

THE CHEMISTRY OF GROUP VII ELEMENTS

Electronic structures/ configurations

Element	Atomic number	Configuration
<i>F</i>	9	$1s^2 2s^2 2p^5$
<i>Cl</i>	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
<i>Br</i>	35	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
<i>I</i>	53	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$

From the above electronic configurations, it can be concluded that the outermost electronic configuration of group VII elements is $ns^2 np^5$

Bonding and structure

Element	Bonding	Structure	Physical state and colour at room temperature
<i>Fluorine</i>	All covalent	All simple molecular	Pale yellow gas
<i>Chlorine</i>			Greenish yellow gas
<i>Bromine</i>			Red liquid
<i>Iodine</i>			Grey/ black solid

Qn. Explain why fluorine and chlorine exist as gases whereas bromine and iodine exist as liquid and solid respectively at room temperature

From fluorine to iodine, atomic radius increases, molecular size and molecular mass increases, hence magnitude of Van der Waals' forces of attraction holding the molecules increases in the order; $F_2 < Cl_2 < Br_2 < I_2$. The Van der Waals' forces in bromine and iodine are strong enough to hold the molecules closer to each other existing as liquid and solid respectively. Fluorine and chlorine have weaker Van der Waals' forces due to their small size and low molecular masses. Their molecules are therefore far apart.

VARIATION IN ATOMIC AND PHYSICAL PROPERTIES OF THE ELEMENTS

1. Melting points/ boiling points

The table below shows the boiling points/melting points of halogens

Element	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
Boiling point($^{\circ}\text{C}$)	-187.9	-34.0	58.2	+184.5
Melting points($^{\circ}\text{C}$)	-219.6	-102.4	-7.2	+113.6

Explain the trend in boiling points/ melting points of the halogens

Boiling point/melting point increases from fluorine to iodine because atomic radius increases, molecular size and molecular mass increases, hence magnitude of Van der Waals' forces of attraction holding the molecules increases in the order $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$. The energy required to break the forces therefore increase from fluorine to iodine.

2. Atomic and ionic radius

The table below shows the atomic radii and ionic radii of the elements in Group VII of the Periodic Table.

Element	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
Atomic radius(nm)	0.072	0.099	0.114	0.133
Ionic radius(nm)	0.136	0.181	0.195	0.216

(a) State and explain the trend in atomic radius of the elements

Atomic radius increases from fluorine to iodine.

This is because from fluorine to iodine, nuclear charge increases because a proton is added to nucleus from element to element. Screening effect also increases, because an extra energy level completely filled with electrons is added. Increase in screening effect outweighs increase in nuclear charge. effective nuclear charge decreases, and outer most electrons are far and weakly attracted by the nucleus.

(b) Explain why the ionic radius is larger than the atomic radius of corresponding neutral atom for each element.

The ions are formed by gaining electrons. When the electrons are gained, the number of electrons becomes greater than the number of existing protons. Screening effect increases. Effective nuclear charge reduces. The electrons become more strongly repelled by the nucleus than they are attracted. In the neutral atom, the screening effect is counterbalanced by nuclear charge.

3. First ionization energy

The table below shows the first ionization energies of Group VII elements.

Element	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
First ionisation energy (kJmol ⁻¹)	1681	1255	1142	1007

(a) Define the term first ionisation energy.

The minimum amount of energy required to remove an electron from a gaseous atom to form a unipositively charged gaseous ion.

or

The minimum amount of energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of unipositively charged gaseous ions.

(b) State and explain the trend in ionization energy of the elements

First ionization energy decreases from fluorine to iodine.

This is because from fluorine to iodine, nuclear charge increases, Screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic radius increases and outer most electron is far and weakly attracted by the nucleus requiring a low amount of energy to be removed.

4. Electron affinity

The table below shows the first electron affinities and atomic numbers of the elements in Group VII

Element	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
Atomic number	9	17	35	53
First electron affinity(kJmol ⁻¹)	-354	-370	-348	-320

(a) Explain what is meant by the term first electron affinity

(b) Plot a graph of first electron affinity against atomic number of the elements.

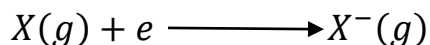
(To be done by student. When plotting the graph, the negative sign may be eliminated since it's on all values and it just indicates that the process is exothermic. The graph below is just a sketch and not on scale)

(c) (i) Explain the general trend in variation of the first electron affinities

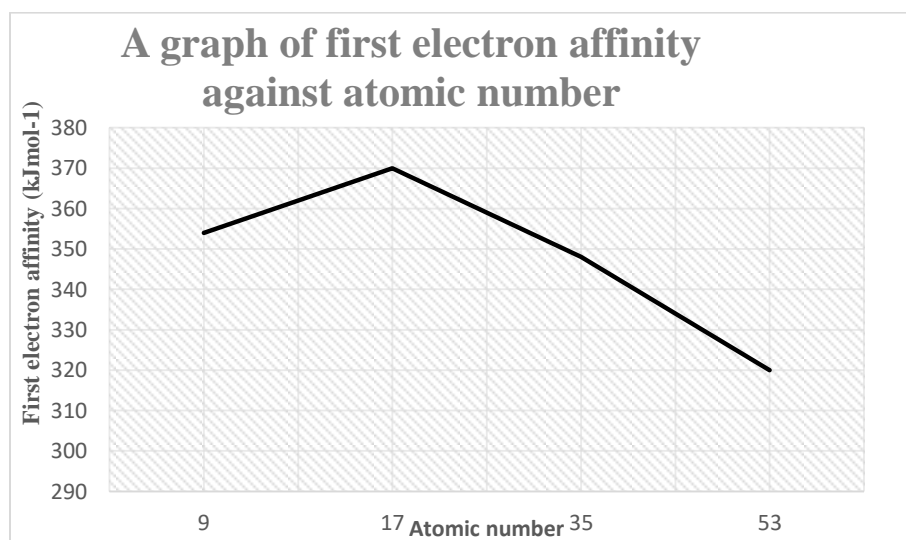
(ii) Explain why fluorine has an abnormal value

(a) This is the energy given out when **one mole** of electrons combines with **one mole** of gaseous atoms to form **one mole** of uninegatively charged gaseous ions

or The energy given out when **an electron** is added to a **gaseous atom** to form a uninegatively charged **gaseous ion**.



(b)



(c) (i) **Generally**, first electron affinity decreases from fluorine to iodine.

This is because from fluorine to iodine, nuclear charge increases, Screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic radius increases and incoming electron is far and weakly attracted by the nucleus giving off a low amount of energy.

(ii) Fluorine has the smallest atomic radius, highest **electron** density, strongly repels the incoming electron and energy is consumed to add the electron to its atom.

5. Electronegativity

The tendency of an atom in a molecule to attract bonding electrons towards itself.

The table below shows the electronegativity values of the elements in Group VII of the Periodic Table.

Element	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
Electronegativity	4.10	2.83	2.74	2.21

State and explain the trend in electronegativity values of the elements

Electronegativity decreases from fluorine to iodine.

