



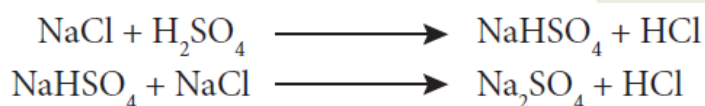
## Warm greetings

Dear students I think previous uploaded notes are very useful to you. Now we learn about the preparation and properties of hydrochloric acid , Acidic properties of hydrogen halides and Inter halogen compounds.

## HYDROCHLORIC ACID

### LABORATORY PREPARATION

It is prepared by the action of sodium chloride and concentrated sulphuric acid.



Dry hydrochloric acid is obtained by passing the gas through conc. sulphuric acid

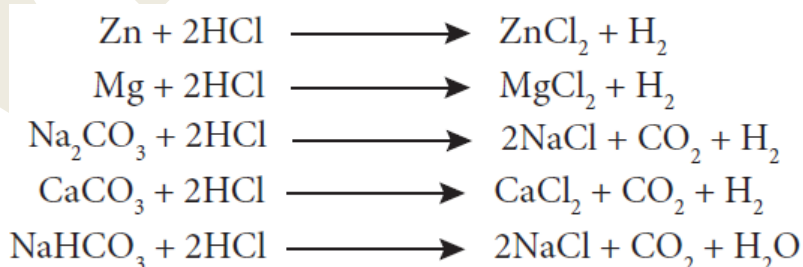
### PROPERTIES

Hydrogen chloride is a colourless, pungent smelling gas, easily liquefied to a colourless liquid (boiling point 189K) and frozen into a white crystalline solid (melting point 159K). It is extremely soluble in water.



### CHEMICAL PROPERTIES

Like all acids it liberates hydrogen gas from metals and carbon dioxide from carbonate and bicarbonate salts.



It liberates sulphur dioxide from sodium sulphate





When three parts of concentrated hydrochloric acid and one part of concentrated nitric acid are mixed, Aquaregia (Royal water) is obtained. This is used for dissolving gold, platinum etc...



### USES OF HYDROCHLORIC ACID

- ❖ Hydrochloric acid is used for the manufacture of chlorine, ammonium chloride, glucose from corn starch etc.,
- ❖ It is used in the extraction of glue from bone and also for purification of bone black.

### TRENDS IN PHYSICAL AND CHEMICAL PROPERTIES OF HYDROGEN HALIDES

#### PREPARATION

Direct combination is a useful means of preparing hydrogen chloride. The reaction between hydrogen and fluorine is violent while the reaction between hydrogen and bromine or hydrogen and iodine are reversible and don't produce pure forms.

#### DISPLACEMENT REACTIONS

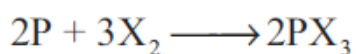
Concentrated sulphuric acid displaces hydrogen chloride from ionic chlorides. At higher temperatures the hydrogen sulphate formed reacts with further ionic chloride. Displacement can be used for the preparation of hydrogen fluorides from ionic fluorides. Hydrogen bromide and hydrogen iodide are oxidised by concentrated sulphuric acid and can't be prepared in this method.

#### HYDROLYSIS OF PHOSPHORUS TRIHALIDES

Gaseous hydrogen halides are produced when water is added in drops to phosphorus trihalides except phosphorus trifluoride.



Hydrogen bromide may be obtained by adding bromine dropwise to a paste of red phosphorous and water while hydrogen iodide is conveniently produced by adding water dropwise to a mixture of red phosphorous and iodine.



(where X=Br or I)

Any halogen vapours which escapes with the hydrogen halide is removed by passing the gases through a column of moist red phosphorous.

**FROM COVALENT HYDRIDES**

Halogens are reduced to hydrogen halides by hydrogen sulphide.



Hydrogen chloride is obtained as a by-product of the reactions between hydrocarbon of halogens.

**General Properties**

	HF	HCl	HBr	HI
Bond dissociation enthalpy	+562	+431	+366	+299
% of ionic character	43	17	113	7

In line with the decreasing bond dissociation enthalpy, the thermal stability of hydrogen halides decreases from fluoride to iodide.

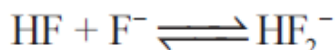
For example, Hydrogen iodide decomposes at 400° C while hydrogen fluoride and hydrogen chloride are stable at this temperature.

At room temperature, hydrogen halides are gases but hydrogen fluoride can be readily liquefied. The gases are colourless but, with moist air gives white fumes due to the production of droplets of hydrohalic acid. In HF, due to the presence of strong hydrogen bond it has high melting and boiling points. This effect is absent in other hydrogen halides.

**ACIDIC PROPERTIES****THE HYDROGEN HALIDES ARE EXTREMELY SOLUBLE IN WATER DUE TO THE IONISATION**

(X – F, Cl, Br, or I)

Solutions of hydrogen halides are therefore acidic and known as hydrohalic acids. Hydrochloric, hydrobromic and hydroiodic acids are almost completely ionised and are therefore strong acids but HF is a weak acid i.e. 0.1mM solution is only 10% ionised, but in 5M and 15M solution HF is stronger acid due to the equilibrium.



At high concentration, the equilibrium involves the removal of fluoride ions is important. Since it affects the dissociation of hydrogen fluoride and increases and hydrogen ion concentration several stable salts  $\text{NaHF}_2$ ,  $\text{KHF}_2$  and  $\text{NH}_4\text{HF}_2$  are known. The other hydrogen halides do not form hydrogen dihalides.

