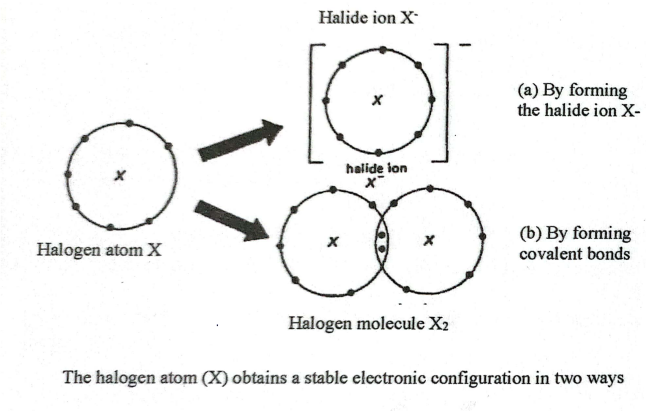
Chapter 6 - Halogens and Its Compounds

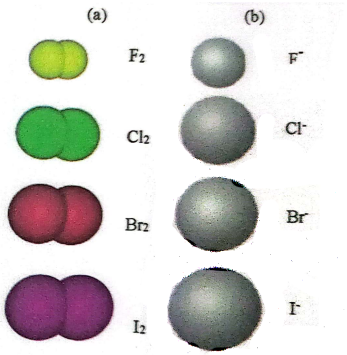
Halogens

General Properties

Electron Configuration



The halogen atom (X) obtains a stable electronic configuration in two ways



Models (to scale) of (a) the halogen molecules, and (b) the halide ions

Appearance

fluorine
pale yellow gas

chlorine
greenish yellow gas

bromine
reddish brown liquid

iodine
dark purple solid

Melting and Boiling Points

- The halogens are diatomic molecules. Thus, their melting points are low. Iodine molecules are the largest among the four halogens. Hence, iodine has the highest melting point.
- A similar trend occurs with the boiling points. There is s gradual increase from fluorine to iodine.

Relative Size

- The increase in size down the group is due to the increase in the number of shells in the atoms.
- Each ion is larger than its atom

Solubility of the halogens

The halogens are only slightly soluble in polar solvents such as water. But they're quite soluble in non-polar solvent. Tetrachloromethane, CCl_4, is a common non-polar solvent used to dissolve the halogens.

halogens in water

halogens in non-polar solvent and water

	chrorine	bromine	iodine
X_2	greenish yellow	reddish brown	dark purple
X_2 in water	light yellow	brown	brown
X_2 in non-polar solvent (CCl_4)	yellow	reddish brown	purple

Electronegativity of the Halogens

- F > Cl > Br > I
- Reactivity: $F_2 > Cl_2 > Br_2 > I_2$

Chemical Properties

Halogens are oxidizing agents.

Reaction with metals

$$
\begin{aligned}
2\,Na_{(s)} + F_{2\,(g)} &\longrightarrow 2\,NaF_{(s)} \\
2\,Na_{(s)} + Cl_{2\,(g)} &\longrightarrow 2\,NaCl_{(s)} \\
2\,Na_{(s)} + Br_{2\,(g)} &\longrightarrow 2\,NaBr_{(s)} \\
2\,Na_{(s)} + I_{2\,(g)} &\longrightarrow 2\,NaI_{(s)} \\
Cu_{(s)} + Cl_{2\,(g)} &\xrightarrow{\Delta} CuCl_{2\,(s)} \\
Cu_{(s)} + Fe_{2\,(g)} &\xrightarrow{\Delta} FeCl_{2\,(s)}
\end{aligned}
$$

- The reaction with **fluorine** is **violent**.
- A small piece of hot sodium in combustion spoon reacts **vigorously** when placed in a gas jar of **chlorine gas**.
- The reaction is less vigorous in **bromine vapor**.
- To react sodium with **iodine**, the iodine is heated to **vaporize** it. The reactions with iodine is less vigorous than with chlorine.
- **Br_2 and I_2 react with metals above Au, Ag and Pt in the reactivity series.**
- **F_2 reacts with all metals.** F_2 reacts with Al , Mg, Cu, Fe will form a **protective layer** of fluoride and prevent further reaction. Thus, F_2 can be stored in steel can.

