TDC Part I
Inorganic Chemistry

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TOPIC:- Polyhalides and polyhaloniumions

Polyhalides and polyhalonium ions

Halide ions associate with molecules of halogens or interhalogens to form polyhalides. The solubility of iodine is enhanced in potassium iodide due to formation of triiodide ion, I_3^-.

$$KI + I_2 \longrightarrow KI_3$$

More complex ions, like I_5^-, I^- are known. Polyhalides containing two or three different halogens are known eg $[ICl_2]^-$, $[BrF_4]^-$, $[BrICl]^-$ etc. polyhalonium cations eg. $[ICl_2]^+$, $[BrF_2]^+$ are obtained as a result of auto ionization of ICl_3 and BrF_3. Other cations e.g. Br_3^+, I_3^+ $[ClF_6]^+$ etc. are also known.

Pseudohalogens

Parallels have been observed between the chemistry of the halogens and other dimeric species. Such molecules are called pseudohalogens eg. Cyanogens $(CN)_2$, thiocyanogen $(SCN)_2$ and selenocyanogen $(SeCN)_2$. A pseudohalogen is a univalent chemical aggregate, comprising of two or more electronegative atoms, which in the free state show properties similar to halogens. They combine with hydrogen to form an acid and with silver, a salt insoluble in water. The anions of pseudohalogens are called pseudohalides. The most important pseudohalide is CN^- and its similarity with Cl^- is shown in Table 30

Table 30: Comparison of a Pseudohalogen with a Halogen

Characterstics	**Examples**	
	Halogen	**Pseudohalogen**
Neutral diatomic species	Cl_2	$(CN)_2$
Anion	Cl^-	CN^-
Acid with hydrogen	HCl	HCN
Insoluble Salts	AgCl	AgCN
Interhalogen compound	ICl, BrCl	ClCN, BrCN, ICN
Anionic Complexes	$[CoCl_6]^{3-}$ $[CuCl_4]^{2-}$	$[Co\ (CN)_6]^{3-}$ $[Cu\ (CN)_4]^{2-}$