

CHLORINE AND ITS COMPOUNDS

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INTRODUCTION

Chlorine is a non-metal assigned atomic number 17

Electronic configuration 2:8:7.

It belongs to group VII and period 3.

Members of group VII are called **halogens**

Other halogens are bromine, fluorine, iodine etc.

Chlorine has a chemical symbol *Cl*

Chlorine forms a diatomic molecule Cl_2

It has two isotopes; chlorine-35 and chlorine-37.

Existence

Chlorine is a greenish yellow poisonous gas which easily attacks the nose and the lungs.

It is formed when hydrochloric acid is oxidized.

On large scale it is prepared by the electrolysis of Brine (concentrated sodium chloride)

The chief source of chlorine is sodium chloride.

Laboratory preparation

In the lab it is usually prepared by the oxidation of concentrated hydrochloric acid. The common oxidizing agents used are manganese (IV) oxide and potassium permanganate and lead (IV) oxide.

Hydrochloric acid + Oxidizing agent \longrightarrow salt(s) + water + chlorine

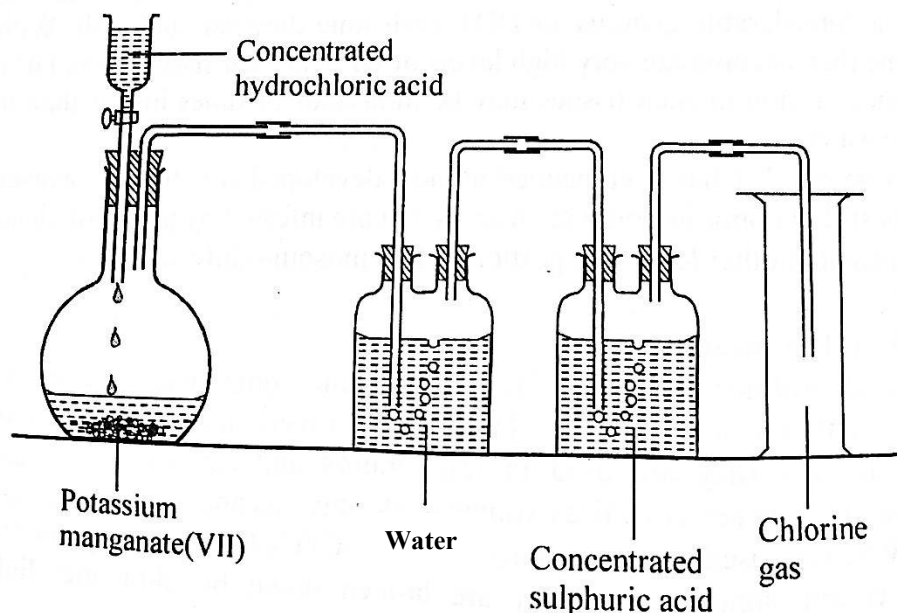
(a) Using potassium permanganate

This is the most convenient method of preparing the gas since the reaction takes place in the cold.

Conditions for the reaction

- No heat is required because potassium permanganate is a very powerful oxidizing agent
- The acid must be concentrated.

Set up of the apparatus



Procedure

Solid Potassium permanganate is placed at the bottom of a flat bottomed flask.

Concentrated hydrochloric acid is then run onto the potassium permanganate by use of a dropping funnel or thistle funnel because it is a liquid.

Effervescence of a greenish yellow gas (chlorine) occurs.

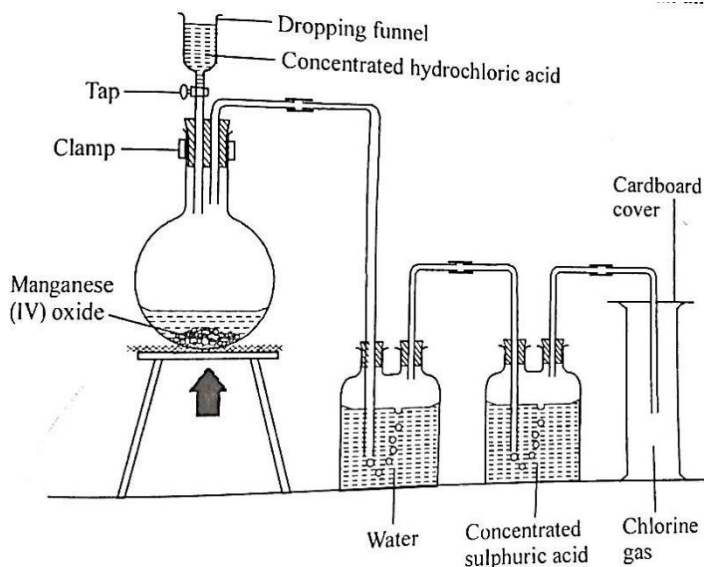
The gas is passed through water to remove misty fumes of hydrogen chloride gas/ any acid spray. It is dried by passing it through concentrated sulphuric acid because it is acidic. (*It can also be dried by using anhydrous calcium chloride*)
The dry gas is then collected by down ward delivery since it is denser than air.

Equation of the reaction



(b) Using manganese (VI) oxide

Set up of apparatus



Conditions for the reaction

- Heat is required
- The acid must be concentrated

Procedure

Solid Manganese (IV) oxide is placed at the bottom of a round bottomed flask and the apparatus arranged as shown above.

Concentrated hydrochloric acid is then run onto the manganese (IV) oxide by use of a dropping funnel or thistle funnel because it is a liquid and the mixture is heated gently.

Effervescence of a greenish yellow gas is evolved and the gas evolved is chlorine.

The gas is then collected over hot water or brine.

If the gas is required pure and dry it is first passed through water to remove traces of hydrogen chloride gas. It is then dried by passing it through concentrated sulphuric acid because it does not react with it/it is acidic.

The dry gas is then collected by downward delivery method because it is denser than air.

Equation for the reaction



Manganese (IV) oxide is a mild oxidizing agent therefore heating is necessary

Preparation of chlorine from sodium chloride

Sodium chloride is first reacted with concentrated sulphuric acid to form hydrogen chloride



The hydrogen chloride formed is then oxidized using manganese (IV) oxide to form chlorine gas



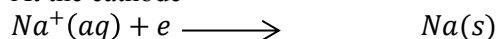
NB: the gas is prepared in a fume cupboard or in open air since chlorine is very poisonous.

