

**Pioneer Junior College  
Higher 2 Chemistry (9647)  
Inorganic Chemistry  
Group VII**

**References**

- 1 Chemistry for advanced level – Peter Cann & Peter Hughes (pg 320 - 331)
- 2 Chemistry in Context 3<sup>rd</sup> Ed. – Graham C. Hill & John S. Holman (pg 263 - 290)
- 3 Chemguide (<http://www.chemguide.co.uk/inorganic/group7menu.html#top>)

**Syllabus Content**

The similarities and trends in the physical and chemical properties of chlorine, bromine and iodine

- I Characteristic physical properties
- II The relative reactivity of the elements as oxidising agents
- III Some reactions of the halide ions
- IV The reactions of chlorine with aqueous sodium hydroxide

**Assessment Objectives**

*You should be able to:*

- (a) *describe the trends in volatility and colour of chlorine, bromine and iodine*
- (b) *analyse the volatility of the elements in terms of van der Waals' forces*
- (c) *describe and deduce from  $E^\circ$  values the relative reactivity of the elements as oxidising agents*
- (d) *describe and explain the reactions of the elements with hydrogen*
- (e)
  - (i) *describe and explain the relative thermal stabilities of the hydrides,*
  - (ii) *interpret these relative stabilities in terms of bond energies*
- (f) *describe and explain the reactions of halide ions with*
  - (i) *aqueous silver ions followed by aqueous ammonia,*
  - (ii) *concentrated sulfuric acid*
- (g) *describe and analyse in terms of changes of oxidation number the reaction of chlorine with cold, and with hot, aqueous sodium hydroxide*

**Lecture Outline**

- 1 **Halogens**
  - 1.1 **Introduction**
  - 1.2 **Physical properties of halogens**
  - 1.3 **Trends in group VII**
  - 1.4 **Chemical properties and reactivity of halogens**
- 2 **Hydrogen halides**
  - 2.1 **Physical properties of hydrogen halides**
  - 2.2 **Thermal stability of hydrogen halides**
  - 2.3 **Acid strength of hydrogen halides**
- 3 **Reaction of halide ions,  $X^-$** 
  - 3.1 **Reaction of halide ions with aqueous silver nitrate, followed by aqueous ammonia**
  - 3.2 **Photochemical reaction of silver halides**
  - 3.3 **Reaction of halide ions with concentrated sulfuric acid**

## 1 Halogens

### 1.1 Introduction

The halogens are the elements in Group VII of the periodic table – fluorine, chlorine, bromine, iodine and astatine. They are known as the *halogens* – a name derived from Greek, meaning “salt formers” because they combine readily with metals to form salts. The halogens exist as diatomic molecules ( $X_2$ ), with the two halogen atoms held together by a single covalent bond.

The group of the halogens is the only Group in the Periodic Table which contains elements in all three physical states at room temperature and pressure. Fluorine and chlorine are gases. Bromine is a liquid. Iodine and astatine are solids.

The halogens comprise the most reactive group of non-metals. They are strong oxidising agents and they are known to exhibit variable oxidation numbers in their compounds.

Although the halogens show distinct trends in behaviour down their group, they also show remarkable similarities. These similarities in their properties and reactions result very largely from their similar electronic configuration. Each of the halogen has an outermost shell containing seven electrons (i.e.  $ns^2 np^5$ ).

### 1.2 Physical properties of Halogens

#### 1.2.1 Physical state and colour

Halogen	Formula	Physical state at room temperature	Colour
Fluorine	$F_2$	Gas	pale yellow
Chlorine	$Cl_2$	Gas	pale yellow-green
Bromine	$Br_2$	Liquid	reddish-brown/orange
Iodine	$I_2$	Solid (but sublimes to form a violet vapour)	black

#### 1.2.2 Volatility

The halogens have **simple molecular structure** with weak **van der Waals forces** between the **non-polar molecules**. Hence, the melting and boiling points of halogens are low.

Going down the group, the **number of electrons** in the halogen molecule **increases**. The **electron cloud** becomes **more polarisable** (i.e. more easily distorted), thus the **strength of van der Waals forces increases**. More energy is required to overcome the stronger van der Waals forces down the group. This results in an increase in boiling point (i.e. **decrease in volatility**).