Reaction with hydrogen

Hydrogen reacts with all the halogens to form hydrogen halides.

$$\mathrm{H_{2\,(g)} + X_{2\,(g)} \longrightarrow \underset{\text{misty fume in moist air}}{2\,HX_{(g)}}}$$

1. With fluorine: violent under all conditions

$$\mathrm{F_{2\,(g)} + H_{2\,(g)} \longrightarrow 2\,HF_{(g)}}$$

2. With chlorine: If the reaction is carried out in bright sunlight or spark, the gaseous mixuture explodes

$$\mathrm{Cl_{2\,(g)} + H_{2\,(g)} \xrightarrow{\text{UV or heating}} 2\,HCl_{(g)}}$$

3. With chlorine: The reaction is slow, even in sunlight or at 500°C.

$$\mathrm{Br_{2\,(g)} + H_{2\,(g)} \overset{\Delta}{\rightleftharpoons} 2\,HBr_{(g)}}$$

4. With iodine: The reaction is slow even when the reactants are heated.

$$\mathrm{I_{2\,(g)} + H_{2\,(g)} \underset{450\,^\circ C}{\overset{\text{Platinium}}{\rightleftharpoons}} 2\,HI_{(g)}}$$

Reaction with water

Fluorine reacts vigorously with water to give o°Cxygen gas.

$$\mathrm{2\,F_{2\,(g)} + 2\,H_2O_{(l)} \longrightarrow 4\,HF_{(aq)} + O_{2\,(g)}}$$

The other three halogens react with water different from fluorine.

$$\mathrm{X_{2\,(g)} + H_2O_{(l)} \rightleftharpoons HX_{(aq)} + HXO_{(aq)}}$$

1. Chlorine
    - Chlorine dissolves moderately in water to give a greenish yellow solution (**chlorine water**)
    - Chlorine water is a mixuture of particles: **Cl_2, H_2O, H^+, Cl^-, ClO^-**
    - It turns blue litmus red then **bleached** as it contains hydrogen ions and chlorate(I) ions.
    - **Chlorine water gives off oxygen gas** when exposed to sunlight

$$\mathrm{Cl_{2\,(g)} + H_2O_{(l)} \rightleftharpoons HCl_{(aq)} + HClO_{(aq)}}$$
$$\mathrm{2\,HClO_{(aq)} \longrightarrow O_{2\,(g)} + 2\,HCl_{(aq)}}$$

        - The formation of chlroic(I) acid is unstable and decompose gradually to hydrochloric acid and oxygen. The decomposition is catalysed by the presence of **sunlight**

2. Bromine
    - Bromine dissolves slightly in water to give a reddish brown colored solution (**bromine water**)
    - The solution is **acidic** but shows **little bleaching action**. This is because the reaction between bromine water only produces a few **bromate(I) ion**.

$$\mathrm{Br_{2\,(g)} + H_2O_{(l)} \rightleftharpoons HBr_{(aq)} + HBrO_{(aq)}}$$

3. Iodine
    - almost insoluble inwater, pale yellow solution is produced when shaking iodine with water

- Iodine is very soluble in aqueous solution of potassium iodide. This is the usual way of obtaining iodine in solution.

$$\mathrm{I^-_{(aq)} + I_{2\,(s)} \longrightarrow \underset{\text{brown}}{I_3{}^-_{(aq)}}}$$

Reaction with alkalis

1. Fluorine

$$\mathrm{2\,F_{2\,(g)} + 2\,OH^-_{(aq)} \longrightarrow OF_{2\,(g)} + 2\,F^-_{(aq)} + 2\,H_2O_{(l)}}$$

2. Other halogens
   - With cold and dilute alkalis to form halide and halate(I) ions

$$\mathrm{\overset{0}{X}_2 + 2\,OH^- \longrightarrow \overset{-1}{X}{}^- + \overset{+1}{X}O^- + H_2O\ (\textit{disproportionation reaction})}$$
$$\mathrm{\overset{0}{Cl}_{2\,(g)} + 2\,\underset{\text{dilute}}{NaOH_{(aq)}} \longrightarrow \overset{-1}{Na}Cl_{(aq)} + \overset{+1}{Na}ClO_{(aq)} + H_2O_{(l)}}$$

   - With hot and concentrated alkalis to form halide and halate(V) ions

$$\mathrm{3\,\overset{0}{X}_2 + 6\,OH^- \longrightarrow 5\,\overset{-1}{X}{}^- + \overset{+5}{X}O_3{}^- + 3\,H_2O}$$
$$\mathrm{3\,\overset{0}{Cl}_{2\,(g)} + 6\,\underset{\text{hot and conc}}{NaOH_{(aq)}} \longrightarrow 5\,\overset{-1}{Na}Cl_{(aq)} + \overset{+1}{Na}ClO_{3\,(aq)} + 3\,H_2O_{(l)}}$$

Displacement reactions

1. Cl_2 + Br^-
   - A few drops of chlorine water are added to an aqueous solution of potassium bromide. the solution changes to a pale red color. Bromine has been formed. (Adding CCl_4 will make the bromine readily dissolves and easier to be observed)

$$\mathrm{Cl_{2\,(aq)} + 2\,Br^-_{(aq)} \longrightarrow Br_{2\,(l)} + 2\,Cl^-_{(aq)}}$$

   - **Chlorine displaces bromine** from the bromide solution.

