CHLORINE AND ITS COMPOUND

The four non metals fluorine, chlorine, bromine and iodine make up a family of related elements called **halogens** meaning salt producers since they react with most metals to form electrovalent salt like compounds.

Preparation of chlorine

Chlorine can be generally prepared by the removal of hydrogen from hydrochloric acid i.e. oxidation of hydrochloric acid. This can be done by a substance containing oxygen (an oxidizing agent) that will combine with the hydrogen to form water. The oxygen for the oxidation of hydrochloric acid is provided by any of the following:

Potassium manganate(VII) or potassium permanganate ($KMnO_4$)

i) Manganese(IV) oxide (MnO_2)

ii) Lead(II) oxide (PbO_2)

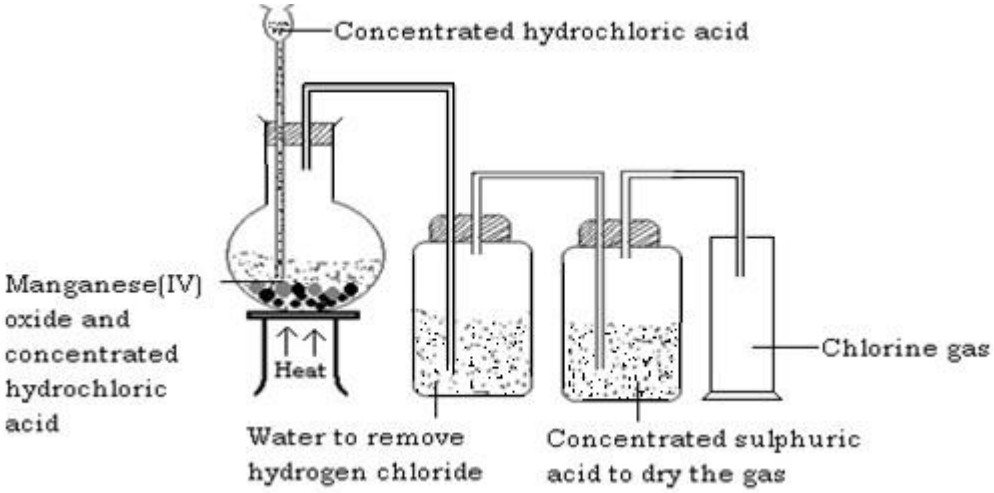
iii) Tri lead tetraoxide (Pb_3O_4)

The common oxidizing agents used in the preparation of chlorine are potassium permanganate and manganese(IV) oxide.

Preparation of chlorine from hydrochloric acid by oxidation with manganese(IV) oxide

Procedure

- Place some manganese(IV) oxide into a flask. Lumps are preferably used as the powder is very reactive
- Fit the apparatus as shown below
- Pour concentrated hydrochloric acid down the thistle funnel
- Heat the mixture in the flask

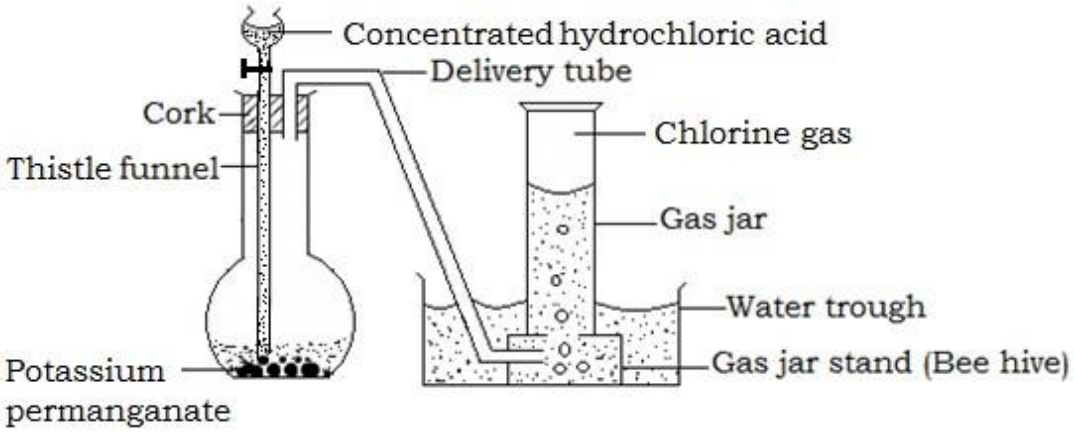


Observation
Effervescence occurs evolving a greenish yellow gas (chlorine gas). Chlorine is evolved together with a small amount of hydrogen chloride gas (misty fumes) which is removed by passing it through the first bottle containing water.