### 1.2.3 Solubility

#### (I) Solubility in water (polar solvent)

All the halogens except fluorine dissolve slightly in water, following coloured aqueous solutions.

Halogen	Solubility In Water	Colour In Water
F <sub>2</sub>	Fluorine is such a powerful oxidising agent that it reacts very vigorously with water to form oxygen and hydrogen fluoride. $2F_2(g) + 2H_2O(l) \rightarrow O_2(g) + 4HF(aq)$	-
Cl <sub>2</sub>	Chlorine reacts slowly with water forming hydrochloric acid and chloric(I) acid. $Cl_2 + H_2O \rightleftharpoons Cl^- + ClO^- + 2H^+$	very pale yellow-green / almost colourless
Br <sub>2</sub>	Bromine is moderately soluble in water.	orange
I <sub>2</sub>	Iodine is slightly soluble in water Solubility increases significantly in the presence of KI(aq) due to the formation of I <sub>3</sub> <sup>-</sup> (aq). $I_2(s) + I^-(aq) \rightleftharpoons I_3^-(aq)$	brown

#### (II) Solubility in Organic Solvent

The halogens, being non-polar, are soluble in non-polar organic solvents, e.g. CCl<sub>4</sub> (denser than water) and cyclohexane / hexane (less dense than water). When dissolved in such organic solvents, characteristic colourations are observed, which are useful for identification in *Qualitative Analysis*.

Halogen	Colour In Organic Solvents
Cl <sub>2</sub>	Pale Yellow / Almost colourless
Br <sub>2</sub>	Reddish-brown
I <sub>2</sub>	Violet / Purple

#### Quick Check 1 [N94/IV/18]

The following report appeared in a newspaper.

*Drums of bromine broke open after a vehicle crash on the motorway. Traffic was diverted as purple gaseous bromine drifted over the road (it is denser than air), causing irritation to drivers' eyes. Firemen sprayed water over the scene of the accident, dissolving the bromine and washing it away.*

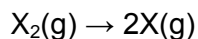
What is wrong with the report?

- A Bromine does not dissolve in water.
- B Bromine does not vaporise readily.
- C Bromine is less dense than air.
- D Bromine is not purple.

### 1.3 Trends in Group VII

#### 1.3.1 Trend in bond energy

Bond energy refers to the amount of energy required to break 1 mole of a covalent bond in the gaseous phase, to form individual gaseous atoms. E.g. for X—X,



The strength of a covalent bond is measured by the bond energy. The greater the magnitude of the bond energy is, the stronger is the covalent bond.

Bond energy, with the exception of fluorine, generally **decreases** down Group VII.

Halogens	F—F	Cl—Cl	Br—Br	I—I
Bond Energy/ kJ mol <sup>-1</sup>	+158	+244	+193	+151

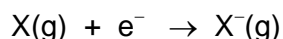
Down the group from chlorine to iodine, the valence orbitals become larger and more diffused. The overlap of orbitals between the two valence np orbitals of halogen becomes less effective. This results in an increase in the X-X bond length and a decrease in X-X bond strength.

Why is F-F bond weaker than expected?

For fluorine, the bond is very short. The lone pairs on the two atoms get close enough to set up a significant amount of repulsion, thus weakening the bond.

#### 1.3.2 Trend in first electron affinity

The first electron affinity of an element is the energy change when one mole of gaseous atoms gain an electron each to form one mole of gaseous singly charged anions.



The first electron affinity becomes less exothermic down the group from chlorine to iodine.

Element	F	Cl	Br	I
Electron Affinity/ kJ mol <sup>-1</sup>	-328	-349	-324	-295

Down Group VII, from chlorine to iodine, the number of filled inner principal quantum shells **increases**. This results in a **decrease** in ability of the halogen atom to accept an extra electron (i.e. lesser energy is released in the addition of one extra electron to the atom). Hence, electron affinity **decreases in magnitude** / becomes **less exothermic** down the group.

Why is the electron affinity of fluorine less exothermic than that of chlorine?

