

GROUP (VII) ELEMENTS

- These include: fluorine, chlorine, bromine and iodine.

General atomic properties

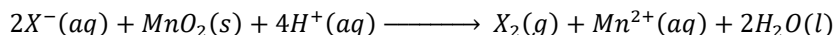
Element	Fluorine	Chlorine	Bromine	Iodine
Atomic radius (nm)	0.72	0.99	1.14	1.33
Boiling point (°C)	-188.0	-34.5	+59.0	+183.0
Bond energy (kJmol ⁻¹)	158.0	242.0	193.0	151.0
Electron affinity (kJmol ⁻¹)	-333	-348	-340	-297

- **The atomic radius** increases down the group. This is because down the group, the nuclear charge increases due to addition of protons to the nucleus of the atoms while the screening effect also increases due to addition of a complete extra shell of electrons from one element to the next. But the increase in the screening effect outweighs the increase in the nuclear charge and the outermost shell of electrons is repelled further away from the nucleus leading to an increase in the atomic radius.
- **The boiling points** of the elements increase down the group. This is because of the increase in the molecular mass of the elements from fluorine to iodine. This increases the magnitude of van der Waals forces holding molecules together so that more heat is required to separate the molecules during boiling.
- **Bond energy** decreases from fluorine to iodine. This is because from fluorine to iodine, the atomic radius increases so that the nuclear attraction for the bonding/ valence electrons also decreases and hence they need less energy to separate.
The bond energy for fluorine is lower than expected because of the strong repulsion between the non-bonding electrons around the fluorine atoms in the molecule. Due to the very small atomic radius of the fluorine atoms, the non-bonding electrons are so close to each other hence much repulsion and reducing the bond energy.
- **The electron affinity** decreases from fluorine to iodine. This is because of the increase in the atomic radius in the same order. The nuclear attraction for the electron to be added decreases, reducing the affinity and less energy is thus given off upon its addition.
Fluorine has a low value of electron affinity because it has a very small atomic radius.
The electron to be added experiences strong repulsion from the electrons already around the small fluorine atom closely shielding its nucleus. This reduces the affinity for the electron and less energy than expected is thus given off.

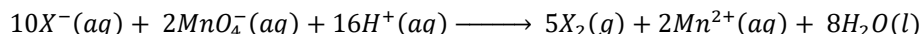
Laboratory preparations of halogens

- Fluorine is not prepared by the ordinary methods in the laboratory
Chlorine, bromine, and iodine can be prepared in the laboratory by:

- Heating a corresponding potassium or sodium halide with concentrated sulphuric acid in the presence of an equal mass of manganese(IV) oxide.



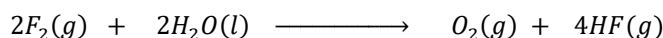
- The action of cold concentrated sulphuric acid on a solid mixture of the sodium or potassium halide salt and potassium permanganate



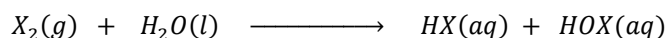
Reaction of group(VII) elements

Reaction with water

- Fluorine oxidises water to oxygen and itself reduced to hydrogen fluoride



- Chlorine and bromine react with water forming a mixture of the corresponding hypohalous and hydrohalic acids (hypochlorous acid and hydrochloric acid for chlorine and hypobromous and hydrobromic acid for bromine)



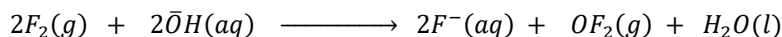
(where X is Cl or Br)

- Iodine does not react with water.

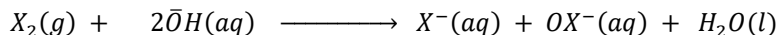
Reaction with caustic alkalis

a. Cold dilute alkalis

- Fluorine reacts with cold dilute alkalis to form a fluoride, oxygen difluoride and water



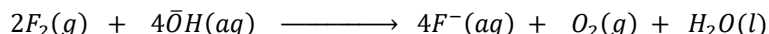
- Chlorine and bromine react with cold dilute alkalis to form the corresponding halide, hypohalite and water



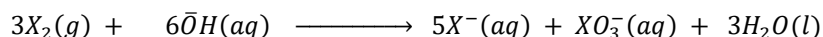
(where X is Cl or Br)

b. Hot concentrated alkalis

- Fluorine reacts with hot concentrated alkalis to form a fluoride, oxygen gas and water



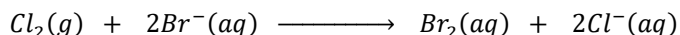
- Chlorine, bromine and iodine react with hot concentrated alkalis to form the corresponding halides, halates and water.