The gas is then dried using concentrated sulphuric acid and collected by down ward delivery method since it is denser than air.
Equation
$MnO_2(s) + 4HCl(aq) \longrightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$

Chlorine being a poisonous gas, it is prepared in the fume cupboard.

Preparation of chlorine from hydrochloric acid by oxidation with potassium permanganate
Procedure
- Place solid potassium permanganate in a flask
- Fit the apparatus as shown below



- Drop on the potassium permanganate concentrated hydrochloric acid from the tap funnel. As each drop reaches the Manganese(IV) oxide, a corresponding quantity of chlorine, a greenish yellow gas is evolved.

Equation

$2KMnO_4(aq) + 16HCl(aq) \longrightarrow 2KCl(aq) + 8H_2O(l) + 2MnCl_2(aq) + 5Cl_2(g)$

The gas collection is by down ward deliver of over brine of hot water of in a gas syringe.

This is the most convenient laboratory method because of the following reasons:
- It does not require heating
- Rate of production of chlorine can be regulated
- If the gas is collected over brine, the experiment can be done out of the fume chamber

Chlorine can be prepared from sodium chloride by adding concentrated sulphuric acid to an intimate mixture of sodium chloride and Manganese(IV) oxide. Traces of hydrogen chloride produced are removed by passing the gas over water. The gas is dried and collected by down ward delivery method.

$2NaCl(s) + MnO_2(s) + 2H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + MnSO_4(aq) + 2H_2O(l) + Cl_2(g)$

Chlorine can also be prepared from bleaching powder. The bleaching powder is placed in a flask and a dilute acid e.g. nitric acid, hydrochloric acid is added to the powder. Effervescence occurs as a greenish yellow gas (chlorine gas) is evolved. The gas is then dried and collected by any of the methods discussed.

$CaOCl_2(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + H_2O(l) + Cl_2(g)$

$CaOCl_2(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + Cl_2(g)$

Industrial manufacture of chlorine

Chlorine is produced commercially by electrolysis of sodium chloride (brine) solution. Chlorine is evolved at the anode of a specially designed cell, and since the other electrode product (sodium hydroxide, at the cathode) reacts with chlorine, they must be kept apart. This is effected by a circulating mercury diaphragm.

When current is passed through the electrolyte, decomposition takes place as follows.

NaCl (aq) $\longrightarrow$ (aq) + (aq)

$H_2O(l) \rightleftharpoons$ (aq) + (aq)

At the cathode

Both sodium and hydrogen ions move towards the cathode. Because of the nature of the mercury electrode, it will influence the discharge of sodium ion ( ) in preference to hydrogen ions ( ) since its discharge requires less energy than the discharge of hydrogen.

(aq) + $\longrightarrow$ Na(s)

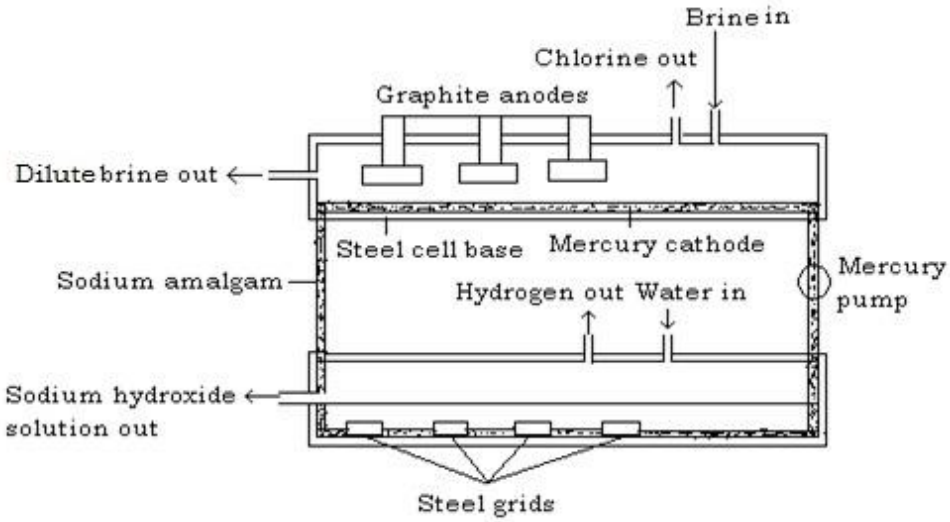
The sodium formed combines with the mercury to form sodium amalgam. The sodium amalgam encounters water in contact with steel grids on which hydrogen has a very low over voltage. Sodium hydroxide is formed and hydrogen gas is liberated.
Equation

