# THE CHEMISTRY OF GROUP VII ELEMENTS

## **Electronic structures/configurations**

Element	Atomic number	Configuration
F	9	$1s^2 2s^2 2p^5$
Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Br	35	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}4s^2 4p^5$
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  $ns^2np^5$ 

## **Bonding and structure**

Element	Bonding	Structure	Physical state and colour at room temperature		
Fluorine	Donuing	Structure	Pale yellow gas		
Chlorine	All covalent		Greenish yellow gas		
Bromine		molecular Red liquid			
Iodine			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	F	Cl	Br	I
Boiling point( <sup>o</sup> C)	-187.9	-34.0	58.2	+184.5
Melting points( <sup>o</sup> 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  $F_2 < Cl_2 < Br_2 < I_2$ . 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	F	Cl	Br	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 DEMYSTIFYING INORGANIC CHEMISTRY BY Joseph Jobs Kayiira, BScED(Hons.CHEM/MTC) Email; josephkayiirab@gmail.com Call 0782601038 WhatsApp 0753247098

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	F	Cl	Br	I
First ionisation energy (kJmol <sup>-1</sup> )	1681	1255	1142	1007

- (a) Define the term first ionisation energy.
- (b) State and explain the trend in ionization energy of the elements

## 4. Electron affinity

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

Element	$\boldsymbol{\mathit{F}}$	Cl	Br	I
Atomic number	9	17	35	53
First electron affinity(kJmol <sup>-1</sup> )	-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.

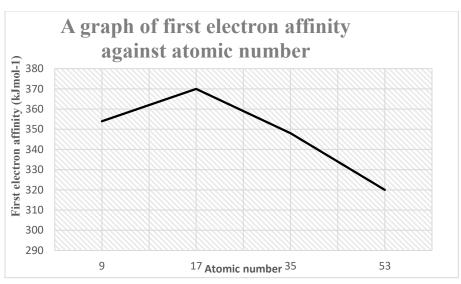
(To be done by student. When plotting the graph, the negative sign may be eliminated since it's on all values and it just indicates that the process is exothermic. The graph below is just a sketch and not on scale)

- (c) (i) Explain the general trend in variation of the first electron affinities
  - (iii) 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**.

$$X(g) + e \longrightarrow X^{-}(g)$$

*(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	F	Cl	Br	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	$\boldsymbol{F_2}$	$Cl_2$	$Br_2$	$I_2$
Bond dissociation energy(kJmol <sup>-1</sup> )	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 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 reducing amount of energy to break the increasingly weakening 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	F	Cl	Br	I
Standard electrode potential( $E^{\theta}$ )				
(Volts) for $\frac{1}{2}X_2/X^-(aq)$	+2.80	+1.36	+1.07	+0.54

- (a) State;
  - (i) the strongest oxidising agent
  - (ii) 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;
    - (i) Chlorine is bubbled through potassium bromide solution
    - (ii) 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) (ii)  $F_2 \gg C l_2 > B r_2 > I_2$ 
  - (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 electron 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  $Cl_2/Cl^-(\alpha q)$  is more positive than that of  $Br_2/Br^-(\alpha q)$  or  $I_2/I^-(\alpha q)$  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.

$$Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(l)$$
  
 $Cl_2(g) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(s)$ 

(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.

$$Sn^{4+}(aq) + 2Br^{-}(aq) \longrightarrow Sn^{2+}(aq) + Br_2(l)$$
  
 $Sn^{4+}(aq) + 2I^{-}(aq) \longrightarrow Sn^{2+}(aq) + I_2(s)$ 

#### 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.

$$2X^{-}(aq) + 4H^{+}(aq) + MnO_2(s) \longrightarrow Mn^{2+}(aq) + 2H_2O(l) + X_2(g/l \text{ or } s)$$
  
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.  $2MnO_4^-(aq) + 16H^+(aq) + 10Cl^-(aq) \longrightarrow 2Mn^{2+}(aq) + 5Cl_2(g) + 8H_2O(l)$  or  $2KMnO_4(s) + 16HCl(aq) \longrightarrow 2KCl(aq) + 2MnCl_2(aq) + 8H_2O(l) + 5Cl_2(g)$ 

