.
$$\begin{array}{l} \text{Cl}_2 + \text{KCl} \rightarrow \text{K}[\text{Cl}_3]; \qquad \text{Br}_2 + \text{KBr} \rightarrow \text{K}[\text{Br}_3] \\ \text{I}_2 + \text{KI} \rightarrow \text{K}[\text{I}_3] \qquad 2 \text{I}_2 + \text{NH}_4\text{I} \rightarrow \text{NH}_4[\text{I}_5] \\ \text{Cl}_2 + \text{K}[\text{ICl}_2] \rightarrow \text{K}[\text{ICl}_4]; \qquad \text{Cl}_2 + \text{K}[\text{IBr}_2] \rightarrow \text{K}[\text{ICl}_2] + \text{Br}_2 \end{array}$$
- ii. By the action of inter-halogens on metals, metallic halides or other polyhalides.
$$\begin{array}{l} 4 \text{BrF}_3 + 3 \text{K} \rightarrow 3 \text{K}[\text{BrF}_4] + \frac{1}{2} \text{Br}_2 \\ \text{ICl} + \text{MCl} (\text{M}=\text{K}, \text{Rb}, \text{NH}_4^+) \rightarrow \text{M}[\text{ICl}_2]; \quad \text{ICl} + \text{KCl} \rightarrow \text{K}[\text{ICl}_2] \\ \text{ICl} + \text{KBr} \rightarrow \text{K}[\text{ClBrI}]; \qquad \text{BrCl} + \text{CsI} \rightarrow \text{Cs}[\text{IBrCl}] \\ \text{BrF}_3 + \text{MF} (\text{M}=\text{Li}, \text{K}, \text{Ag}) \rightleftharpoons \text{M}[\text{BrF}_4]; \\ \text{ClF}_5 + \text{AsF}_5 \rightarrow [\text{ClF}_4]^+[\text{AsF}_6]^- \\ \text{IF}_7 + \text{MF}_5 (\text{M}=\text{As}, \text{Sb}) \rightarrow [\text{IF}_6]^+[\text{MF}_6]^- \\ \text{ICl} + \text{K}[\text{ClBrI}] \rightarrow \text{K}[\text{ICl}_2] + \text{IBr} \end{array}$$
- iii. By action of I_2 or Cl_2 on solution of metallic chlorides in HCl.
$$\text{I}_2 + 3 \text{Cl}_2 + 2 \text{MCl} (\text{Li}, \text{Na}) \rightarrow 2 \text{M}^+[\text{ICl}_4]^-$$
- iv. $\text{I}_2 + \text{Cl}_2 + 2 \text{RbCl} (\text{in HCl}) \rightarrow 2 \text{Rb}^+[\text{ICl}_2]^-$
By action of an appropriate gaseous halogen on metallic halide in absence of solvent.
$$\text{F}_2 + \text{CsCl} \rightarrow \text{Cs}[\text{ClF}_4]$$
- v. I_2 dissolve in highly acidic oxidizing media to give I_2^+ ion. The salts of X_2^+ are best prepared by action of $\text{S}_2\text{O}_6\text{F}_2$ on X_2 molecule and then SbF_5 is added.
$$\text{X}_2 + \text{S}_2\text{O}_6\text{F}_2 (\text{then add SbF}_5) \rightarrow [\text{X}_2]^+[\text{Sb}_3\text{FI}_6]^-$$
- vi. Salts of X_3^+ ions can be prepared by a number of methods. For example:
$$2 \text{I}_2 + \text{ICl} + \text{AlCl}_3 \rightarrow [\text{I}_5]^+[\text{AlCl}_4]^-$$

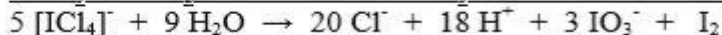
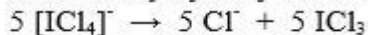
$$\text{Cl}_2 + \text{ClF} + \text{AsF}_5 \xrightarrow{-78^\circ\text{C}} [\text{Cl}_3]^+[\text{AsF}_6]^-$$

$$3 \text{I}_2 + 3 \text{AsF}_5 \xrightarrow{\text{in SO}_2} 2 [\text{I}_3]^+[\text{AsF}_6]^- + \text{AsF}_3$$