This is because from fluorine to iodine, nuclear charge increases, screening effect also increases, because an extra energy level completely filled with electrons is added from element to element. Increase in screening effect outweighs increase in nuclear charge. Effective nuclear charge decreases, atomic radius increases, and the bonding electrons experience a greater repulsion than nuclear attraction.

6. Bond dissociation energy

The table below shows the values of Bond dissociation energy of halogens.

Element	<i>F₂</i>	<i>Cl₂</i>	<i>Br₂</i>	<i>I₂</i>
Bond dissociation energy(kJmol ⁻¹)	158.1	242.2	193	151

(a) State the difference between bond dissociation energy and bond energy.

(b) Explain the trend, stating any anomalies in the bond dissociation energy of the halogens.

- (a) Bond dissociation energy is the heat change that occurs when one mole of a covalent bond is broken down into its constituent gaseous atoms whereas Bond energy is the standard enthalpy change that occurs when one mole of a covalent bond is formed from its constituent gaseous atoms.
- (b) Bond dissociation energy decreases from chlorine to iodine but with fluorine having an abnormally low value of bond dissociation energy.

This is because from one chlorine to iodine, atomic radius increases, bond length increases and bond strength decreases, resulting into weaker attraction between the atoms in the molecule, requiring a low amount of energy to break the bonds.

Fluorine has an abnormally low value of bond dissociation energy because fluorine has the smallest atomic radius, and the non-bonding electrons in the molecule repel each other strongly. This strong repulsion tends to force the fluorine atoms far apart thus weakening the F-F bond, requiring low amount of energy to break it.

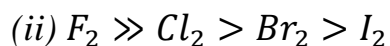
7. Electrode potential

The table below shows the standard electrode potential values of Group VII elements.

Element	<i>F</i>	<i>Cl</i>	<i>Br</i>	<i>I</i>
Standard electrode potential(E^θ) (Volts) for $\frac{1}{2}X_2/X^-(aq)$	+2.80	+1.36	+1.07	+0.54

- (a) State;
- the strongest oxidising agent
 - order of oxidising strength of the halogens
- (b) Explain the trend in standard electrode potential of the elements
- (c) State what would be observed when;
- Chlorine is bubbled through potassium bromide solution
 - Chlorine is bubbled through potassium iodide solution
- (d) Explain your observations in c(i) and (ii) basing on the table above
- (e) Explain why tin(IV) chloride exists but tin(IV) bromide and tin(IV) iodide do not exist.

(a)(i) Fluorine or F_2 (but not F)

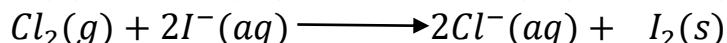
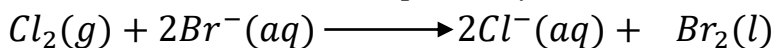


(b) *Standard electrode potential becomes less positive (increases) from fluorine to iodine because ionic radius increases, electron affinity decreases, bond dissociation energy generally decreases and hydration energy also decreases. However, the decrease in electro affinity and bond dissociation energy is more rapid than decrease in hydration energy.*

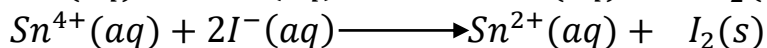
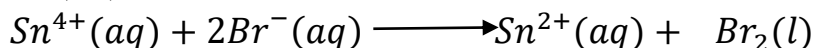
(c) (i) *The greenish-yellow gas dissolves and the colourless solution forms a red liquid.*

(ii) *The greenish-yellow gas dissolves and the colourless solution turns dark brown finally forming a black solid deposit.*

(d) *The standard electrode potential for $Cl_2/Cl^-(aq)$ is more positive than that of $Br_2/Br^-(aq)$ or $I_2/I^-(aq)$ and the chloride ion has a smaller ionic radius than bromide and iodide ions respectively. Chlorine therefore a stronger oxidising agent than bromine or iodine. Chlorine oxidises bromide and iodide ions to bromine and iodine respectively.*



(e) *Bromide ions and iodide ions have a larger ionic radius than chloride ion. The ions are therefore strongly reducing. They reduce tin(IV) ions to tin(II) ions, as they are oxidised to bromine and iodine respectively. Chloride ions cannot reduce tin(IV) ions.*

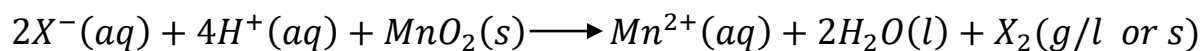


METHODS OF PREPARATION OF HALOGENS

Qn. Describe the general method of preparing halogens except fluorine

All halogens apart from fluorine are prepared by;

Heating a solid halide salt with concentrated sulphuric acid in presence of manganese(IV) oxide.



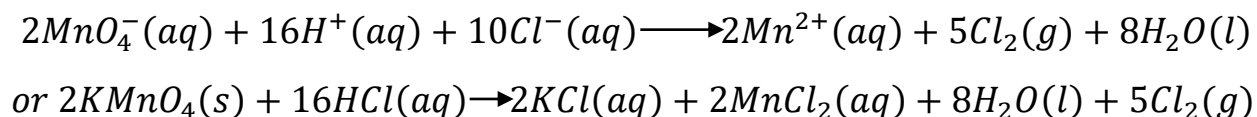
Where $X = Cl, Br \text{ or } I$

N.B. The Chemistry in action here is that concentrated sulphuric acid acts upon the halide salt (KCl/KBr/KI or NaCl/NaBr /NaI) to form a hydrogen halide (HCl or HBr or HI) which is then oxidised to the halogen by manganese(IV) oxide.

Qn. Describe the reactions, stating the conditions and under which chlorine can be prepared in the laboratory. State any observations made.

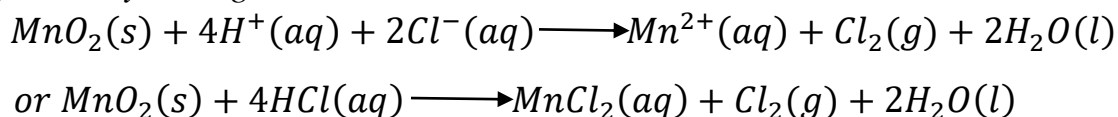
1. Chlorine can be prepared by the reaction between cold concentrated hydrochloric acid and potassium manganate(VII).

The purple solution turns colourless and bubbles of a greenish yellow gas.



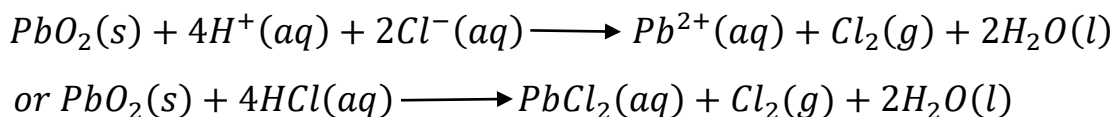
2. Chlorine can also be prepared by heating concentrated hydrochloric acid with manganese(IV) oxide.

The black solid dissolves forming a colourless solution and bubbles of a greenish yellow gas.