Hydrohalic acid shows typical acidic properties. They form salts with acids, bases and reacts with metals to give hydrogen. Moist hydrofluoric acid (not dry) rapidly react with silica and glass.



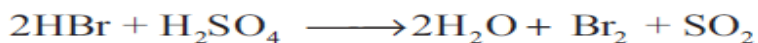
## OXIDATION

Hydrogen iodide is readily oxidised to iodine hence it is a reducing agent.

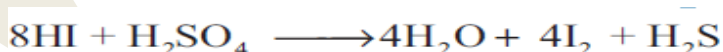


Acidic solution of iodides is readily oxidised. A positive result is shown by liberation of iodine which gives a blue-black colouration with starch.

Hydrogen bromide is more difficult to oxidise than HI. HBr reduces slowly  $\text{H}_2\text{SO}_4$  into  $\text{SO}_2$



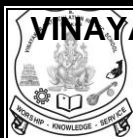
But hydrogen iodide and ionic iodides are rapidly reduced by  $\text{H}_2\text{SO}_4$  into  $\text{H}_2\text{S}$  and not into  $\text{SO}_2$ .



Reducing property of hydrogen iodide can be also explained by using its reaction with alcohols into ethane. It converts nitric acid into nitrous acid and dinitrogen dioxide into ammonium.

Hydrogen chloride is unaffected by concentrated sulphuric acid by only strong oxidising agents like  $\text{MnO}_2$ , potassium permanganate or potassium chlorate.

To summarize the trend,



Property	Order
Reactivity of hydrogen	Decreases from fluorine to iodine
Stability	Decreases from HF to HI
Volatility of the hydrides	HF < HI < HBr < HCl
Thermal stability	HF > HI > HBr > HCl
Boiling point	HCl < HBr < HI
Acid strength	Increases from HF to HI

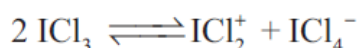
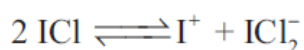
## INTER HALOGEN COMPOUNDS

Each halogen combines with other halogens to form a series of compounds called inter halogen compounds. In the given table of inter halogen compounds a given compound A is less electronegative than B.

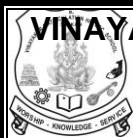
AB	AB <sub>3</sub>	AB <sub>5</sub>	AB <sub>7</sub>
ClF	ClF <sub>3</sub>	IF <sub>5</sub>	IF <sub>7</sub>
BrF	BrF <sub>3</sub>	BrF <sub>5</sub>	
IF	IF <sub>3</sub>		
BrCl	ICl <sub>3</sub>		
ICl			
IBr			

## PROPERTIES OF INTER HALOGEN COMPOUNDS

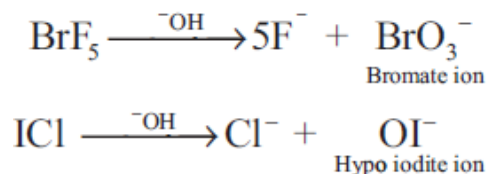
- ❖ The central atom will be the larger one
- ❖ It can be formed only between two halogen and not more than two halogens.
- ❖ Fluorine can't act as a central metal atom being the smallest one
- ❖ Due to high electronegativity with small size fluorine helps the central atom to attain high coordination number
- ❖ They can undergo the auto ionization.



- ❖ They are strong oxidizing agents

**REACTION WITH ALKALI**

When heated with the alkalis, larger halogen form oxyhalogens and the smaller forms halide.

**STRUCTURE OF INTER HALOGEN COMPOUNDS**

The structures of different type of inter halogen compounds can be easily explained using VSEPR theory.

Type	Structure	Hybridisation	bond pairs / lone pairs
AX	Linear	$\text{sp}^3$	1 / 3
$\text{AX}_3$	T shaped	$\text{sp}^3\text{d}$	3 / 2
$\text{AX}_5$	Square pyrimidal	$\text{sp}^3\text{d}^2$	5 / 1
$\text{AX}_7$	Pentagonal bipyramidal	$\text{sp}^3\text{d}^3$	7 / 0

**OXIDES OF HALOGEN**

Fluorine reacts readily with oxygen and forms difluorine oxide ( $\text{F}_2\text{O}$ ) and difluorine dioxide ( $\text{F}_2\text{O}_2$ ) where it has a -1 oxidation state. Other halogens do not react with oxygen readily. But the following oxides can be prepared by some indirect methods. Except fluorine all the other halogens have positive oxidation states.

Type	$\text{X}_2\text{O}$	$\text{XO}_2$	$\text{XO}_3$	$\text{X}_2\text{O}_6$	$\text{X}_2\text{O}_7$	Others
Oxidation state	+1	+4	+5	+6	+7	-
F	-	-	-	-	-	$\text{OF}_2$ (-1) $\text{O}_2\text{F}_2$ (-1) $\text{O}_4\text{F}_2$ (-1)
Cl	$\text{Cl}_2\text{O}$	$\text{ClO}_2$	-	$\text{Cl}_2\text{O}_6$	$\text{Cl}_2\text{O}_7$	$\text{Cl}_2\text{O}_4$ (+4)
Br	$\text{Br}_2\text{O}$	$\text{BrO}_2$	-	-	-	-
I	-	-	$\text{I}_2\text{O}_5$	-	-	$\text{I}_4\text{O}_9$ $\text{I}_2\text{O}_4$ (+4)

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