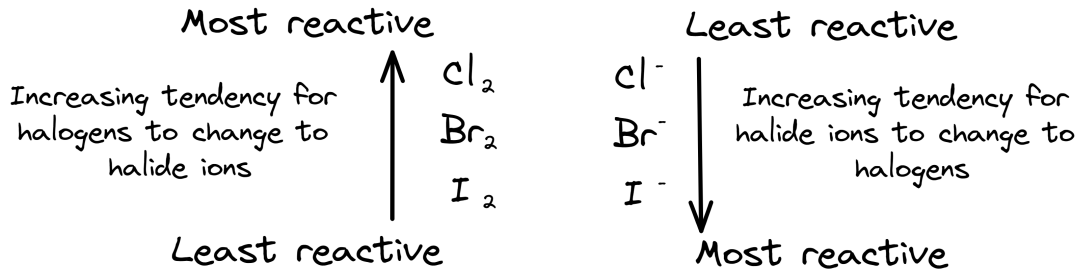
2. Cl_2 + I^-
   - Chlroine displaces iodine from iodide solution. The CCL_4 layer turns purple when iodine is present.

$$\mathrm{Cl_{2\,(aq)} + 2\,I^-_{(aq)} \longrightarrow I_{2\,(s)} + 2\,Cl^-_{(aq)}}$$

3. Br_2 + I^-
   - Bromine displaces iodine from iodide solution, but no reaction takes place when bromine is added to chloride solution.

$$\mathrm{Br_{2\,(aq)} + 2\,I^-_{(aq)} \longrightarrow 2\,Br^-_{(aq)} + I_{2\,(s)}}$$

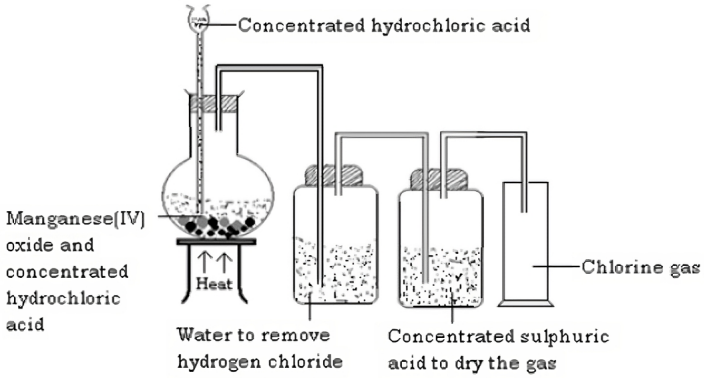
4. Iodine cannot displace either chlorine or bromine from their halide solutions.
   - Therefore, iodide ions readily lose electrons to become iodine molecules.
   - Chlorine ions are the most stable, it's more difficult to change them back to chlorine.



Chlorine

Preparation

1. Oxidation of concentrated hydrochloric acid with manganese(VI) oxide



$$\mathrm{MnO_{2\,(s)} + 4\,HCl_{(aq)} \xrightarrow{\Delta} MnCl_{2\,(aq)} + 2\,H_2O_{(l)} + Cl_{2\,(g)}}$$

   - Heat the mixture and pass the gas fromed through water and then concentrated sulfuric acid before collecting it by downward delivery. If the gas is not required dry, it can be collected over brine.

2. Oxidation of concentrated hydrochloric acid with potassium manganate(VII)

$$\mathrm{2\,KMnO_{4\,(aq)} + 16\,HCl_{(aq)} \longrightarrow 2\,MnCl_{2\,(aq)} + 2\,KCl_{(aq)} + 8\,H_2O_{(l)} + Cl_{2\,(g)}}$$

3. Oxidation of sodium chloride with manganese(VI) oxide

$$\mathrm{MnO_{2\,(s)} + 2\,NaCl_{(s)} + 2\,H_2SO_{4\,(aq)} \xrightarrow{\Delta} MnSO_{4\,(aq)} + Na_2SO_{4\,(aq)} + 2\,H_2O_{(l)} + Cl_{2\,(g)}}$$

