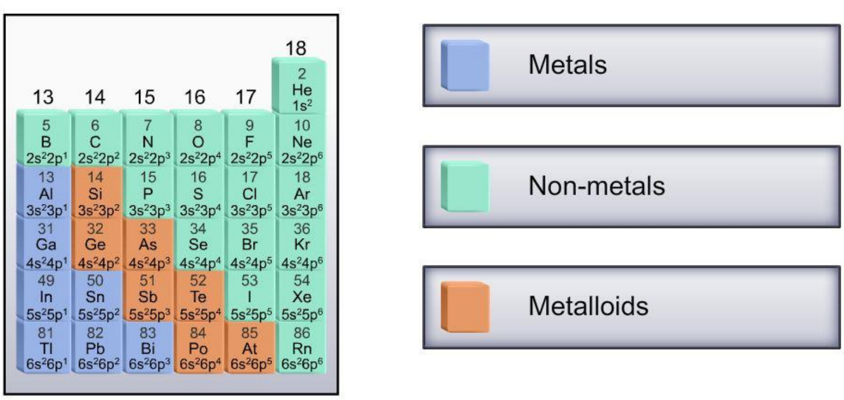
HALOGENS

Group 7A (17) Elements



- **None of the Group 7A elements behaves as a typical metal.**

The Halogens

- Most reactive nonmetal group;
- Not found as free elements in nature.
- Mainly found as halide ions (X^-) in various minerals and in seawater.
- Very reactive non-metals
  - ✓High electronegativity
  - ✓High electron affinity
- Bonding and Oxidation states
- Colour

Halides

- When halogens react with another substance, they become ions. When this happens, they are called **halides**.

Halogen	reaction	Halide
fluorine (F)	→	fluoride (F^-)
chlorine (Cl)	→	chloride (Cl^-)
bromine (Br)	→	bromide (Br^-)
iodine (I)	→	iodide (I^-)

Why are they called the 'halogens'?

These halogen-metal compounds are salts, which give halogens their name – '**halo-gen**' means '**salt-former**'.

Electron structure

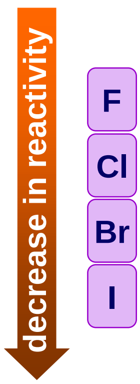
- All halogens have 7 electrons in their outer shell, **ns^2, np^5**.

This means that:

- They can easily obtain a full outer shell by gaining 1 electron.
- They all gain an electron in reactions to form **negative ions** with a -1 charge.
- They have similar chemical properties.

Electron structure and reactivity

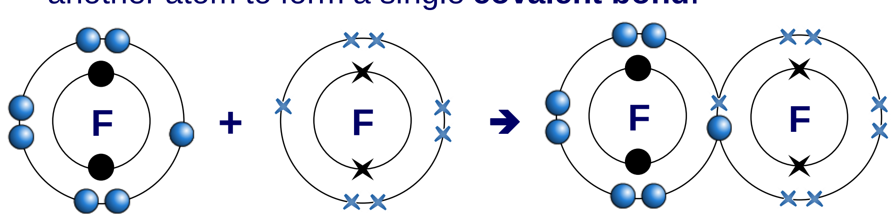
All halogens are reactive, and the reactivity decreases down the group. What is the reason for this?



- This means that, down the group, the outer shell gets further away from the nucleus and is shielded by more electron shells.
- The further the outer shell is from the positive attraction of the nucleus, the harder it is to attract another electron.
- This means that reactivity decreases with the size of the atom.

How do halogen molecules exist?

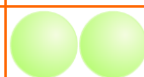
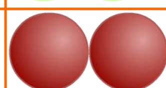
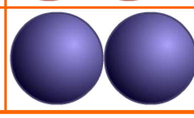
All halogen atoms require one more electron to obtain a full outer shell and become stable.
Each atom can achieve this by sharing one electron with another atom to form a single **covalent bond**.



This means that all halogens exist as diatomic molecules: $\mathbf{F_2}$, $\mathbf{Cl_2}$, $\mathbf{Br_2}$ and $\mathbf{I_2}$.

What is the physical state of the halogens?