Industrial preparation of chlorine

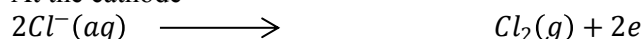
This is done by electrolysis of concentrated solution of sodium chloride using mercury as a cathode and carbon as anode. Sodium is deposited at the cathode and chlorine gas is liberated at the anode.

Reaction:

At the cathode



At the anode



Test for chlorine gas

Pass chlorine gas through damp litmus paper

The greenish yellow gas turns moist blue litmus paper to red and then rapidly bleaches it.

Physical properties

Chlorine is a greenish yellow gas

It is a very poisonous gas

It is denser than air

It is fairly/ moderately soluble in water

It has a pungent choking smell

It turns blue litmus paper red and then bleaches it.

NB: the gas does not burn and it extinguishes a burning flame

Chemical properties

Reaction with water

Chlorine reacts with water to form a mixture of hydrochloric acid and hypochlorous acid.

When chlorine is dissolved in water, the green-yellow solution formed is called chlorine water



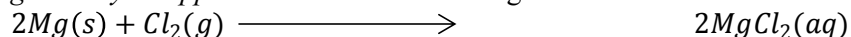
Reaction with metals

Most metals react with chlorine forming the corresponding metal chlorides.

Where a metal exhibits more than one Valency, the chloride of the higher Valency is formed. For example, with iron, which exhibits valency of 2 and 3, iron (III) chloride is formed. With copper, copper (II) chloride is formed. This shows that chlorine is a strong oxidizing agent.

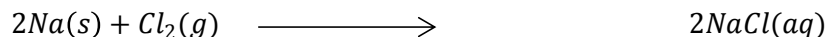
(a) sodium and magnesium

Magnesium ribbon burns in chlorine with a *bright white flame*. The *greenish -yellow* colour of chlorine *gradually disappears*. A *white solid* of magnesium chloride is formed.



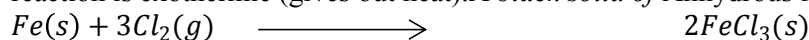
This is an oxidation -reduction reaction. Chlorine is acting as an oxidizing agent.

Sodium also forms white sodium chloride.

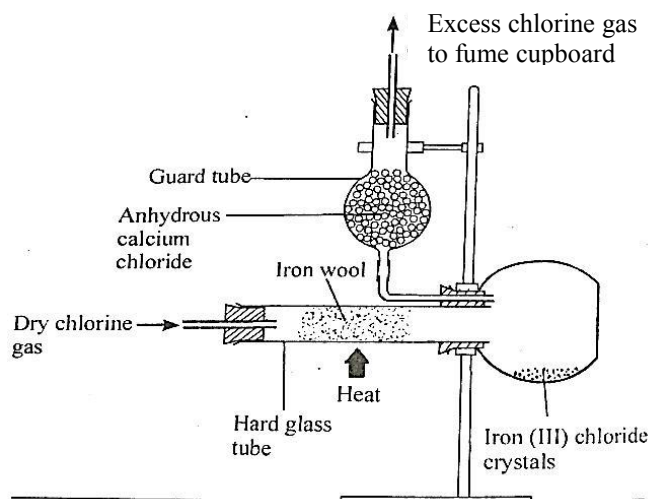


(b) Iron

When dry chlorine is passed over heated iron wire, a *red glow* spreads through the wire indicating that the reaction is exothermic (gives out heat). A *black solid* of Anhydrous iron (III) chloride is then formed.



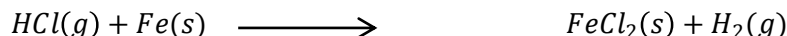
Set up



The above method is a convenient method for preparing iron (III) chloride

NB: 1. Iron (III) chloride is formed instead of iron (II) chloride because the iron (II) chloride formed is further oxidized by the chlorine forming Iron (III) chloride.

However if hydrogen chloride is used instead of chlorine, a *white solid* of Anhydrous Iron (II) chloride will be formed



2. The reaction between iron and chlorine forms *brown fumes* of gaseous iron (III) chloride which turns directly to *black crystals* of iron (III) chloride. This shows that iron (III) chloride sublimates.

3. Anhydrous calcium chloride is used to prevent iron (III) chloride from absorbing moisture and forming a solution since iron (III) chloride is **deliquescent**.

Calcium oxide may be used to replace calcium chloride because being basic; it reacts with acidic chlorine gas to form a salt, thus preventing air pollution.

4. Aluminium chloride is also prepared using the same apparatus.

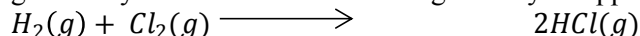
Qn: Explain why chlorine forms iron (III) chloride when reacted with iron and not iron (II) chloride.

Chlorine is a strong oxidizing agent so it oxidizes iron to its higher oxidation state of Iron (III)

Reaction with non-metals

(a) Hydrogen

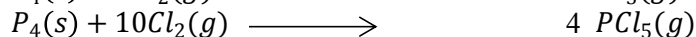
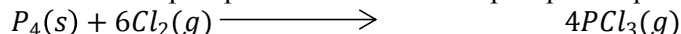
It burns in chlorine with a white flame forming misty/ steamy fumes of hydrogen chloride. The greenish-yellow Colour of chlorine gradually disappears



In bright sunlight, hydrogen combines with chlorine explosively forming hydrogen chloride gas.

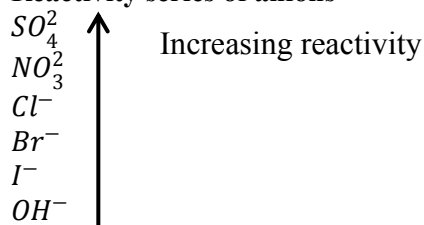
(b) Phosphorus

White phosphorus burns in chlorine with a *bright yellow flame* forming *white fumes* of the phosphorus chlorides i.e. phosphorus trichloride and phosphorus pentachloride.



Displacement reactions of chlorine

Reactivity series of anions

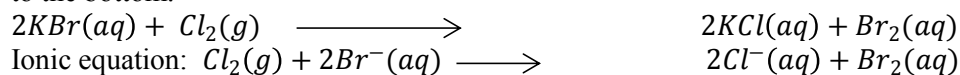


Reaction with bromides and iodides/ displacement reactions of chlorine

Chlorine is a very strong oxidizing agent. It therefore displaces bromine and iodine from their salts

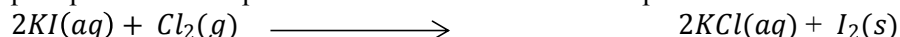
(a) with bromides

When chlorine gas is bubbled through a solution of potassium bromide, chlorine will displace the bromide from the solution and the colourless solution turns reddish brown, this is due to the formation of bromine water. Later the solution becomes saturated with bromine and a dark red liquid of bromine sinks to the bottom.