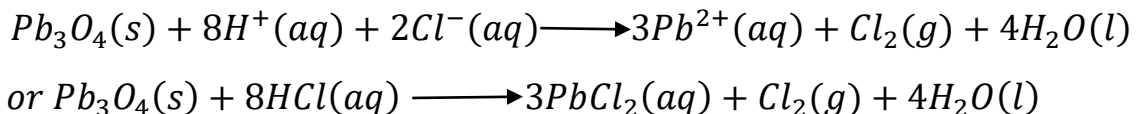
3. Chlorine can also be prepared by heating concentrated hydrochloric acid with lead(IV) oxide.

The dark brown solid dissolves forming a colourless solution and bubbles of a greenish yellow gas.

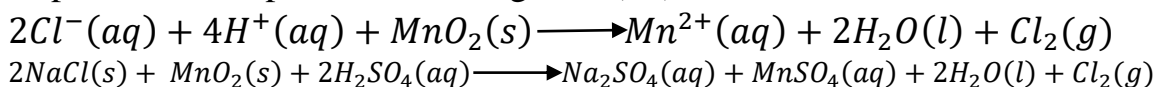


4. Chlorine can as well be prepared by heating concentrated hydrochloric acid with Dilead(II) lead(IV) oxide.

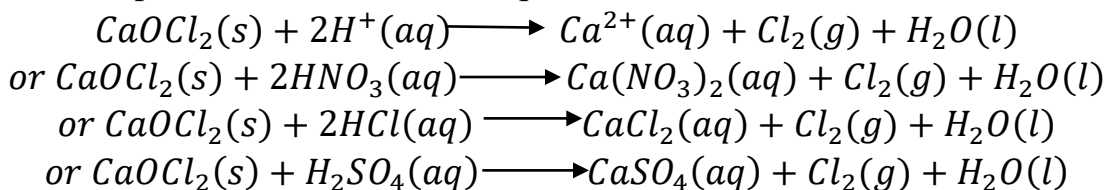
The red solid dissolves forming a colourless solution and bubbles of a greenish yellow gas.



5. Chlorine can be prepared by heating solid sodium chloride with concentrated sulphuric acid in presence of manganese(IV) oxide.



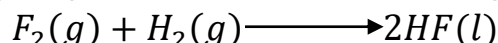
6. Chlorine is also prepared by the reaction between bleaching powder (Calcium hypochlorite with dilute nitric acid or dilute hydrochloric acid or dilute sulphuric acid. No heat is required.



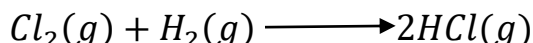
CHEMICAL PROPERTIES OF THE ELEMENTS

1. Describe the reactions of Group VII elements react with hydrogen. State the conditions for the reactions.

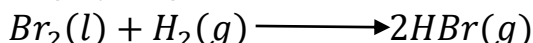
Fluorine explodes in hydrogen even in darkness forming hydrogen fluoride



Chlorine does not react with hydrogen in the dark or at room temperature but the mixture explodes on heating or presence of sunlight or ultraviolet light to form hydrogen chloride



Bromine reacts with hydrogen only on heating or in the presence of platinum catalyst at 300 °C forming hydrogen bromide

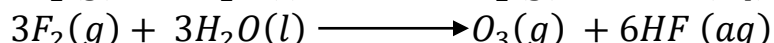
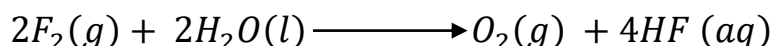


Iodine reacts with hydrogen in the presence of platinum catalyst at 400 °C forming hydrogen iodide

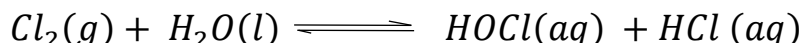


2. Describe the reactions of halogens with water.

Fluorine reacts vigorously with water, oxidising it to oxygen/ozone and itself reduced to hydrofluoric acid.



Chlorine disproportionates in water to form chloric(I) acid and hydrochloric acid



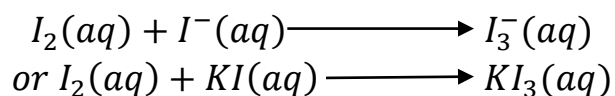
Bromine disproportionates in water to form bromic(I) acid and hydrobromic acid



Iodine is insoluble in water.

3. Explain why iodine is insoluble in water but soluble in potassium iodide solution.

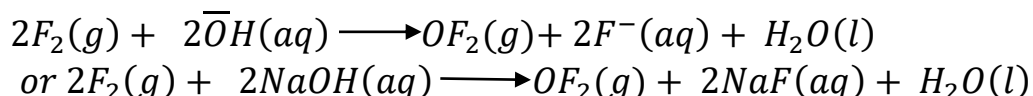
Iodine is non-polar yet water is polar. Intermolecular forces of attraction between individual molecules of water and individual molecules of iodine are on average stronger than intermolecular forces of attraction between molecules of water and molecules of iodine. When the two are combined, repulsion occurs. However, iodine reacts with potassium iodide to a soluble complex of potassium triiodide.



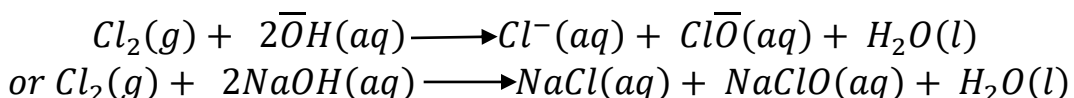
4. Describe how fluorine, chlorine, bromine and iodine react with sodium hydroxide under various conditions.

(i) cold dilute sodium hydroxide

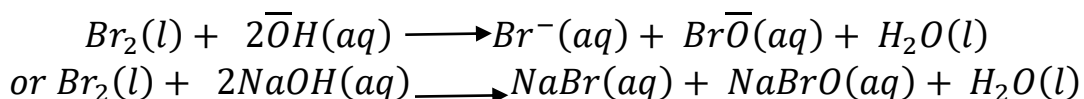
Fluorine reacts with cold dilute sodium hydroxide solution to form oxygen difluoride, fluoride ions and water



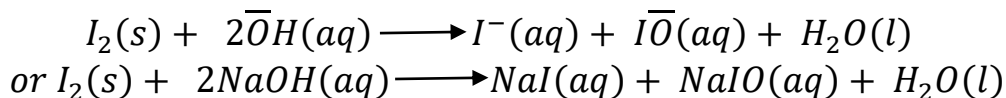
Chlorine disproportionates in cold dilute sodium hydroxide to form chloride ions, chlorate(I) ions and water



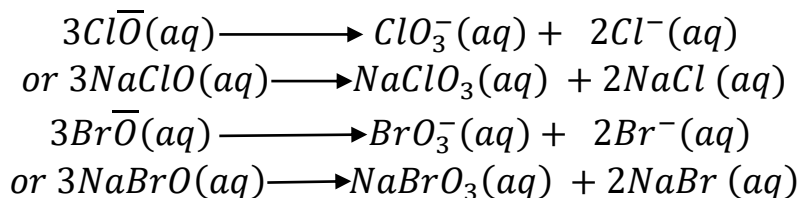
Bromine also disproportionates in cold dilute sodium hydroxide to form bromide ions, bromate(I) ions and water



Iodine disproportionates in cold dilute sodium hydroxide to form iodide ions, iodate(I) ions and water

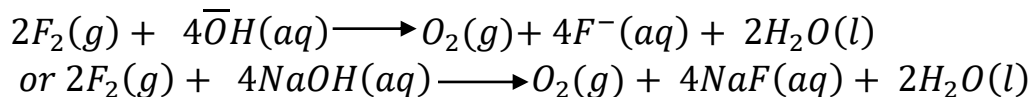


N.B; The chlorate(I) ions and bromate(I) ions formed by the above reactions undergo further disproportionation if heated/ warmed to form chlorate(V) ions and chloride ions, bromate(V) ions and bromide ions respectively. The yellow solution turns colourless during this reaction

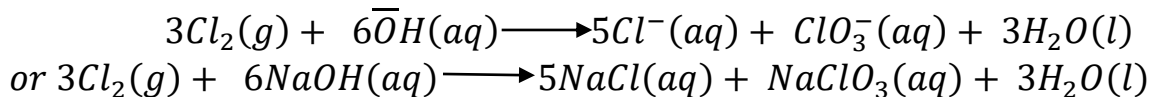


(ii) hot concentrated sodium hydroxide.