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.

$$MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \longrightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$$
  
or  $MnO_2(s) + 4HCl(aq) \longrightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$ 

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.

$$PbO_2(s) + 4H^+(aq) + 2Cl^-(aq) \longrightarrow Pb^{2+}(aq) + Cl_2(g) + 2H_2O(l)$$
  
or  $PbO_2(s) + 4HCl(aq) \longrightarrow PbCl_2(aq) + Cl_2(g) + 2H_2O(l)$ 

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.

$$Pb_3O_4(s) + 8H^+(aq) + 2Cl^-(aq) \longrightarrow 3Pb^{2+}(aq) + Cl_2(g) + 4H_2O(l)$$
  
or  $Pb_3O_4(s) + 8HCl(aq) \longrightarrow 3PbCl_2(aq) + Cl_2(g) + 4H_2O(l)$ 

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

$$2Cl^{-}(aq) + 4H^{+}(aq) + MnO_{2}(s) \longrightarrow Mn^{2+}(aq) + 2H_{2}O(l) + Cl_{2}(g)$$
  
 $2NaCl(s) + MnO_{2}(s) + 2H_{2}SO_{4}(aq) \longrightarrow Na_{2}SO_{4}(aq) + MnSO_{4}(aq) + 2H_{2}O(l) + Cl_{2}(g)$ 

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.

$$CaOCl_2(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + Cl_2(g) + H_2O(l)$$

$$or CaOCl_2(s) + 2HNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + Cl_2(g) + H_2O(l)$$

$$or CaOCl_2(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + Cl_2(g) + H_2O(l)$$

$$or CaOCl_2(s) + H_2SO_4(aq) \longrightarrow CaSO_4(aq) + Cl_2(g) + H_2O(l)$$

#### 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.

$$F_2(g) + H_2(g) \longrightarrow 2HF(l)$$

Chlorine explodes with hydrogen on heating or presence of sunlight or ultraviolet light to form hydrogen chloride.

$$Cl_2(g) + H_2(g) \longrightarrow 2HCl(g)$$

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

$$Br_2(l) + H_2(g) \longrightarrow 2HBr(g)$$

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

$$I_2(s) + H_2(g) - 2HI(g)$$

2. (a) Describe the reactions of halogens with water.

Fluorine reacts vigorously with water to form oxygen/ozone and hydrofluoric acid.

$$2F_2(g) + 2H_2O(l) \longrightarrow O_2(g) + 4HF(aq)$$
  
 $3F_2(g) + 3H_2O(l) \longrightarrow O_3(g) + 6HF(aq)$ 

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

$$Cl_2(g) + H_2O(l) \longrightarrow HOCl(aq) + HCl(aq)$$

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

$$Br_2(l) + H_2O(l) \longrightarrow HOBr(aq) + HBr(aq)$$

Iodine **does not react** with water.

(b) 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.

$$I_2(aq) + I^-(aq) \longrightarrow I_3^-(aq)$$
  
or  $I_2(aq) + KI(aq) \longrightarrow KI_3(aq)$ 

- 3. 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**.

$$2F_2(g) + 2\overline{O}H(aq) \longrightarrow OF_2(g) + 2F^-(aq) + H_2O(l)$$
  
or  $2F_2(g) + 2NaOH(aq) \longrightarrow OF_2(g) + 2NaF(aq) + H_2O(l)$ 

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

$$Cl_2(g) + 2\overline{O}H(aq) \longrightarrow Cl^-(aq) + Cl\overline{O}(aq) + H_2O(l)$$
  
or  $Cl_2(g) + 2NaOH(aq) \longrightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$ 