*As the fluorine atom is very small, the existing electron density is very high. When an electron is added to the atom, it enters a region of space with a very high negative charge. Due to the strong electrostatic repulsion which offsets the nuclear attraction, the electron affinity of fluorine is less exothermic than that of chlorine.*

### 1.3.3 Trend in first ionisation energy

First ionisation energy of an element is the energy required to remove one mole of electrons from one mole of gaseous atoms of the element, producing one mole of gaseous singly charged cations.



The first ionisation energy decreases down the group.

Element	F	Cl	Br	I
Ionisation Energy / $\text{kJ mol}^{-1}$	+1680	+1260	+1140	+1010

Down Group VII, there is an **increase** in number of **filled inner** principal quantum shells. Valence electrons are further away from the nucleus. Less energy is required to remove the outermost electron from the gaseous atoms. Hence, ionisation energy **decreases** / becomes **less endothermic** down the group

### 1.3.4 Trend in electronegativity

Electronegativity of an atom refers to the tendency / relative ability of an atom to attract the bonding pair of electrons in a covalent bond (i.e. its electron-pulling power).

Electronegativity decreases down the group.

Element	F	Cl	Br	I
Electronegativity	4.0	3.0	2.8	2.5

Down Group VII, there is an **increase** in number of **filled inner** principal quantum shells. The distance between the nucleus of the halogen atom and the bonding pair electrons **increases**. Hence, the halogen atom is less able to attract bonding pair electrons to itself (i.e. electronegativity **decreases** down the group).

## 1.4 Chemical properties and reactivity of halogens

### 1.4.1 Relative oxidising power of halogens

All halogen atoms have 7 valence electrons. In order to attain the stable octet structure and due to their high electron affinity, halogen atoms tend to gain one electron (hence reduced to  $X^-$ ) from other substances. Thus, they are **good oxidising agents**.

The standard electrode potential,  $E^\ominus$ , is a measure of the tendency for  $X_2$  to be reduced to  $X^-$ . The more positive the  $E^\ominus(X_2/X^-)$  value, the greater the tendency for reduction to occur (i.e. higher oxidising power of  $X_2$ ).



$E^\circ (X_2/X^-)$  becomes **less positive** down the group, indicating a decrease in oxidising power of halogen.

**Oxidising power:**  $F_2 > Cl_2 > Br_2 > I_2$ .

Conversely, the reducing power of the halide ions,  $X^-$ , **increases** down the group.

**Reducing power :**  $I^- > Br^- > Cl^- > F^-$

To account for the decrease in oxidising power of the halogens down the group, there is a need to consider the enthalpy change of formation of  $X^-(aq)$  from  $X_2$ (standard state) using the energy cycle below.



	F	Cl	Br	I
$\Delta H_{at} / \text{kJ mol}^{-1}$	+79	+121	+112	+107
1 <sup>st</sup> E.A. / $\text{kJ mol}^{-1}$	-328	-364	-342	-295
$\Delta H_{hyd} / \text{kJ mol}^{-1}$	-506	-381	-351	-307
$\Delta H_f / \text{kJ mol}^{-1}$	-755	-592	-547	-481

The more exothermic the enthalpy change of formation of  $X^-(aq)$  is, the more favourable the reaction is and hence the stronger is the oxidising power of the halogen. The most important factor to account for the decrease in oxidising power down the group is actually the less exothermic enthalpy change of hydration of the halide ion.

#### 1.4.2 Redox reaction of halogens (displacement reactions)

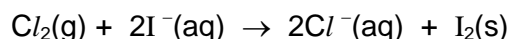
The stronger oxidising halogen will displace the weaker oxidising halogen from its aqueous ion.

##### Quick Check 2

*The use of the Data Booklet is relevant to this question.*

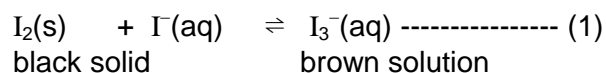
Use the  $E^\circ(X_2/X^-)$  values to predict if any of the following reaction may occur. If a reaction occurs, write the balanced equation and state the observation.