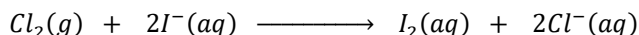
(where X is Cl, Br or I)

Displacement reactions

- Each halogen can displace those below it in the group from their halide solutions.
- Chlorine displaces bromine and iodine from the solutions containing bromides and iodides respectively. This is because chlorine is a stronger oxidising agent than bromine or iodine. E.g.
- When chlorine is bubbled through an aqueous solution of potassium or sodium bromine, the colourless solution turns reddish-brown.

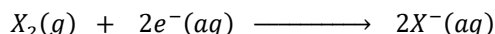


- When chlorine is bubbled through an aqueous solution of potassium or sodium iodide, the colourless solution turns brown.



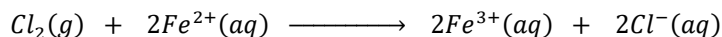
Other oxidation reactions

- Halogens act as oxidising agents by accepting electron from the reducing agent



a. Oxidation of iron(II) to iron(III)

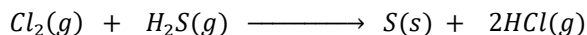
- When chlorine is bubbled through a solution of iron(II) sulphate, the pale solution turns pale yellow.
- This is due to oxidation of iron(II) ions to iron(III) ions



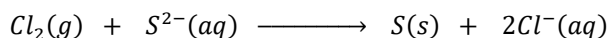
- Bromine has a similar reaction but **not** iodine.

b. Oxidation of hydrogen sulphide to sulphur

When chlorine is passed through a gas jar containing hydrogen sulphide (or hydrogen sulphide solution), a yellow deposit of sulphur is formed. This is due to oxidation of hydrogen sulphide (or sulphide ions) to sulphur

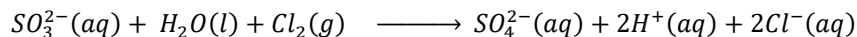


or



c. Oxidation of sulphur dioxide or sulphites to sulphates

- Chlorine oxidises sulphur dioxide in the presence of water or sulphite in aqueous solution to sulphates



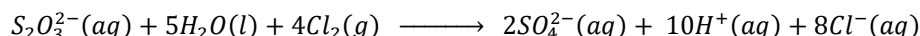
- Bromine and iodine give a similar reaction.
- The halogens are decolourised resulting in a colourless solution

d. Oxidation of thiosulphate

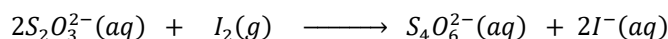
- Limited chlorine (or bromine) oxidises sodium thiosulphate partially to sodium sulphate and sulphur



- Excess chlorine (or bromine) oxidises sodium thiosulphate to sodium sulphate



- Iodine oxidises sodium thiosulphate to sodium tetrathionate. The brown solution turns colourless during the process

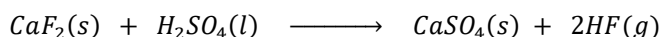


Compounds of group (VII) elements

a. Hydrides

i. Hydrogen fluoride

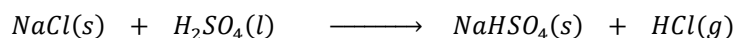
- This can be prepared by distilling calcium fluoride with concentrated sulphuric acid.



- The solution of hydrogen fluoride in water is called *hydrofluoric acid*.

ii. Hydrogen chloride

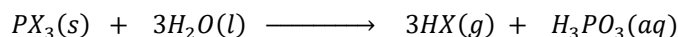
- It can be prepared by the action of cold concentrated sulphuric acid on sodium chloride.