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

$$Br_2(l) + 2\overline{O}H(aq) \longrightarrow Br^-(aq) + Br\overline{O}(aq) + H_2O(l)$$
  
or  $Br_2(l) + 2NaOH(aq) \longrightarrow NaBr(aq) + NaBrO(aq) + H_2O(l)$ 

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

$$I_2(s) + 2\overline{O}H(aq) \longrightarrow I^-(aq) + I\overline{O}(aq) + H_2O(l)$$
  
or  $I_2(s) + 2NaOH(aq) \longrightarrow NaI(aq) + NaIO(aq) + H_2O(l)$ 

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

$$3Cl\overline{O}(aq) \longrightarrow ClO_3^-(aq) + 2Cl^-(aq)$$
  
 $or\ 3NaClO(aq) \longrightarrow NaClO_3(aq) + 2NaCl\ (aq)$   
 $3Br\overline{O}(aq) \longrightarrow BrO_3^-(aq) + 2Br^-(aq)$   
 $or\ 3NaBrO(aq) \longrightarrow NaBrO_3(aq) + 2NaBr\ (aq)$ 

(ii) hot concentrated sodium hydroxide.

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

$$2F_2(g) + 4\overline{O}H(aq) \longrightarrow O_2(g) + 4F^-(aq) + 2H_2O(l)$$
  
or  $2F_2(g) + 4NaOH(aq) \longrightarrow O_2(g) + 4NaF(aq) + 2H_2O(l)$ 

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

$$3Cl_2(g) + 6\overline{O}H(aq) \longrightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$$
or  $3Cl_2(g) + 6NaOH(aq) \longrightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$ 

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

$$3Br_2(g) + 6\overline{O}H(aq) \longrightarrow 5Br^-(aq) + BrO_3^-(aq) + 3H_2O(l)$$
  
or  $3Br_2(g) + 6NaOH(aq) \longrightarrow 5NaBr(aq) + NaBrO_3(aq) + 3H_2O(l)$ 

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

$$3I_2(s) + 6\overline{O}H(aq) \longrightarrow 5I^-(aq) + IO_3^-(aq) + 3H_2O(l)$$
  
or  $3I_2(s) + 6NaOH(aq) \longrightarrow 5NaI(aq) + NaIO_3(aq) + 3H_2O(l)$ 

#### 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.

$$2Fe^{2+}(aq) + Cl_2(g) \longrightarrow 2Fe^{3+}(aq) + 2Cl^{-}(aq)$$
  
 $2Fe^{2+}(aq) + Br_2(l) \longrightarrow 2Fe^{3+}(aq) + 2Br^{-}(aq)$   
 $or \ 2FeCl_2(aq) + Cl_2(g) \longrightarrow 2FeCl_3(aq)$ 

(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.

 $NO_2^-(aq) + 3H_2O(l) + Cl_2(g) \rightarrow NO_3^-(aq) + 2H^+(aq) + 2Cl^-(aq)$ Silver ions react with the chloride ions to form insoluble silver chloride

$$Ag^{+}(aq) + Cl^{-}(aq) \longrightarrow AgCl(s)$$

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

$$AgCl(s) + 2NH_3(aq) \longrightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

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.

$$SO_3^{2-}(aq) + H_2O(l) + Cl_2(g) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2Cl^-(aq)$$
  
Barium ions react with sulphate ions to form insoluble barium sulphate  
 $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$ 

3. Chlorine gas was bubbled through potassium manganate(VI) solution and to the resultant solution was dilute sulphuric acid and tin(II) sulphate solution. State what was observed and explain your answer.

**Observation;** Greenish yellow gas dissolved and the green solution turned to a purple solution which then turned colourless.

**Explanation;** Chlorine oxidises manganate(VI) ions to manganate(VII) ions and itself reduced to chloride ions.

$$2MnO_4^{2-}(aq) + Cl_2(g) \longrightarrow 2MnO_4^{-}(aq) + 2Cl^{-}(aq)$$
  
$$2K_2MnO_4(aq) + Cl_2(g) \longrightarrow 2KMnO_4(aq) + 2KCl(aq)$$

The acidified manganate(VII) ions then oxidise tin(II) ions to tin(IV) ions as they are reduced to manganese(II) ions.

$$2MnO_4^-(aq) + 16H^+(aq) + 5Sn^{2+}(aq) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Sn^{4+}(aq)$$