(a) Excess  $Cl_2(g)$  is bubbled into  $KI(aq)$



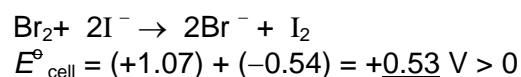
$$E^\circ_{\text{cell}} = (+1.36) + (-0.54) = +0.82 \text{ V} > 0$$

Reaction is **energetically feasible**.



A **brown** solution is formed initially as the  $\text{I}_2$  produced reacts with  $\text{I}^-(\text{aq})$  to form  $\text{I}_3^-$ . However, as more  $\text{I}^-(\text{aq})$  gets oxidised to  $\text{I}_2(\text{aq})$  by the excess  $\text{Cl}_2(\text{g})$  bubbled into the solution,  $[\text{I}^-]$  decreases. This shifts equilibrium (1) to the left. Eventually, black solid will be observed remaining in the solution.

(b)  $\text{KI}(\text{aq})$  is shaken with  $\text{Br}_2$  in hexane.

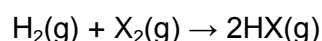


Reaction is **energetically feasible**.

Reddish-brown  $\text{Br}_2$  decolourises and the top hexane layer turns **violet** due to  $\text{I}_2$  dissolving in hexane.

### 1.4.3 Reactions with hydrogen

The halogens react with  $\text{H}_2$  in the gaseous phase to give covalent hydrogen halides,  $\text{H-X}$ .



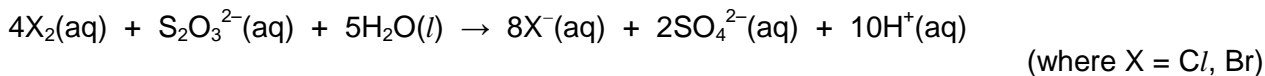
The reaction between halogen and hydrogen becomes **less vigorous** down the group as the strength of the  $\text{H-X}$  bond formed decreases. The reactivity of fluorine is particularly high as the weak  $\text{F-F}$  bond breaks to form two very strong  $\text{H-F}$  bonds.

The decrease in reactivity is also consistent with the **decreasing oxidising power** of halogens down the group.

Reactions with $\text{H}_2(\text{g})$	Observations
$\text{F}_2$	Reaction is extremely rapid. Explodes with $\text{H}_2$ under all conditions.
$\text{Cl}_2$	Explodes with $\text{H}_2$ when exposed to ultraviolet light. Reaction is slow in the dark.
$\text{Br}_2$	Reaction is slow. Need to heat to $200^\circ\text{C}$ in the presence of Pt catalyst.
$\text{I}_2$	No reaction unless strongly heated at $400^\circ\text{C}$ over Pt catalyst. Reaction is reversible and an equilibrium mixture is obtained.  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

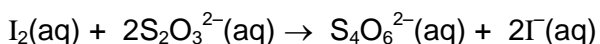
#### 1.4.4 Reaction with sodium thiosulfate

##### Reactions of thiosulfate with $\text{Cl}_2$ and $\text{Br}_2$



$\text{Cl}_2$  and  $\text{Br}_2$ , being **stronger oxidising agents** than  $\text{I}_2$ , can oxidise thiosulfate ion ( $\text{S}_2\text{O}_3^{2-}$ ) to sulfate ion ( $\text{SO}_4^{2-}$ ). Oxidation state of sulfur increases from +2 to +6.

##### Reactions of thiosulfate with $\text{I}_2$

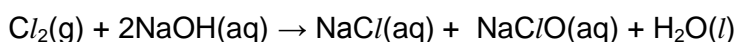


$\text{I}_2$ , the **weakest** oxidising agent among the halogens, can only oxidise thiosulfate ion ( $\text{S}_2\text{O}_3^{2-}$ ) to tetrathionate ion ( $\text{S}_4\text{O}_6^{2-}$ ). Average oxidation number of sulfur increases from +2 to +2.5.

This reaction is used for titrimetric analysis (in titrations) of iodine. Starch indicator is added to the titration mixture only when the mixture is pale yellow, then the titration is continued until the blue-black colour is just discharged.

