

HALOGENS

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HALOGENS

Introduction

The elements Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I) and Astatine (At) which belong to group 17 or VII A of periodic table are commonly called halogens. The term halogen means salt producer. None of the halogens occur in native or free state in nature because of their high reactivity. The last element of this group is Astatine (At) which is radioactive and quite rare.

General Characteristics of Halogens

a) Electronic configuration

All the elements of this family have the outer ns^2np^5 electronic configuration. That is, they all have seven electrons (ns^2np^5) in their outermost valence shell and are p block elements.

Group VII A (Elements)	Electronic Configuration
${}_9\text{F}$	$[\text{He}] 2s^2 2p^5$
${}_{17}\text{Cl}$	$[\text{Ne}] 3s^2 3p^5$
${}_{35}\text{Br}$	$[\text{Ar}] 3d^{10} 4s^2 4p^5$
${}_{53}\text{I}$	$[\text{Kr}] 4d^{10} 5s^2 5p^5$
${}_{85}\text{At}$	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^5$

b) Atomic radii: They have small atomic radius, smallest in the period.

c) Ionization energy: They have high ionization energy next to noble gases.

d) Electronegativity: Halogens have high electronegativity; highest in the period. This is because of smallest size and high nuclear charge. Fluorine is the most electronegative element known.

e) Electron affinity: Halogens have high electron affinity (EA), highest in the period. This is due to smallest atomic size and high nuclear charge.

f) Oxidation state: The most common oxidation state in their combined form is -1 . Fluorine is the most electronegative element hence always show only -1 oxidation state in its compounds. Chlorine, Bromine and Iodine show wide range of oxidation states from -1 to $+7$.

g) Oxidizing agent: They have high tendency to gain electron. Hence, they are oxidizing agents and the oxidizing power is in the order: $F_2 > Cl_2 > Br_2 > I_2$

h) Atomicity: They all exist as non-polar diatomic molecule (F_2, Cl_2, Br_2, I_2) containing single covalent bond.

i) Melting and boiling points: There is regular increase in melting point and boiling point with increasing atomic number. At room temperature, F_2 and Cl_2 are gases, Br_2 is liquid and I_2 is volatile crystalline solid.

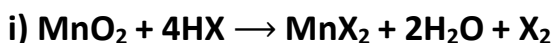
Melting point: $F_2 (-219^\circ C) < Cl_2 (-101^\circ C) < Br_2 (-7^\circ C) < I_2 (114^\circ C)$

Boiling point: $F_2 (-188^\circ C) < Cl_2 (-34^\circ C) < Br_2 (59^\circ C) < I_2 (185^\circ C)$

Comparative Study of Preparation of Halogens

1. By chemical oxidation of halo acids:

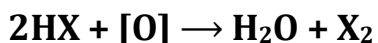
Chlorine, bromine and iodine can be prepared by the oxidation of respective halo acids with powerful oxidizing agents such as MnO_2 , $KMnO_4$ and $K_2Cr_2O_7$.

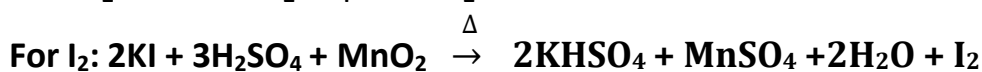
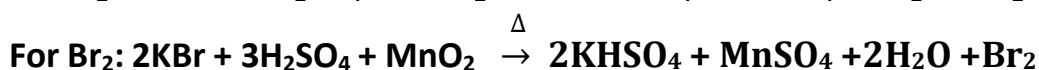
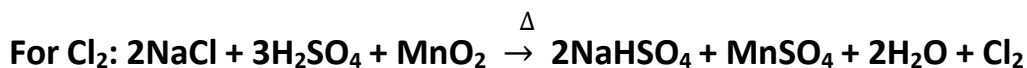


Where, $X = Cl, Br$ or I .