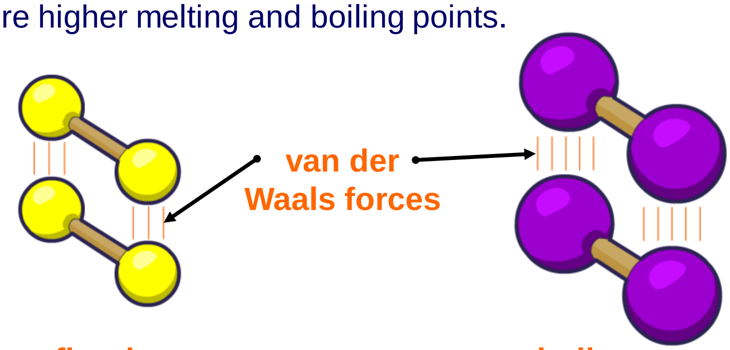
The melting and boiling points of the halogens increase down the group, as the molecules become bigger.

Halogen	Relative size	Melting point (°C)	Boiling point (°C)	State
fluorine		-220	-118	**gas**
chlorine		-101	-34	**gas**
bromine		-7	59	**liquid**
iodine		114	184	**solid**

What is the state of each halogen at room temperature?

Trends in boiling point

Halogen molecules increase in size down the group. This leads to greater van der Waals forces between molecules, increasing the energy needed to separate the molecules and therefore higher melting and boiling points.



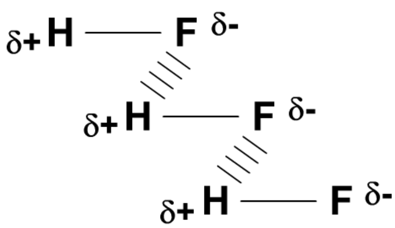
fluorine
atomic radius = 42 × 10^{-12} m
boiling point = -118 °C

iodine
atomic radius = 115 × 10^{-12} m
boiling point = 184 °C

Hydrogen halides

The hydrogen halides are colourless gases at room temperature.

Hydrogen halide	Boiling point (°C)
HF	20
HCl	-85
HBr	-67
HI	-35

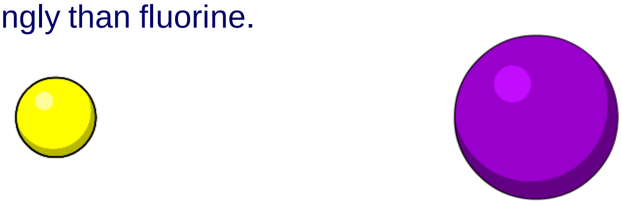


Hydrogen fluoride has an unexpectedly high boiling point compared to the other hydrogen halides. This is due to hydrogen bonding between the H–F molecules.

Trends in electronegativity

Electronegativity of the halogens decreases down the group due to an increase in atomic radius.

Increased nuclear charge has no significant effect because there are more electron shells and more shielding. Iodine atoms therefore attract electron density in a covalent bond less strongly than fluorine.



fluorine
atomic radius = 42×10^{-12} m
electronegativity = 4.0

iodine
atomic radius = 115×10^{-12} m
electronegativity = 2.5

Electronegativity

A measure of the attracting ability of bonding electrons.

Due to their large effective nuclear charge, halogens are the most electronegative element in the periodic table.

Element	EN value
F	4.0
Cl	3.0
Br	2.8
I	2.5

Astatine

The name astatine comes from the Greek word for **unstable.**

Astatine exists in nature in only very tiny amounts. It is estimated that only 30 grams of astatine exist on Earth at any one time. This is because it is **radioactive**, and its most stable isotope (**^{210}At**) has a half-life of only 8 hours.

[210]
At
85

It was first made artificially in 1940, by bombarding ^{209}Bi with α-radiation. What do you predict for these properties of astatine?

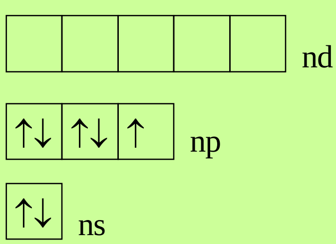
- colour
- state at room temperature
- electronegativity.

