

9.5 HALOGENS

Learning outcomes

Learners should be able to:

- 9.14 Explain general characteristics of halogens.
- 9.15 Compare the methods of preparation of halogens without a diagram and description.
- 9.16 Explain chemical properties of halogens [With water, alkali, ammonia, oxidizing 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).

Group 17 (or VII A) in the periodic table

Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I) and astatine (At)

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: They have the highest electronegativity in the period. This is because of the small atomic size and high nuclear charge. Fluorine is the most electronegative element in the periodic table.
4. Electron affinity: They have the highest EA in the period.
5. Atomicity: They all exist as non-polar diatomic molecules.
6. Melting point and boiling point: The melting and boiling point is in the order Fluorine < Chlorine < bromine < iodine. Therefore, at room temperature, F_2 and Cl_2 are gases, Br_2 is liquid and I_2 is solid.
7. Ionization energy: Their ionization energies are high.
8. Atomic radius: They have a small atomic radius; the smallest in their period.
9. Halogens are the most reactive elements. With metals, they form typical salts.
10. Oxidizing agents: Due to high electron affinity and high electronegativity, they tend to gain electrons and get reduced. Hence, they are oxidizing agents.

1. Which has maximum electron affinity?
 - a. F
 - b. Cl
 - c. Br
 - d. I
2. Which is most reactive?
 - a. F
 - b. Cl
 - c. Br
 - d. I
3. Which of the following is radioactive?
 - a. F
 - b. I
 - c. At
 - d. Br
4. Which of the following is liquid at room temperature?
 - a. F_2
 - b. Cl_2
 - c. Br_2
 - d. I_2
5. The electronegativity of the halogen is in the order

- a. $F > Cl > Br > I$ c. $I > Br > Cl > F$ b. $Cl > F > Br > I$ d. $I < Br < F < Cl$

6. The Strongest oxidizing agent among the following is

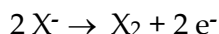
- a. O_3 b. O_2 c. F_2 d. Cl_2

1. Why halogens are never found in the free state in nature? 2

{Hint: high electronegativity, electron affinity and Low dissociation energy}

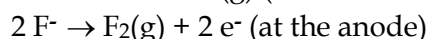
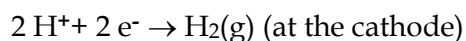
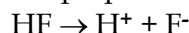
General methods of preparation

Halogens are prepared by the **oxidation** of respective halides either by electrolytic oxidation or chemical oxidation of halides.

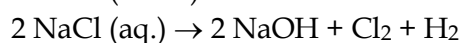
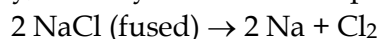


1. By the electrolytic oxidation of halides

Fluorine is prepared by electrochemical oxidation in perfectly anhydrous conditions.



Similarly, electrolysis of fused or aqueous sodium chloride gives 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 **oxidizing agents** like MnO_2 , $K_2Cr_2O_7$, $KMnO_4$ etc.



Br_2 & I_2 are unstable, they are not prepared as laboratory reagents.

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.

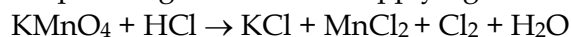


3. Laboratory preparation of iodine with the application of heat



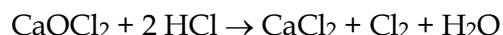
III. Laboratory preparation of chlorine without application of heat

Chlorine can be prepared in the laboratory by the action of concentrated hydrochloric acid on powdered potassium permanganate without applying heat.



(Balance the above equation with the oxidation number method.)

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

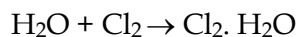


2. Give the balanced chemical equation for the preparation of chlorine in the laboratory. 1

Chemical Properties of halogens

1. With water:

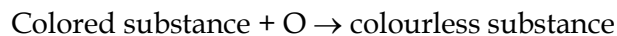
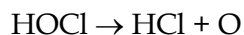
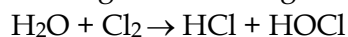
Chlorine dissolves in water to some extent forming hydrated chlorine, Cl^- (chloride) and OCl^- (hypochlorite)



Bromine dissolves in water in a similar manner. Iodine shows a similar behaviour but to a minimal extent.

2. Bleaching action:

Chlorine changes colored organic compounds into colorless form.



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

7. The bleaching action of Cl_2 is due to

- a. Oxidation b. Reduction c. Dehydration d. Polymerization

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 .