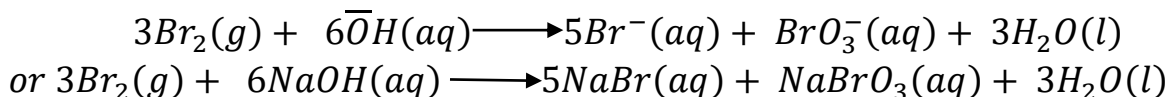
Fluorine reacts with hot concentrated sodium hydroxide to form oxygen, fluoride ions and water.



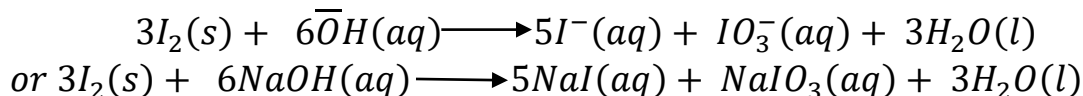
Chlorine disproportionates in hot concentrated sodium hydroxide to form chloride ions, chlorate(V) ions and water.



Bromine also disproportionates in hot concentrated sodium hydroxide to form bromide ions, bromate(V) ions and water.



Iodine also disproportionates in hot concentrated sodium hydroxide to form iodide ions, iodate(V) ions and water.



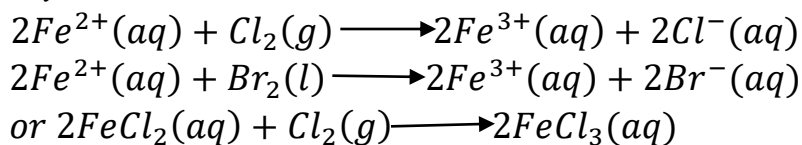
OXIDISING ACTION OF HALOGENS

1. State what would be observed and explain your observations when;

- (i) **chlorine and bromine are separately added to iron(II) chloride solution.**
- (ii) **chlorine is bubbled through potassium nitrite solution and silver nitrate solution followed by excess ammonia added to the resultant solution.**

(i) **Observation;** In each case, the green solution turns brown

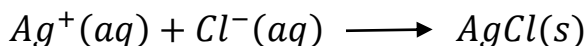
Explanation; chlorine and bromine oxidise iron(II) ions to iron(III) ions as they are reduced to chloride ions and bromide ions respectively.



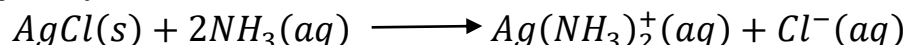
(ii) **Observation;** Greenish yellow gas dissolves and the colourless solution formed a white precipitate soluble in excess ammonia to form a colourless solution.

Explanation; chlorine oxidises nitrate ions to nitrite ions and itself reduced to chloride ions.

$\text{NO}_2^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow \text{NO}_3^-(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq})$
 Silver ions react with the chloride ions to form insoluble silver chloride



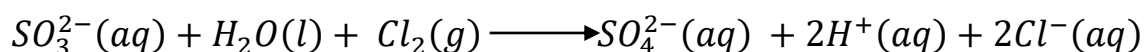
Silver chloride reacts with excess ammonia to form a soluble complex of diammine silver(I) ion.



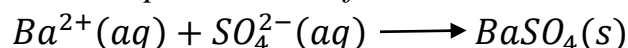
- 2. Chlorine gas was bubbled through sodium sulphite solution and to the resultant solution was added barium nitrate solution. State what was observed and explain your answer.**

Observation; Greenish yellow gas dissolved and the colourless solution formed a white precipitate with barium nitrate solution.

Explanation; Chlorine oxidises sulphite ions to sulphate ions and itself reduced to chloride ions.



Barium ions react with sulphate ions to form insoluble barium sulphate

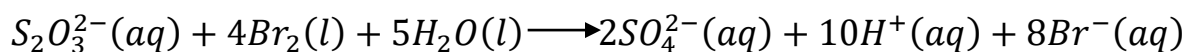
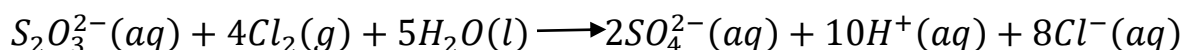


- 3. Describe the reactions of chlorine, bromine and iodine react with;**

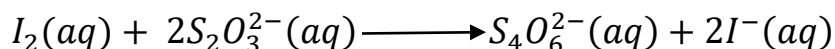
(i) **sodium thiosulphate solution**

(ii) **hydrogen sulphide.**

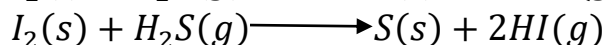
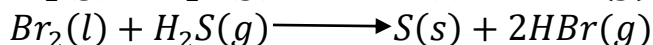
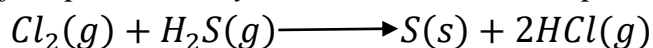
- (i) Chlorine and bromine oxidise thiosulphate ions to sulphate ions as they are reduced to chloride ions and bromide ions respectively.



Iodine being a weaker oxidising agent oxidises thiosulphate ions to tetrathionate ions and itself reduced to iodide ions.



- (ii) Chlorine, bromine and iodine oxidise hydrogen sulphide to deposit a yellow solid of sulphur as they are reduced to corresponding hydrides.



HYDRIDES OF GROUP(VII) ELEMENTS

1. The table below shows the chemical formulae of the hydrides of Group VII elements and their physical states at room temperature.

Element	Formula of hydride	Physical state at room temperature
Fluorine	<i>HF</i>	<i>Liquid</i>
Chlorine	<i>HCl</i>	<i>Gas</i>
Bromine	<i>HBr</i>	<i>Gas</i>
Iodine	<i>HI</i>	<i>Gas</i>

Explain why hydrogen fluoride is a liquid whereas other hydrides are gases at room temperature.

Fluorine has the highly electronegative making the hydrogen-fluorine bond highly polar. The molecules of hydrogen fluoride are held by strong intermolecular hydrogen bonds which keep the molecules closer to each other. Molecules of hydrogen chloride, hydrogen bromide and hydrogen iodide are held by weak Van der Waals' forces that keep the molecules far apart.