Bonding and Oxidation State

F shows (–1) only

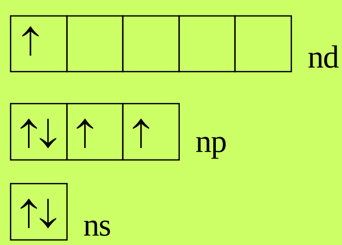
- ns^2np^5
- Ionic or covalent bond with oxidation state –1 or +1
- Except F, all other halogens can expand their octet by using the low-lying, vacant d-orbitals to form bonding.
- Their oxidation states range from –1 to +7.

Bonding and Oxidation State



(0, +1, -1 states)

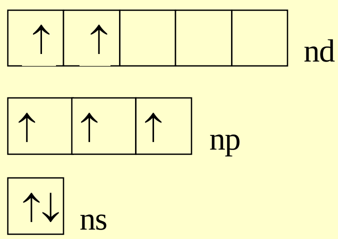
Cl_2, Cl^-, OCl_2



(+3 states)

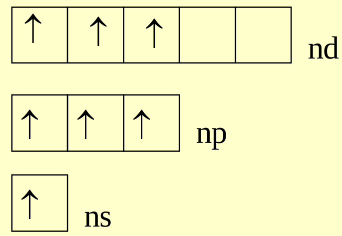
$HClO_2$, ClO_2^-

Bonding and Oxidation State



(+5 state)

$HClO_3$, $HBrO_3$, I_2O_5



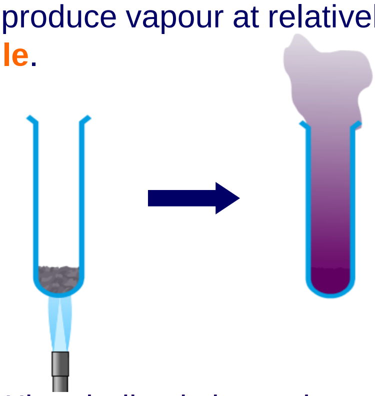
(+7 state)

Cl_2O_7, HIO_4

Halogen vapours

Bromine and iodine are not gaseous, but have low boiling points. This means that they produce vapour at relatively low temperature. They are **volatile**.

Bromine produces some red-brown vapour, seen here above the liquid bromine in the jar.



When iodine is heated gently, it changes directly from a solid to a gas without first becoming a liquid. This is called **sublimation**.

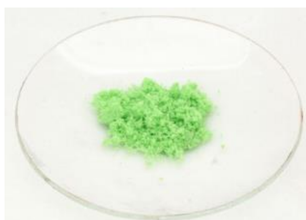
How do the halogens react with metals?

The reactivity of halogens means that they readily react with most metals.

Halogens need to gain electrons for a full electron shell and metals need to lose electrons for a full electron shell.

This means that halogens and metals react to form **ionic compounds**.

These are **metal halides**, which are a type of salt.



nickel (II) chloride

copper (II) chloride

Halogens and iron

When a halogen reacts with iron it forms an iron halide:

$$3Cl_2(g) + 2Fe(s) \rightarrow 2FeCl_3(s)$$

$$3Br_2(g) + 2Fe(s) \rightarrow 2FeBr_3(s)$$

Iodine reacts **slowly** with iron when heated constantly.

$$3I_2(g) + 2Fe(s) \rightarrow 2FeI_3(s)$$

Halogen displacement reactions

Halogen displacement reactions

Halogen displacement reactions are **redox** reactions.

$Cl_2 + 2KBr \rightarrow 2KCl + Br_2$

To look at the transfer of electrons in this reaction, the following two half equations can be written:

$Cl_2 + 2e^- \rightarrow 2Cl^-$

$2Br^- \rightarrow Br_2 + 2e^-$

What has been oxidized and what has been reduced?

- Chlorine has gained electrons, so it is **reduced** to Cl^- ions.
- Bromide ions have lost electrons, so they have been **oxidized** to bromine.