- 4. Describe the reactions of chlorine, bromine and iodine react with;
  - (i) sodium thiosulphate solution
  - (ii) hydrogen sulphide.
  - (iii) sulphurous acid
  - (i) Chlorine and bromine oxidise thiosulphate ions to sulphate ions as they are reduced to chloride ions and bromide ions respectively.

$$S_2O_3^{2-}(aq) + 4Cl_2(g) + 5H_2O(l) {\longrightarrow} 2SO_4^{2-}(aq) + 10H^+(aq) + 8Cl^-(aq)$$

$$S_2O_3^{2-}(aq) + 4Br_2(l) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 10H^+(aq) + 8Br^-(aq)$$

However, if limited chlorine is used, thiosulphate ions disproportionate into sulphate ions and sulphur as the chlorine is reduced to chloride ions.

$$S_2O_3^{2-}(aq) + Cl_2(g) + H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 2H^+(aq) + 2Cl^-(aq) + S(s)$$

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

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^{-}(aq)$$

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

$$Cl_2(g) + H_2S(g) \longrightarrow S(s) + 2HCl(g)$$
  
 $Br_2(l) + H_2S(g) \longrightarrow S(s) + 2HBr(g)$   
 $I_2(s) + H_2S(g) \longrightarrow S(s) + 2HI(g)$ 

(iii) Chlorine and bromine oxidise sulphurous acid to sulphuric acid as they are reduced to chloride ions and bromide ions respectively.

$$Cl_2(g) + H_2O(l) + H_2SO_3(aq) \longrightarrow H_2SO_4(aq) + 2HCl(aq)$$
  
 $Br_2(l) + H_2O(l) + H_2SO_3(aq) \longrightarrow H_2SO_4(aq) + 2HBr(aq)$ 

### **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	HF	Liquid
Chlorine	HCl	Gas
Bromine	HBr	Gas
Iodine	HI	Gas

Explain why hydrogen fluoride is a liquid at 19°C whereas hydrogen bromide is a gas at the same temperature.

Fluorine atom is more electronegative than the bromine atom. The fluoride ion in hydrogen fluoride has a smaller ionic radius than the bromide ion in hydrogen bromide. This makes the hydrogen-fluorine bond more polar than the hydrogen-bromine bond. The molecules of hydrogen fluoride are held by stronger intermolecular hydrogen bonds which keep the molecules closer to each other whereas the molecules of hydrogen bromide 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

$$F_2(g) + H_2(g) \longrightarrow 2HF(l)$$

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

$$Cl_2(g) + H_2(g) \longrightarrow 2HCl(g)$$

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

$$Br_2(l) + H_2(g) \longrightarrow 2HBr(g)$$

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

$$I_2(s) + H_2(g) \longrightarrow 2HI(g)$$

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

$$X_2 + H_2(g) \longrightarrow 2HX(g \text{ or } l) \text{ where } X = F, Cl, Br \text{ or } l$$

(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.

$$CaF_2(s) + H_2SO_4(l) \longrightarrow CaSO_4(aq) + 2HF(l)$$

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

$$KCl(s) + H_2SO_4(l) \longrightarrow KHSO_4(s) + HCl(g)$$
  
 $NaCl(s) + H_2SO_4(l) \longrightarrow NaHSO_4(s) + HCl(g)$ 

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

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$$P_4(s) + 6Br_2(l) \longrightarrow 4PBr_3(l)$$
  
 $PBr_3(l) + 3H_2O(l) \longrightarrow H_3PO_3(aq) + 3HBr(g)$ 

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

$$P_4(s) + 6I_2(s) \longrightarrow 4PI_3(s)$$
  
 $PI_3(s) + 3H_2O(l) \longrightarrow H_3PO_3(aq) + 3HI(g)$   
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.

$$KCl(s) + H_2SO_4(l) \longrightarrow KHSO_4(s) + HCl(g)$$

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.