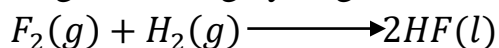
METHODS OF PREPARATION OF THE HYDRIDES.

2. (a) Describe the general methods of preparing the hydrides in above.

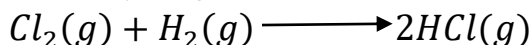
The hydrides can be formed by three main general methods;

- (i) *Direct combination of the elements with hydrogen.*

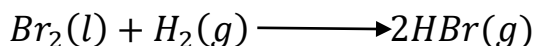
Fluorine is reacted with hydrogen forming hydrogen fluoride



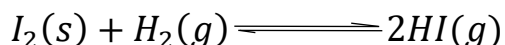
Chlorine is reacted with hydrogen and the mixture is heated or exposed to sunlight or ultraviolet light to form hydrogen chloride



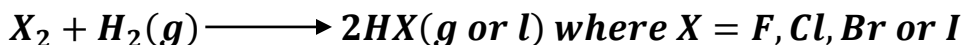
Bromine is reacted with hydrogen in the presence of platinum catalyst at 300 °C to form hydrogen bromide



Iodine is reacted with hydrogen in the presence of platinum catalyst at 400 °C to form hydrogen iodide

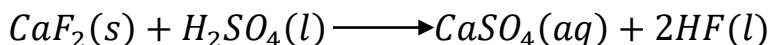


In general, the hydrides can be formed by the reaction between hydrogen and the halogen

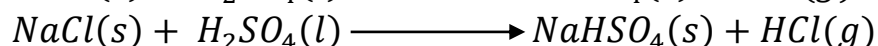
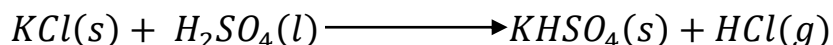


(ii) **Reaction between concentrated sulphuric acid and the halide salts**

Hydrogen fluoride can **best** be formed by reaction between cold concentrated sulphuric acid calcium fluoride.



Hydrogen chloride is also **best** formed by heating concentrated sulphuric acid with either solid potassium chloride or solid sodium chloride.

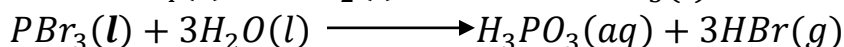
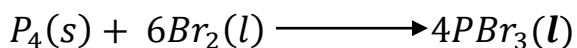


However, this method is inconvenient for preparation of hydrogen bromide and hydrogen iodide which are progressively stronger reducing agents than hydrogen chloride.

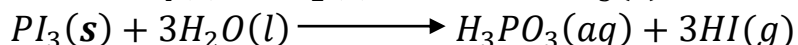
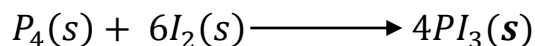
(iii) **Hydrolysis of corresponding phosphorus trihalides prepared in situ.**

This is the best method for preparation of hydrogen bromide and hydrogen iodide.

Hydrogen bromide is formed by adding bromine to a paste of red phosphorus and water forming phosphorus(III) bromide which is then hydrolysed to form hydrogen bromide and phosphorous acid



Hydrogen iodide is formed by adding water to a mixture of red phosphorus and iodine forming phosphorus(III) iodide which is then hydrolysed to form hydrogen iodide and phosphorous acid

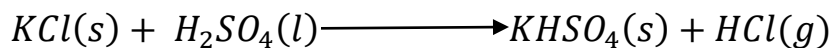


No heat is required in each of these two reactions.

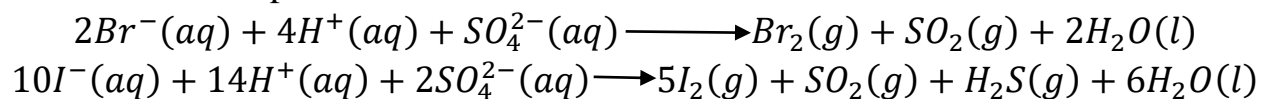
N.B. Note that although the above methods can prepare the hydrides in general, there is a more convenient method to prepare each of the hydrides.

(b) Hydrogen chloride can be prepared by the action of concentrated sulphuric acid on potassium chloride but hydrogen iodide and hydrogen bromide cannot be prepared by the action of concentrated sulphuric acid on potassium iodide and potassium bromide respectively.

Potassium chloride reacts with concentrated sulphuric acid to form hydrogen chloride gas which is a weak reducing agent due to the smaller ionic radius of chloride ion.



On the other hand, hydrogen iodide and hydrogen bromide that would be formed are strong reducing agents due to the large ionic radius of iodide and bromide ions. They reduce sulphuric acid to sulphur dioxide as they are oxidised to iodine and bromine respectively. The iodine is observed as purple vapours and bromine as reddish brown vapours



BOILING POINTS/ MELTING POINTS OF THE HYDRIDES

3. The table below shows both boiling points of group VII hydrides.

Hydride	<i>HF</i>	<i>HCl</i>	<i>HBr</i>	<i>HI</i>
Boiling point(°C)	+19.9	-85.0	-66.7	-35.4

Explain the variation in melting/ boiling points, including any anomalies involved.

Boiling points **generally** increase from hydrogen fluoride to hydrogen iodide. However, hydrogen fluoride has an abnormally high value of boiling point. The increase in melting point from hydrogen chloride to hydrogen iodide is because the three hydrides have simple molecular structures held by weak Van der Waals' forces whose magnitude increases with the increasing molecular weight leading to an increase in amount of energy required to break the forces. Hydrogen fluoride has an abnormally high melting point because fluorine has the highest electronegativity, making the hydrogen-fluorine highly polar. The hydrogen fluoride molecules are therefore held by strong intermolecular hydrogen bonds which require a high amount of energy to break.

ACID STRENGTHS

4. The table below shows acid dissociation constants, K_a , of group VII hydrides.

Hydride	<i>HF</i>	<i>HCl</i>	<i>HBr</i>	<i>HI</i>
K_a (mol dm^{-3}) at 25 °C	6.6×10^{-4}	1.3×10^6	1.0×10^9	3.2×10^9

Explain the trend in K_a values of the hydrides.

The K_a values increase in the order $HF < HCl < HBr < HI$ indicating that acid strength increases in the same order. This is because atomic radius of the halogen atoms increases from fluorine to iodine. This makes the hydrogen-halogen bond length longer, reducing the bond strength from hydrogen fluoride to hydrogen iodide, releasing many hydrogen ions in solution.

Hydrofluoric acid is a very weak acid because it dissociates to a considerably smaller extent and also the fluoride ions produced tend to combine with the undissociated hydrogen fluoride molecules especially in concentrated solutions.

In dilute solution; $HF(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

In concentrated solution; $HF(l) + F^-(aq) \rightleftharpoons HF_2^-(aq)$

THERMOSTABILITY

5. Explain the trend in thermostability of the hydrides.

REDUCING ACTION

6. State and explain the trend in reducing action of the hydrides

Reducing strength increases in the order $HF < HCl < HBr < HI$ because ionic radius halide ions increases and electronegativity decreases from fluorine to iodine. Hydrogen fluoride has no reducing action.