(b) with iodides

When chlorine gas is bubbled through a solution of potassium iodide, the colourless solution turns deep brown due to the formation of iodine. Since iodine is only slightly soluble in water, it will form a black precipitate/ solid deposit. This shows that chlorine displaces iodide ions from the solution.



Chlorine as an oxidizing agent

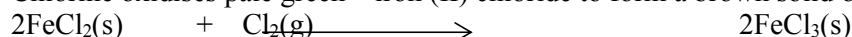
(a) reaction with hydrogen sulphide

Chlorine oxidizes hydrogen sulphide to a yellow solid of sulphur and itself reduced to steamy fumes of hydrogen chloride



(ii) Reaction with iron (II) chloride

Chlorine oxidises pale green iron (II) chloride to form a brown solid of iron (III) chloride

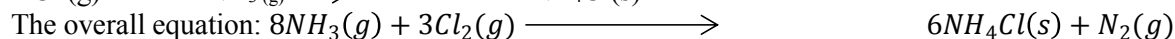
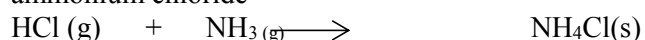


(d) Reaction with ammonia

Ammonia burns spontaneously in chlorine gas and it is oxidized to nitrogen gas. Hydrogen chloride is also formed.



In excess ammonia, the hydrogen chloride formed combines with ammonia to form dense white fumes of ammonium chloride

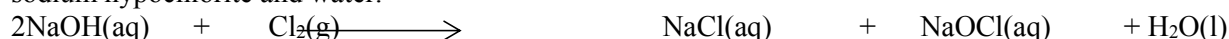


Action of chlorine on alkalis

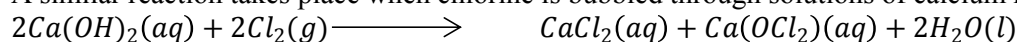
The product formed when chlorine reacts with alkalis depends on the temperature and concentration of the alkali.

(a) With cold dilute alkalis

Chlorine reacts with cold dilute sodium hydroxide to form a pale yellow solution of sodium chloride, sodium hypochlorite and water.



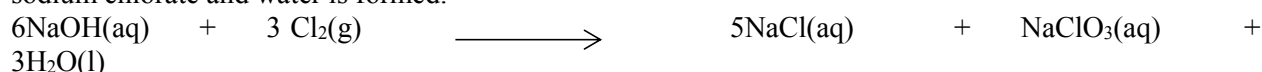
A similar reaction takes place when chlorine is bubbled through solutions of calcium hydroxide.



Calcium hypochlorite is commonly known as bleaching powder.

(b) With hot concentrated sodium hydroxide.

When chlorine is passed through hot concentrated sodium hydroxide, a mixture of sodium chloride, sodium chlorate and water is formed.



Reaction with hydrocarbons e.g. turpentine

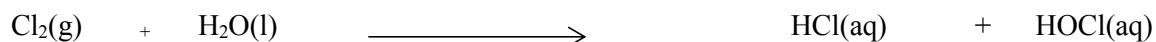
Burning hydrocarbons continue to burn in chlorine to form a black solid of carbon and hydrogen chloride is formed.

If cotton wool is soaked in warm turpentine ($C_{10}H_{16}$) and placed in a jar of chlorine, it bursts into a red flame and a black solid will be formed



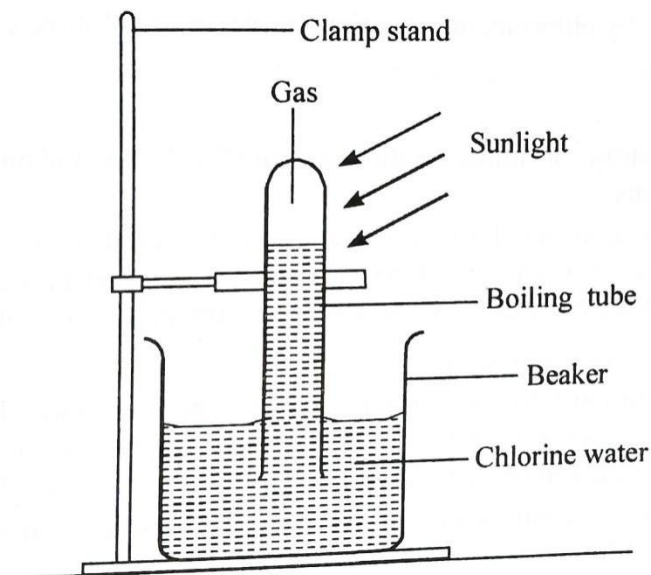
Chlorine water

Chlorine water is a mixture of hydrochloric acid and hypochlorous acid obtained by passing chlorine through water. it is yellow in colour.



Effect of sunshine on chlorine water

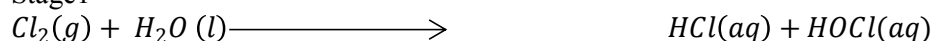
When a glass tube filled with chlorine water is exposed to sunlight for some time, the *greenish yellow* chlorine water turns to *colourless*. This is because the greenish yellow hypochlorous acid is slowly decomposed by sunlight to form hydrochloric acid which is colourless. Oxygen gas is also formed. The rate of the reaction is greatly increased by sunlight.



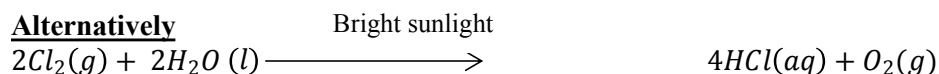
Equations

It can take two steps

Stage 1



Alternatively



Bleaching action of chlorine

When coloured flowers (red or blue) or a damp blue litmus paper are placed in a gas jar containing chlorine, the flowers are bleached (their Colour is removed)/ turns colourless. The bleaching action is due to the formation of hypochlorous acid formed due to the reaction of the moisture in the flower with chlorine.



