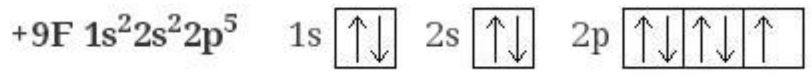
General characteristics of halogens. Halogen compounds

Position in the periodic system of chemical elements

- Halogens are located in the **main subgroup of group VII** (or group 17 in the modern form of the ETS) of the periodic system of chemical elements by D.I. Mendeleev.

The electronic structure of halogens

- The electronic configuration of the halogens in the ground state corresponds to the formula ns np^{25} .
- For example, the electronic configuration of fluori 

- Halogen atoms contain 1 unpaired electron on the outer energy level and three unpaired electron pairs in the ground energy state. Consequently, in the ground state the halogen atoms can form 1 bond by the exchange mechanism.
- In this case the fluorine has no excited state, i.e. the maximum valence of the fluorine in the compound is I.
- However, unlike fluorine, chlorine, bromine and iodine atoms can move into an excited energy state due to their vacant d-orbitals.
- Thus, the maximum valence of halogens (except fluorine) in compounds is VII. Halogens are also characterised by valences I, III, V.
- The oxidation states of the halogen atom are from -1 to +7. The characteristic oxidation states are -1, 0, +1, +3, +5, +7. For fluorine the characteristic oxidation state is -1 and valence I.

Physical properties and patterns of property change

- Halogens form bi-atomic molecules with the composition Hal_2 . In the solid state have a molecular crystalline lattice. They are poorly soluble in water, all have an odour and are volatile.

Halogen	F	Cl	Br	I
Oxidation grades	-1	-1, +1, +3, +5, +7	-1, +1, +3, +5, +7	-1, +1, +3, +5, +7
Aggregate state	Gas	Gas	Liquid	Solid crystals
Colour	Light yellow	Yellow-green	Brownish	Dark grey with a metallic sheen
Smell	Sharp	Sharp, suffocating	Pungent, stinky	Sharp
T melting	-220^{o} C	-101^{o} C	-7^{o} C	113.5^{o} C
Boiling point	-188^{o} C	-34^{o} C	58^{o} C	185^{o} C

Halogen compounds

Oxidation degree	Typical connections
+7	Chloric acid $HClO_4$ Perchlorates $MeClO_4$
+5	Chloric acid $HClO_3$ Chlorates $MeClO_3$
+3	Chloric acid $HClO_2$
+1	Chlorous acid HClO Hypochlorites MeClO
-1	Hydrogen chloride HCl, Chlorides MeCl

Bromine and iodine form similar compounds

Methods of producing halogens

Obtaining chlorine

- **In industry,** chlorine is produced by the electrolysis of molten or dissolved sodium chloride.
- **Electrolysis of molten sodium chloride**.

$2NaCl \rightarrow 2Na + Cl_2$

- **Electrolysis of a sodium chloride solution**.

$2NaCl + 2H_2 O \rightarrow H_2 \uparrow + 2NaOH + Cl_2 \uparrow$

- **In the laboratory,** chlorine is produced by reacting concentrated hydrochloric acid with strong oxidising agents.
- **For example,** by reacting hydrochloric acid with manganese oxide (IV)

$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 \uparrow + 2H O_2$

- Or potassium permanganate:

$2KMnO_4 + 16HCl \rightarrow 2MnCl_2 + 2KCl + 5Cl_2 \uparrow + 8H O_2$

- Bertholite salt also oxidises hydrochloric acid:

$KClO_3 + 6HCl \rightarrow KCl + 3Cl_2 \uparrow + 3H O_2$

- Potassium bichromate oxidises hydrochloric acid:

$K_2 Cr O_{27} + 14HCl \rightarrow 2CrCl_3 + 2KCl + 3Cl_2 \uparrow + 7H O_2$

Obtaining fluorine

- Fluorine is produced **by the electrolysis of molten potassium hydrofluoride.**

$2KHF_2 \longrightarrow 2K + H_2 + 2F_2$

Obtaining bromine

- Bromine can be obtained by oxidising Br ions$^-$ with strong oxidising agents.
- **For example**, bromohydrogen is oxidised by chlorine:

$2HBr + Cl_2 \longrightarrow Br_2 + 2HCl$

- Manganese compounds also oxidise bromide ions.
- **For example**, manganese oxide (IV):

