TDC Part I
Inorganic Chemistry

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TOPIC:- Compounds (Hydrogen Halides)

Compounds Hydrogen Halides

Binary compounds of hydrogen and halogen are formulated as HX and in the anhydrous state are referred to as hydrogen halides. Their aqueous solutions are called hydrohalic acids. The halogens react with hydrogen forming HX. The reaction with fluorine is violent and explosive while that with iodine is slow illustrating decrease in reactivity on moving down the group. At room tempera HF is a liquid due to strong intermolecular hydrogen bonding, while others are gases. The melting and boiling points shows a gradual increase in the order HCl < HBr < HI.

The hydrogen halides are covalent in the gaseous state, but in aqueous solution they ionize and behave as strong acids (except HF, which is a weak acid, pKa = 3.2 at 25^0 C). The ionization may be represented as

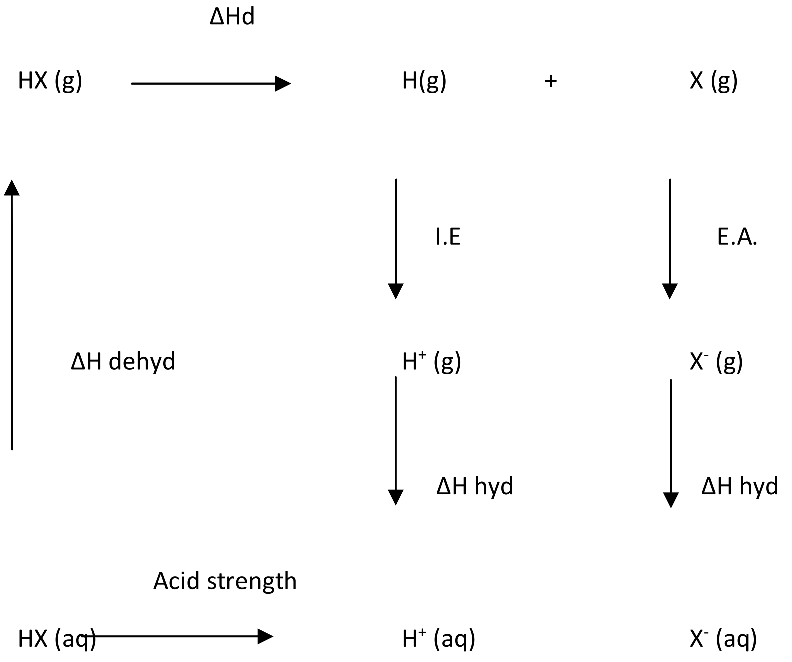
$$HX + H_2O \longrightarrow H_3O^+ + X^- \text{ (X= Cl, Br, I)}$$

The aqueous solutions form isotopes with maximum boiling points (negative deviation from Raoult's Law).

As fluorine is the most electronegative element, the H-F bond has maximum ionic character and HF should be the strongest acid, however the reverse is true. The paradox arises due to the fact that acid strength which is given by the following reaction

$$HX \text{ (hydrated)} + H_2O \longrightarrow H_3O^+ + X^- \text{ (hydrated)}$$

It involves various enthalpy parameters as shown:



Thus acid strength = ΔH dehyd + ΔHd + I.E. + E.A. + ΔHhyd of H^+ and X^- Where

ΔHdehyd = enthalpy of dehydration
ΔHd = enthalpy of dissociation
I.E. = ionization enthalpy
E.A. = electron affinity
Δ Hhyd = enthalpy of hydration

For HF, the enthalpy of dehydration and enthalpy of dissociation are very high. The high enthalpy of hydration of F^- cannot compensate for the same and the total enthalpy change for HF is least negative. Due to strong hydrogen bonding between F^- and H_3O^+ ($F \;\; H^+$------OH_2), ion pairs of the type $H_3O^+F^-$ are formed, lowering the concentration of H_3O^+ and decreasing acidity. As the concentration of HF increases, the tendency to form H_3O^+ increases:

$$H_3O^+F^- + HF \rightleftharpoons H_3O^+ + HF_2^-$$