Displacement reactions

- If a halogen is added to a solution of a compound containing a less reactive halogen, it will react with the compound and form a new one. This is called **displacement**.

$$F_2(aq) + 2NaCl(aq) \rightarrow 2NaF(aq) + Cl_2(aq)$$

A more reactive halogen will **always** displace a less reactive halide from its compounds in solution.

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Oxidizing ability of halogens

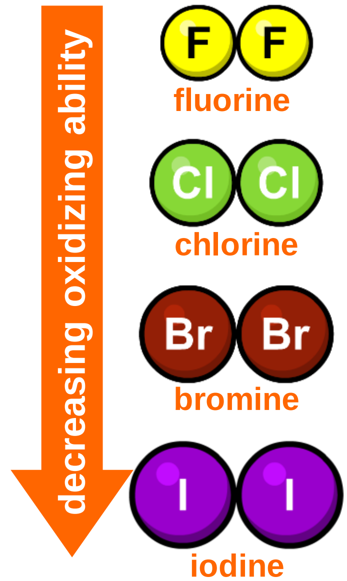
Oxidizing ability of halogens

In displacement reactions between halogens and halides, the **halogen** acts as an **oxidizing agent**.

This means that the halogen:

- **oxidizes** the halide ion to the halogen
- **gains** electrons
- is **reduced** to form the halide ion.

What is the order of oxidizing ability of the halogens?

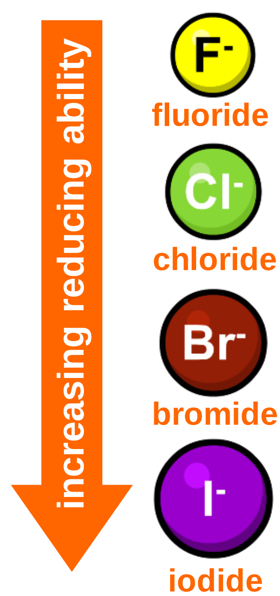


Halides as reducing agents

A substance that donates electrons in a reaction (i.e. is oxidized) is a **reducing agent** because it reduces the other reactant.

The larger the halide ion, the easier it is for it to donate electrons and therefore the more reactive it is.

This is because its outermost electrons are further from the attraction of the nucleus and more shielded from it by other electrons. The attraction for the outermost electrons is therefore weaker.



Reaction with water

Fluorine oxidizes water to form HF and O_2

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

Chlorine undergoes disproportionation(self oxidation and reduction) to form HCl and HOCl.

$Cl_2 + H_2O \rightarrow HCl + HOCl$

Reaction with water

A mixture of Cl_2(aq), HCl(aq) and HOCl(aq) is called ***chlorine water***.

OCl^- , chloric(I) ion

1. Strong oxidizing agent with bleaching property
   OCl^- + dye (coloured) $\rightarrow$ Cl^- + dye (colourless)

2. Unstable to heat and light
   $2OCl^- \rightarrow O_2 + 2Cl^-$

Reaction of chlorine with water

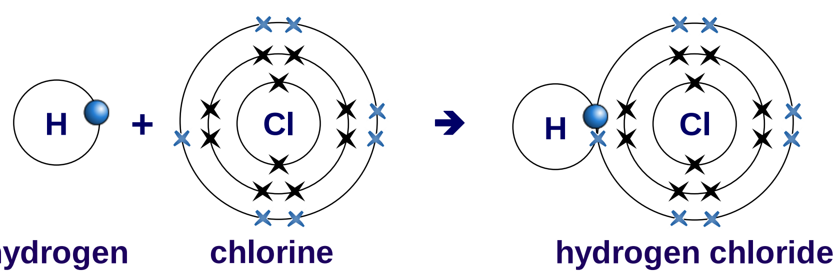
Chlorine is used to purify water supplies because it is toxic to bacteria, some of which can cause disease. Adding it to water supplies is therefore beneficial for the population.

However, chlorine is also toxic to humans, so there are risks associated with gas leaks during the chlorination process. There is also a risk of the formation of chlorinated hydrocarbons, which are also toxic.

How do the halogens react with non-metals?

Halogens also react with non-metals.