$MnO_2 + 4HBr \longrightarrow MnBr_2 + Br_2 + 2H\ O_2$

Obtaining iodine

- Iodine is produced by the oxidation of I ions$^-$ with strong oxidizing agents.
- **For example**, chlorine oxidises potassium iodide:

$$2KI + Cl_2 \rightarrow I_2 + 2KCl$$

- Manganese compounds also oxidise iodide ions.
- **For example**, manganese oxide (IV) oxidises potassium iodide in an acidic environment:

$$2KI + MnO_2 + 2H_2 SO_4 \rightarrow I_2 + K_2 SO_4 + MnSO_4 + 2H O_2$$

Chemical properties of halogens

The chemical activity of halogens increases from the bottom to the top - from astatine to fluorine.

1. Halogens exhibit **oxidising** properties. Halogens react with **metals** and **non-metals**.

1.1 Halogens do not **burn** in air. Fluorine oxidises oxygen to form oxygen fluoride:

$2F_2 + O_2 \rightarrow 2OF_2$

1.2 The interaction of halogens with **sulphur** produces sulphur **halides:**

$S + Cl_2 \rightarrow SCl_2\ (S_2Cl)_2$

$S + 3F_2 \rightarrow SF_6$

1.3 When **phosphorus** and **carbon** interact with halogens, **phosphorus and carbon halides** are formed:

$2P + 5Cl_2 \rightarrow 2PCl_5$

$2P + 3Cl_2 \rightarrow 2PCl_3$

$2F_2 + C \rightarrow CF_4$

Chemical properties of halogens

1.4 When interacting with **metals,** halogens exhibit **oxidising** properties, forming **halides**.

For example, **iron** reacts with halogens to form **halides**. Fluorine, chlorine and bromine form iron (III) halides and iron (II) with iodine:

$3Cl_2 + 2Fe \rightarrow 2FeCl_3$

$I_2 + Fe \rightarrow FeI_2$

The situation with **copper** is similar: fluorine, chlorine and bromine oxidise copper to copper (II) halides and iodine to copper (I) iodide:

$Cl_2 + Cu \rightarrow 2CuCl_2$

$I_2 + 2Cu \rightarrow 2CuI$

Active metals react violently with halogens, especially fluorine and chlorine (burn in an atmosphere of fluorine or chlorine).

Another **example**: **aluminium** reacts with chlorine to form aluminium chloride:

$3Cl_2 + 2Al \rightarrow 2AlCl_3$

Chemical properties of halogens

1.5 Hydrogen burns in a **fluorine** atmosphere:

$F_2 + H_2 \rightarrow 2HF$

Hydrogen only reacts **with chlorine** when heated or illuminated. In this case, the reaction proceeds with an explosion:

$Cl_2 + H_2 \rightarrow 2HCl$

Bromine also reacts with hydrogen to form hydrogen bromide:

$Br_2 + H_2 \rightarrow 2HBr$

Iodine interacts with hydrogen only when strongly heated, the reaction is reversible, with heat absorption (endothermic):

$I_2 + H_2 \leftrightarrow 2HI$

Chemical properties of halogens

Halogens react with **halogens**. The more active halogens oxidise the less active ones.

For example, fluorine oxidises chlorine, bromine and iodine:

$Cl_2 + F_2 \rightarrow 2ClF$

2. Halogens react **with complex substances**, also showing predominantly oxidative properties. Halogens readily **disproportionate** when dissolved in water or in alkalis.

2.1 When dissolved **in water, chlorine and bromine** partially disproportionate, increasing and decreasing the oxidation degree. **Fluorine** oxidises water.