The hypochlorous acid then gives away its oxygen to the coloured dye in the flower (oxidation)



Chlorine will bleach the Colour from most dyes including writing ink. However it does not bleach printer ink since it is made up of carbon which it does not attack.

Nb: dry chlorine does not bleach or a dry litmus paper will not be bleached by chlorine.

Reason: this lack water and hence no hypochlorous acid will be formed.

Uses of chlorine

- It is used as a bleaching agent. It bleaches cotton, linen and paper
- Chlorine is added in water to kill bacteria

- Used in the manufacture of hydrochloric acid
- Used in making insecticides such as DDT
- Used in the manufacture of plastics e.g. Polyvinyl chloride (P.V.C) which is used for making pipes, chairs and tables.
- Used in the manufacture of weed killers e.g sodium chlorate.
- Manufacture of antiseptics e.g. sodium hypochlorite.
- manufacture of anaesthetics such as chloroform ($CHCl_3$)
- used in the manufacture of hydrochloric acid
- used in the manufacture of organic solvents such as tetrachloromethane

HYDROGEN CHLORIDE GAS

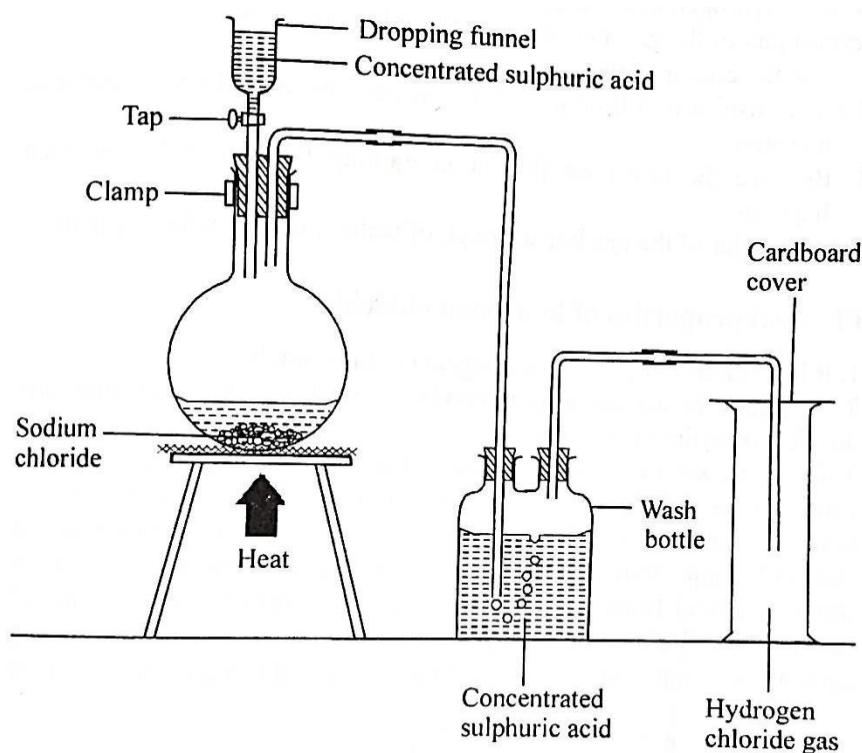
Lab preparation

Hydrogen chloride is prepared in the laboratory by the action of concentrated sulphuric acid on a solid chloride. Sodium chloride is one of the most commonly used because it is cheap and readily available.

Potassium chloride may also be used

Chlorides of lead, calcium and barium are not used. This is because they form insoluble sulphates which coat the chloride preventing further reaction.

Set up of apparatus



Procedure

Sodium chloride is placed in a round bottomed flask, and the apparatus arranged as shown above. Concentrated sulphuric acid is then added through the thistle funnel to the sodium chloride and the reaction mixture is then heated.

Effervescence of a colourless gas occurs and misty fumes of hydrogen chloride gas are given off.

The gas is passed through a wash bottle containing concentrated sulphuric acid to dry the gas.

The gas is then collected by downward delivery method because it is denser than air

equation



NB: Sodium hydrogen sulphate is formed instead of sodium hydrogen sulphate because the conditions in the glass apparatus will not favour the removal of both hydrogen ions from the acid.

1. Conditions for the reaction

- No heat is required
- The acid must be concentrated

2. the rate of reaction can be increased by

- heating the mixture gently
- using powdered/ crushed lumps of sodium chloride

3. Hydrogen chloride gas cannot be collected over water since the gas is very soluble in water to form hydrochloric acid.

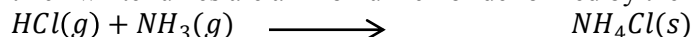
Physical Properties of hydrogen chloride

- It is a colourless gas
- It forms misty fumes in damp air because it forms tiny drops of hydrochloric acid.
- It has a choking irritating smell
- It is denser than air
- It is very soluble in water, forming hydrochloric acid (1 cm³ of water can dissolve about 450cm³ of the gas)
- The gas shows the usual acidic properties e.g. Turns moist blue litmus paper to red
- It reacts with carbonates and hydrogen carbonates to give off Carbon dioxide gas
- It reacts with bases to form a salt and water

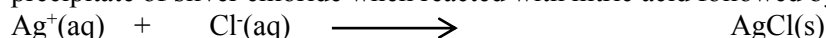
Test for the gas.

Hydrogen chloride forms misty fumes in moist air; it turns moist blue litmus to red.

It is confirmed *using concentrated ammonia solution*. When a bottle containing concentrated ammonia solution is opened near a test tube containing hydrogen chloride gas, *thick white fumes* are formed. The thick white fumes are ammonium chloride formed by the reaction



The gas may also be confirmed by bubbling it through a solution of silver nitrate. It produces a white precipitate of silver chloride when reacted with nitric acid followed by silver nitrate.



Effect of solvent on the properties of hydrogen chloride gas

Hydrogen chloride is soluble in both polar solvents such as water and non-polar solvents such as benzene, methyl benzene and carbon tetrachloride.

When dissolved in water, hydrogen chloride gas ionized forming hydrogen ions and chloride ions.



This ionization is responsible for the acidic properties of the solution of hydrogen chloride in water. The ions also conduct electricity.