#### 1.4.5 Reaction of halogens with sodium hydroxide

##### With cold dilute aqueous NaOH

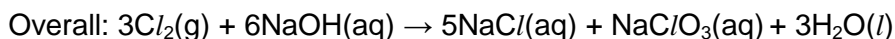
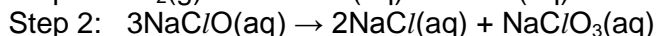
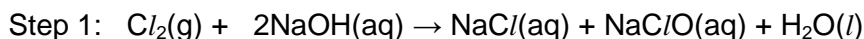


In the above reaction, chlorine undergoes **disproportionation**, i.e. chlorine is simultaneously oxidised to  $\text{ClO}^-$  and reduced to  $\text{Cl}^-$ . Chlorine is **reduced** as its oxidation number decreases from 0 in  $\text{Cl}_2$  to -1 in  $\text{Cl}^-$ . Chlorine is **oxidised** as its oxidation number increases from 0 in  $\text{Cl}_2$  to +1 in  $\text{ClO}^-$ .

*\*\*Note: Bromine and iodine react similarly.*

##### With hot aqueous NaOH

The reaction of chlorine with hot aqueous NaOH takes place in two steps:



In the above reaction, chlorine undergoes **disproportionation**, i.e. chlorine is simultaneously oxidised to  $\text{ClO}_3^-$  and reduced to  $\text{Cl}^-$ . Chlorine is **reduced** as its oxidation number decreases from 0 in  $\text{Cl}_2$  to -1 in  $\text{Cl}^-$ . Chlorine is **oxidised** as its oxidation number increases from 0 in  $\text{Cl}_2$  to +5 in  $\text{ClO}_3^-$ .

*\*\*Note:  $\text{BrO}^-$  and  $\text{IO}^-$  disproportionate similarly and **more readily** than  $\text{ClO}^-$ . Disproportionation in step 2 occurs more readily down the group. With  $\text{I}_2$ , disproportionation of  $\text{IO}^-$  occurs rapidly even with **cold** dilute aqueous NaOH.*





## 2 Hydrogen halides

### 2.1 Physical properties of hydrogen halides

All hydrogen halides, H-X, are colourless and pungent gases at room temperature and pressure (often observed as steamy / white fumes).

H-X	Boiling point / °C
HF	20
HCl	-85
HBr	-67
HI	-35

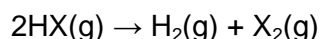
H-F has **exceptionally high** melting & boiling points (compared to other HX) because of the **strong hydrogen bonds between H-F molecules** in both the gaseous & liquid states.

HCl, HBr and HI have **low** melting and boiling points because little energy is required to overcome the weak van der Waals' forces.

The boiling point increases down the group because the total number of electrons in each molecule increases from HCl to HI. With more electrons that can be polarised, the strength of the van der Waals' forces of attractions increases. More energy is required to overcome the stronger van der Waals' forces down the group.

### 2.2 Thermal stability of hydrogen halides

Upon heating, hydrogen halides decompose to form halogen and hydrogen. HI can be decomposed to H<sub>2</sub>(g) and I<sub>2</sub>(g) by putting a red hot iron wire in the gas.



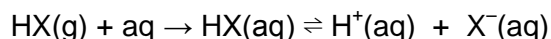
Thermal stability: **HF > HCl > HBr > HI**

	H — F	H — Cl	H — Br	H — I
Bond Energy / kJ mol <sup>-1</sup>	+562	+431	+366	+299

Going down Group VII, the valence np orbital of the halogen atom is larger and more diffused. Thus, the overlap of orbitals between the 1s orbital of H and the np orbital of halogen atom becomes less effective. Consequently, the H-X bond is longer and weaker as indicated by the bond energies. Less energy is required to break the H-X bond going down the group, i.e. thermal stability decreases.

## 2.3 Acid strength of hydrogen halides

In the presence of water, hydrogen halides dissociate / ionise to form acids:



The acidity (i.e. acid strength) of hydrogen halides depends on the readiness to release  $\text{H}^+$  ions, i.e. strong acids dissociate more readily to release  $\text{H}^+$  while weak acids dissociate less readily to release  $\text{H}^+$ .