Physical Properties

1. Chlorine is a greenish yellow gas with an unpleasent choking smell.
2. It's moderately soluble in water.
3. It's about 2.5 times heavier than air.
4. It can be liquified under a pressure of about 6 atm.
5. It's poisonous

Chemical Properties

General Properties of Halogens

Reaction with slaked lime (formation of bleaching powder)

$$2\,\mathrm{Cl_{2\,(g)}} + \mathrm{Ca(OH)_{2\,(s)}} \longrightarrow \underset{\text{bleaching powder}}{\mathrm{Ca(ClO)_{2\,(s)}}} + \mathrm{CaCl_{2\,(s)}} + 2\,\mathrm{H_2O_{(;)}}$$

When using bleaching powder, **calcium chlorate(I)** reacts with carbon dioxide and water to form **chloric(I) acid**, which performs bleaching action.

$$\mathrm{Ca(ClO)_{2\,(s)}} + \mathrm{CO_{2\,(g)}} + \mathrm{H_2O_{(l)}} \longrightarrow \mathrm{CaCO_{3\,(s)}} + 2\,\mathrm{HClO_{(aq)}}$$

As a bleaching agent

- A moist litmus paper will turn colorless when it's placed in a jar of chlorine
- The bleaching action of chlroine is due to its ability to react with water to form chloric(I) acid, Dry chlorine does not bleach.
- Chloric(I) acid is unstable and will subsequently decompose to release oxygen atom (nascent oxygen). The oxygen is then accepted by the dye, which is oxidized to form a colorless compound.

$$\mathrm{Cl_{(g)}} + \mathrm{H_2O_{(l)}} \rightleftharpoons \mathrm{HCl_{(aq)}} + \underset{\text{bleaching agent}}{\mathrm{HOCl_{(aq)}}}$$

$$\mathrm{HOCl_{(aq)}} \longrightarrow \mathrm{HCl_{(aq)}} + \underset{\text{nascent oxygen}}{\mathrm{O}}$$

$$\mathrm{HOCl_{(aq)}} + \underset{\text{colored}}{\mathrm{dye}} \longrightarrow \mathrm{HCl_{(aq)}} + \underset{\text{colorless}}{\mathrm{dye}} + \mathrm{O}$$

Test

1. color & smell: greenish yellow gas with irritating smell
2. damp litmus paper
    - Drop a piece of damp blue litmus paper into a gas jar of the unknown gas. If the paper turns **red** then **bleached**, the gas is chlorine
3. starch-iodide paper test
    - Drop a piece of **damp starch-iodide paper** (paper dipped in a mixuture of starch and solution of potassium iodide) into a gas jar of the unknown gas. If the paper turns **blue**, the gas is chlorine.
        - chlorine displaces iodide from potassium iodide to form iodine and potassium chloride, iodine then form **blue starch-iodine complex** with starch.

Uses

1. Germicide
2. Bleaching agent
3. Manufacture of certain compounds

Bromine and Iodine

Preparation

Bromine

$$2\,\mathrm{Br^-}_{(aq)} + \mathrm{MnO_{2\,(s)}} + 4\,\mathrm{H^+}_{(aq)} \longrightarrow \mathrm{Mn_2}^{+}{}_{(aq)} + 2\,\mathrm{H_2O_{(l)}} + \mathrm{Br_{2\,(g)}}$$
$$2\,\mathrm{KBr}_{(aq)} + \mathrm{MnO_{2\,(s)}} + 2\,\mathrm{H_2SO_{4\,(aq)}} \longrightarrow \mathrm{MnSO_{4\,(aq)}} + 2\,\mathrm{H_2O_{(l)}} + \mathrm{Br_{2\,(g)}} + \mathrm{K_2SO_{4\,(aq)}}$$

Iodine

$$2\,\mathrm{I^-}_{(aq)} + \mathrm{MnO_{2\,(s)}} + 4\,\mathrm{H^+}_{(aq)} \longrightarrow \mathrm{Mn_2}^{+}{}_{(aq)} + 2\,\mathrm{H_2O_{(l)}} + \mathrm{I_{2\,(g)}}$$

Test for iodine

Add a few drop of the unknown solution to **starch solution.** If iodine is present, a **dark blue** coloration appears due to the formation of an **iodine-starch complex**.

Uses

1. Bromine is used in the manufacture of 1,2-dibromoethane, in making dyestuffs, silver bromide (photographic films) and fire **retardant materials** 防火材料
2. Iodine is used in **medicine** to treat cases of **goitre** 甲状腺肿 and used for radiation emergencies to protect the **tyroid gland** against radioactive iodides (potassium iodide tablets). **Tincture of iodine** 碘酊 (sol`n of iodine in ethanol) is used as an **antiseptic**.