$$2HBr(g) + H_2SO_4(l) \longrightarrow Br_2(g) + SO_2(g) + 2H_2O(l)$$
or  $2Br^-(aq) + 4H^+(aq) + SO_4^{2-}(aq) \longrightarrow Br_2(g) + SO_2(g) + 2H_2O(l)$ 

$$2HI(g) + H_2SO_4(l) \longrightarrow I_2(g) + SO_2(g) + 2H_2O(l)$$
or  $2I^-(aq) + 4H^+(aq) + SO_4^{2-}(aq) \longrightarrow I_2(g) + SO_2(g) + 2H_2O(l)$ 
or  $10HI(aq) + 2H_2SO_4(l)(aq) \longrightarrow 5I_2(g) + SO_2(g) + H_2S(g) + 6H_2O(l)$ 
or  $10I^-(aq) + 14H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 5I_2(g) + SO_2(g) + H_2S(g) + 6H_2O(l)$ 

## **BOILING POINTS/ MELTING POINTS OF THE HYDRIDES**

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

Hydride	HF	HCl	HBr	HI
<b>Boiling point(OC)</b>	+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 increasing amount of energy required to break the increasingly stronger forces.

Hydrogen fluoride has an abnormally high melting point because the fluorine atom has the highest electronegativity, the fluoride ion has the smallest ionic radius, making the hydrogen-fluorine bond highly polar. The hydrogen fluoride molecules are therefore held by strong intermolecular hydrogen bonds which require a high amount of energy to break.

Explain why hydrogen fluoride has a higher boiling point than hydrogen iodide.

The fluorine atom is more electronegative than the iodine atom. The fluoride ion in hydrogen fluoride has a smaller ionic radius than the iodide ion in hydrogen iodide. This makes the hydrogen-fluorine bond more polar than the hydrogen-iodine bond. The molecules of hydrogen fluoride are held by stronger intermolecular hydrogen bonds which require a higher amount of energy to break whereas the molecules of hydrogen iodide are held by weak Van der Waals' forces that require a lower amount of energy to break.

#### THERMAL STABILITY

# 4. (a) State and explain the trend in thermal stability of the hydrides.

Thermal stability of the hydrides decreases in the order HF > HCl > HBr > HI. This is because the 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, reducing the amount of energy required to dissociate the hydrogen-halogen bond.

#### **ACID STRENGTHS**

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

Hydride	HF	HCl	HBr	HI
$K_a$ (moldm <sup>-3</sup> ) at 25 $^{\circ}$ C	$6.6 \times 10^{-4}$	$1.3 \times 10^{6}$	$1.0 \times 10^{9}$	$3.2 \times 10^{9}$

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 ionic radius of the halide ions increases from the fluoride ion to the iodide ion. 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 **the weakest acid** because the **fluorine atom is most electronegative** and the **fluoride ion has the smallest ionic radius**. Therefore the **hydrogen-fluorine bond** is **the shortest, most polar** and **strongest** making the acid to **dissociate to a considerably smaller extent**.

Explain why hydrofluoric acid is a weaker acid than hydroiodic acid

The fluorine atom is more electronegative than the iodine atom and the fluoride ion in hydrofluoric acid has a smaller ionic radius than the iodide ion in hydroiodic acid. Therefore the hydrogen-fluorine bond is the shorter, more polar and stronger than the hydrogen-iodine bond in hydroiodic acid hence the hydrogen-fluorine bond does not easily break, releasing fewer hydrogen ions in solution than the hydrogen-iodine bond which easily breaks.

# Qn. Explain why hydrofluoric acid is a weak acid in dilute solution but its acid strength increases with increasing concentration

The fluorine atom in hydrogen fluoride is highly electronegative due to a very small atomic radius. Therefore the hydrogen- fluorine bond is highly polar and very strong. When hydrogen fluoride is dissolved in water, the hydrofluoric acid formed only partly ionises, doesn't easily release hydrogen ions making it a weak acid.

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

However, in concentrated solution, the fluoride ions released react with hydrofluoric acid to form hydrogen difluoride ion.

In concentrated solution;  $HF(l) + F^{-}(aq) \longrightarrow HF_{2}^{-}(aq)$ 

This reduces the concentration of fluoride ions at equilibrium. The equilibrium shifts from left to right as more of the hydrogen fluoride dissociates releasing more hydrogen ions making the solution a strong acid at high concentration.