$$Na/Hg(l) + H_2O(l) \longrightarrow NaOH(aq) + H_2(l) + Hg(l)$$

At the anode
Both chloride and hydroxyl ions move to the anode. Due to the high concentration of the chloride ions, it is discharged in preference to hydroxyl ions, therefore forming chlorine gas at the anode.

$$(aq) - \longrightarrow Cl_2(g)$$

NB. Carbon anode is used as it is relatively inert and not easily attacked by chlorine. Chlorine is very reactive and attacks most metals.



Properties of chlorine
Physical properties
- It is a greenish yellow gas with a chocking, unpleasant, irritating smell.
- It is slightly soluble in water forming a yellowish chlorine water which is a mixture of hydrochloric acid and hypochlorous acid.

$$H_2O(l) + Cl_2(g) \longrightarrow HOCl(aq) + HCl(aq)$$

- It is denser than air.
- It turns damp blue litmus paper red the bleaches it. Its bleaching action is due to the formation of hypochlorous acid. Dry chlorine does not bleach.
- Dry Chlorine does not bleach and extinguishes a burning splint.

Test for chlorine:
It is a greenish yellow gas which turns moist blue litmus paper red then bleaches it. This is because, the gas is acidic.

Chemical properties

1. Chlorine as a bleaching agent
Pour a little litmus solution into a gas jar of chlorine.

Observation: The litmus immediately turns colourless.
Chlorine bleaches colour from most dyes and will remove colour from writing ink (but not printer's ink, which consists mainly of carbon which chlorine does not attack.)

The bleaching action
Chlorine reacts with water to form hypochlorous acid

$$H_2O(l) + Cl_2(g) \longrightarrow HOCl(aq) + HCl(aq)$$

The hypochlorous acid is a very reactive compound and readily gives up its oxygen to the dye, to form a colourless compound.

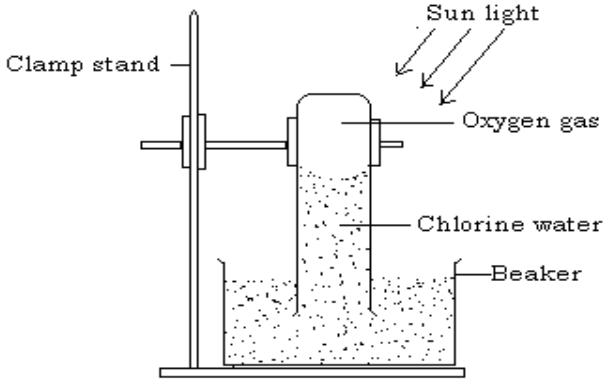
$$\underset{\text{(Coloured)}}{\text{Dye}} + HOCl \longrightarrow HCl(aq) + \underset{\text{(Colourless)}}{(\text{Dye} + O)}$$

The hypochlorous acid turns the coloured dye to colourless by **oxidation** reaction since it gives up its oxygen to the coloured dye.

This indicates that dry chlorine will not bleach since there will be no hypochlorous acid formed.

Hypochlorous acid is also used to kill bacteria and germs in drinking water, swimming pools and in sewage treatment.

2. Effect of sunlight on chlorine water
Pass chlorine gas into water in a beaker until water becomes yellow green in colour i.e. chlorine water is formed. Fill a long tube with this chlorine water and invert it in a beaker containing some of the water and expose it to bright sunlight.



After some times, a gas collects in the tube and on applying a glowing splint, the gas rekindled it showing that the gas is oxygen.

Equation

$2Cl_2(g) + 2H_2O(aq) \longrightarrow 4HCl(aq) + O_2(g)$

The above reaction occurs instantaneously in two stages as

$H_2O(l) + Cl_2(g) \longrightarrow HOCl(aq) + HCl(aq)$

$2HOCl(aq) \longrightarrow 2HCl(aq) + O_2(g)$

3. Action of chlorine on alkali

a) On cold dilute alkaline solution

Chlorine reacts with dilute aqueous solution of sodium and potassium forming pale yellow solution of the hypochlorite and chloride of the metal.