Summary Comparison of the Halogen Elements

Summary Comparison of the Halogen Elements			
	Chlorine	**Bromine**	**Iodine**
Appearance	Greenish yellow; poisonous gas; irritating smell	Dark red; poisonous liquid; volatile with irritating smell	Black crystalline solid, sublimes to form purple fumes on heating, posonous at high concentration
Solubility	Moderately soluble, yields acidic solution of HCl and HClO	Slightly soluble, yields acidic solution of HBr and HBrO	Sparingly soluble, but readily soluble in ethanol, ether and potassium iodide solution
Electronegativity and reactivity	$\xrightarrow[\text{Decreasing reactivity}]{\text{Decreasing electronegativity}}$		
Affinity for hydrogen	Direact combination, combines explosively in sunlight	Direact combination, combines only on heating or in the present of a platinum catalyst	Direact combination, combines slowly and reversibly on heating at about 400°C in the presence of a platinum catalyst
Reaction with metals and non-metals	vigorous	moderate	least vigorous
Reaction with dilute alkalis	yields chlorides and chlorates(I)	yields bromides and bromates(I)	yields iodides and iodates(I)
Reaction with concentrated alkalis	yields chlorides and chlorates(V)	yields bromides and bromates(V)	yields iodides and iodates(V)
Bleaching actions	Strong	Weak	None
Oxidizing actons	Strong	Moderate	Weak
Displacement reactions	Displace bromine and iodine from bromides and iodides	Displace iodine from iodides	None
Hydrogen halides	Colorless gas, denser than air, dissolves to give an acidic constant boiling mixutre		
	$\xrightarrow[\text{Increasing reducing power}]{\text{Decreasing thermal stability}}$		
Silver halide	AgCl: white solid; soluble in aqueous ammonia; reduced to silver by light	AgBr: pale yellow solid; sparingly soluble in aqueous ammonia; reduced to silver by light	AgI: yellow solid; insoluble in aqueous ammonia; reduced to silver by light

Hydrogen Halides

Hydrogen Fluoride

Hydrofluoric acid is a weak acid. It attacks glass and sand. Hence, it can't be stored in glassware.

$$\mathrm{SiO_{2\,(s)} + 4\,HF_{(aq)} \longrightarrow SiF_{4\,(g)} + 2\,H_2O_{(l)}}$$
$$\mathrm{SiO_{2\,(s)} + 2\,NaOH_{(aq)} \xrightarrow[\text{hot and conc.}]{} \underset{\text{sodium silicate}}{Na_2SiO_{3\,(aq)}} + H_2O_{(l)}}$$

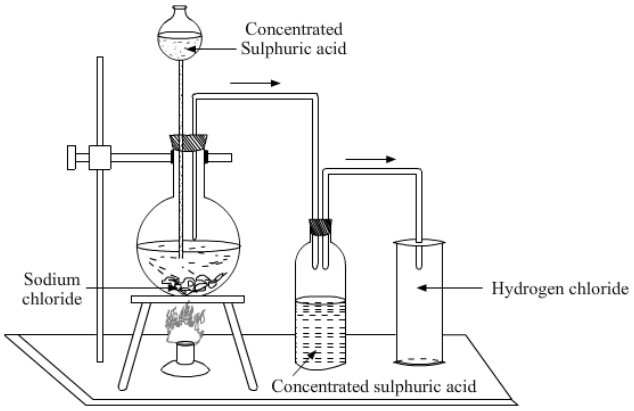
Thermal stability: HF > HCl > HBr > HI

Acid strength: HI > HBr > HCl >> HF, weak acid due to extra strong hydrogen bond

Hydrogen chloride

Hydrogen chloride exists as a gas at r.t.p. When it dissolves in water, it forms hydrochloric acid.

Laboratory preparation



Hydrogen chloride is prepared by the action of **hot concentrated sulfuric(VI) acid on any soluble chloride**, e.g. sodium chloride.

The acid reacts with the chloride to produce **misty fumes of hydrogen chloride**, which turns the damp blue litmus paper red.