When dissolved in benzene, hydrogen chloride gas does not ionize.

polar solvent (water)	non polar solvent (methyl benzene)
the solution turns blue litmus paper red	the solution has no effect on litmus paper
the solution liberates carbon dioxide from carbonates	the solution does not liberates carbon dioxide from carbonates
when reacted with metals, hydrogen gas is liberated	when reacted with metals, hydrogen gas is not liberated
the solution conducts electricity (an electrolyte)	the solution does not conduct electricity (non-electrolyte)
the solution neutralizes bases	the solution does not neutralize bases

The fountain experiment

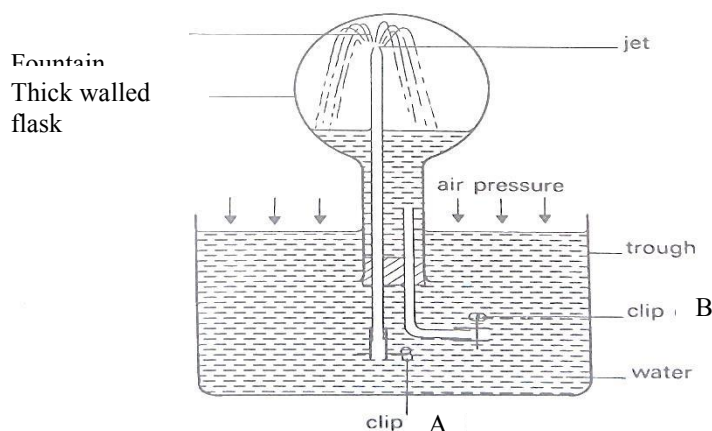
The very high solubility of hydrogen chloride gas in water can be showed using the fountain experiment.

Procedure

A thick walled round bottomed flask is filled with hydrogen chloride gas .

It is thick walled so as to resist the high pressure that will be built up in the flask.

The round bottomed flask is then fitted with a stopper carrying tubes with clips and it is inverted in water as shown below.



Clip B is opened for a short time so as to allow some little water into the flask. Close it and allow the few drops of water to dissolve the gas in the flask.

Clip A is then opened.

Observation:

Water moves up by capillary and comes out of the capillary tube at the jet in form of a fountain. This continues until the flask is filled with water.

Explanation

The little water allowed into the flask when clip B was opened absorbed all the hydrogen chloride. This created a partial vacuum in the flask so that atmospheric pressure forces the water in the trough to rise when clip A is opened.

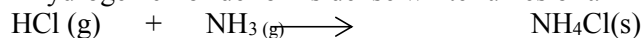
Chemical properties

Combustion

Hydrogen chloride does not burn, and it extinguishes a burning flame.

Reaction with ammonia

Hydrogen chloride forms dense white fumes of ammonium chloride when reacted with ammonia gas.



Reaction with metals

Hydrogen chloride gas reacts with heated iron, magnesium, and aluminium forming the metal chloride and hydrogen gas.

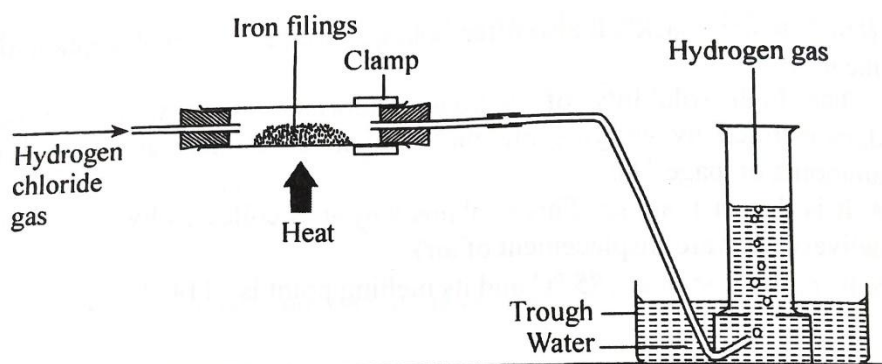
Where the metal exhibits more than one valency, the chloride of the lower valency is formed. This is unlike the reaction of chlorine with metals where the chloride of the higher valency is formed.

Hydrogen chloride gas does not react with copper because copper is lower than hydrogen in the reactivity series.

Reaction with iron

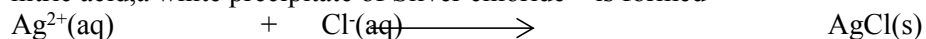
When hydrogen chloride is passed through heated iron wire, a white solid of iron (II) chloride is formed. Hydrogen gas is also formed which burns with a pop sound.





Reaction with silver nitrate

When dry hydrogen chloride gas is bubbled through silver nitrate solution which has been acidified with nitric acid, a white precipitate of Silver chloride is formed



This test can be used to confirm the presence of a chloride in qualitative analysis

Uses of hydrogen chloride

In manufacture of vinyl chloride, fertilizers, dyes etc.

Used in the separation of cotton from wool

Used in delinting of cotton

Used in the manufacture of hydrochloric acid.

HYDRO CHLORIC ACID

Preparation

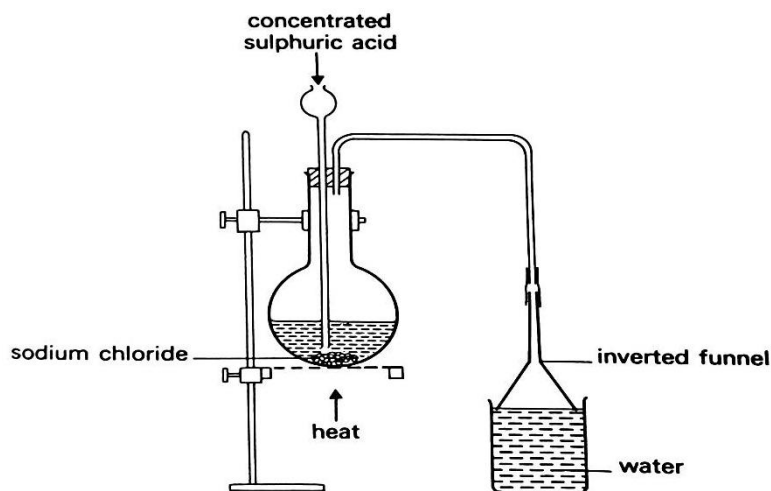
An aqueous solution of hydrochloric acid is prepared by dissolving hydrogen chloride gas in water.

Procedure

Concentrated sulphuric acid is added to sodium chloride in a flat bottomed flask using a thistle funnel.

Effervescence of a colourless gas is formed.