$Cl_2(g) + 2NaOH(aq) \longrightarrow NaOCl(aq) + NaCl(aq) + H_2O(l)$

(Sodium hypochlorite) (Sodium chloride)

$Cl_2(g) + 2KOH(aq) \longrightarrow KOCl(aq) + KCl(aq) + H_2O(l)$

(Potassium hypochlorite) (Potassium chloride)

Ionically

$Cl_2(g) +$ (aq) $\longrightarrow$ (aq) + (aq) + $H_2O(l)$

b) On hot concentrated aqueous solution

If chlorine is passed into a hot concentrated solution of potassium, a mixture of potassium chlorate and potassium chloride are formed. A similar reaction occurs when chlorine reacts with concentrated sodium and calcium hydroxide.

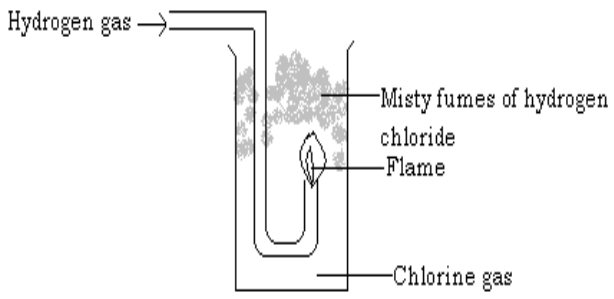
$6KOH(aq) + 3Cl_2(g) \longrightarrow KClO_3(aq) + 5KCl(aq) + 3H_2O(l)$

Or

$3Cl_2(g) +$ (aq) $\longrightarrow$ (aq)+ (aq) + $3H_2O(l)$

4. Reaction of chlorine with hydrogen

When a jet of burning hydrogen is lowered into a gas jar of chlorine, it continuous to burn with a white flame producing steamy fumes of hydrogen chloride and the greenish yellow colour of chlorine disappears.



$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

A mixture of hydrogen and chlorine also explodes when exposed to bright sunlight. This shows the great affinity of chlorine for hydrogen. The reaction is slow in dim sun light and reaction does not take place in the absence of light.

5. Chlorine as an oxidizing agent

An oxidizing agent is one which can

i) Remove hydrogen from a compound
ii) Accept electrons donated by metals

Chlorine removes hydrogen from many compounds as well as accepts electrons from metals. The oxidizing property of chlorine is illustrated by the following reactions.

i) Reaction with hydrogen sulphide

When a gas jar of hydrogen sulphide is inverted over a gas jar of chlorine, yellow solids of sulphur and white fumes of hydrogen chloride are formed.

$H_2S(g) + Cl_2(g) \longrightarrow 2HCl(g) + S(s)$

Hydrogen sulphide has been oxidized to sulphur and chlorine itself was reduced to hydrogen sulphide.

The reaction proceeds as follows

$H_2S \longrightarrow +$

$\longrightarrow S +$ (oxidation)

$Cl_2 + \longrightarrow$ (reduction)

ii) Reaction with ammonia

Ammonia burns in chlorine and is oxidized to nitrogen and chlorine itself is reduced to hydrogen chloride.

$2NH_3(g) + 3Cl_2(g) \longrightarrow N_2(g) + 6HCl(g)$

The hydrogen chloride produced reacts with excess ammonia forming white fumes of ammonium chloride.

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

Overall equation for the reaction is

$8NH_3(g) + 3Cl_2(g) \longrightarrow N_2(g) + 6NH_4Cl(s)$

iii) Oxidation of iron(II) to iron(III)

Chlorine accepts electrons like other oxidizing agents and is converted to chlorine ion.

$Cl_2 + \longrightarrow$

The electron that the chlorine accepts is supplied by a reducing agent which in this case is iron(II).

$\longrightarrow + e^-$

When chlorine gas is bubbled through a pale green solution of iron(II) chloride, it changes to yellow due to the formation of iron(III) chloride. When sodium hydroxide is added to this solution it forms red brown precipitates. This indicates that iron(II) chloride has been oxidized to iron(III) chloride.

$2FeCl_2(aq) + Cl_2(g) \longrightarrow 2FeCl_3$

Or

(aq) + $Cl_2(g) \longrightarrow$ (aq) + (aq)

iv) **Reaction of chlorine with hydrocarbons e.g. turpentine** ($C_{10}H_{16}$)

Hydrocarbons consist of only carbon and hydrogen. Chlorine removes hydrogen from hydrocarbon to form hydrogen chloride and black carbon particles are left.