Properties:

- i. All polyhalides are coloured compounds and depth of colour increases with the increase of the atomic number of halogen atoms.
- ii. Polyhalides are highly soluble in water and get dissociated in water. The stability of metallic trihalides of MX_3 type having the same cation in the same oxidation state is in the order: $MI_3 > MBr_3 > MCl_3$. And the stability of metallic trihalides, having the same trihalide anion and different cation increases with the increase in size of the cation. For example:
 $NaI_3 < KI_3 < RbI_3 < CsI_3$.

The polyhalides, containing ICl_4^- anion, dissociate in aqueous solution followed by hydrolysis to iodate, IO_3^- .



- iii. Polyhalide ions form complexes with organic donor molecules. Examples: $LiI_3 \cdot 4 C_6H_5CN$, $MI_3 \cdot 2 C_6H_5CN$ (M=Na or K)
- iv. They undergo thermal decomposition when heated. The ease of dissociation decreases with the increase of the size of the cation. On thermal dissociation, the polyhalides give metal monohalides and halogen molecule or inter-halogen molecule.



The stability of trihalide ions formed by the same metal, decreases in the order: $I_3^- > IBr_2^- > ICl_2^- > I_2Br^- > Br_2^- > BrCl_2^- > Br_2Cl^-$

- v. When polyhalide is allowed to react with halogen molecule, it undergoes substitution reaction.
 $KIBr_2 + Cl_2 \rightarrow KICl_2 + Br_2; \quad CsBr_3 + I_2 \rightarrow CsIBr_2 + IBr$
 Sometimes a higher polyhalide is formed. $KICl_2 + Cl_2 \rightarrow KICl_4$
- vi. Polyhalides may dissolve in liquid halogen or in inter-halogen to give solution from which original polyhalide may be crystallised by evaporation.

Structure of Polyhalide ions:

Geometry of cations	Examples	Structure	Explanation
Tri-atomic inter-halogen cations	ICl_2^+ , IBr_2^+ , BrF_2^+ , ClF_2^+	sp^3 hybridisation (V-shaped)	Angular geometry which arises from sp^3 hybridisation of central positively-charged bigger halogen atom and due to presence of two lps of electrons on the central atom.
Penta-atomic inter-halogen cations	IF_4^+ , ClF_4^+ , BrF_4^+	sp^3d hybridisation distorted-tetrahedral structure	All these cations have distorted-tetrahedral or see-saw structure. This structure arises from sp^3d hybridisation of central positively-charged bigger halogen atom and due to presence of one lone pair of electrons on the central atom.
Hepta-atomic inter-halogen cations	IF_6^+ , BrF_6^+	sp^3d^2 hybridisation octahedral structure	All these ions have octahedral structure corresponding to sp^3d^2 hybridisation of the central positively-charged bigger halogen atom and due to absence of lp of electrons on the central atom

Geometry of anions	Examples	Structure	Explanation
Tri-atomic inter-halogen anions	ICl_2^- , IBr_2^- , BrCl_2^- , ClF_2^- , I_3^- , ClBrI^-	sp^3d hybridisation linear structure	All these ions have linear structure which due to sp^3d hybridisation of central atom and presence of three lps of electrons on the axial site of central atom.
Penta-atomic inter-halogen anions	ICl_4^- , BrF_4^- , I_5^-	sp^3d^2 hybridisation square planar	All these ions have square planar geometry which arises due to sp^3d^2 hybridisation of central atom and presence of two lps of electrons on the axial sites.
Hepta-atomic inter-halogen anions	IF_6^- , BrF_6^-	sp^3d^3 hybridisation distorted octahedral	These ions have distorted octahedral structure which is because of sp^3d^3 hybridisation of central atom and presence of one lone pair of electrons on the central atom.