ANOMALOUS BEHAVIOUR OF FLUORINE AND HYDROGEN FLUORIDE

7. Although fluorine is an element in group VII of the Periodic Table, it behaves differently from other members of the group.

(a) State the reasons why fluorine behaves differently from the other members of the group.

(b) State the differences between the Chemistry of fluorine as an element and other halogens

Reasons / causes for anomalous behaviour of fluorine

(a)

- Fluorine has the smallest atomic radius compared to other elements
- Fluorine has the highest electronegativity among the elements
- Fluorine has an abnormally low value of bond dissociation energy of the $F-F$ bond
- Unlike other elements, fluorine cannot expand its octet
- Fluorine has the most positive standard electrode potential among the elements
- High exothermic hydration energy of the fluoride ion

(b)

- Fluorine oxidises water to oxygen and itself reduced to hydrofluoric acid. Iodine does not react with water and other halogens disproportionate in water
- Fluorine oxidises cold dilute sodium hydroxide solution to oxygen difluoride gas, itself reduced to fluoride ions. Other halogens disproportionate to form halide ions and halate(I) ions and water.
- Fluorine oxidises hot concentrated sodium hydroxide solution to oxygen gas, itself reduced to fluoride ions. Other halogens disproportionate to form halide ions and halate(V) ions and water.
- Fluorine combines directly with carbon. Other halogens do not react directly with carbon.

Note with concern that the chemistry of compounds of fluorine is not required here as the question is specific to fluorine.

8. Although hydrogen fluoride is a group VII hydride, it behaves differently from hydrides of other members in the group.

(a) State the reasons why hydrogen fluoride behaves differently from the hydrides of other members of the group.

(b) State the differences between the properties on hydrogen fluoride and other group VII hydrides.

(a)

- Hydrogen fluoride is strongly hydrogen bonded unlike other hydrides
- It has a very low value of acid dissociation constant at room temperature
- The fluoride ion in it has the smallest ionic radius compared to other halide ions
- The fluorine atom, to which hydrogen is bonded, has the highest electronegativity among the halogen atoms

(b)

- Hydrogen fluoride is a liquid at room temperature whereas other hydrides are gases
- Hydrogen fluoride has an abnormally high value of boiling point compared to other hydrides
- Hydrofluoric acid is a very weak acid in contrast to hydrochloric acid, hydrobromic acid and hydroiodic acid which are all strong acids
- Hydrogen fluoride has no reducing action yet other hydrides are reducing

9. The bond angle in phosphorus trifluoride is 96° while that of phosphorus trichloride is 100° . Explain this observation.

Both phosphorus trifluoride and phosphorus trichloride adopt a trigonal pyramidal shape. However, the fluorine atom is more electronegative than the chlorine atom. The fluorine atom therefore draws away the bonded pairs of electrons from the phosphorus atom more than the chlorine atom does. This makes the bonded pairs to be far apart reducing the repulsion between them. Therefore phosphorus trifluoride has a smaller bond angle than phosphorus trichloride.

POLARISABILITY OF HALIDE IONS

As anionic radius of the anions increases, the anions become more polarisable. This increases the tendency forming covalent compounds.

10. Explain why the solubility of lead(II) halides increases in the order;



The cationic radius and cationic charge are the same in all compounds. However, anionic radius decreases from the iodide ion to the chloride ion. The halide ions therefore become less polarisable and the ionic character increases from lead(II) iodide to lead(II) chloride. Since water is a polar solvent, the compounds become more soluble in that order.

OCCURRENCE, EXTRACTION AND UTILISATION OF NATURAL SALT (SODIUM CHLORIDE)

11. Describe the extraction of sodium chloride from natural deposits

QUALITATIVE ANALYSIS FOR Cl^- , Br^- AND I^- IONS

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
Cl^-	To a spatula endful of the solid, add 2-3 drops of concentrated sulphuric acid and heat	White fumes turn blue litmus red and form dense white fumes with concentrated ammonia	HCl gas evolved Cl^- present	Concentrated sulphuric acid reacts with chloride ions to form hydrogen chloride gas. $Cl^-(s) + H_2SO_4(l) \longrightarrow HCl(g) + HSO_4^-(aq)$ Hydrogen chloride gas reacts with concentrated ammonia to form ammonium chloride $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$
	To the solution, add dilute nitric acid followed lead(II) nitrate solution	White precipitate	$C_2O_4^{2-}$, SO_3^{2-} , SO_4^{2-} , Cl^- probably present	Lead(II) ions react with chloride ions to form insoluble lead(II) chloride $Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2(s)$
	Add lead(II) nitrate followed by dilute nitric acid	White precipitate insoluble in acid	SO_4^{2-} , Cl^- probably present	Lead(II) ions react with chloride ions to form insoluble lead(II) chloride $Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2(s)$

To the acidified solution, lead(II) nitrate solution and heat/boil/warm	White precipitate soluble on heating/boiling/warming and reprecipitates on cooling	Cl^- present	Lead(II) ions react with chloride ions to form insoluble lead(II) chloride $\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \longrightarrow \text{PbCl}_2(\text{s})$
Add dilute nitric acid followed by silver nitrate solution	White precipitate	$\text{C}_2\text{O}_4^{2-}$, SO_3^{2-} , Cl^- probably present	Silver ions react with chloride ions to form insoluble silver chloride $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$
Add silver nitrate solution followed by dilute nitric acid	White precipitate insoluble in acid	Cl^- present	Silver ions react with chloride ions to form insoluble silver chloride $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$
Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia dropwise until in excess.	White precipitate soluble in excess ammonia to form a colourless solution	Cl^- confirmed	Silver ions react with chloride ions to form insoluble silver chloride $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$ Silver chloride reacts with excess ammonia to form a soluble complex of diammine silver(I) ion. $\text{AgCl}(\text{s}) + 2\text{NH}_3(\text{aq}) \longrightarrow \text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{Cl}^-(\text{aq})$
To the solution, add bleaching powder then dilute nitric acid (or add chlorine water) followed by tetrachloromethane and shake. Allow to stand	Tetrachloromethane layer remains colourless	Cl^- present	The acidified bleaching powder or chlorine water produces Chlorine. The chlorine cannot oxidise chloride ions. hence the tetrachloromethane layer remains colourless
To a spatula endful of the solid, add 2-3 drops of concentrated sulphuric acid and heat (the reaction may	Reddish brown vapours	Br_2 evolved Br^- present	Bromide ions are strongly reducing due to their large ionic radius. They reduce hot concentrated sulphuric acid to sulphur dioxide as they are oxidised to bromine.