Procedure

Warm a little turpentine in a dish. Dip into it a filter paper and drop the filter paper with turpentine in a gas jar containing chlorine

Observation

A red flash accompanied by a violent reaction occurs. Black cloud of solid particles of carbon is produced and hydrogen chloride gas is also formed.

$C_{10}H_{16}(l) + 8Cl_2(g) \longrightarrow 10C(s) + 16HCl(g)$

The presence of hydrogen chloride can be shown by blowing the fumes from ammonia bottle across the top of the jar. Dense white fumes of ammonium chloride are formed.

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

6) Displacement reaction of chlorine

Chlorine being more reactive than the other halogens displaces them from their salts.

i) Reaction of chlorine with potassium bromide

When chlorine is bubbled through a saturated solution of potassium bromide, the clear solution immediately turns red (due to formation of bromine water) and a drop of a red liquid (bromine) is observed at the bottom of the boiling tube.

$2KBr(aq) + Cl_2(g) \longrightarrow 2KCl(aq) + Br_2(l)$

Ionically

(aq) + $Cl_2(g) \longrightarrow$ (aq) + $Br_2(l)$

Bromine dissolves in tetra chloromethane to form a reddish brown solution.

ii) Displacement of iodine

When chlorine is bubble through a solution of potassium iodide, the clear solution turns to the characteristic dark brown ―iodine‖ colour and a black solid (iodine) is deposited as iodine is only slightly soluble in water. On warming the solution, the characteristic violet vapour of iodine is seen.

$2KI(aq) + Cl_2(g) \longrightarrow 2KCl(aq) + I_2(l)$

Ionically

(aq) + $Cl_2(g) \longrightarrow$ (aq) + $I_2(l)$

Iodine dissolves in tetra chloromethane to form a violet solution.

7) Reaction of chlorine with non metals

i) Phosphorus

When a piece of dry yellow phosphorus is lowered in a gas jar of chlorine, it burns spontaneously giving off white fumes of chlorides of phosphorus mainly phosphorus tri chloride (PCl_3)

$$P_4(s) + 6Cl_2(g) \longrightarrow 4PCl_3(g)$$

(Phosphorus(III) chloride)

$$P_4(s) + 10Cl_2(g) \longrightarrow 4PCl_5(g)$$

(Phosphorus(V) chloride)

ii) Sulphur

When dry chlorine is passed over molten sulphur in a distilling flask, connected to a condenser, a reddish liquid distills over.

$$2S(l) + Cl_2(g) \longrightarrow S_2Cl_2(l)$$

(disulphur dichloride)

8) Reaction of chlorine with metals

i) Reaction with sodium and magnesium

Burning sodium and magnesium continue to burn is chlorine forming white fumes of sodium and magnesium chlorides respectively.

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$

ii) Reaction with Dutch metal

Dutch metal is an alloy of copper and zinc. When a piece of Dutch metal is dropped in a gas jar of chlorine and heated, it burns with a green flame to form copper(II) chloride and Zinc chloride.

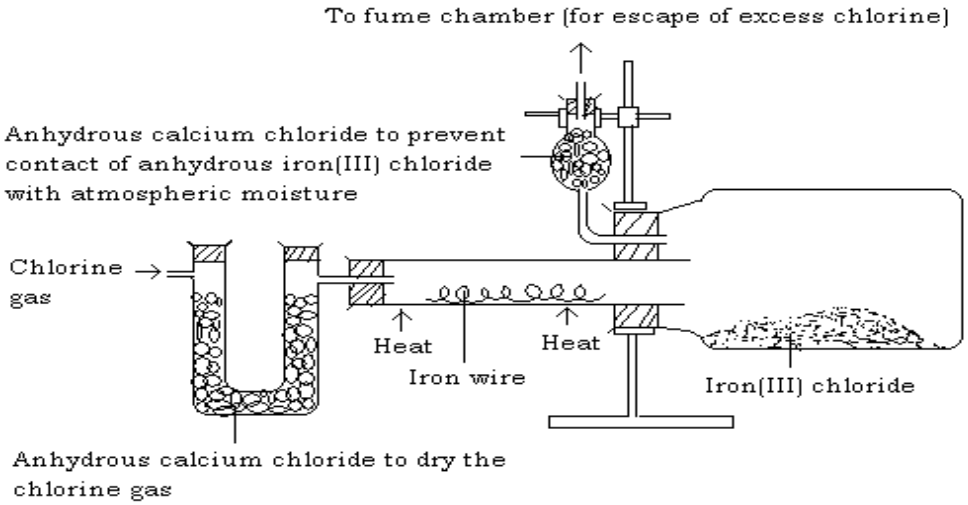
$$Cu(s) + Cl_2(g) \longrightarrow CuCl_2(s)$$

$$Zn(s) + Cl_2(g) \longrightarrow ZnCl_2(s)$$

iii) Action of chlorine on iron (preparation of iron(III) chloride by direct synthesis)