#### 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 atom has the smallest atomic radius compared to other elements
- Fluorine atom has the highest electronegativity among the elements
- Fluorine molecule has the lowest value of bond dissociation energy of the F—F bond
- Unlike other elements, fluorine atom cannot expand its octet
- Fluorine has the largest positive standard electrode potential among the elements

(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
- Hydrogen fluoride has the smallest bond length.
- Hydrogen fluoride has the highest electronegativity difference between its atoms among the hydrides.

**(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

Polarisability is the ease by which the electron cloud of the anion can be distorted.

The greater the polarisability of the anion, the greater the tendency of the anion to form a covalent bond.

Polarisability of an anion depends on the size of the anion

The smaller the anion, the lower it is polarizable and the larger the anion, the easier it is polarized.

If we consider the halide ions, polarisability increases in the order

$$F^- < Cl^- < Br^- < I^-$$

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

$$PbI_2 < PbBr_2 < PbCl_2$$

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.

Qn. Explain why aluminium chloride is soluble in methylbenzene and has a low melting point yet aluminium fluoride is soluble in water and has a higher melting point.

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

ION	TEST	OBSERVATION	DEDUCTION	EXPLANATION
	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 $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$
Cl-	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 <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> 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/wa rming and reprecipitates on cooling	Cl <sup>-</sup> present	Lead(II) ions react with chloride ions to form insoluble lead(II) chloride $Pb^{2+}(aq) + 2Cl^{-}(aq) \longrightarrow PbCl_{2}(s)$
	Add dilute nitric acid followed by silver nitrate solution	White precipitate	$C_2O_4^{2-}$ , $SO_3^{2}$ , $Cl$ probably present	Silver ions react with chloride ions to form insoluble silver chloride $Ag^{+}(aq) + Cl^{-}(aq) \longrightarrow AgCl(s)$

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		T	1	<del></del>
	Add silver nitrate solution followed by dilute nitric acid	White precipitate insoluble in acid	Cl <sup>-</sup> present	Silver ions react with chloride ions to form insoluble silver chloride $Ag^{+}(aq) + Cl^{-}(aq) \longrightarrow AgCl(s)$
Cl <sup>-</sup>	Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia drop wise until in excess.  White precipitate soluble in excess ammonia to form a colourless solution		$Cl^ confirmed$ $AgCl(s) + 2N$	Silver ions react with chloride ions to form insoluble silver chloride $Ag^{+}(aq) + Cl^{-}(aq) \longrightarrow AgCl(s)$ Silver chloride reacts with excess ammonia to form a soluble complex of diammine silver(I) ion. $H_{3}(aq) \longrightarrow Ag(NH_{3})^{+}_{2}(aq) + Cl^{-}(aq)$
	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 <sup>-</sup> present	The acidified bleaching powder or chlorine water produces Chlorine. The chlorine cannot oxidise chloride ions. hence the tetrachloromethane layer remains colourless
Br-	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)	Reddish brown vapours $2Br^{-}(aq) + 4H^{+}(aq)$	$Br_2$ evolved $Br^-$ present $aq) + SO_4^{2-}(aq)$	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. $\Rightarrow Br_2(g) + SO_2(g) + 2H_2O(l)$