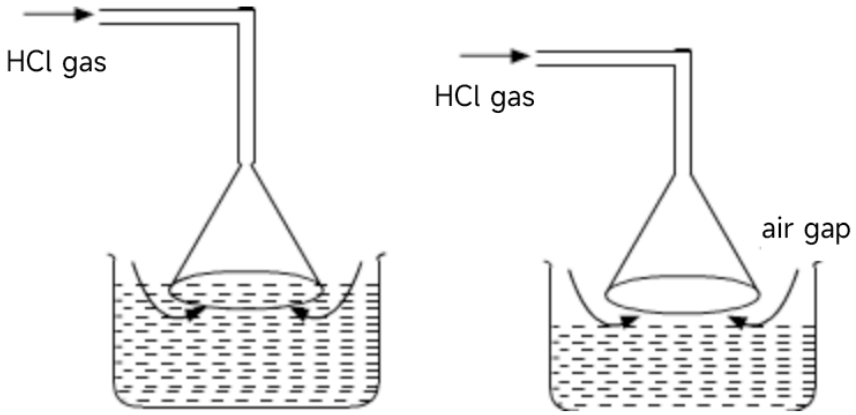
At **lower temperature**, sodium hydrogensulfate(VI) is formed together with some hydrogen chloride.

$$\mathrm{NaCl_{(s)} + H_2SO_{4\,(aq)} \longrightarrow HCl_{(g)} + NaHSO_{4\,(aq)}}$$

At **higher temperature**, the reaction goes to **completion**, forming sodium sulfate and more hydrogen chloride.

$$\mathrm{NaCl_{(s)} + NaHSO_{4\,(aq)} \xrightarrow{500-600^\circ C} HCl_{(g)} + Na_2SO_{4\,(aq)}}$$

For storage pupose, hydrogen chloride is dissolved in water to form **hydrochloric acid**. However, if the delivery tube is dipped back directly into the water in a beaker, the water is likely to be sucked back into the reacting flask. **To prevent "sucking back", an inverted filter funnel is attached to the end of the delivery tube by means of a short rubber tubing. The rim of the funnel is placed just beneath the surface of the water.** Concentrated hydrochloric acid, wchih contains about 36% by mass of hydrogen chloride, is obtained by passing the gas into water until no more gas can be absorbed.



Industrial preparation

It's made in industry by the direact combination of hydrogen and chlorine gases.

$$\mathrm{H_{2\,(g)} + Cl_{2\,(g)} \longrightarrow 2\,HCl_{(g)}}$$

Physical Properties

1. colorless gas with choking, iritating smell
2. turns damp blue litmus paper red, showing that it's acidic in aqueous solution
3. It's about 1.25 times denser than air. Therefore can be scollected by downward delivery.
4. It forms misty fumes in moist air as it dissolves in the moisture to form tiny droplets of hydrochloric acid.
5. It's very soluble in water, forming an aqueous solution of hydrochloric acid.
6. Dry hydrogen chlrodei readily dissolves in non-polar solvents, but preserves its covalent nature becuase it does not ionize.
7. Hydrogen chloride neither burns nor supports combustion, hence it extinguishes a burning splinter.

Chemical properties of hydrogen chloride

1. Direct combination with ammonia
    - When a gas jar of hydrogen chloride is inverted over a gas full of ammonia, dense white funmes are formed. (test for HCl)

$$\mathrm{HCl_{(g)} + NH_{3\,(g)} \longrightarrow NH_4Cl_{(s)}}$$

Chemical properties of hydrochloric acid

As an acid

hydrochloric acid is a strong acid

1. reaction with metals

$$\mathrm{2\,HCl_{(aq)} + Mg_{(s)} \longrightarrow MgCl_{2\,(aq)} + H_{2\,(g)}}$$

2. reaction with bases

$$\mathrm{2\,HCl_{(aq)} + CuO_{(s)} \longrightarrow CuCl_{2\,(aq)} + H_2O_{(l)}}$$

3. reaction of carbonates

$$\mathrm{2\,HCl_{(aq)} + CaCO_{3\,(s)} \longrightarrow CaCl_{2\,(aq)} + H_2O_{(l)} + CO_{2\,(g)}}$$

4. reaction with sulfate(IV) or hydrogensulfate(IV)

$$\mathrm{2\,HCl_{(aq)} + CaSO_{3\,(s)} \longrightarrow CaCl_{2\,(aq)} + H_2O_{(l)} + SO_{2\,(g)}}$$
$$\mathrm{2\,HCl_{(aq)} + Ca(HSO_3)_{2\,(s)} \longrightarrow CaCl_{2\,(aq)} + 2\,H_2O_{(l)} + 2\,SO_{2\,(g)}}$$

5. reaction with sulfides

$$\mathrm{2\,HCl_{(aq)} + CuS_{(s)} \longrightarrow CuCl_{2\,(aq)} + H_2S_{(g)}}$$