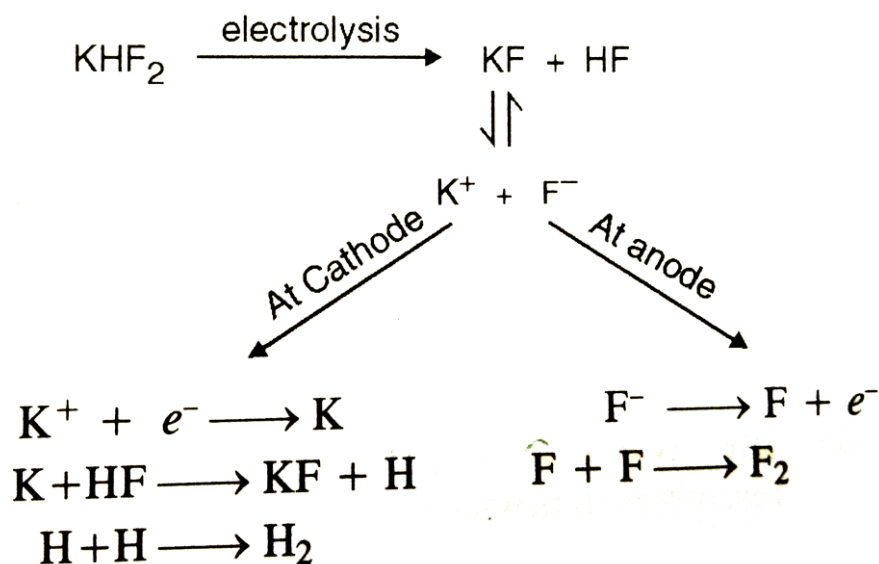
2. Laboratory preparation:

In laboratory, chlorine, bromine and iodine are prepared by heating their respective halide salts (MX) with manganese dioxide and concentrated sulphuric acid. Here, $M = Na$ or K and $X = Cl, Br$ or I .





Note: Fluorine cannot be prepared by chemical oxidation method since fluorine is the most powerful oxidizing agent. However, it can be prepared by electrolytic oxidation of KF and HF.



Chemical Properties of Halogens

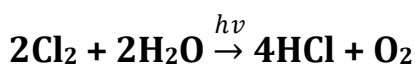
Halogens are most reactive non-metals. This is because of low bond dissociation energy of their molecules, high electronegativity and electron affinity. The reactivity of halogens is in the order: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

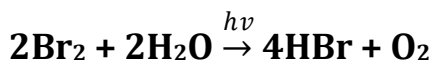
1. Action with water

Fluorine being strong oxidizing agents oxidizes water to O_2 and O_3 .



At ordinary temperature, in absence of sunlight, Cl_2 , Br_2 and I_2 dissolve slowly in water to give chlorine water, bromine water and iodine water. But, in presence of sunlight they decompose water slowly.





Iodine has little action with water, but it dissolves readily in aq. solution of KI due to formation of KI_3 .

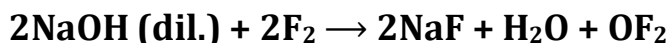


2. Action with alkali (imp)

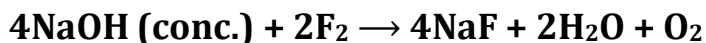
Halogens react with alkali solutions (NaOH or KOH) in two different conditions: i) Cold and dilute alkali solution and ii) Hot and concentrated alkali solution to give different products.

a) Reaction with F_2

i) Cold and dilute alkali:

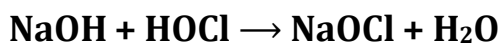
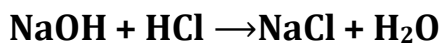


ii) Hot and concentrated alkali:



b) Reaction with Cl_2

i) Cold and dilute alkali: Cl_2 reacts with dilute NaOH at or below room temperature (15°C) to give sodium chloride (NaCl) and sodium hypochlorite (NaOCl).



(sodium hypochlorite)

This is disproportionation reaction in which chlorine is oxidized as well as reduced.

ii) Hot and concentrated alkali (NaOH): Cl_2 reacts with hot and conc. NaOH to give sodium chloride (NaCl) and sodium chlorate (NaClO_3).





(Sodium Chlorate)

This is also a disproportionation reaction.

c) Reaction with Br₂

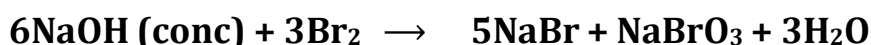
Br₂ reacts with NaOH similar to chlorine.

i) With cold and dilute alkali:



(Sodium hypobromite)

ii) With hot and concentrated alkali:



(Sodium bromate)

d) Reaction with I₂

Iodine reacts with NaOH similar to chlorine and bromine.

i) With cold and dilute NaOH



(Sodium hypoiodite)

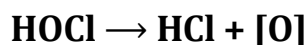
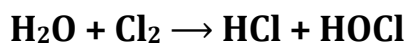
ii) With hot and Concentrated NaOH



(Sodium Iodate)

3. Bleaching action

Decolorization of a substance by a reagent is termed as bleaching action. Most halogens can bleach the colour of organic and vegetable matter by oxidation. The bleaching action is effective for chlorine, mild for bromine and iodine doesnot show any bleaching action. The bleaching action is due to oxidation which is permanent.

