

9.5 HALOGENS

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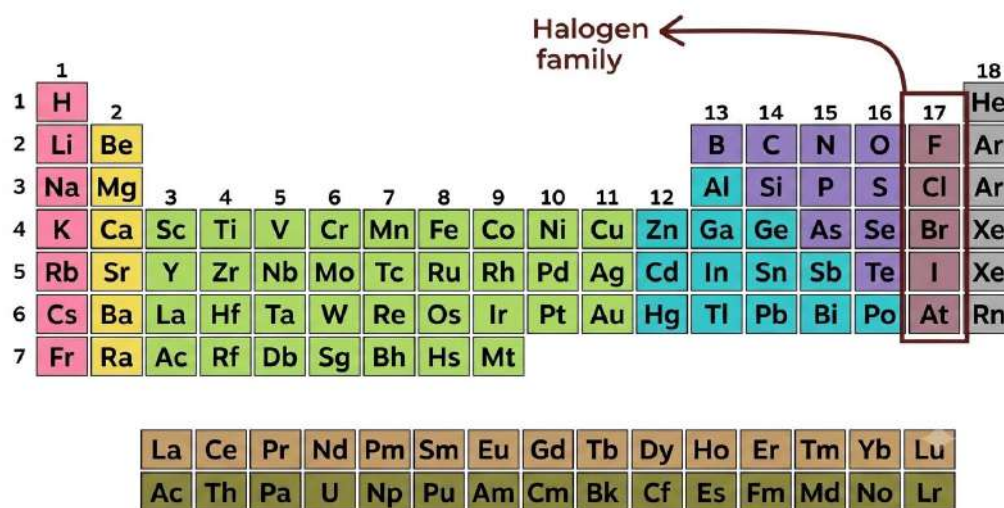
Learning outcomes

By the end of this chapter, Students should be able to:

- 9.14 Explain general characteristics of halogens.
- 9.15 Compare the methods of preparation of halogens (no diagram and description required).
- 9.16 Explain chemical properties of halogens [With water, alkali, ammonia, oxidising character, bleaching action] and uses of halogens (Cl_2 , Br_2 , and I_2).
- 9.17 Explain laboratory preparation of Cl_2 , Br_2 and I_2 .
- 9.18 Show preparation of haloacids (without diagram and description) and properties (reducing strength, acidic nature, and solubility).
- 9.19 State the uses of haloacids (HCl , HBr , and HI).

 To help reinforce your skills, most chemical equations are intentionally left unbalanced—test yourself by balancing them as you study!

The word **halogen** means "**salt former**." Halogens readily react with metals to form salts such as NaCl and KBr . They are highly reactive non-metals found in Group 17 (or VIIA) of the periodic table. Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I) and astatine (At)



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General characteristics

1. Valence shell electronic configuration: ns^2np^5
2. Oxidation state: The most common oxidation state in their combined form is -1.
3. Electronegativity: Halogens have the highest electronegativity in their respective period. This is because of the small atomic size and relatively high effective nuclear charge. Fluorine is the most electronegative element.
4. Electron affinity: They have the highest EA in their period.
5. Atomicity: They all exist as diatomic molecules, X_2 . Because the two atoms are identical, X_2 molecules are non-polar.
6. Melting point and boiling point: The melting and boiling points are in the order Fluorine < Chlorine < Bromine < Iodine. Therefore, at room temperature, F_2 and Cl_2 are gases, Br_2 is a liquid, and I_2 is a solid.
7. Ionisation energy: Their ionisation energies are high.

8. Atomic radius: They have a relatively small atomic radius; the atomic radius increases down the group.
9. Halogens are highly reactive non-metals. Reactivity generally decreases down the group. They react with metals to form metal halides (salts).
10. Oxidising agents: Due to high electron affinity and high electronegativity, they tend to gain electrons and are therefore reduced. Hence, they are oxidising agents.

Physical properties summary table

Property	Down Group 17
Atomic radius	↑
Melting/boiling points	↑
Electronegativity	↓
Ionisation energy	↓
Oxidizing power(of X₂)	↓
Reactivity	↓
Reducing power of X⁻	↑

💡 Why does reactivity decrease down the group?

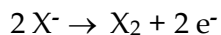
Halogens react by gaining one electron. Down the group, atomic size and shielding increase, and the nucleus attracts an incoming electron less strongly. Therefore, the tendency to gain an electron decreases.

1. Why are halogens never found in the free state in nature? 2
 {Hint: high electronegativity, high electron affinity, and low bond dissociation energy}

Most of the reactions in this material are left unbalanced, intentionally. Try balancing; this enhances your balancing skills, while helping you remember reactions at the same time.