For example, **chlorine,** when dissolved in cold water, disproportions to the nearest stable oxidation states (+1 and -1) and forms hydrochloric acid and hypochlorous acid (chlorine water):

$Cl_2 + H_2O \leftrightarrow HCl + HClO$

When dissolved in hot water, chlorine disproportionates to oxidation states -1 and +5, forming hydrochloric acid and perchloric acid:

$Cl_2 + 6H_2O \leftrightarrow 5HCl + HClO_3$

Fluorine reacts with water with an explosion:

$2F_2 + 2H_2O \rightarrow 4HF + O_2$

Chemical properties of halogens

2.2 When dissolved **in alkalis, chlorine, bromine and iodine** disproportionate to form different salts**. Fluorine** oxidises alkalis**.**

For example, chlorine reacts with a **cold** solution of sodium hydroxide:

$Cl_2 + 2NaOH_{(хол.)} \rightarrow NaCl + NaClO + H\ O_2$

When interacting with **hot** sodium hydroxide solution, chloride and chlorate are formed:

$3Cl_2 + 6NaOH_{(гор.)} \rightarrow 5NaCl + NaClO_3 + 3H\ O_2$

Another **example**: chlorine dissolves in a cold solution of calcium hydroxide:

$2Cl_2 + 2Ca(OH)_{2(хол.)} \rightarrow CaCl_2 + Ca(ClO)_2 + 2H\ O_2$

2.3 More active halogens displace less active halogens from **salts** and **halogen hydrocarbons.**

For example, chlorine displaces iodine and bromine from a solution of potassium iodide and potassium bromide respectively:

$Cl_2 + 2NaI \rightarrow 2NaCl + I_2$

$Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2$

Another property: the **more active halogens oxidise the less active ones**.

Chemical properties of halogens

2.4 Halogens exhibit **oxidising properties** and interact with **reducing agents**.

For example, chlorine oxidises hydrogen sulphide:

$Cl_2 + H_2 S \longrightarrow S + 2HCl$

Chlorine also oxidises sulphites:

$Cl_2 + H_2 O + Na_2 SO_3 \longrightarrow 2HCl + Na_2 SO_4$

Halogens also oxidise peroxides:

$Cl_2 + H O_{22} \longrightarrow 2HCl + O_2$

Or, when heated or exposed to light, water:

$2Cl_2 + 2H_2 O \longrightarrow 4HCl + O_2$ (light or boiling)

Halogen hydrocarbons

Halogen hydrocarbons

- **Halogen hydrocarbons HHal are** binary compounds of hydrogen with halogens, which are **volatile hydrogen compounds**. Halogen hydrocarbons are colourless, poisonous gases with a pungent odour, well soluble in water.
- In the series HCl - HBr - HI the bond length increases and the covalence of the bond decreases the polarity of the H - Hal bond.
- Halogen-hydrogen solutions in water (except hydrogen fluoride) are **strong acids**. Aqueous hydrogen fluoride solution is a weak acid.

Methods of producing halogen hydrocarbons

- **In the laboratory,** halogen hydrocarbons are produced **by the action of non-volatile acids on metal chlorides**.
- **For example,** by the action of concentrated sulphuric acid on sodium chloride:
- $H_2\ SO_{4(конц.)} + NaCl_{(solid)} \rightarrow NaHSO_4 + HCl\uparrow$
- Halogen hydrocarbons are also obtained by direct interaction of simple substances:
- $Cl_2 + H_2 \rightarrow 2HCl$

Chemical properties of halogen hydrocarbons

1. In aqueous solution, hydrogen halides exhibit **acidic properties**. They react with **bases, basic oxides, amphoteric hydroxides, amphoteric oxides**. Acidic properties **increase** in the series HF - HCl - HBr - HI.

- **For example**, hydrogen chloride reacts with **calcium oxide, aluminium oxide, sodium hydroxide, copper (II) hydroxide, zinc (II) hydroxide, ammonia**:
- $2HCl + CaO \rightarrow CaCl_2 + H\ O_2$
- $6HCl + Al\ O_{23} \rightarrow 2AlCl_3 + 3H\ O_2$
- $HCl + NaOH \rightarrow NaCl + H\ O_2$
- $2HCl + Cu(OH)_2 \rightarrow CuCl_2 + 2H\ O_2$
- $2HCl + Zn(OH)_2 \rightarrow ZnCl_2 + 2H\ O_2$
- $HCl + NH_3 \rightarrow NH_4\ Cl$
- As typical mineral acids, aqueous solutions of halogen hydrocarbons react with **metals** in the metal activity series before hydrogen. This produces **a metal salt and hydrogen**.
- **For example**, hydrochloric acid dissolves iron. This produces hydrogen and iron(II) chloride:
- $Fe + 2HCl \rightarrow FeCl_2 + H_2$

Chemical properties of halogen hydrocarbons

2. In aqueous solution, hydrogen halides **dissociate** to form acids. An aqueous solution **of hydrogen fluoride** (hydrofluoric acid) is a weak acid:

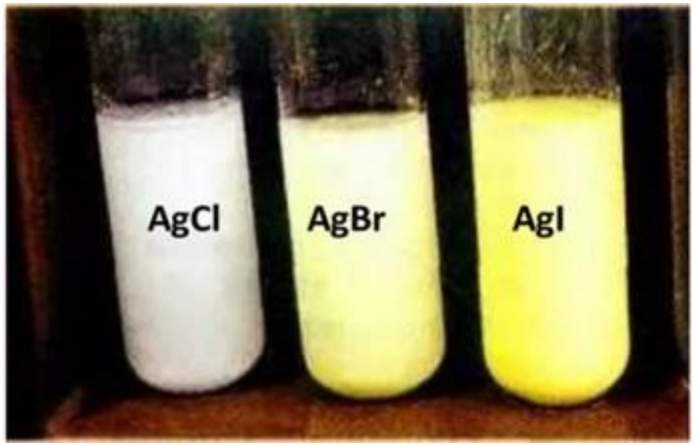
- $HF \leftrightarrow H^+ + F^-$
- Aqueous solutions **of hydrogen chloride** (hydrochloric acid), **hydrogen bromide** and **hydrogen iodide** are strong acids and dissociate almost completely in dilute solution:
- $HCl \leftrightarrow H^+ + Cl^-$

3. Aqueous solutions of halogenated hydrocarbons react **with salts of weaker acids** and with some **soluble salts** (if a gas, precipitate, water or weak electrolyte is formed).

- **For example**, hydrochloric acid reacts with calcium carbonate:
- $2HCl + CaCO_3 \rightarrow CaCl_2 + 2H_2O + CO_2$

Chemical properties of halogen hydrocarbons

- **Qualitative reaction** for halide ions - interaction with **soluble silver salts.**
- When hydrochloric acid reacts with **silver nitrate (I)**, a white precipitate of silver chloride is formed:
- $HCl + AgNO_3 = AgCl\downarrow + HNO_3$
- The **silver bromide** precipitate is a pale yellow colour:
- $HBr + AgNO_3 = AgBr\downarrow + HNO_3$
- The **silver iodide** precipitate is yellow in colour:
- $HI + AgNO_3 = AgI\downarrow + HNO_3$



Chemical properties of halogen hydrocarbons

4. The reducing properties of halogen hydrocarbons increase in the series HF - HCl - HBr - HI.

- Halogen hydrocarbons react with **halogens**. The **more active halogens displace the less active ones.**
- **For example**, bromine displaces iodine from iodine-hydrogen:
- $Br_2 + 2HI \rightarrow I_2 + 2HBr$
- **Chlorine**, on the other hand, cannot displace fluorine from **hydrogen fluoride**.
- **Hydrogen bromide** is a strong reducing agent and is oxidised by manganese compounds, chromium (VI), concentrated sulphuric acid and other strong oxidising agents:
- **For example**, bromohydrogen is oxidised **with concentrated sulphuric acid**:
- $2HBr + H_2 SO_{4(конц.)} \rightarrow Br_2 + SO_2 + 2H O_2$
- Hydrogen bromide reacts with **potassium bichromate** to form molecular bromine:
- $14HBr + K_2 Cr O_{27} \rightarrow 2KBr + 2CrBr_3 + 3Br_2 + 7H O_2$
- Or with **manganese (IV) oxide**:
- $4HBr + MnO_2 \rightarrow MnBr_2 + Br_2 + 2H O_2$
- **Hydrogen peroxide** also oxidises hydrogen bromide to molecular bromine:
- $2HBr + H O_{22} \rightarrow Br_2 + 2H O_2$