For example, halogens react with hydrogen to create **hydrogen halides**.



Unlike their reactions with metals, halogens share electrons with non-metals, and so react to form **covalent compounds**.

All hydrogen halides are gases. They dissolve easily in water and become strong acids.

Halide + c. H_2SO_4

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$
$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + HCl$ (500°C)

$2NaBr + 2H_2SO_4 \rightarrow 2HBr + Na_2SO_4$
$2HI + H_2SO_4 \rightarrow SO_2 + Br_2 + 2H_2O$

$2NaI + 2H_2SO_4 \rightarrow 2HI + Na_2SO_4$
$8HI + H_2SO_4 \rightarrow H_2S + 4I_2 + 4H_2O$

Relative reducing power: HCl < HBr < HI

Halide + c. H_3PO_4

$3NaCl + H_3PO_4 \rightarrow Na_3PO_4 + 3HCl$
$3NaBr + H_3PO_4 \rightarrow Na_3PO_4 + 3HBr$
$3NaI + H_3PO_4 \rightarrow Na_3PO_4 + 3HI$

H_3PO_4 is NOT a strong oxidizing agent.
It reacts with halides to form HX.

Halides + $Ag^+(aq)$

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$, white precipitate

$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$, pale yellow precipitate

$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$, yellow precipitate

Halides + $Ag^+(aq)$

Ion	Action of $AgNO_{3=}$	Effect of Standing in sunlight	Effect of adding excess aq. NH_3
Cl^-	White ppt.	Turns grey	White ppt. dissolves
Br^-	Pale yellow ppt.	Turns yellowish grey	Pale yellow ppt. slightly dissolves
I^-	Yellow ppt.	Remains yellow	Yellow ppt. does not dissolve

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Uses of Halogens

Uses of fluorine

Fluoridation of water, to prevent tooth decay

Toothpaste, to prevent tooth decay

fluorine and its compounds

Polymers, e.g. Teflon for non-stick pans

Processing uranium nuclear fuel

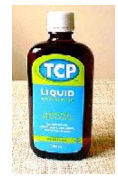
Uses of chlorine

chlorine and its compounds

Pesticides and weed killers

Treatment of drinking water

Antiseptics and disinfectants



Chlorinated carbon compounds, e.g. solvents and plastics (PVC)

Bleach to kill bacteria and to make paper white

Uses of bromine and iodine

bromine and its compounds

Leaded petrol

Medicines

Photography

Agriculture

iodine and its compounds

Animal feed supplements

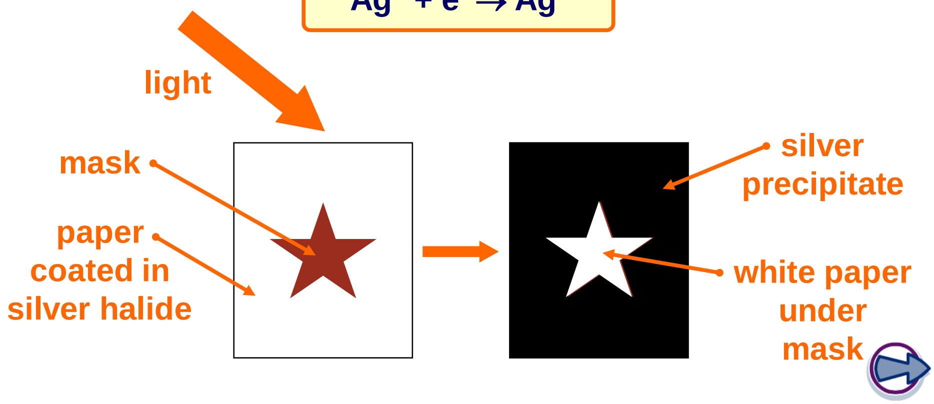
Antiseptics and water purification tablets

Uses of halides in photography

Silver halides are used in photography.

Photographic film coated with a silver halide is exposed to light, causing the halide to decompose to form silver. This appears as a black precipitate on the photographic film.

$$Ag^{+} + e^{-} \rightarrow Ag$$



silver iodide crystals can be used to cause rainfall