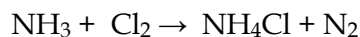
With hot and concentrated NaOH, bromate is obtained.



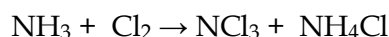
3. What happens when bromine reacts with hot and conc. NaOH? 1
4. What happens when gas obtained by heating NaCl and conc. H_2SO_4 is passed through hot and conc. solution of NaOH? 3
5. What happens when chlorine gas is passed into a dilute solution of caustic soda? 1
6. How will Cl_2 react with conc. NaOH? 1

4. With ammonia

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



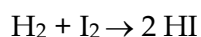
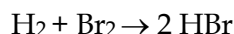
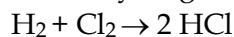
With chlorine in excess



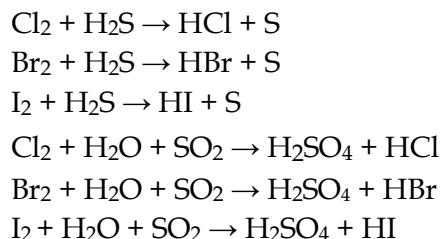
7. Write the equation for the reaction between ammonia and chlorine.
8. How does ammonia react with chlorine? 1
9. How does ammonia react with chlorine in excess? 1

5. Oxidising character of halogens:

These oxidize hydrogen into hydrogen halides.



These oxidize, H_2S into S, SO_2 into H_2SO_4 etc.



Uses of halogens

Uses of fluorine:

- To prepare chlorofluorocarbons which are used as refrigerants & fuel.
- For the manufacture of Teflon
- To prepare NaF which is used in drinking water and fluoride toothpaste because it reduces the incidence of tooth decay
- For etching glass to achieve an artistic effect.

Uses of chlorine:

- To prepare organic compounds like PVC, plastic, ethyl chloride, chloroform, BHC, DDT (insecticides) etc.
- Chloride is used for bleaching textile, wood, and paper.
- As a disinfectant in drinking water and swimming pools.

Uses of Bromine:

- To prepare 1,2-dibromoethane which is added to petrol to remove lead.
- To prepare organic compounds like methyl bromide, ethyl bromide etc.
- KBr is used as a sedative and in treating epilepsy.

Uses of iodine:

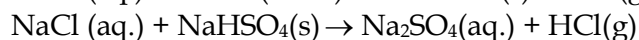
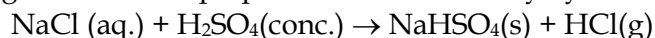
- To prepare iodoform, methyl iodide etc.
- As antiseptic, in the form of tincture of iodine.
- As a food supplement, in the form of iodized salt.

10. Mention the uses of chlorine. 2
8. In the conversion of Br_2 to BrO_3^- , the ON of Br changes from
 a. 0 to +5 b. -1 to +5 c. 0 to +3 d. +2 to +5
9. A red flower and a piece of paper dipped in printer ink are placed in two test tubes, then Cl_2 gas is passed into both the test tubes then
 a. The paper is bleached. d. Both are bleached.
 b. Only the flower is bleached. c. None are bleached.
10. Which of the following halogen is used as an analgesic?
 a. Fluorine b. Chlorine c. Bromine d. Iodine
11. Bleaching of Cl_2 is
 a. Oxidation and permanent c. Reduction and temporary
 b. Oxidation and temporary d. Reduction and permanent
12. The deficiency of iodine causes
 a. Rickets b. Goitre c. Scurvy d. Tuberculosis
11. Write the action of sulphur dioxide with chlorine in presence of water. Writing the Oxidation Numbers, specify which element is oxidised and which element is reduced in that reaction. 2
12. Write full forms of PVC, BHC and DDT. 1
13. Write the structure of BHC. How is it prepared?# 1
14. Write the structures and IUPAC names of chloroform, iodoform, methyl chloride, ethyl bromide, and 1,2-dibromoethane.

