

Polyhalides

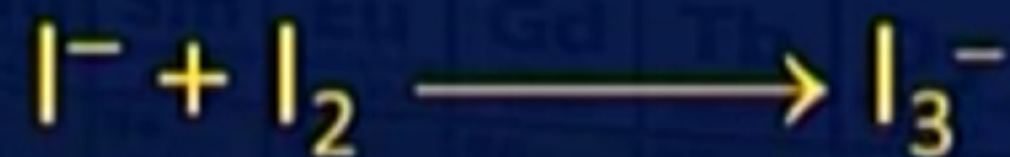
- Polyhalide is a halide containing more than one halogen atom in a molecule.
- Halogens or interhalogens react with halide ions to form polyhalide ions.

Polyhalides

Solubility of iodine and formation of triiodide ion

ion: Iodine is only slightly soluble in water (0.34g l^{-1}). Its solubility increases in presence of small amount of iodide ions in solution. It is due to formation of polyhalide ion : triiodide ion I_3^- .

It is quite stable in ionic crystal and aqueous solution.



Structure of Polyhalides

- They always have the heaviest and least electronegative halogen as central atom, making the ion asymmetric in some cases.
- Structures of most heteropolyhalogen ions and lower isopolyhalogen ions follow VSEPR theory. However, there are some exceptional cases. For example, when central atom is heavy and contain seven lone pairs, such as $[\text{BrF}_6]^-$ and $[\text{IF}_6]^-$, they have a regular octahedral arrangement of fluoride ligands instead of a distorted one due to the presence of stereochemically inert lone pair.

Structure of Polyhalide ions

- The polyiodide ions have much more complicated structures.
- (i) Cl_3^- , Br_3^- , ICl_2^- , IBr_2^- including I_3^- . In these ions, one of the halogen atoms or halogen atom larger in size undergoes sp^3d -hybridization giving a linear shape with three lone pairs at equatorial positions.
- (ii) Cl_3^+ , Br_3^+ , I_3^+ , ICl_3^+ , IBr_2^+ . Central atom is sp^3 hybridized giving a bent shape with two lone pairs of electrons on the central atom.

Structure of Polyhalide ions

- The polyiodide ions have much more complicated structures.
- (iii) ICl_4^- , BrF_4^- , I_3^- . Central atom involves sp^3d^2 hybridization giving square planar shape with two lone pairs of electrons on axial positions.
- (iv) ICl_4^- , BrF_4^- , I_5^- . Central atom involves sp^3d hybridization giving a distorted tetrahedral structure with one lone pair of electrons on equatorial position.

Structure of Polyhalide ions

- The polyiodide ions have much more complicated structures.
- (v) I_7^- , IF_6^+ . Central iodine atom undergoes sp^3d^3 hybridization giving a distorted octahedral structure with one lone pair of electrons.
- (vi) I_7^+ , Central iodine atom involves sp^3d^2 hybridization giving an octahedral structure.

Structure of Polyhalide ions

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(vii) Fluorine due to its highest electronegativity (and only -1 oxidation state) does not form polyhalide ions where it acts as a central atom.

Properties of Polyhalides

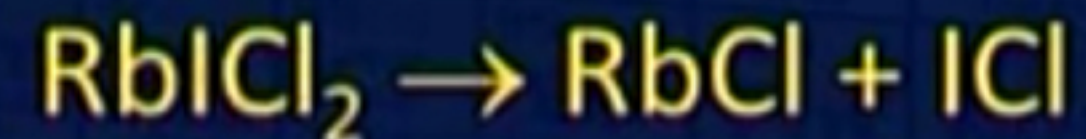
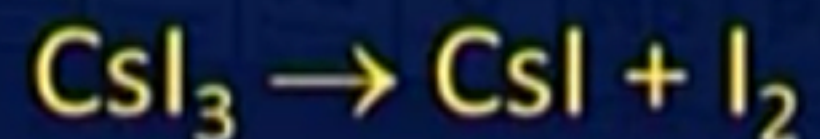
- All the polyhalides are colored compounds.
- The depth of color increases with increase in atomic number of the halogen atoms present. Thus bromoiodides are red and chlorobromides are yellow.
- Polyhalides are usually soluble in water, from which they can be crystallized.

Properties of Polyhalides

- Some of them get dissociated in water to free halogen and halide ion. $I_3^- \rightarrow I_2 + I^-$.
- Stability of metal trihalide is in order as :
 $MI_3 > MBr_3 > MCl_3$
- Some of polyhalide ions form complexes with organic donor molecules such as $LiI_3 \cdot 4C_6H_5CN$.

Properties of Polyhalides

- When solid polyhalides are heated, they dissociate, more or less, readily. Ease of dissociation of a given polyhalide decreases with increase of size of cation with which the polyhalide anion is associated.
- On thermal dissociation, the polyhalide give metal monohalide and halogen or interhalogen molecule.



Summary

- Major applications of halogens
- Basic properties of halogens
- Interhalogens
- Classification and structure of interhalogens
- Structure based properties of diatomic, tetra-atomic, and hexa-atomic interhalogens