The gas is absorbed in water using filter funnel inverted over a beaker of water to prevent suck back.



Properties

The acid behaves chemically in two ways: as an acid and as a reducing agent.

As an acid

- ✓ It shows all the properties typical of acids i.e.
- ✓ It has a sour taste
- ✓ Turns moist blue litmus paper to red
- ✓ The solution conducts electricity
- ✓ It reacts with metals and hydrogen gas is liberated

✓ It reacts with carbonates and hydrogen carbonates to give off Carbon dioxide gas

✓ It reacts with bases to form a salt and water only

As a reducing agent; see preparation of chlorine gas

The acid reacts as a reducing agent when reacted with strong oxidizing agents i.e. it forms chlorine when reacted with potassium permanganate or when heated with manganese (IV) oxide

Uses of hydrochloric acid

- To stabilize pH in the manufacture of beers and wines
- To remove oxides of metals from the surfaces on metals (pickling)
- Manufacture of chlorine gas
- Preparation of soluble chlorides such as calcium chloride.

Chlorides: these are salts of hydrochloric acid

Properties of chlorides

(a) Action of heat

(b) Action of concentrated sulphuric acid

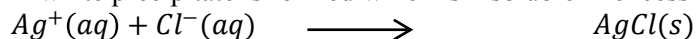
(c) Solubility in water

Tests for chlorides

(a) Using nitric acid followed by silver nitrate

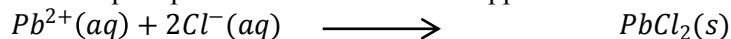
Observation

A white precipitate is formed which is insoluble in excess acid.

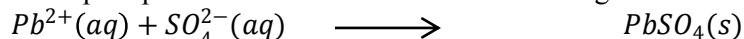


(b) Using Nitric acid followed by lead (ii) nitrate followed by heating

A white precipitate is formed which disappears/dissolves on heating and reappears on cooling



NB: warming helps to differentiate lead (II) chloride from lead (II) sulphate which if present also give a white precipitate but does not dissolve on warming.



Preparation of chlorides

1. Soluble chlorides:

(a) Sodium, potassium and ammonium salts use the alkali and hydrochloric acid.

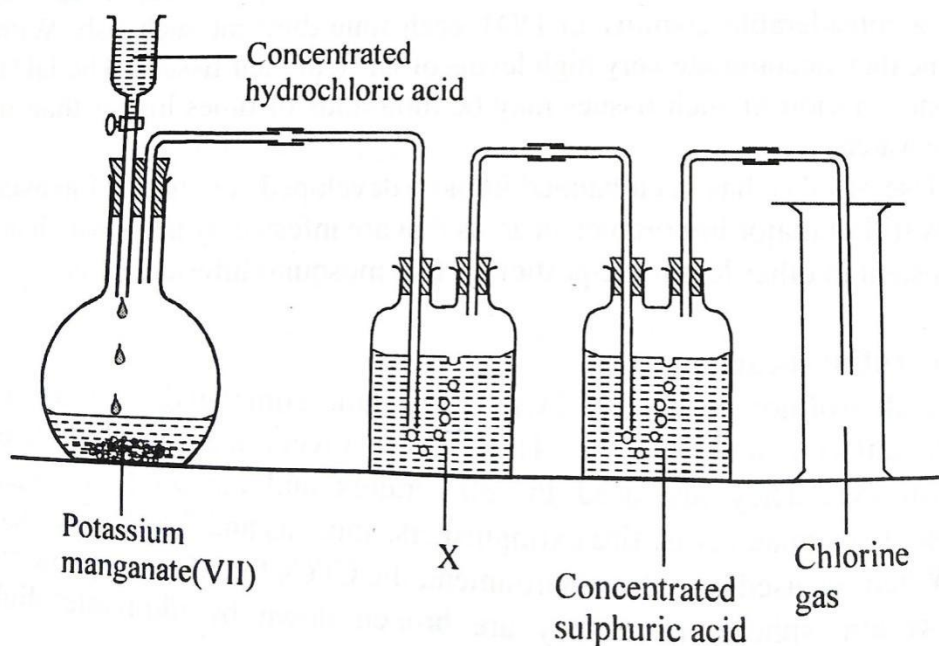
(b) Chlorides of magnesium, calcium, aluminium, zinc and iron are prepared by either reacting the metal, its oxide or carbonate with dilute hydrochloric acid.

2. Insoluble chlorides

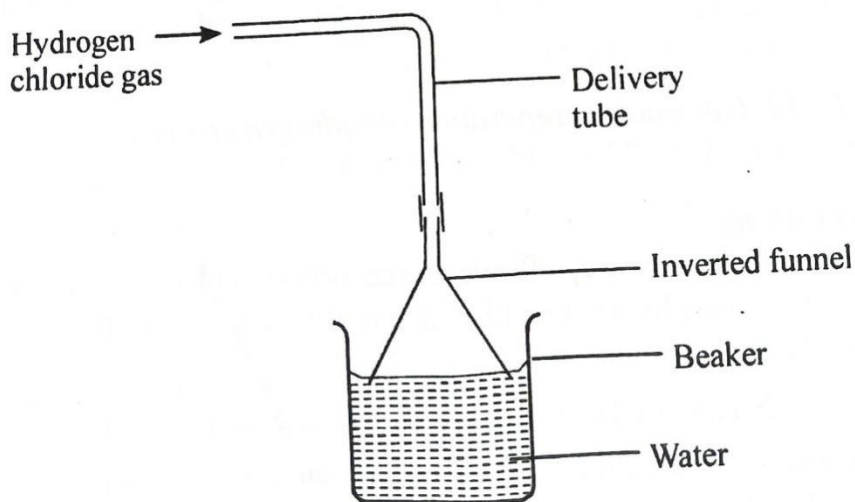
Lead and silver chlorides are prepared by double decomposition/ precipitation method i.e. to a soluble salt of lead and silver is added a soluble salt solution containing chloride ion.