Procedure

- Place a coil of iron wire in a hard glass tube in the apparatus below. The iron coil must be free of rust.



- Pass a stream of dry chlorine over it.
- Heat the wire and stop the heating the moment the reaction starts.

Observation

The wire glows and the reaction continues without application of heat indicating that the reaction is **exothermic.** Black crystals of iron(III) chloride sublimes and collects in the small bottle which acts as a condenser.

$$2Fe(s) + 3Cl_2(g) \longrightarrow 2FeCl_3(s)$$

Formation of iron(III) chloride shows that chlorine is an oxidizing agent. The iron (II) chloride formed is immediately oxidized to iron(III) chloride.

The black crystals of anhydrous iron(III) chloride should be placed in a desiccator as they are very deliquescent.

Note

1. Sodium chloride can be made in a similar way.

   $$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

2. Iron(II) chloride (white solid) is made in the same way using dry hydrogen chloride instead of chlorine.

   $$Fe(s) + 2HCl(g) \longrightarrow FeCl_2(s) + H_2(g)$$

Uses of chlorine

1. Chlorine is extensively used as a bleaching agent and in the manufacture of bleaching agents.
2. It is used for making domestic antiseptic solutions such as sodium hypochlorite.
3. Chlorine is used in the manufacture of chlorates used for example as weed killers.
4. Manufacture of hydrogen chloride which is used in the manufacture of plastic like PVC (polyvinylchloride).

5. Manufacture of many organic chemicals e.g. tetra chloromethane (CCl_4), 1,1,2-trichloroethene (C_2HCl_3). These compounds are solvents used to remove grease from other substances (degreasing agents), dry cleaning fluids.
6. Chlorine is used to sterilize water for domestic and industrial uses i.e. it kills bacteria and other germs in water and is used in water purification process.

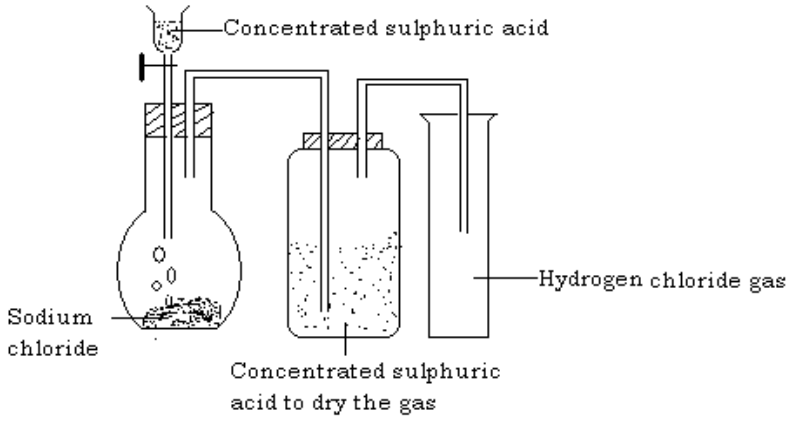
HYDROGEN CHLORIDE

Laboratory preparation

Hydrogen chloride can be prepared in the laboratory by the action of concentrated sulphuric acid on common salt (rock salt).

Procedure

- Place sodium chloride in flask and fit the apparatus as shown below.



- Add concentrated sulphuric acid down the funnel.

Effervescence occurs and misty fumes are observed. The gas is passed through a wash bottle containing concentrated sulphuric acid to dry the gas and it is collected by down ward delivery method as it is denser than air.

$H_2SO_4(l) + NaCl(s) \longrightarrow NaHSO_4(s) + HCl(g)$

Note

1. Sodium chloride is used because it is cheap and readily available.
2. The reaction proceeds in the cold though a further yield is obtained in the industrial process by heating.
3. The sulphate is not obtained under laboratory conditions because its formation requires a higher temperature but is obtained during the industrial process.