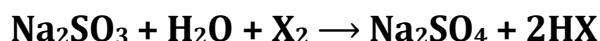
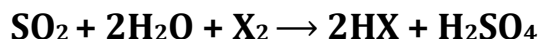
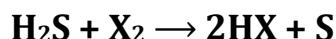


Chlorine is used industrially to bleach textiles, wood, paper etc. Fluorine being highly reactive destroys organic matter.

4. Oxidizing character

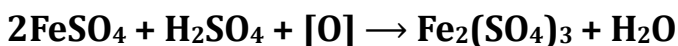
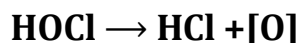
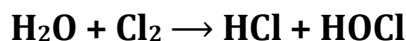
All halogens are good oxidizing agents. The oxidizing power is in the order: $F_2 > Cl_2 > Br_2 > I_2$

a) Action with H_2S , SO_2 and metal sulphites: Chlorine, bromine and iodine oxidize H_2S to sulphur, SO_2 to H_2SO_4 , and sulphites to sulphates.

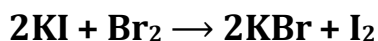
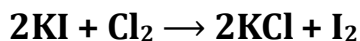
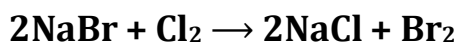
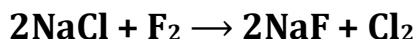


Where, $X = Cl, Br$ or I

b) Action with ferrous salts: Chlorine also oxidizes ferrous salts to ferric salts whereas bromine and iodine cannot do so.



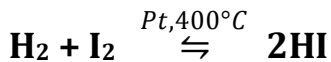
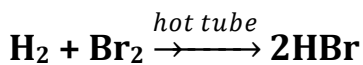
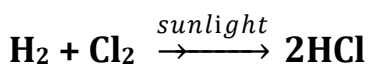
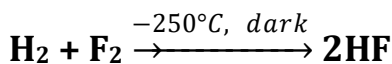
c) Displacement reactions: F_2 displaces Cl_2 , Br_2 and I_2 from their aqueous salt. Cl_2 displaces Br_2 and I_2 from their aqueous salt. Br_2 displaces I_2 from its aqueous salt.



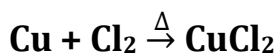
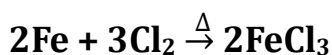
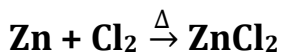
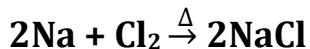
I_2 cannot displace other halogens. This shows the oxidizing strength of halogens is in the order: $F_2 > Cl_2 > Br_2 > I_2$

d) Addition reactions: Halogens undergo addition reactions with many non-metals and metals

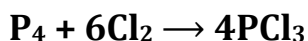
i) Action with hydrogen: All the halogens combine with hydrogen under different conditions to form corresponding hydrogen halides.



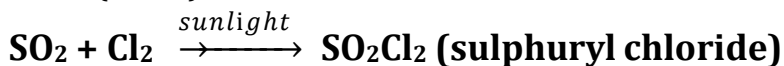
ii) Action with metals: Chlorine is non-combustible gas but supports the combustion of a number of substances.



iii) Action with non-metals: Chlorine reacts with some non-metals such as P_4 and non-metallic compounds to give different products.



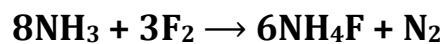
(Excess)



5. Action with ammonia (imp)

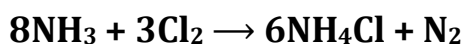
a) Reaction with F_2

Ammonia reacts violently with F_2 to produce nitrogen.