Chemical properties of halogen hydrocarbons

- **Iodohydrogen is an** even stronger **reducing agent**, and is oxidised by other non-metals and even oxidising agents such as iron (III) compounds and copper (II) compounds.
- **For example**, iodohydrogen reacts with **iron (III) chloride** to form molecular iodine:
- $2HI + 2FeCl_3 \rightarrow I_2 + 2FeCl_2 + 2HCl$
- or with **ferrous (III) sulphate:**
- $2HI + Fe_2 (SO)_{43} \rightarrow 2FeSO_4 + I_2 + H_2 SO_4$
- Iodohydrogen is easily oxidised by nitrogen compounds **such** as **nitric oxide (IV)**:
- $2HI + NO_2 \rightarrow I_2 + NO + H O_2$
- or molecular **sulphur** when heated:
- $2HI + S \rightarrow I_2 + H S_2$
- **5. Hydrofluoric acid** reacts with **silicon (IV) oxide** (dissolves glass):
- $SiO_2 + 4HF \rightarrow SiF_4 + 2H O_2$
- $SiO_2 + 6HF_{(изб)} \rightarrow H_2 [SiF_6] + H O_2$

Metal halides

- Halogenides are binary compounds of halogens and metals or certain non-metals, salts of halogen hydrocarbons.

Methods of producing halides

1. Metal halides are produced by the interaction of halogens with metals. The halogens exhibit the properties of an oxidising agent.

- For example, chlorine interacts with magnesium and calcium:
- $Cl_2 + Mg \rightarrow MgCl_2$
- $Cl_2 + Ca \rightarrow CaCl_2$

2. Metal halides can be obtained by the interaction of metals with **hydrogen halides**.

- **For example**, hydrochloric acid reacts with iron to form ferric chloride (II):
- $Fe + 2HCl \rightarrow FeCl_2 + H_2$

Metal halides

3. Metal halides can be obtained by the interaction of **basic and amphoteric oxides** with **hydrogen halides**.

- **For example**, when calcium oxide and hydrochloric acid interact:
- $2HCl + CaO \rightarrow CaCl_2 + H\ O_2$
- Another **example**: the interaction of aluminium oxide with hydrochloric acid:
- $6HCl + Al\ O_{23} \rightarrow 2AlCl_3 + 3H\ O_2$

4. Metal halides can be obtained by the interaction of **bases and amphoteric hydroxides** with **hydrogen halides**.

- **For example,** when sodium hydroxide and hydrochloric acid interact:
- $HCl + NaOH \rightarrow NaCl + H\ O_2$

Metal halides

5. Some **salts** react with **hydrogen halides** to form metal halides.

- **For example**, sodium hydrogen carbonate reacts with hydrogen bromide to form sodium bromide:
- $HBr + NaHCO_3 \rightarrow NaBr + CO_2 \uparrow + H\ O_2$

Chemical properties of halides

1. Soluble halides enter into exchange reactions with **soluble salts, acids and bases** if a precipitate, gas or water is formed.

- **For example**, bromides, iodides and chlorides react with **silver nitrate** to form yellow, yellow and white precipitates respectively.
- $NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$

2. Heavy metal halides react **with the more active metals**. The more active metals displace the less active ones.

- **For example**, magnesium displaces copper from molten copper(II) chloride:
- $Mg + CuCl_2 \rightarrow MgCl_2 + Cu$

Chemical properties of halides

3. Halogenides are subjected **to electrolysis** in solution or melt. This produces **halogens** at the anode.

- **For example**, the electrolysis of **a** potassium bromide **melt** produces potassium at the cathode and bromine at the anode:
- $2KBr \rightarrow 2K + Br_2$
- **When a solution of** potassium bromide is electrolysed, hydrogen is released at the cathode and bromine is also produced at the anode:
- $2KBr + 2H_2O \rightarrow H_2\uparrow + 2KOH + Br_2\uparrow$

4. Metal halides exhibit **reducing properties**. Chlorides are oxidising only strong oxidising agents, but iodides are already very strong reducing agents. In general, the reducing properties of halides are similar to those of hydrogen halides.

- **For example**, potassium bromide is oxidised with concentrated sulphuric acid:
- $2KBr + 2H_2SO_{4\,(конц.)} \rightarrow 4K_2SO_4 + 4Br_2 + SO_2 + 2H\,O_2$

Chemical properties of halides

5. Insoluble metal halides are dissolved by an excess of **ammonia**.

- **For example**, silver (I) chloride dissolves when exposed to an excess of ammonia solution:
- $AgCl + NH_3 \longrightarrow [Ag(NH\ )_{32}\ ]Cl$

6. Insoluble halides **decompose** into halogen and metal when exposed to light.

- **For example**, silver chloride decomposes when exposed to ultraviolet light:
- $2AgCl \longrightarrow 2Ag + Cl_2$