Test for hydrogen chloride

1. When the gas is bubbled through a solution of silver nitrate and nitric acid, it forms white precipitates of silver chloride.

$AgNO_3(aq) + HCl(g) \longrightarrow AgCl(s) + HNO_3(aq)$

Or

(aq) + (aq) $\longrightarrow$ AgCl(s)

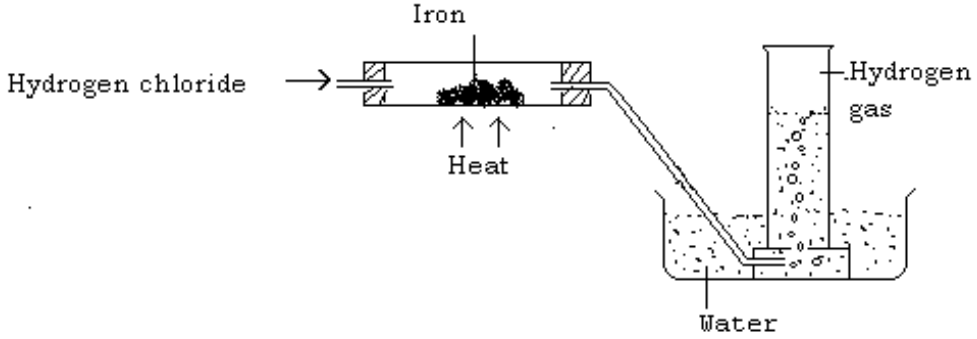
2. Hydrogen chloride forms dense white fumes of ammonium chloride with ammonia.

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

Properties of hydrogen chloride gas
Physical properties
1. It is a colourless gas with an irritating, choking smell.
2. It forms misty fumes in damp air as it forms tiny droplets of hydrochloric acid.
3. It turns moist blue litmus paper red.
4. It is also soluble in methyl benzene (toluene)
5. Hydrogen chloride gas is denser than air.
6. It is very soluble in water. When it dissolves in air, it forms hydrochloric acid.

The high solubility of hydrogen chloride gas in water can be demonstrated by the fountain experiment as that of ammonia.

Chemical properties
1. Deduction of the composition of hydrogen chloride
a) Action of dry hydrogen chloride gas on heated iron
When dry hydrogen gas is passed over heated iron, the gaseous product that is collected over water burns with a pop sound indicating that the gas is hydrogen.



$Fe(s) + 2HCl(g) \longrightarrow FeCl_2(s) + H_2(g)$

b) Reaction with potassium permanganate ($KMnO_4$)
When hydrogen chloride gas is slowly passed over potassium permanganate, a greenish yellow gas is formed. The greenish yellow gas is chlorine.

$2KMnO_4(s) + 16HCl(g) \longrightarrow 2KCl(aq) + 2MnCl_2(aq) + 8H_2O(l) + 5Cl_2(g)$

From the above two reactions, conclusions can be made that the components of hydrogen chloride are chlorine and hydrogen.

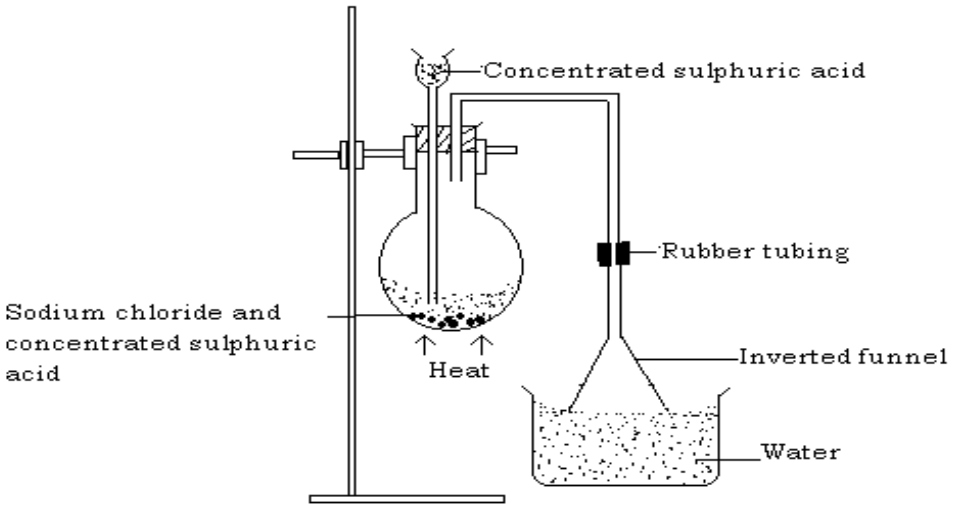
2. Reaction with ammonia
Hydrogen chloride reacts with ammonia forming white fumes of ammonium chloride.

