VINAYAKAR MATRICULATION HIGHER SECONDARY SCHOOL, SIVAKASI.

12th Standard - CHEMISTRY

DATE: 02 – August - 2021 **CH - 23** **No. of Pages: 06**

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.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$
$$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$$

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.

$$HCl\,(g) + H_2O\,(l) \longrightarrow H_3O^+ + Cl^-$$

CHEMICAL PROPERTIES

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

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$
$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$
$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2$$
$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2$$
$$NaHCO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

It liberates sulphur dioxide from sodium sulphate

$$Na_2SO_4 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$$

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...

$$Au + 4H^+ + NO_3^- + 4\,Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$$

$$Pt + 8H^+ + 4NO_3^- + 6Cl^- \longrightarrow [PtCl_6]^{2-} + 4NO_2 + 4H_2O$$

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 react 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 tri halides except phosphorus trifluoride.

$$PX_3 + 3H_2O \longrightarrow H_3PO_3 + 3HX$$

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.

$$2P + 3X_2 \longrightarrow 2PX_3$$

$$2PX_3 + 3H_2O \longrightarrow H_3PO_3 + 3HX$$

(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.

$$H_2S + X_2 \longrightarrow 2HX + S$$

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

General Properties

	HF	HCl	HBr	HI
Bond dissolution enthalphy	+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

$$HX + H_2O \longrightarrow H_3O^+ + X^-$$

$$(X – F, Cl, Br, or I)$$

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.

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

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

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 $NaHF_2$, KHF_2 and NH_4HF_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.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$$

OXIDATION

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

$$2HI \rightleftharpoons 2H^+ + I_2 + 2e^-$$

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 H_2SO_4 into SO_2

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + Br_2 + SO_2$$

But hydrogen iodide and ionic iodides are rapidly reduced by H2SO4 into H2S and not into SO2.

$$8HI + H_2SO_4 \longrightarrow 4H_2O + 4I_2 + H_2S$$

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 aid by only strong oxidising agents like MnO_2, potassium permanganate or potassium chloride.

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_3	AB_5	AB_7
ClF	ClF_3	IF_5	IF_7
BrF	BrF_3	BrF_5	
IF	IF_3		
BrCl	ICl_3		
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.

$$2\,ICl \rightleftharpoons I^+ + ICl_2^-$$

$$2\,ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$$

- They are strong oxidizing agents

REACTION WITH ALKALI

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

$$BrF_5 \xrightarrow{^-OH} 5F^- + \underset{\text{Bromate ion}}{BrO_3^-}$$

$$ICl \xrightarrow{^-OH} Cl^- + \underset{\text{Hypo iodite ion}}{OI^-}$$

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	sp^3	1 / 3
AX_3	T shaped	sp^3d	3 / 2
AX_5	Square pyrimidal	sp^3d^2	5 / 1
AX_7	Pentagonal bipyramidal	sp^3d^3	7 / 0

OXIDES OF HALOGEN

Fluorine reacts readily with oxygen and forms difluorine oxide (F_2O) and difluorine dioxide (F2O2) 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	X_2O	XO_2	XO_3	X_2O_6	X_2O_7	Others
Oxidation state	+1	+4	+5	+6	+7	-
F	-	-	-	-	-	OF_2 (-1) O_2F_2 (-1) O_4F_2 (-1)
Cl	Cl_2O	ClO_2	-	Cl_2O_6	Cl_2O_7	Cl_2O_4 (+4)
Br	Br_2O	BrO_2	-	-	-	-
I	-	-	I_2O_5	-	-	I_4O_9 I_2O_4 (+4)

@@@@@@@@@