END OF CHAPTER QUESTIONS

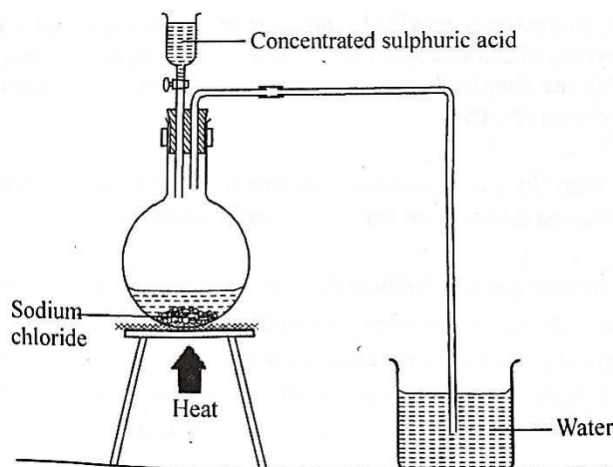
- When chlorine water was added to sodium bromide which contained a small amount of tetrachloromethane, an orange colour was observed. When bromine water was added to sodium iodide in the presence of a little amount of tetrachloromethane, a violet colour was observed.
 - Name the type of reactions taking place.
 - Write ionic equations for the reactions between
 - Chlorine and NaBr(aq)
 - Bromine and NaI(aq)
 - Write the order of reactivity of the three halogens starting with the most reactive.
- The diagram below illustrates a setup that is used for the laboratory preparation of chlorine gas. Study it carefully and answer the questions that follow.
 - Give an equation for the reaction that takes place in the flask.
 - Name liquid X and state its role in the set up
 - Name the method used to collect the gas and state the property of the gas that enables it to be collected using the method.
 - State the change that would have to be made in the above setup if chlorine gas was to be prepared using manganese (IV) oxide instead of potassium manganate (VII). Give a reason for the change.
 - What is the maximum volume of chlorine gas measured at room temperature and pressure that can be obtained if 17.4g manganese (IV) oxide is reacted completely with concentrated hydrochloric acid? ($\text{Mn}=55$, $\text{O}=16$, molar gas volume at r.t.p.= 24000cm^3).



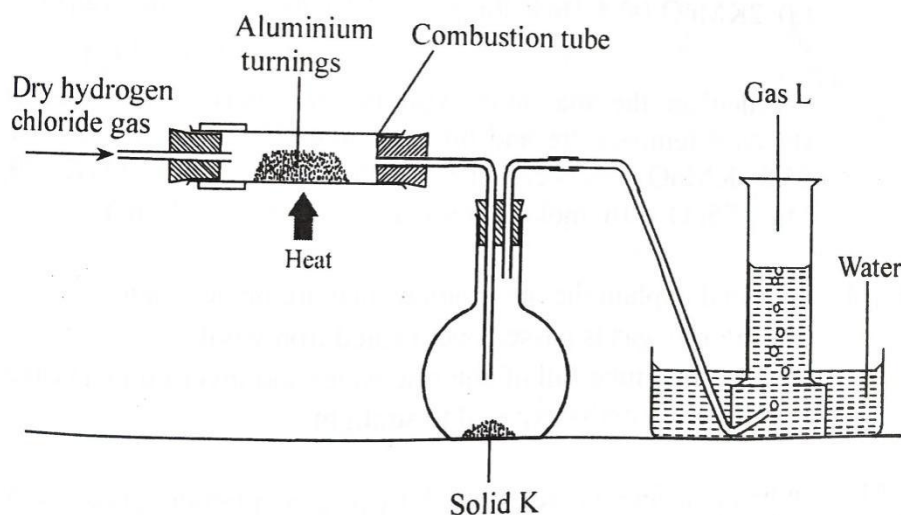
- A student was provided with a jar of chlorine gas and a jar of hydrogen chloride gas. Give (a) one simple physical property and (b) one simple chemical property that can be used to distinguish between the two.
- Chlorine gas was bubbled through a potassium iodide solution.
 - State the observations that would be made.
 - Give a net ionic equation for the reaction that takes place.
 - State with a reason which is the oxidizing agent in this reaction.
- The figure below shows the method used for dissolving hydrogen chloride gas in water. Study it and answer the questions that follow.



- (a) What property of hydrogen chloride gas makes this the method of choice?
 - (b) Explain the importance of the inverted funnel.
 - (c) Name two other gases that are dissolved using this method.
6. The figure below is an experimental set up by a student for the preparation of aqueous hydrogen chloride. Study it and answer the questions that follow.
- (a) Give an equation for the reaction that takes place in the flask.



- (b) (i) state one mistake in the set up.
 - (ii) what would happen if the experiment was carried out as it is?
 - (iii) How can the mistake be corrected?
 - (c) What is the other name for aqueous hydrogen chloride?
 - (d) How is the pH of water affected by dissolving hydrogen chloride?
 - (e) Name the ion responsible for the change you have stated in (d) above.
7. (a) Give an equation for the reaction between chlorine gas and dilute sodium hydroxide solution.
- (b) explain with the aid of an equation how the product formed by reacting chlorine gas with dilute sodium chloride solution acts as a bleaching agent.
8. The diagram below shows a set up in which dry hydrogen chloride gas was reacted with aluminium turnings. Study it and answer the questions that follow.