As a precipitating agent

When hydrochloric acid is added to silver nitrate(V) or lead(II) nitrate(V) solution, a white precipitate of silver chloride or lead(II) chloride is formed.

$$\mathrm{HCl_{(aq)} + AgNO_{3\,(aq)} \longrightarrow AgCl_{(s)} + HNO_{3\,(aq)}}$$
$$\mathrm{2\,HCl_{(aq)} + Pb(NO_3)_{2\,(aq)} \longrightarrow PbCl_{2\,(s)} + 2\,HNO_{3\,(aq)}}$$

Reaction with strong oxidizing agents

Concentrated hydrochloric acid is **easily oxidised** by strong oxidising agents, such as manganese (IV) oxide, potassium manganate(VII), potassium dichromate(VI) and lead(IV) oxide to **liberate chlorine**.

Therefore, it is **never used to acidifying solutions of oxidising agents** like manganese (IV) oxide, potassium manganate(VII), potassium dichromate(VI) and lead(IV) oxide before reacting with reducing agents. (sulphuric acid is used instead)

$$\ce{MnO2 (s) + 4 HCl (aq) ->[\Delta] MnCl2 (s) + 2 H2O (l) + Cl2 (g)}$$
$$\ce{2 KMnO4 (aq) + 16 HCl (aq) -> 2 MnCl2 (aq) + 2 KCl (aq) + 8 H2O (l) + 5 Cl2 (g)}$$
$$\ce{K2Cr2O7 (aq) + 14 HCl (aq) -> 2 KCl (aq) + 2 CrCl3 (s) + 7 H2O (l) + 3 Cl2 (g)}$$

Test for hydrogen chloride

1. It's a clear gas with irritating smell (appear misty in damp air). The gas is acidic to litmus.
2. It produces a **white precipitate** of silver chloride in a drop of silver nitrate and nitric acid (remove other ions that might also give a confusing precipitate with silver nitrate). The precipitate is **soluble in ammonia equation**.

$$\ce{AgNO3 (aq) + HCl (aq) -> AgCl (s) + HNO3 (aq)}$$
$$\ce{AgCl (s) + 2 NH3 (aq) -> [Ag(NH3)2]Cl (aq)}$$

3. It also produces **dense white fumes** in the presence of **ammonia**.

Uses

1. It is used in the **synthesis of PVC**, in the production of glucose from starch and e.t.c.
2. It is used to **remove oxides from metals prior to electroplating** (known as pickling).
3. Laboratory reagent.

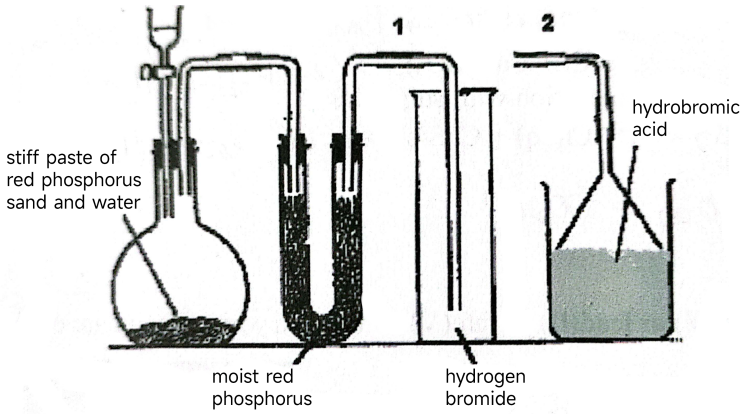
Hydrogen bromide

Laboratory preparation

Hydrogen bromide is not as stable as hydrogen chloride and is decomposed to some extent by the action of heat. This, together with the fact that hot concentrated sulphuric acid is an oxidising agent, makes it **impossible to prepare pure hydrogen bromide by the action of heat on a mixture of concentrated sulphuric acid**. The products of such an attempt would be hydrogen bromide, bromine, and sulphur dioxide.

$$\ce{2 KBr (aq) + 2 H2SO4 (aq) -> K2SO4 (aq) + Br2 (g) + SO2 (g) + 2 H2O (l)}$$

It may be made by the action of bromine on a mixture of red phosphorus and water.



$$\underset{\text{moist red phosphorus}}{\mathrm{P_{4\,(s)}}} + 6\,\mathrm{Br_{2\,(l)}} \longrightarrow 4\,\mathrm{PBr_{3\,(g)}}$$
$$\mathrm{PBr_{3\,(g)}} + 3\,\mathrm{H_2O_{(l)}} \longrightarrow \mathrm{H_3PO_{3\,(aq)}} + 3\,\mathrm{HBr_{(g)}}$$
$$\mathrm{P_{4\,(s)}} + 6\,\mathrm{Br_{2\,(l)}} \longrightarrow 4\,\mathrm{H_3PO_{3\,(aq)}} + 12\,\mathrm{HBr_{(g)}}$$