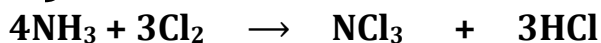
b) Reaction with Cl_2

i) Excess ammonia condition:



(Excess)

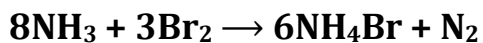
ii) Excess Cl_2 condition:



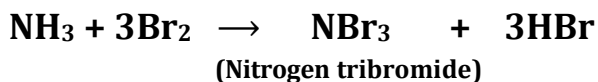
(Excess) (Nitrogen trichloride)

c) Reaction with Br_2

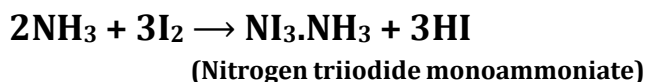
i) Excess NH_3 condition:



ii) Excess Br_2 condition:



d) Reaction with I_2



$\text{NI}_3 \cdot \text{NH}_3$ is an explosive substance and produces noise on rubbing giving nitrogen and free iodine.



Uses of Halogens

Uses of fluorine

- i) To prepare chlorofluorocarbons (Freons) which are used as refrigerants and aerosol propellants
- ii) For the separation of isotopes of Uranium.
- iii) To prepare NaF this prevents decaying of teeth.
- iv) For the manufacture of Teflon which is unreactive plastic and is used as non-stick coating in frying pan.

Uses of chlorine

- i) As a disinfectant and germicide for sterilization of drinking water.
- ii) It is used as bleaching agent in paper, rayon, cotton industries etc.
- iii) It is used to prepare insecticides such as BHC (Benzene hexa chloride), and DDT (Dichlorophenyl Trichloroethane).
- iv) Large amount of chlorine is used to prepare organic compounds like PVC (polyvinyl chloride), plastic, chloroform, chlorobenzene etc.
- v) It is used to prepare poisonous gases like phosgene gas (COCl_2) and tear gas (Cl_3CNO_2).

Uses of bromine

- i) It is used to prepare silver bromide which is used in photography.
- ii) It is used for unsaturation test in organic compounds as bromine water.

- iii) As a germicide and disinfectant.
- iv) Metal bromides such as NaBr, KBr etc are used in medicine as nerve sedative.

Uses of iodine

- i) To prepare organic compound like iodoform which is used as antiseptic.
- ii) AgI is used to prepare photographic film in the same manner like AgCl and AgBr.
- iii) Iodine is best known for its use in antiseptic in the form of tincture of iodine which is solution of iodine in alcohol.
- iv) Used as laboratory reagent.
- v) Iodine salts like NaI, KI are used for treatment of goiter (enlargement of thyroid gland).

Test of Halogens

a) Physical test

Chlorine	Bromine	Iodine
Greenish yellow pungent gas	Dark red pungent liquid	Dark violet slight pungent Solid

b) Chemical test

Test of chlorine

- i) It turns starch iodide paper blue but with fresh starch solution it produces no colour.

$$2KI + Cl_2 \rightarrow 2KCl + I_2$$

$$I_2 + starch \rightarrow blue\ colour$$
- ii) Bleaches moist red flower.

Test of bromine

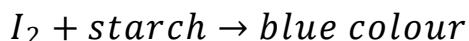
- i) It turns starch iodide paper into blue but with fresh starch solution an orange yellow colour is produced.

$$2KI + Br_2 \rightarrow 2KBr + I_2$$

$$I_2 + starch \rightarrow blue\ colour$$
- ii) Bromine water decolorizes blue litmus paper.

Test of iodine

i) It turns both starch paper and starch solution to blue.

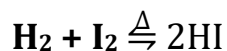
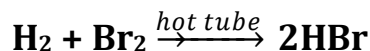
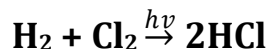
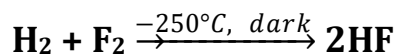


ii) It dissolves in Chloroform and Carbon tetrachloride solution giving violet solution.

Comparative Study of Preparation of Halo Acids (Hydrogen halides: HCl, HBr, HI)

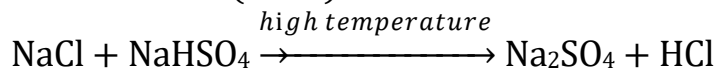
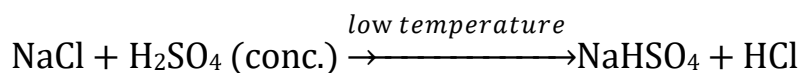
1. Halo acids from hydrogen and halogens:

All halogens directly combine with hydrogen to form corresponding hydrogen halides with decreasing order of reactivity.