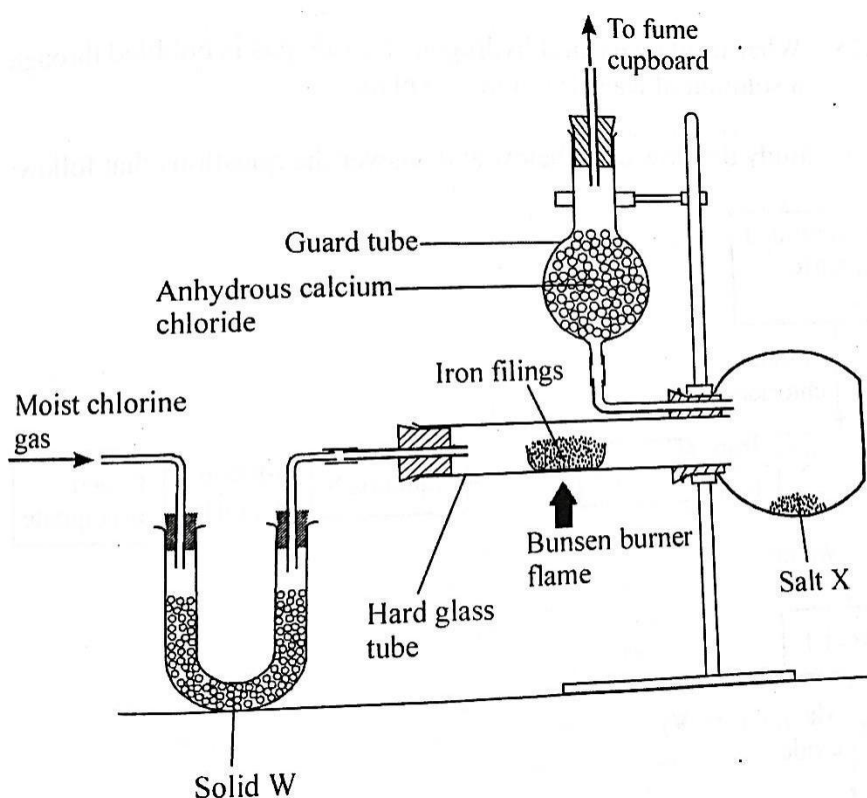


- Name two reagents that are commonly used to prepare hydrogen chloride gas and write an equation for the reaction.
 - Name two reagents that would be used to dry hydrogen chloride gas.
 - Name solid K and gas L.
 - Explain why it is possible to collect solid K using the method shown.
 - Give an equation for the reaction that takes place in the combustion tube.
 - After the reaction has gone on for some time, the water in the trough turns litmus paper red. Explain.
 - State and explain what would happen if copper was replaced with aluminium in the combustion tube.
9. Potassium manganate (VII) oxidizes concentrated hydrochloric acid forming chlorine gas according to the following equation.

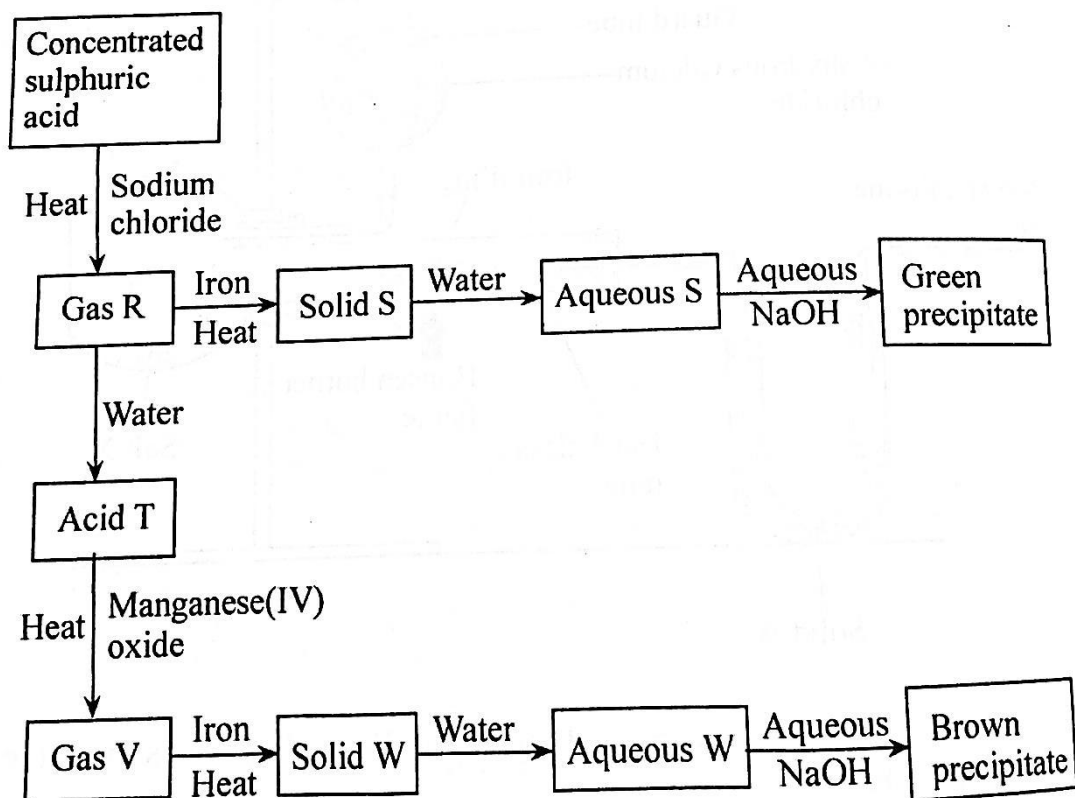


Calculate the maximum volume of chlorine measured at s.t.p that can be obtained when 15.8g KMnO_4 reacts completely with hydrochloric acid. (K=39, Mn=55, O=16. Molar gas volume at s.t.p=22.4 dm³)

- State and explain the observations that are made when:
 - Chlorine gas is passed over heated iron wool.
 - A boiling tube full of chlorine water and inverted in a beaker of chlorine water is exposed to sunlight.
- When chlorine gas reacts with hydrogen sulphide gas a yellow deposit is formed.
 - Name the yellow deposit and give an equation that leads to its formation.
 - Which of the two, chlorine or hydrogen sulphide is the oxidizing agent in this reaction. Explain.
- Chlorine bleaches dyes in presence of moisture but not in its absence. Explain.
- The diagram below shows a setup in which dry chlorine gas was reacted with iron filings. Study it and answer the questions that follow.



- State the role played by solid W and give its possible identity.
 - Name two reagents that could be reacted to produce chlorine without heating. Give a balanced equation for the reaction.
 - Name salt X and give an equation for its formation.
 - State with a reason one other metal chloride that could be collected using the same method.
 - Why is it not possible to collect sodium chloride using the same method?
 - Phosphorous (III) chloride can also be prepared using this method but it is advisable to remove one of the conditions.
 - Explain how you would separate a mixture of sodium chloride and iron (III) chloride.
- What would happen if hydrogen chloride gas is bubbled through a solution of lead (II) nitrate? Explain.
 - Study the flow chart below and answer the questions that follow.



(a) Name the following:

- (i) Gas R
- (ii) Solid S
- (iii) Acid T
- (iv) Gas V
- (v) Solid W

(b) Give the equations for the formation of:

- (i) solid S
- (ii) solid W

(c) Give equations for the formation of

- (i) Green precipitate
- (ii) brown precipitate

(d) Explain why gas R reacts with iron to form solid S while gas V reacts with iron to form solid W.

16. Chlorine gas was bubbled through a potassium bromide solution.

(a) State the observations that would be made.

(b) Give a net ionic equation for the reaction that takes place.

(c) State with a reason which is the oxidizing agent in the reaction.

17. State and explain the observation that is made when dry solid calcium hydroxide is shaken with chlorine gas.