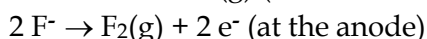
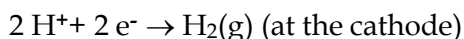
General methods of preparation

Halogens are prepared by the **oxidation** of respective halides either by electrolytic oxidation or chemical oxidation of halides. Halide ions are oxidised to halogens.



1. By the electrolytic oxidation of halides

Fluorine is prepared by electrolysis of anhydrous hydrogen fluoride containing a suitable fluoride salt such as KF. Water must be absent, because fluorine reacts with water.



Similarly, electrolysis of fused or aqueous sodium chloride gives Cl₂.

Electrolyte	Cathode product	Anode product
Molten NaCl	Na	Cl ₂
Aqueous NaCl	H ₂	Cl ₂

2. By chemical oxidation of halides

Cl_2 , Br_2 and I_2 can be prepared by the oxidation of halides with strong **oxidising agents like MnO_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4** etc.



II. Laboratory preparation of chlorine, bromine, and iodine with the application of heat

Cl_2 , Br_2 , and I_2 are prepared in the laboratory by heating respective halides with manganese dioxide and concentrated sulphuric acid.



1. Laboratory preparation of chlorine with the application of heat

Chlorine is prepared in the laboratory by heating sodium chloride with manganese dioxide and concentrated sulphuric acid.



2. Laboratory preparation of bromine with the application of heat

Bromine is prepared similarly.

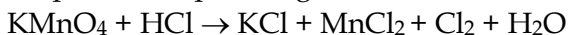


3. Laboratory preparation of iodine with the application of heat



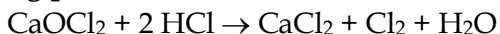
III. Laboratory preparation of chlorine without application of heat

Chlorine can be prepared in the laboratory by allowing concentrated hydrochloric acid to react with powdered potassium permanganate. No external heating is required.



 Practice: Balance this equation using the oxidation-number method

Chlorine gas is also prepared in the laboratory by the action of concentrated hydrochloric acid on **bleaching powder**.



Chemical Properties of Halogens

1. With water:

Chlorine is moderately soluble in water and reacts reversibly with it to form hydrochloric acid and hypochlorous acid

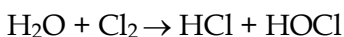


Bromine also dissolves in water and undergoes a similar reaction. The reaction becomes less significant from chlorine to iodine because the oxidising power of the halogen decreases down the group.

2. Bleaching action:

Chlorine changes many coloured substances into a colourless form.

Chlorine reacts with water to form hypochlorous acid (HOCl). HOCl is a strong oxidising agent and oxidises coloured substances to colourless products.



The bleaching action of bromine is, to a lesser extent, compared to that of chlorine. Iodine does not bleach.

3. With caustic alkali or caustic soda (NaOH)

• Reaction of Cl_2

Cl_2 reacts with **cold and dil. NaOH** to form NaCl and sodium hypochlorite (NaOCl).



Cl_2 reacts with **hot and concentrated NaOH** to form NaCl and sodium chlorate (NaClO_3).



- **Reaction of Br_2**

With cold and dilute NaOH, hypobromite is obtained at 0°C .

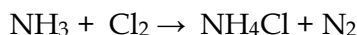


With hot and concentrated NaOH, bromate is obtained.

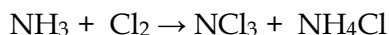


4. With ammonia

With ammonia in excess, chlorine reacts to form ammonium chloride and nitrogen gas

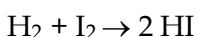
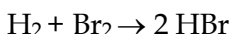
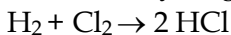


With chlorine in excess

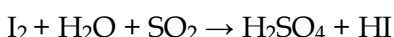
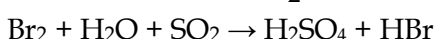
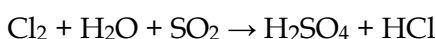
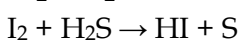
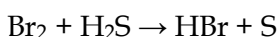
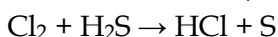


5. Oxidising character of halogens:

Halogens oxidise hydrogen into hydrogen halides.



Halogens oxidise H_2S to S, and SO_2 to H_2SO_4 , etc.



Uses of halogens

Uses of fluorine:

- To prepare chlorofluorocarbons, which are used as refrigerants.
- For the manufacture of Teflon
- Fluoride compounds such as NaF are used in dental products and, in some places, for water fluoridation.
- For etching glass (as HF) to achieve an artistic effect.

Uses of chlorine:

- To prepare organic compounds like plastics (e.g., PVC), ethyl chloride, chloroform, insecticides (e.g., BHC, DDT), etc.
- Chlorine and its compounds are used for bleaching textiles, wood, and paper.
- As a disinfectant in drinking water and swimming pools.