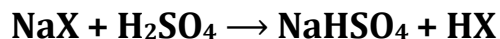


2. Halo acids from alkali metal halides (imp)

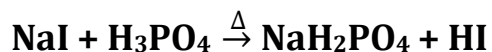
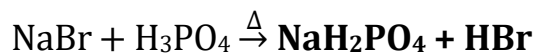
Hydrogen chloride gas is prepared in laboratory by heating common salt with concentrated sulphuric acid.



HBr and HI cannot be prepared in the same way as HCl by using conc. H_2SO_4 . It is because HBr and HI being stronger reducing agents, reduce conc. H_2SO_4 to sulphur dioxide. As a result, HBr and HI themselves get oxidized to Br_2 and I_2 respectively.

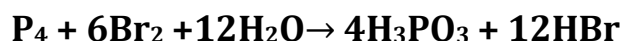
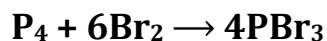


Instead, HBr and HI can be prepared by heating bromide and iodide salts with phosphoric acid which is non-oxidizing acid.

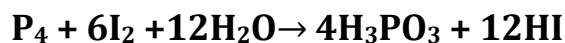
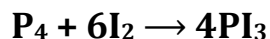


3. Halo acids from red phosphorous, halogen and water

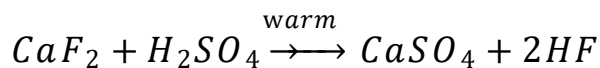
Hydrogen bromide and hydrogen iodide gases are prepared in laboratory by the action of bromine and iodine respectively on moist red phosphorous.



Similarly,



Note: Hydrogen fluoride is prepared in laboratory by heating calcium fluoride with conc. H_2SO_4 .

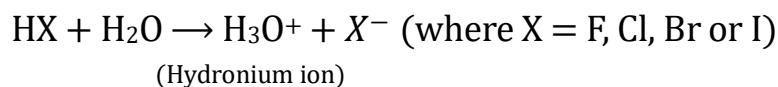


Chemical Properties of Halo Acids

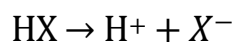
The bond dissociation energy of halo acids decreases from HF to HI. Accordingly, the reactivity increases in the order: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.

1. Acidic nature

Hydrogen halides are soluble in water and their aqueous solutions are called hydrohalic acid or simply halogen acids or halo acids. They ionize in water to give the hydronium ion.



or, simply

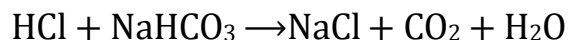
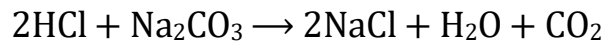
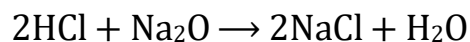
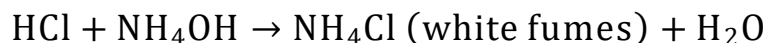
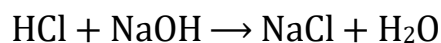


The order of acidic strength of halogen acid is: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.

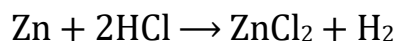
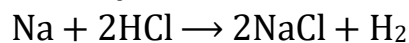
In case of HF, the ionization is not complete and is a weak acid. On the other hand, ionization is complete for HCl, HBr, and HI and are regarded as strong acids. Hydrohalic acids show typical acidic character as shown below:

i. They turn blue litmus to red and methyl orange to red.

ii. They react with bases:



iii. They react with metals:



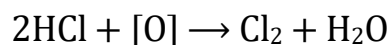
2. Reducing nature (imp)

Hydrogen halides act as reducing agent. The reducing power is in the order: $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$. Since HF is least reactive, it does not act as a reducing agent unlike other hydrogen halides.

a. Action with MnO_2 , KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$

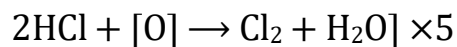
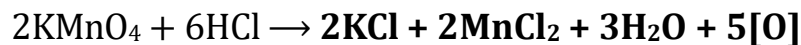
HCl, HBr and HI reduce solid MnO_2 , KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ which are powerful oxidizing agents.

i) With MnO_2

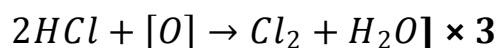
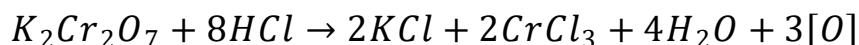