- Hydrogen chloride is manufactured by direct combination of hydrogen and chlorine.
- It can be converted to hydrochloric acid by dissolving it in distilled water.

iii. Hydrogen bromide and hydrogen iodide

- These can be prepared by the action of water on phosphorus tribromide or phosphorus triiodide



(where X is Br or I)

Properties of the hydrides

i. Boiling points

Hydride	HF	HCl	HBr	HI
Boiling point (°C)	+19.9	-85.0	-66.0	-35.4

- The boiling points of the hydrides increase in the order: $HCl < HBr < HI < HF$

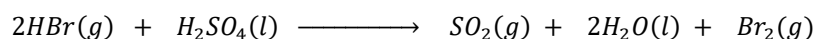
- Van der Waals holding the molecules together, hence increasing the energy required to separate the molecules during boiling.
- Hydrogen fluoride has the highest boiling point even though it has the smallest molecular mass. This is due to hydrogen bonding between the HF molecules. Fluorine is highly electronegative and thus leads to formation of very strong intermolecular hydrogen bonds in hydrogen fluoride.

ii. Acid strength

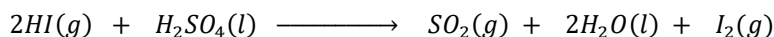
- The acid strength increases in the order. $HF < HCl < HBr < HI$.
- This is because the bond strength of the hydrogen-halogen bond decreases in the order $H - F > H - Cl > H - Br > H - I$ so that the ease with which the proton is lost increases from HF to HI and hence the acid strength.
- The decrease in the bond strength is due to increase in atomic radius which reduces the nuclear attraction for the bonding electrons thus weakening the bond in the same order

iii. Hydrides as reducing agents

- Hydrogen fluoride and hydrogen chloride are not reducing agents.
- Concentrated sulphuric acid oxidises hydrogen bromide to bromine and the acid reduced to sulphur dioxide and water.



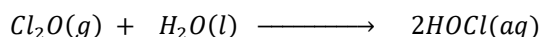
- Concentrated sulphuric acid oxidises hydrogen iodide to iodine and the acid reduced to sulphur dioxide and water.



b. Oxides and oxy-acids

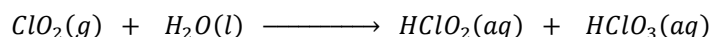
i. Dichlorine oxide

- It is a yellow gas soluble in water to form hypochlorous acid (also called *chloric(I) acid*)



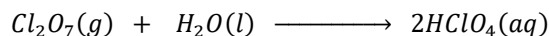
ii. Chlorine dioxide

- Occurs as a red gas soluble in water forming a mixture of chlorous (*chloric(III)*) acid and chloric (*chloric(V)*) acid



iii. Dichlorine heptaoxide

- It is an acid anhydride of perchloric (*chloric(VII)*) acids



- The acids $HOCl$, $HClO_2$, $HClO_3$ and $HClO_4$ are called the oxyacids of chlorine

Acid strength of the oxy-acids

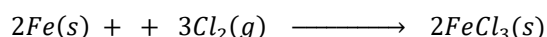
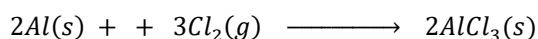
The acid strength increases in the order $\text{HOCl} > \text{HClO}_2 > \text{HClO}_3 > \text{HClO}_4$.

- This is due to the increase in the number of oxygen atoms bonded directly to the chlorine atom.
- Oxygen is more electronegative compared to chlorine so it withdraws electrons away from the chlorine atom
- This withdrawal is transferred through the chlorine atom to the $\text{O} - \text{H}$ bond which increases the partial positive charge on the hydrogen atom
- The $\text{O} - \text{H}$ bond weakens and the proton is easily lost.
- The magnitude of the partial positive charge on the hydrogen atom increases with the number of oxygen atoms attached to the chlorine atom

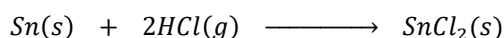
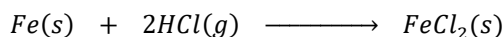
c. Chlorides

- Anhydrous chlorides can be prepared by:

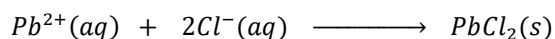
i. Heating the metal in a stream of dry chlorine e.g.



ii. Heating the metal in a stream of dry hydrogen chloride gas



- Insoluble chlorine can be prepared by precipitation reaction. For example lead(II) chloride can be prepared by adding a solution of sodium chloride to a solution of lead(II) nitrate. The precipitate obtained is the filtered off and dried.



Unique behaviour of fluorine

- Fluorine shows many properties in which it differs from the rest of the members of group(VII).

