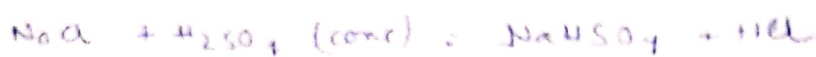
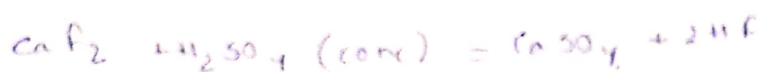


Hydrogen Halides :

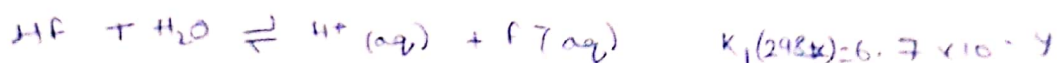
The hydrogen halides or the halogen hydroacids may be conveniently prepared by reactions of the following type :



Only HF is a low boiling liquid associated through H-bonding. Others are gases, and all are colourless.

All the acids are freely soluble in water.

Crystalline hydrate $\text{H}_2\text{O} \cdot n\text{HF}$ ($n = 1, 2, 4$) show the presence of H_3O^+ ion in tight H-bonded association with F^- , HF_2^- or H_3F_4^- . High HF bond strength makes HF a weak acid in dilute aq. solⁿ.



weaker bond dissociation energy makes all these other hydroacids strong acids in aq. solution. pK values are $\text{HCl} : -7$, $\text{HBr} : -9$, $\text{HI} : -10$. acid strength $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

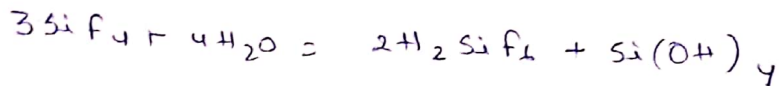
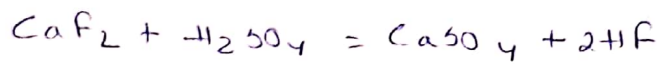
HF and its vapours are highly poisonous. The aqueous solution attacks all metals and evolves H_2 .

It also attacks glass & porcelain. The use of HF in etching glass is based on



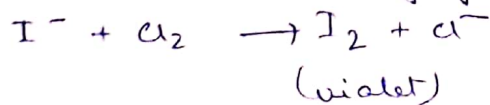
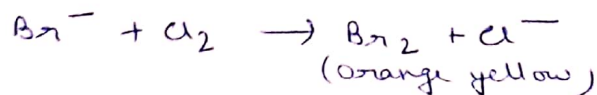
Detection of Fluorides:

Fluorides are detected by heating the sample with conc. H_2SO_4 & sand when bubbles of SiF_4 rise giving the test tube an oily appearance. A drop of water held in the flame turns opaque due to formation of ~~si~~ insoluble silicic acid.



Detection of Br^- & I^- : ~~By Cl_2 water test~~

Layer test is carried out by adding organic solvent such as CS_2 or $CHCl_3$ in presence of chlorine water. When



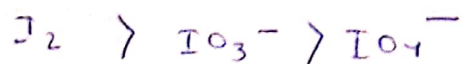
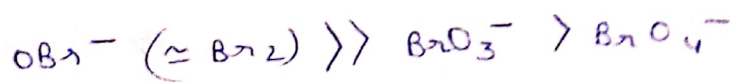
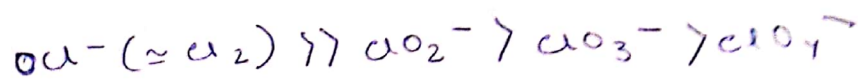
out of the liberated Br_2 and I_2 , I_2 will go first into the organic layer because distribution ^{coefficient} of I_2 is greater than that of Br_2 . On further addition of chlorine water iodine is oxidized to iodate which produces colourless solution and reddish brown colouration of organic layer will appear due to dissolved Br_2 .

Although iodine forms HIO_4 and the corresponding octahedral IO_4^- ion, a variety of other peroxide acids & their derivatives are also known. Perchloric acid H_5IO_6 has an octahedral environment of 5 OH groups plus an O atom. O-bridged dimers are also formed at higher pH .

Strong p-d pi bonding between filled 2p orbitals on O & empty d-orbitals on the halogens (their energy lowered by presence of the O-atoms) further stabilize the bonds. The absence of d-orbitals & steric congestion around small F-atom appears to be responsible for non-existence of higher oxoacids containing F.

Acid strength strengths of the oxoacids increase with increasing oxidation state of the halogen. Approximate pK_a values are HOCl : 7.52, HOClO : 1.94, HOClO_2 : -3, HOClO_3 : -10. Acid strength among related acids by different halogens follows the sequence $\text{Cl} < \text{Br} < \text{I}$.

Rates of oxidation by oxoacids and their ions appear to decrease with increase in the oxidation number of the halogen.



Rates of oxidation by different oxoanions containing the halogens in same oxidation state increase from Cl^- to Br^- to I^-
 $\text{IO}_4^- > \text{BrO}_4^- > \text{ClO}_4^-$