Properties of hydrogen bromide

1. It's a fuming gas with choking smell and its density is almost three times that or air.
2. It's very soluble in water, forming a strongly acid solution.
3. It's less stable than hydrogen chloride, being more easily decomposed into its elements.
4. Its general chemical properties are similar to hydrogen chloride

Test for hydrogen bromide

Hydrogen bromide turns damp blue litmus paper red and gives a pale yellow precipitate of silver bromide with a mixture of silver nitrate(V) and nitric acid. The precipitate is only sparingly soluble in ammonia water.

$$\mathrm{Br^-{}_{(aq)}} + \mathrm{Ag^+{}_{(aq)}} \longrightarrow \mathrm{AgBr_{(s)}}$$

Hydrogen iodide

The gas is less stable than hydrogen bromide. A solution of hydrogen iodide in water quickly darkens because of the formation of iodine.

Properties of hydrogen iodide

1. It's a fuming, choking gas, very soluble in water forming hydroiodic acid.
2. It dissociates reversibly above 180°C.
3. The acid usually used as acidified potassium iodide solution, is a strong reducing agent.

Test for hydrogen iodide

Add a little chlorine water to a gas jar of the gas, add a few drops of the liquid into starch past. A dark blue color is observed.

The halides

Chlorides

Most chlorides are soluble, except $CuCl_2$, Hg_2Cl_2, AgCl, $PbCl_2$ is insoluble in cold water but dissolves gradually when warmed.

Properties

1. Action of heat: Chlorides **aren't decomposed** by heat.
2. Volatility
    - Chlorines are more **volatile** than most salts when heated. They're therefore the most suitable compounds for **flame tests**.

Metal	Flame color
Potassium	Lilac
Sodium	Golden yellow

Metal	Flame color
Lithium	Red
Calcium	Brick red
Copper	Bluish green
Barium	Yellowish green

3. Action of concentrated sulfuric(VI) acid
    - All chlorides react with hot concentrated sulfuric acid to produce hydrogen chloride. (H_2SO_4 isn't strong enough to produce $Cl_{2(g)}$)

$$2\,Cl^-_{(aq)} + H_2SO_{4\,(aq)} \longrightarrow 2\,HCl_{(g)} + {SO_4}^{2-}{}_{(aq)}$$

4. In the presence of a strong oxidizing agent
    - When a metallic chloride is heated with concentrated sulfuric acid and a strong oxidizing agent, chlorine gas is produced. This is the basis of the laboratory preparation of chlorine from sodium or potassium chloride.

$$2\,MCl_{(s)} + 2\,H_2SO_{4\,(aq)} + MnO_{2\,(s)} \longrightarrow M_2SO_{4\,(aq)} + MnSO_{4\,(aq)} + 2\,H_2O_{(l)} + Cl_{2\,(g)}$$

Test for soluble halides

Most metal halides are soluble except **lead and silver halides**. Therefore solutions of lead and silver ions are used to test for the presence of halide ions in solution.

Test for Soluble Halides			
Reagent	$Cl^-_{(aq)}$	$Br^-_{(aq)}$	$I^-_{(aq)}$
$Pb(NO_3)_{2\,(aq)}$ $Pb^{2+}_{(aq)} + 2\,X^-_{(aq)} \longrightarrow PbX_{2\,(s)}$	White precipitate of $PbCl_2$	White precipitate of $PbBr_2$	Yellow precipitate of PbI_2
$AgNO_{3\,(aq)}$ $Ag^+_{(aq)} + X^-_{(aq)} \longrightarrow AgX_{(s)}$	White precipitate of $AgCl$	Pale yellow precipitate of $AgBr$	Yellow precipitate of AgI
Solubiltiy of silver halides in (a) dil. $NH_{3\,(aq)}$ (b) conc. $NH_{3\,(aq)}$ (c) dil. $HNO_{3\,(aq)}$	 soluble soluble insoluble	 insoluble insoluble insoluble	 insoluble insoluble insoluble
Effect of sunlight	white ppt. turns purple/grey	pale yellow ppt. turns green/yellow	yellow ppt. turns grey

The cyrstalline structure of **AgI** is similar to ice, allowing it to induce freezing in cloud seeding for the purpose of **rainmaking**.

`相当炸裂 by jiahuiiiii @ 6th Nov 2023 1750`