	-			
	To the solution, add dilute nitric acid followed lead(II) nitrate solution	White precipitate	$C_2O_4^{2-}$ , $SO_3^{2-}$ , $SO_4^{2-}$ , $Cl$ $Br^-$ probably present	Lead(II) ions react with bromide ions to form insoluble lead(II) bromide $Pb^{2+}(aq) + 2Br^{-}(aq) \longrightarrow PbBr_{2}(s)$
Br-	Add dilute nitric acid followed by silver nitrate solution	Pale yellow precipitate	Br <sup>-</sup> present	Silver ions react with bromide ions to form insoluble silver bromide $Ag^{+}(aq) + Br^{-}(aq) \longrightarrow AgBr(s)$
	Add silver nitrate solution followed by dilute nitric acid	Pale yellow precipitate insoluble in acid	Br <sup>-</sup> present	Silver ions react with bromide ions to form insoluble silver bromide $Ag^{+}(aq) + Br^{-}(aq) \longrightarrow AgBr(s)$
	Add dilute nitric acid followed by silver nitrate solution. Then add aqueous ammonia drop wise until in excess.	Pale yellow precipitate soluble in excess ammonia	Br <sup>-</sup> present	Silver ions react with bromide ions to form insoluble silver bromide $Ag^{+}(aq) + Br^{-}(aq) \longrightarrow AgBr(s)$ Silver bromide is sparingly soluble in ammonia.
	To the solution, add bleaching powder then dilute nitric acid (or add chlorine water) followed by tetrachloromet hane and shake. Allow to stand	Reddish brown liquid in tetrachloromethan e layer	Br <sup>-</sup> present	The acidified bleaching powder or chlorine water produces Chlorine which oxidises bromide ions to bromine. $Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(l)$ Bromine is covalent hence dissolves in tetrachloromethane to form the reddish brown layer.

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I-	To a spatula endful of the solid, add 2-3 drops of concentrated sulphuric acid and heat (the reaction may take place even before	Purple vapours $2I^{-}(aq) + 4H^{+}(aq)$	$I_2$ evolved $I^-$ present $+ SO_4^{2-}(aq)$ —	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.
	heating)			$q) \rightarrow 5I_2(g) + SO_2(g) + H_2S(g) + 6H_2O(l)$
	To the solution, add dilute nitric acid followed lead(II) nitrate solution	Yellow precipitate	I <sup>-</sup> 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 <sup>–</sup> 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 <sup>–</sup> 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 drop wise until in excess.	Yellow precipitate insoluble in ammonia	I <sup>-</sup> 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

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I-	To the solution, add bleaching powder then dilute nitric acid (or add chlorine water) followed by tetrachloromet hane and shake. Allow to stand	Violet colouration in tetrachloromethan e layer	I <sup>–</sup> 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 <sup>-</sup> 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;
 (a) Sodium iodide solution.
 (03 marks)

(b) Sodium thiosulphate solution (03 marks)

(c) Cold dilute sodium hydroxide (03 marks)

2. (a) Write equation for the reaction that takes place when hot concentrated potassium hydroxide is added to;

(i) fluorine. (01 mark)

(ii) chlorine. (01 mark)

(b) Write equation(s) for the reaction(s) of

(i) fluorine and water (1 ½ marks)

(ii) hydrofluoric acid and silicon(IV) oxide (1 ½ marks)

(c) Arrange the following hydrogen halides; *HCl*, *HI* and *HBr* in order of decreasing acid strength. Give a reason for your answer. (03 marks)

3. (a)Fluorine, chlorine, bromine and iodine are diatomic molecules of group VII elements of the Periodic Table. Briefly describe how the elements react with;

(i) Potassium bromide. (02 marks)

(ii) Hydrogen sulphide (02 marks)

(b) The hydrides of the elements in (a) above boil at different temperatures shown in the table below.

Hydride	HF	HCl	HBr	HI
<b>Boiling point(OC)</b>	+20	-85	-67	-35

State and explain the trend in boiling points of the hydrides.

(03 marks)

(c) (i) State the order in reducing strength of the hydrides.

(01 mark)

(ii) 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
<b>Boiling point(K)</b>	293	188	206	238
Bond length(nm)	0.086	0.128	0.142	0.160

(a) Explain the observed trend in;

(i) Boiling points

(02 marks)

(ii) Bond length

(02 marks)

(b) 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. State what would be observed and write equation for the reaction that would take place when;
  - (a) Copper(II) sulphate solution was added to potassium iodide solution. (2 ½ marks)
  - (b) Potassium iodide solution is added to chlorine water. (02 marks)
  - (c) Chlorine is bubbled through iron(II) chloride solution (2 ½ marks)
  - (d) Solid sodium iodide is heated with concentrated sulphuric acid.