Why fluorine differs from the rest of the group(VII)

- Fluorine has a very small atomic radius, forms fluoride ions with very small ionic radii and high hydration energy,
- Fluorine has a very high electronegativity, low bond energy, oxidising power compare to the rest of the members of the group.

Ways in which fluorine differs from the rest of the group(VII)

- Fluorine oxidises water to oxygen and hydrogen fluoride whereas chlorine and bromine form a mixture hypochlorous and hydrohalic acids, while iodine does not react with water
- Fluorine reacts directly with carbon while other group(VII) elements do not

- Fluorine reacts with hot concentrated alkalis to form oxygen, fluorides and water while others form halides, halates and water
- Fluorine reacts with cold dilute alkalis to form oxygen difluoride, fluorides and water while others halogens form hypohalites, halides and water
- Fluorine does not form oxyacids while other halogens do
- Fluorine has only one oxidation state while other halogens have several oxidation states
- Hydrogen fluoride is a weak acid while other halogen acids are strong acids
- Hydrogen fluoride is a room at temperature while other halogen hydrides are gases

Qualitative analysis of group(VII) ions

Reagent; Lead(II) nitrate solution and dilute nitric acid

Observations with		
Cl^-	Br^-	I^-
White precipitate insoluble in the acid (soluble on warming and re-precipitates on cooling)	White precipitate insoluble in the acid	Yellow precipitate insoluble in the acid

Reagent; Silver nitrate solution, dilute nitric acid, and ammonia solution

Observations with		
Cl^-	Br^-	I^-
White precipitate insoluble in the acid but soluble in ammonia solution	Pale yellow precipitate insoluble in the acid but soluble in concentrated ammonia solution	Yellow precipitate insoluble in the acid and concentrated ammonia solution

Reagent; bleaching powder (or chlorine water) carbon tetrachloride

Observations with		
Cl^-	Br^-	I^-
	Orange colour in the tetrachloromethane layer	Purple colour in the tetrachloromethane layer

GROUP (VII) QUESTIONS

1. (a) State four properties in which fluorine differs from iodine
 (b) State the conditions and write the equations for the reaction between sodium hydroxide and

- (i) Fluorine
- (ii) Iodine
- (c) Compare the oxidizing powers of fluorine and iodine using their reactions with water

2. The boiling points of the hydrides of group (VII) elements are given in the table below

Compound	HF	HCl	HBr	HI
B.P/ °C	+199	-85.0	66.7	-35.5

- (a) Explain the trend in boiling points of the hydrides
 - (b) Giving reasons, suggest the trend in the acid strength of the hydrides
 - (c) Using equations where applicable, explain what happens when conc. Sulphuric acid is mixed with each of the hydrides.
 - (d) Arrange the following in order of their increasing acid strength. HClO , HClO_2 , HClO_3 , HClO_4 .
 - (e) Explain your answer in d.
3. Explain the following observations
- (a) Fluorine is more reactive than any other halogen
 - (b) Lead (IV) chloride exists while lead (IV) bromide does not
 - (c) Lead (IV) fluoride is ionic while lead (IV) chloride is covalent
 - (d) Despite the electron affinity of chlorine being highest, fluorine is the strongest oxidizing agent.
4. (a) Describe briefly how chlorine can be produced on a large scale.
- (b) Describe briefly how chlorine can be converted into potassium chlorate (V) crystals in the laboratory.
- (c) 2.0g of a mixture of potassium chloride and potassium chlorate were dissolved in 250cm³ of water. 10cm³ of the solution was shaken with potassium iodide solution. The iodine liberated required 8.0cm³ of 0.2M sodium thiosulphate solution for complete reaction.
- Potassium chlorate and potassium iodide react according to the equation.
- $$\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + \text{I}^-(\text{aq}) \longrightarrow 3\text{I}_2(\text{aq}) + \text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$$
5. (a) Explain why fluorine shows some differences in its properties from the rest of the group (VII) members of the periodic table.
- (b) State the difference between the chemistry of fluorine and the rest of the elements of group (VII) of the periodic table.
- (c) Write equations to compare the reactions of chlorine and fluorine when they react with
- (i) Water
 - (ii) Sodium hydroxide solution
- (d) Write equation for the reaction between hydrofluoric acid and silicon dioxide