Uses of Bromine:

- Manufacture of brominated compounds like methyl bromide, ethyl bromide, etc.
- Used in some **flame-retardant materials and water-treatment chemicals**.
- Manufacture of **pharmaceuticals and other speciality chemicals**.
- Photographic chemicals (historical but chemically relevant)

- To prepare 1,2-dibromoethane, which is added to petrol to remove lead (historical only).
- KBr as a sedative and in treating epilepsy (historical use).

Uses of iodine:

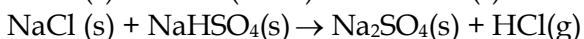
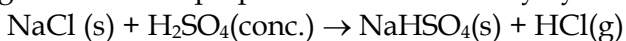
- To prepare iodoform, methyl iodide, etc.
- As an antiseptic, in the form of tincture of iodine.
- As a food supplement, in the form of iodised salt.
- Manufacture of iodine-containing pharmaceuticals and other speciality chemicals.

Hydrohalic acids

Hydrogen chloride (HCl) is a gas. Its aqueous solution is called hydrochloric acid. Similarly, HBr and HI are hydrogen halides, while their aqueous solutions are called hydrobromic acid and hydroiodic acid, respectively.

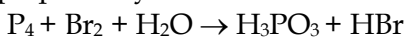
Laboratory preparation of hydrogen chloride

Hydrogen chloride is prepared in the laboratory by heating common salt with conc. sulphuric acid.



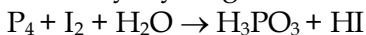
Laboratory preparation of hydrogen bromide (HBr)

HBr is prepared by the action of bromine on moist red phosphorus.



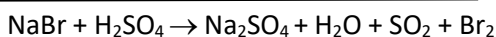
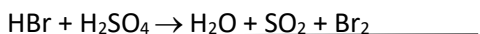
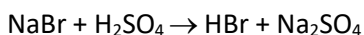
Laboratory preparation of hydrogen iodide

In the laboratory, hydrogen iodide is formed by the action of iodine on moist red phosphorus.



2. Why can't HBr and HI be prepared by treating conc. H_2SO_4 with bromide and iodide? 2

Answer: HBr and HI cannot be prepared using concentrated H_2SO_4 because HBr and HI are strong reducing agents and reduce H_2SO_4 . HI reduces H_2SO_4 more strongly than HBr. E.g.,



Properties of hydrogen halides (HCl, HBr and HI)

- All halogen acids are polar covalent molecules.

HCl, HBr and HI are highly soluble in water. Their solubility slightly increases in the order $\text{HCl} < \text{HBr} < \text{HI}$.

3. Acidic nature

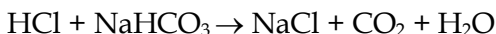
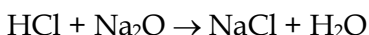
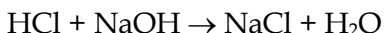
The aqueous solutions of HCl, HBr and HI behave as typical acids.

They turn blue litmus red, phenolphthalein from pink in base to colourless, and methyl orange from yellow in base, orange in the transition range, and red in acid.

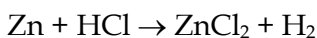
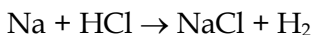
Acidic strength: $\text{HI} > \text{HBr} > \text{HCl}$

Down the group, the H-X bond becomes weaker, so H^+ is released more easily. Therefore, acidic strength increases down the group.

a. Reaction with base:



b. Reaction with metals:



4. Reducing nature:

The reducing power of halogen acids follows the order $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

HCl reduces MnO_2 , $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 .

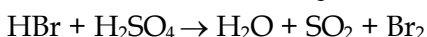
a. With MnO_2 :



b. With KMnO_4



HBr and HI also reduce KMnO_4 . HBr and HI can reduce even conc. H_2SO_4 .



HI is a more powerful reducing agent; it also reduces copper sulphate.



Uses of HCl

1. Used in the preparation of aqua regia, which is used to dissolve gold, platinum, etc. (aqua regia is a mixture of conc. HCl and conc. HNO_3 in the ratio 3:1)
2. As a laboratory reagent
3. To clean iron sheets for pickling before galvanisation or plating.
4. For the manufacture of chlorine, metal chlorides, chlorine dyes, and many other chemicals.
5. Naturally, gastric juice contains HCl in the stomach, which helps to digest the food.
6. To hydrolyse starch to glucose in the manufacture of corn syrup (historical use)

Uses of HBr

- Used in the manufacture of brominated organic compounds.
 - Used in the pharmaceutical industry to prepare hydrobromide salts of medicines.
 - Used as a reagent in organic synthesis.

Uses of HI

- Used in the preparation of alkyl iodides and other iodine-containing organic compounds.
- Used as a strong reducing and iodinating reagent in organic synthesis.
- Used in the manufacture of pharmaceuticals and other speciality chemicals.

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