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

Preparation of a solution of hydrogen chloride in water (hydrochloric acid)

The solution of the gas in water forms hydrochloric acid. When the gas is bubbled through water until no more of the gas can dissolve, then the product is concentrated hydrochloric acid and contains 36% by mass of hydrogen chloride.

When dissolving, the apparatus should be arranged as below. The method is only suitable if the gas is very soluble.



The rim of the funnel must just be at the surface of water in the beaker this avoids water being sucked into the preparation apparatus; a delivery tube cannot also be used because it would suck up water in to the preparation apparatus.

Properties of hydrochloric acid

It has all the properties typical of an acid like

- Sour taste
- Turns blue litmus paper red
- It is fully ionized in aqueous solution indicating that it is a strong acid

$HCl(aq) \longrightarrow (aq) + \quad (aq)$

$H_2O(l) + HCl(aq) \longrightarrow (aq) + \quad (aq)$

- It liberates carbon dioxide with carbonates

$ZnCO_3(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + CO_2(g) + H_2O(l)$

Ionically

$(aq) + 2 \quad (aq) \longrightarrow CO_2(g) + H_2O(l)$

- It forms hydrogen with metals above hydrogen in the electrochemical series.

$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$

- It neutralizes bases to form salts and water

$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$

Ionically

(aq) + (aq) $\longrightarrow$ $H_2O(l)$

$CuO(s) + 2HCl(aq) \longrightarrow CuCl_2(aq) + H_2O(l)$

- Oxidizing agents e.g. Manganese (IV) oxide and potassium permanganate oxidize the concentrated hydrochloric acid to chlorine.

$2KMnO_4(s) + 16HCl(aq) \longrightarrow 2KCl(aq) + 2MnCl_2(aq) + 8H_2O(l) + 5Cl_2(g)$

These properties are due to the fact that hydrogen chloride although a covalent compound ionizes completely when dissolved in water and therefore show typical acidic characteristics.

Uses of hydrochloric acid

- It is used in the removal of rust from iron (descaling) before it is galvanized.
- It is used in cleaning metals before they are electroplated.
- It is used in the manufacture of plastics like polyvinylchloride
- Used in the preparation of soluble chlorides

Preparation of solution of hydrogen chloride in methyl benzene

The preparation is done the same way as above. Hydrogen chloride dissolves but does not ionize in organic solvents like methyl benzene and exists as a covalent compound. Therefore, the solution does not conduct electricity; has no effect on litmus paper; does not react with metals above copper and does not react with carbonates or hydrogen carbonates but reacts with ammonia to form white precipitates of ammonium chloride since the salt is insoluble in organic solvents.

Test for chlorides

Solid chlorides

When concentrated sulphuric acid is added to any chloride, hydrogen chloride gas is evolved.

The gas forms fumes in moist air; turns moist blue litmus paper red; and forms thick white fumes of ammonium chloride with ammonia; and forms white precipitates of silver chloride with acidified silver nitrate solution.

Chloride in solution

To a solution of chloride, add a little nitric acid and then silver nitrate solution. White precipitates of silver chloride are seen.

(aq) + (aq) $\longrightarrow$ AgCl(s)

When a little ammonia solution is added to the above solution, the white precipitates dissolve. The precipitates are insoluble in nitric acid. The only two insoluble chlorides are lead(II) chloride and silver chloride.

Sample questions on Chlorine and its compound

1. *Describe and explain the laboratory preparation and manufacture of chlorine. Using equations, describe the reactions of chlorine with: metals, non metals, water, dilute acids and hydrocarbons. How would you show experimentally that hydrogen chloride is very soluble in water? Outline the uses of chlorine.*
2. *With the aid of a labeled drawing, explain how hydrogen chloride and hydrochloric acid are prepared in the laboratory. Describe experiments to deduce the composition of hydrogen chloride. Describe the reactions of hydrogen chloride with ammonia. Explain the behaviour of hydrogen chloride in (i) water and (ii) methyl benzene.*
3. *Describe one experiment in each case to show (a) how hydrochloric acid acts as a reducing agent (b) how hydrogen chloride can be identified. Give the uses of hydrochloric acid.*