(2 ½ marks)

- (e) Warm concentrated hydrochloric acid is added to manganese(IV) oxide. (02 marks)
- (f) Sodium iodide is added to acidified sodium chlorate(I) solution.

(02 marks)

- (g) Chlorine is bubbled through sodium thiosulphate solution (2 ½ marks)
- (h) Sodium iodide solution is added to acidified hydrogen peroxide solution. (1 ½ marks)
- (i) Chlorine is bubbled through potassium manganate(VI) solution

(2 ½ marks)

6.	(a) The (i)	chemistry of fluorine differs from that of chlorine.  State two differences between the chemistry of fluorin	e and chlorine
		apart from their reactions with sodium hydroxide.	(02 1 )
	(··)		(02 marks)
	(ii)	Write the equation for the reaction between cold	allute soalum
		hydroxide and;	
		• Fluorine	(02 1 )
		• chlorine	(03 marks)
7.	(a) The	e oxidising strength of group VII elements decreases in th	e order;
	$F_2 \gg C$	$l_2 > Br_2 > l_2$	
	(i)	State three reasons to account for the high oxidising	ng strength of
		fluorine relative to other halogens.	(1 ½ marks)
	(ii)	State two other anomalous properties of fluorine.	(02 marks)
(	(b) Desc	cribe the reactions of chlorine and iodine with;	
	(i)	sodium thiosulphate solution.	(3 ½ marks)
	(ii)	iron(II) sulphate.	(02 marks)
8.	(a) (i) S	State the condition(s) under chlorine reacts with sulphur of	lioxide.
			(01 mark)
	(ii) W	rite equation for the reaction.	(01 mark)
-		e was bubbled through sodium thiosulphate solution ion was added to the resultant solution.	n and lead(II)
	(i) State	e what was observed.	(01 mark)
	(ii) Wri	te equation(s) for the reaction(s) that took place.	(02 marks)
9.	` '	te three reasons why fluorine differs in some of its prop group VII elements.	erties from the (03 marks)
(	(b) Wri	te equations for ionisation of hydrogen fluoride in aqu	eous solutions
1	that are;		
	(i) di	lute	
	(ii) c	oncentrated	(03 marks)
	(c) Expl	ain why hydrogen fluoride is a weaker acid than hydroge	en chloride.

(03 marks)

- 10. 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)  $I^-$  and  $Br^-$  (4 ½ marks)
  - (ii)  $Cl^-$  and  $Br^-$  (4 ½ marks)
  - (iii)  $I^-$  and  $Cl^-$  (4 ½ marks)
- 11.(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.  $(2 \frac{1}{2} \text{ marks})$
  - (c) Explain why unlike other halogens, fluorine liberates oxygen from cold water. (02 marks)
- 12.(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)
  - (b) Sodium thiosulphate solution was added to the mixture in (a), state what was observed and write equation for the reaction that took place.

 $(2 \frac{1}{2} \text{ marks})$ 

13.(a) The table below shows the melting points of magnesium halides.

Formula of halide	$MgF_2$	$MgCl_2$	$MgBr_2$	$MgI_2$
Melting point( <sup>o</sup> 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 <sup>-1</sup> )	-813	-710	-643

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

14. 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.

 $(2 \frac{1}{2} \text{ marks})$ 

- (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

- 15. 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)
    - (iii) sulphurous acid (2 ½ marks)
  - (d) Hydrofluoric acid is a weaker acid than hydrochloric acid. Explain.

(02 marks)

- 16.(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
- 17.(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<sub>2</sub>, HClO<sub>3</sub> and HClO<sub>4</sub>.
- (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)
- 18.(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(IV) 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)

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

$H \longrightarrow X$	H - F	<i>H</i> — <i>Cl</i>	H—Br	H - I
Bond energy(kJmol <sup>-1</sup> )	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)
- 20.(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:
    - (i) why hydrogen fluoride is a liquid whereas hydrogen chloride is a gas at 18 °C. (04 marks)
    - (ii) why aluminium fluoride has a higher melting point than aluminium chloride. (03 marks)
- 21.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)