6. (a) Describe how you would determine the percentage
 - (i) Amount of chlorine in bleaching powder
 - (ii) Of available chlorine in jik.
 - (b) 1.2g of bleaching powder was ground up with water and the whole diluted to make 250cm³. 25cm³ of this solution were added to an excess of potassium iodide acidified with ethanoic acid, and this required 22.3cm³ of 0.05M sodium thiosulphate. Calculate the percentage of available chlorine in the bleaching powder
 - (c) 10cm³ of jik was diluted to make 250cm³. 25cm³ of this solution were added to an excess of potassium iodide acidified with ethanoic acid, and this required 20.4cm³ of 0.10M sodium thiosulphate. Calculate the percentage of available chlorine in the jik.
7. Explain the following observations
 - (a) Hydrofluoric acid forms acid salts while hydrochloric acid does not.
 - (b) Hydrogen fluoride is a liquid at room temperature while hydrogen chloride is a gas
 - (c) Hydrogen chloride can be prepared by the action of conc. Sulphuric acid on sodium chloride, while hydrogen iodide cannot be obtained in a similar way.
 - (d) Hydrogen fluoride is a stronger acid at higher concentration than when its dilute
 - (e) Hydrogen chloride is a stronger acid than hydrogen fluoride.
 8. (a) Describe how you would distinguish the following pairs of ions
 - (i) Cl⁻ and Br⁻
 - (ii) Br⁻ and I⁻
 - (iii) I⁻ and Cl⁻
 - (b) Write equations for the following
 - (i) Addition of hydrogen chloride to bleaching powder, CaOCl₂
 - (ii) Heating sodium chlorate (I)
 - (iii) Addition of hydrogen iodide to sodium hypochlorite.
 - (c) sodium chlorate is a strong oxidizing agent and in acidic medium, it behaves as

$$\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \longrightarrow \text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{aq})$$

Write equations for the reactions between sodium chlorate (acidified) and

 - (i) Iron (II) sulphate solution
 - (ii) Potassium iodide solution
 - (iii) Sodium sulphite solution
 9. (a) Describe one general method of preparing halogens (except fluorine) in the laboratory. Write equation for the reaction
 - (b) Describe the reaction of fluorine, chlorine and bromine with
 - (i) Water
 - (ii) Sodium hydroxide
 - (c) How would you distinguish between sodium bromide and sodium iodide, given chlorine and tetrachloromethane

10. (a) Explain how the following vary within group (VII)
- atomic radius
 - Boiling point
 - Ionization energy.
- (b) The table below shows the bond energy and electron affinity of group (VII) elements

Element	Bond energy (kJmol ⁻¹)	Electron affinity (kJmol ⁻¹)
Fluorine	158.1	333
Chlorine	242.0	348
Bromine	193.0	340
Iodine	151.0	297

Describe and explain the trend in

- Bond energy
 - Electron affinity
11. (a) Hypochlorite, chlorate (I) is a component of domestic bleaching compounds and undergoes disproportionation.
- State the oxidation state of chlorine in chlorate (I)
 - Explain what the term disproportionation means. Use chlorate (I) to illustrate your answer
- (b) Excess chlorine was bubbled through a hot conc. Solution of potassium hydroxide. Write an equation for the reaction that took place.
- (c) 1.6g of the salt mixture above was dissolved in water to make 250cm³. 25cm³ of this solution were added to an excess of potassium iodide acidified with sulphuric acid,
- State what is observed and write equation for the reaction.
 - If the product of the reaction required 12.8cm³ of 0.1M sodium thiosulphate. Calculate the percentage of potassium chlorate in the mixture
12. State what is observed and write equation for the reaction when
- Chlorine is bubbled through a cold dilute solution of potassium hydroxide
 - Bromine is bubbled through a solution of potassium iodide
 - Iodine solution is added to sodium thiosulphate solution
 - Excess chlorine is bubbled through a solution of sodium thiosulphate and barium chloride solution is added
 - Chlorine is mixed with hydrogen sulphide gas
 - Moderate amount of chlorine is bubbled through a solution of sodium thiosulphate
 - Bromine is bubbled through a solution of iron (III) sulphate
 - Potassium iodide solution is mixed with iron (III) sulphate solution
 - Chlorine gas bubbled through sodium sulphite solution and barium chloride added
 - Chlorine is bubbled through potassium iodide solution