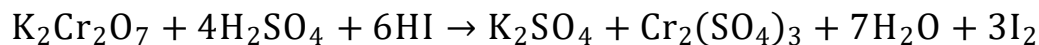
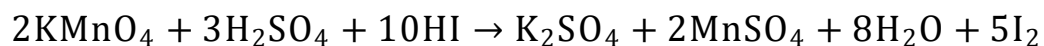
ii) With KMnO_4



iii) With $\text{K}_2\text{Cr}_2\text{O}_7$

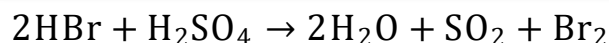
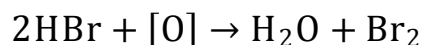
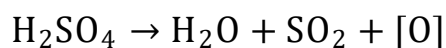


HBr and HI can also reduce less powerful oxidizing agents such as acidified KMnO_4 and acidified $\text{K}_2\text{Cr}_2\text{O}_7$.

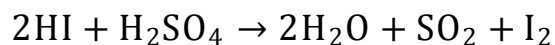


b. Action with conc. H_2SO_4

HBr and HI (not HCl) can reduce conc. H_2SO_4 .

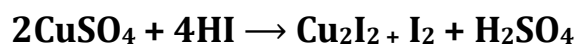


Similarly,



c. Action with CuSO_4 solution

Only HI (not HCl and HBr) can reduce CuSO_4 solution.



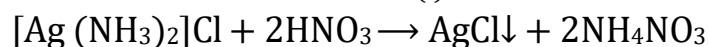
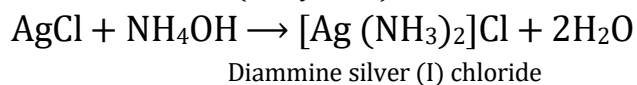
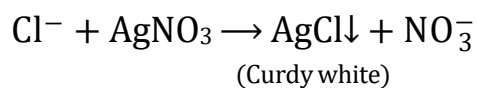
Detection of Halide Ions/Halo acids (imp)

Halide ions (Cl^- , Br^- and I^-) present in aqueous solutions of metal halides (MX) or halo acids (HX) can be detected by following tests:

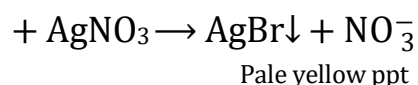
1. Silver nitrate test

In this test, the solution containing halide ion is first boiled with dil. HNO_3 , cooled and then treated with a few drops of $AgNO_3$ solution.

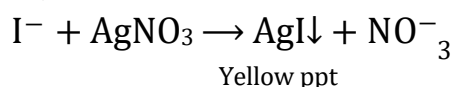
i) Cl^- gives curdy white precipitate which dissolves in ammonia solution but reappears on adding nitric acid.



ii) Br^- gives a pale yellow precipitate which is slightly soluble in ammonia. Br^-



iii) I^- gives yellow precipitate which is insoluble in ammonia solution.



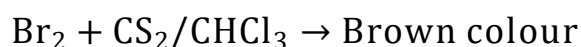
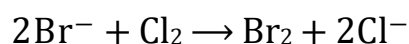
Note: The reason for boiling the solution with dil. HNO_3 before $AgNO_3$ test is to remove the interfering radicals such as CN^- , S^{2-} etc.

2. Chlorine water test

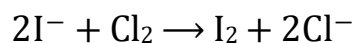
In this test, the solution containing halide ion is treated with chlorine water in the presence of a little carbon disulphide (CS_2) or chloroform ($CHCl_3$).

i. Cl^- has no action with chlorine water.

ii. With Br^- , Br_2 is set free which gives brown colour in the bottom layer of CS_2 or $CHCl_3$.



iii. With I^- , I_2 is set free which gives violet colour in the bottom layer of CS_2 or $CHCl_3$.



$I_2 + CS_2/CHCl_3 \rightarrow$ Violet colour

Uses of Halo Acids

A) Uses of HCl

- a) As an important reagent in laboratory.
- b)** In the preparation of aqua-regia (HCl and HNO_3 in the ratio of 3:1 by volume)
- c) For the manufacture of textile, dyes etc.
- d)** In the manufacture of Cl_2 gas

B) Uses of HBr

- a) As a laboratory reagent.
- b) In organic chemistry as brominating reagent.
- c) In the preparation of silver bromide ($AgBr$) which is used in photography.

C) Uses of HI

- a) For preparation of iodides (KI) and Iodine.
- b) As a reducing agent