Br⁻	take place even before heating)	$2\text{Br}^-(\text{aq}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \longrightarrow \text{Br}_2(\text{g}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$		
	To the solution, add dilute nitric acid followed lead(II) nitrate solution	White precipitate	$\text{C}_2\text{O}_4^{2-}$, SO_3^{2-} , SO_4^{2-} , Cl^- Br^- probably present	Lead(II) ions react with bromide ions to form insoluble lead(II) bromide $\text{Pb}^{2+}(\text{aq}) + 2\text{Br}^-(\text{aq}) \longrightarrow \text{PbBr}_2(\text{s})$
	Add dilute nitric acid followed by silver nitrate solution	Pale yellow precipitate	Br^- present	Silver ions react with bromide ions to form insoluble silver bromide $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \longrightarrow \text{AgBr}(\text{s})$
	Add silver nitrate solution followed by dilute nitric acid	Pale yellow precipitate insoluble in acid	Br^- present	Silver ions react with bromide ions to form insoluble silver bromide $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \longrightarrow \text{AgBr}(\text{s})$
	Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia dropwise until in excess.	Pale yellow precipitate soluble in excess ammonia	Br^- present	Silver ions react with bromide ions to form insoluble silver bromide $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \longrightarrow \text{AgBr}(\text{s})$ Silver bromide is sparingly soluble in ammonia.
	To the solution, add bleaching powder then dilute nitric acid (or add chlorine water) followed by tetrachloromethane and shake. Allow to stand	Reddish brown liquid in tetrachloromethane layer	Br^- present	The acidified bleaching powder or chlorine water produces Chlorine which oxidises bromide ions to bromine. $\text{Cl}_2(\text{g}) + 2\text{Br}^-(\text{aq}) \longrightarrow 2\text{Cl}^-(\text{aq}) + \text{Br}_2(\text{l})$ Bromine is covalent hence dissolves in tetrachloromethane to form the reddish brown layer.
	To a spatula endful of the solid, add 2-3 drops of concentrated sulphuric acid and heat (the reaction may take place even before heating)	Purple vapours	I_2 evolved I^- present	Iodide ions are strongly reducing due to their large ionic radius. They reduce hot concentrated sulphuric acid to sulphur dioxide as they are oxidised to iodine. Sometimes oxidation result into formation of hydrogen sulphide gas, as well, with a smell of rotten eggs. $2\text{I}^-(\text{aq}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \longrightarrow \text{I}_2(\text{g}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ or $10\text{I}^-(\text{aq}) + 14\text{H}^+(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq}) \longrightarrow 5\text{I}_2(\text{g}) + \text{SO}_2(\text{g}) + \text{H}_2\text{S}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$

I^-	To the solution, add dilute nitric acid followed lead(II) nitrate solution	Yellow precipitate	I^- present	Lead(II) ions react with iodide ions to form insoluble lead(II) iodide $Pb^{2+}(aq) + 2I^-(aq) \longrightarrow PbI_2(s)$
	Add dilute nitric acid followed by silver nitrate solution	Yellow precipitate	I^- present	Silver ions react with iodide ions to form insoluble silver iodide $Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$
	Add silver nitrate solution followed by dilute nitric acid	Yellow precipitate insoluble in acid	I^- present	Silver ions react with iodide ions to form insoluble silver iodide $Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$
	Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia dropwise until in excess.	Yellow precipitate insoluble in ammonia	I^- present	Silver ions react with iodide ions to form insoluble silver iodide $Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$ Silver iodide is insoluble in ammonia
	To the solution, add bleaching powder then dilute nitric acid (or add chlorine water) followed by tetrachloromethane and shake. Allow to stand	Violet colouration in tetrachloromethane layer	I^- present	The acidified bleaching powder or chlorine water produces Chlorine which oxidises iodide ions to iodine. $Cl_2(g) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(aq)$ Iodine is covalent hence dissolves in tetrachloromethane.
	Add copper(II) sulphate solution	White precipitate in a brown solution	I^- present	Copper(II) ions oxidises iodide ions to iodine and itself reduced copper(I) iodide. $2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow Cu_2I_2(s) + I_2(aq)$

MISCELLANEOUS TOPICAL QUESTIONS

Short answer type questions

- Write equations to show how chlorine and iodine react with;
 - Sodium iodide solution. (03 marks)
 - Sodium thiosulphate solution (03 marks)
 - Cold dilute sodium hydroxide (03 marks)
- Write equation for the reaction that takes place when hot concentrated potassium hydroxide is added to;
 - fluorine. (01 mark)
 - chlorine. (01 mark)
 - Write equation(s) for the reaction(s) of
 - fluorine and water (1 ½ marks)
 - hydrofluoric acid and silicon(IV) oxide (1 ½ marks)
 - Arrange the following hydrogen halides; HCl , HI and HBr in order of decreasing acid strength. Give a reason for your answer. (03 marks)
- Fluorine, chlorine, bromine and iodine are diatomic molecules of group VII elements of the Periodic Table. Briefly describe how the elements react with;
 - Potassium bromide. (02 marks)
 - Hydrogen sulphide (02 marks)
 - The hydrides of the elements in (a) above boil at different temperatures shown in the table below.

Hydride	HF	HCl	HBr	HI
Boiling point($^{\circ}C$)	+20	-85	-67	-35

- State and explain the trend in boiling points of the hydrides. (03 marks)
- State the order in reducing strength of the hydrides. (01 mark)
 - Write a general equation for the reaction between aqueous solutions of the hydrohalic acids with sodium carbonate. (01 mark)
4. The table below gives some physical properties of hydrogen halides.

Hydride	HF	HCl	HBr	HI
Boiling point(K)	293	188	206	238
Bond length(nm)	0.086	0.128	0.142	0.160

- Explain the observed trend in;
 - Boiling points (02 marks)
 - Bond length (02 marks)
- Arrange the hydrogen halides in order of the expected increase in acid strength of their aqueous solutions, giving reason for your answer. (02 marks)

5. (a) Draw the structure and name the shape of the following compounds

Structure	Shape
PH_3	
SF_4	

(03 marks)

(b) Write equation for the reaction between ammonia and aluminium chloride.
(01 mark)

6. State what would be observed and write equation for the reaction that would take place when;

(i) Copper(II) sulphate solution was added to potassium iodide solution.
(2 ½ marks)

(ii) Potassium iodide solution is added to chlorine water. (02 marks)

(iii) Solid sodium iodide is heated with concentrated sulphuric acid.
(2 ½ marks)

(iv) Warm concentrated hydrochloric acid is added to manganese(IV) oxide. (02 marks)

(v) Sodium iodide is added to acidified sodium chlorate(I) solution.
(02 marks)

(vi) Sodium iodide solution is added to acidified hydrogen peroxide solution.
(1 ½ marks)

7. (a) The chemistry of fluorine differs from that of chlorine.