Hydrohalic acids

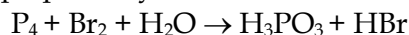
Laboratory preparation of hydrogen chloride

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



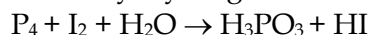
Laboratory preparation of hydrogen bromide (HBr)

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



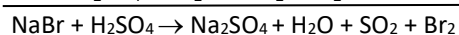
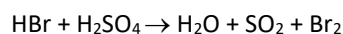
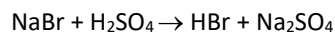
Laboratory preparation of hydrogen iodide

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



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

Answer: because HBr and HI formed, being strong reducing agents, reduce conc. H_2SO_4 to give SO_2



16. Concentrated sulphuric acid can be used in the laboratory to produce hydrogen chloride gas by the reaction with solid sodium chloride. Hydrogen iodide is not produced by the same method as hydrogen chloride. Why? 1

Properties of hydrogen halides (halogen acids)

- All halogen acids are polar covalent molecules.

Properties	HCl	HBr	HI
Solubility in water	Least soluble	Less soluble	Most soluble
Acidic nature and ionization constant	Acidic $K_a \sim 10^8$	More acidic $K_a \sim 10^{10}$	Most acidic $K_a \sim 10^{11}$

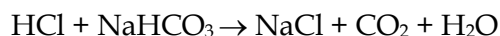
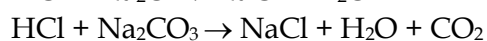
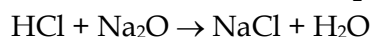
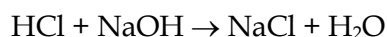
3. Acidic nature

Halogen acids are soluble in water & their aqueous solutions are called hydrohalic acids or halogen acids. They behave as typical acids.

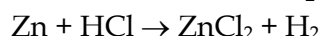
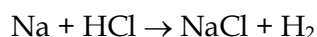
They turn blue litmus to red, phenolphthalein from pink to colourless, methyl orange from yellow to orange.

17. What is the difference between hydrogen chloride gas and hydrochloric acid? 1

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 .

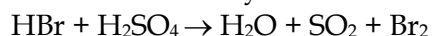
a. With MnO_2 :



b. With KMnO_4



HBr and HI react similarly as HCl does. HBr and HI can reduce even conc. H_2SO_4 .



HI is a more powerful reducing agent, hence reduces copper sulphate too.



18. How does hydroiodic acid (HI) react with MnO_2 ?
19. How does hydroiodic acid (HI) react with CuSO_4 solution? 2
20. How does hydroiodic acid (HI) react with MnO_2 & CuSO_4 solutions?
21. Compare and contrast the properties of HCl, HBr and HI. 4

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 and in industries.
3. To clean iron sheets for pickling before galvanization or plating.
4. To hydrolyze starch to glucose in the manufacture of corn syrup.
5. For the manufacture of chlorine, metal chlorides, chlorine dyes and many other chemicals.
6. Naturally gastric juice contains HCl in the stomach which helps to digest the food.

Uses of HBr

Uses of HI

(study from the book)

Many of these reactions are not balanced. Practice balancing.

13. Bond in HCl molecule is
 - a. Pure covalent
 - b. Highly polar
 - c. Polar covalent
 - d. H-bonding
14. Which are the most and least acidic among the given hydrohalic acids?
 - a. HCl and HBr
 - b. HI and HF
 - c. HF and HI
 - d. HI and HCl
15. The reducing nature of halo acids is in the order
 - a. $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$
 - b. $\text{HCl} > \text{HBr} > \text{HI} > \text{HF}$
 - c. $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
 - d. $\text{HCl} > \text{HF} > \text{HBr} > \text{HI}$
16. The acidic strength of the halogen acids is in the order
 - a. $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$
 - b. $\text{HCl} > \text{HBr} > \text{HI} > \text{HF}$
 - c. $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$
 - d. $\text{HCl} > \text{HF} > \text{HBr} > \text{HI}$
17. The reaction of chlorine with hot and conc. NaOH gives
 - a. NaClO
 - b. NaClO_2
 - c. NaClO_3
 - d. NaClO_4
18. Which of the following is obtained when bromine reacts with cold and dilute NaOH?
 - a. NaBrO
 - b. NaBrO_2
 - c. NaBrO_3
 - d. NaBrO_4
19. Aqua regia is a mixture of
 - a. $\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4$
 - b. $3 \text{HCl} + \text{HNO}_3$
 - c. $\text{HCl} + \text{CH}_3\text{COOH}$
 - d. $3 \text{HNO}_3 + \text{HCl}$

*** This is not a complete note. It is just to guide you. It is recommended to study prescribed textbooks along with this material. ***