(i) State two differences between the chemistry of fluorine and chlorine apart from their reactions with sodium hydroxide.
(02 marks)

(ii) Write the equation for the reaction between cold dilute sodium hydroxide and;

- Fluorine
- chlorine

(03 marks)

8. (a) The oxidising strength of group VII elements decreases in the order;
 $F_2 \gg Cl_2 > Br_2 > I_2$
- State three reasons to account for the high oxidising strength of fluorine relative to other halogens. (1 ½ marks)
 - State two other anomalous properties of fluorine. (02 marks)
- (b) Describe the reactions of chlorine and iodine with;
- sodium thiosulphate solution. (3 ½ marks)
 - iron(II) sulphate. (02 marks)
9. (a) (i) State the condition(s) under chlorine reacts with sulphur dioxide. (01 mark)
- (ii) Write equation for the reaction. (01 mark)
- (b) Chlorine was bubbled through sodium thiosulphate solution and lead(II) nitrate solution was added to the resultant solution.
- State what was observed. (01 mark)
 - Write equation(s) for the reaction(s) that took place. (02 marks)
- 10.(a) State three reasons why fluorine differs in some of its properties from the rest of group VII elements. (03 marks)
- (b) Write equations for ionisation of hydrogen fluoride in aqueous solutions that are;
- dilute
 - concentrated (03 marks)
- (c) Explain why hydrogen fluoride is a weaker acid than hydrogen chloride. (03 marks)
11. Name the reagent(s) that can be used to distinguish between the following pair(s) of compounds. In each case state the observations made and write equation(s) for the reaction.
- I^- and Br^- (4 ½ marks)
 - Cl^- and Br^- (4 ½ marks)
 - I^- and Cl^- (4 ½ marks)

- 12.(a) (i) What is the electronic configuration of the bromide ion. (01 mark)
 (ii) With the aid of a suitable diagram(s), show how the bonding of the chlorate(III) oxo-anion of chlorine. (1 ½ marks)
 (b) When iodine is added to aqueous sodium hydroxide, the initial product formed disproportionates. Explain the meaning of this term and write an ionic equation for the changes that take place. (2 ½ marks)
 (c) Explain why unlike other halogens, fluorine liberates oxygen from cold water. (02 marks)
- 13.(a) State what would be observed and write equation for the reaction that would take place if potassium iodide was added to acidified potassium dichromate solution. (2 ½ marks)
 (c) Sodium thiosulphate solution was added to the mixture in (a), state what was observed and write equation for the reaction that took place. (2 ½ marks)
- 14.(a) The table below shows the melting points of magnesium halides.

Formula of halide	MgF_2	$MgCl_2$	$MgBr_2$	MgI_2
Melting point($^{\circ}C$)	1263	714	711	634

Explain the trend in melting points of the halides. (04 marks)

(b) The values of lattice energies of potassium halides are given below.

Formula of halide	KF	KCl	KI
Lattice energy($kJmol^{-1}$)	-813	-710	-643

Explain the trend in these values for the potassium halides. (03 marks)

15.Explain the following observations

- (a) Lead(IV) chloride exists but lead(IV) bromide does not. (02 marks)
 (b) Tin and lead do not form tetraiodides. (03 marks)
 (c) When hydrogen iodide is treated with concentrated sulphuric acid, iodine is liberated, whereas when hydrogen chloride is similarly treated, chlorine is not evolved. (03 marks)
 (d) When added separately to copper(II) sulphate solution, potassium iodide forms a white precipitate in a brown solution while potassium chloride gives no observable change. (03 marks)
 (e) The boiling point of hydrogen fluoride is higher than that of hydrogen chloride. (03 marks)

- (f) Both halogens and oxygen are diatomic. However, halogens react more readily with metals than oxygen. (02 marks)
- (g) Iodine is insoluble in water but soluble in potassium iodide solution. (2 ½ marks)
- (h) The bond in hydrogen chloride is polar. (1 ½ marks)
- (i) Hydrofluoric acid is weaker than hydrobromic acid. (03 marks)

Long answer type questions

16. Fluorine, chlorine, bromine and iodine are elements in group VII of the Periodic Table.
- (a) Describe the general method of preparing chlorine, bromine and iodine in the laboratory. (02 marks)
- (b) Fluorine differs in some of its properties from chlorine, bromine and iodine.
- (i) Explain why fluorine differs from other Group VII elements. (02 marks)
- (ii) State four properties in which fluorine differs from other Group members. (04 marks)
- (c) Describe the reactions of group VII elements with:
- (i) Water (04 marks)
- (ii) Sodium hydroxide (08 marks)
- (d) Hydrofluoric acid is a weaker acid than hydrochloric acid. Explain. (02 marks)
- 17.(a)(i) Sketch a graph of first electron affinity against atomic number of group VII elements. (3 ½ marks)
- (ii) Explain the shape of the graph (6 ½ marks)
- (b) State two reasons why fluorine differs in some of its properties from bromine. (02 marks)
- (c) State three properties in which fluorine differs from bromine. (03 marks)
- (d) Describe the reaction of sulphuric acid with hydrogen bromide. Write the equation for the reaction. (03 marks)

18.(a) The boiling points of group VII elements are in the order
 $I_2 > Br_2 > Cl_2 > F_2$ whereas the dissociation energy is in the reverse order.
 Briefly explain this observation. (06 marks)

(b) Discuss the chemical differences between fluorine and bromine with respect to;

- (i) Water
- (ii) Sodium hydroxide (08 marks)

(c) The oxy-acids of chlorine include; $HOCl$, $HClO_2$, $HClO_3$ and $HClO_4$.

- (i) Write and name the shapes adopted by the oxy-acids. (04 marks)
- (ii) Which of the oxy-acids is the strongest acid. Give a reason for your answer. (02 marks)

19.(a) State and explain the trend in the boiling points of group VII elements. (03 marks)

(b) Explain why hydrogen fluoride;

- (i) is a weaker acid in dilute aqueous solution than in concentrated solution. (03 marks)
- (ii) has a higher boiling point than hydrogen iodide (03 marks)

(c) Write equation for the reaction between hydrogen fluoride and silicon(V) oxide. (01 mark)

(d) Describe the reactions of group (VII) elements with sodium hydroxide. (07 marks)

(e) Write the equation for the reaction between sulphuric acid

- (i) Sodium chloride
- (ii) Potassium bromide
- (iii) Sodium iodide (03 marks)

20.(a) The bond energies of halogen acids are given in the table below.

$H-X$	$H-F$	$H-Cl$	$H-Br$	$H-I$
Bond energy(kJmol⁻¹)	556	431	336	299

- (i) Explain the variation in bond energy. (03 marks)
- (ii) State two properties of the halogen acids whose variation is caused by the trend in bond energies. (02 marks)

(b) Describe the reaction of the halogen acids with;

- (i) Concentrated sulphuric acid (05 marks)
- (ii) Sodium carbonate (2 ½ marks)

(c) Describe the reaction of the halogens with concentrated potassium hydroxide. (7 ½ marks)

21.(a) Describe the industrial preparation of chlorine. (04 marks)

- (b) Describe the reaction of chlorine with;
- (i) iron (02 marks)
 - (ii) potassium hydroxide (04 marks)
- (c) Describe the reaction of fluorine with
- (i) Water (02 marks)
 - (ii) Potassium hydroxide (04 marks)
- (d) Explain why hydrogen fluoride is a liquid whereas hydrogen chloride is a gas at 18 °C. (04 marks)
22. Explain the following observations.
- (a) When iodine crystals are added to cold dilute sodium hydroxide solution, the grey solid dissolves to form a pale yellow solution which turned colourless on standing. (04 marks)
 - (b) When acidified potassium manganate(VII) solution was added to aqueous potassium iodide solution, the solution turns brown. (03 marks)
 - (c) The first electron affinities of the halogens generally decrease down the group. However, the first electron affinity of fluorine is abnormally high. (04 marks)
 - (d) When a limited amount of chlorine is bubbled through sodium thiosulphate solution, a yellow precipitate is formed. (05 marks)
 - (e) The fluorine molecule has a low bond dissociation enthalpy yet it has a short bond length. (04 marks)