Degree of Dissociation in a  $0.10 \text{ mol dm}^{-3}$  solution of HX

	H — F	H — Cl	H — Br	H — I
Degree of Dissociation (%)	8.5	92	93	95
Acid strength	weak	strong		

Hydrochloric acid  $\text{HCl(aq)}$ , hydrobromic acid  $\text{HBr(aq)}$  and hydriodic acid  $\text{HI(aq)}$  are **strong acids** as they dissociate **completely** in water to form  $\text{H}^+(\text{aq})$  and  $\text{X}^-(\text{aq})$  ions.

Down Group VII, strength of  $\text{H—X}$  bond **decreases**. The ease of breaking the  $\text{H—X}$  bond to release  $\text{H}^+(\text{aq})$  ions **increases**. Hence, acid strength **increases** down the group. Acid strength:  **$\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$**

**HF is a weak acid.** HF dissociates only partially in water to form  $\text{H}^+(\text{aq})$  and  $\text{F}^-(\text{aq})$  ions, leaving behind a large proportion of undissociated HF molecules.

### Why is hydrofluoric acid a weak acid? (For self-read)

There are two factors to account for the low acid strength of hydrofluoric acid.

- Very strong hydrogen bonds exist between the un-ionised hydrogen fluoride molecules and water molecules. A lot of energy is required to overcome them (not seen in the other hydrogen halides).
- There is also a large decrease in entropy when the hydrogen fluoride molecules ionise in water to form very small fluoride ions which impose a lot of order on the surrounding water molecules. The effect is less significant for the halide ions which are bigger.

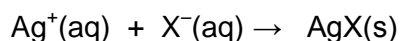
	$\Delta H / \text{kJ mol}^{-1}$	$T\Delta S / \text{kJ mol}^{-1}$	$\Delta G / \text{kJ mol}^{-1}$	$K_a / \text{mol dm}^{-3}$
HF	– 13	– 29	+ 16	$1.6 \times 10^{-3}$
HCl	– 59	– 13	– 46	$1.2 \times 10^8$
HBr	– 63	– 4	– 59	$2.2 \times 10^{10}$
HI	– 57	+ 4	– 61	$5.0 \times 10^{10}$

<http://www.chemguide.co.uk/inorganic/group7/acidityhx.html> & Peter Cann Page 328

### 3 Reaction of halide ions, $X^-$

#### 3.1 Reaction with $\text{AgNO}_3(\text{aq})$ , followed by addition of aqueous $\text{NH}_3$

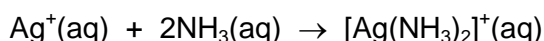
When a solution of  $\text{AgNO}_3(\text{aq})$  is added to an aqueous solution containing the halide ions, precipitation of silver halide takes place.



	$\text{Cl}^-(\text{aq})$	$\text{Br}^-(\text{aq})$	$\text{I}^-(\text{aq})$
$\text{AgNO}_3(\text{aq})$	White ppt of $\text{AgCl}$	Cream ppt of $\text{AgBr}$	Yellow ppt of $\text{AgI}$
Solubility of $\text{AgX}$ in			
(i) excess dilute aq. $\text{NH}_3$	soluble	insoluble	insoluble
(ii) excess concentrated aq. $\text{NH}_3$	soluble	soluble	insoluble

*(will be discussed further in 2016 in acid-base equilibria)*

When  $\text{NH}_3(\text{aq})$  is added,  $\text{Ag}^+$  forms a stable diamminesilver(I) complex  $[\text{Ag}(\text{NH}_3)_2]^+$ .



The formation of this complex **reduces**  $[\text{Ag}^+(\text{aq})]$ . Hence, ionic product of  $\text{AgX}$  decreases (where ionic product =  $[\text{Ag}^+(\text{aq})][\text{X}^-(\text{aq})]$ ).



$$K_{\text{sp}}(\text{AgCl}) > K_{\text{sp}}(\text{AgBr}) > K_{\text{sp}}(\text{AgI}).$$

For  $\text{AgCl}$ :

The formation of diamminesilver(I) complex in dilute aqueous ammonia is **sufficient to cause the ionic product of  $\text{AgCl}$  to fall below its  $K_{\text{sp}}$  value** (as the  $K_{\text{sp}}$  value of  $\text{AgCl}$  is highest). Thus,  $\text{AgCl}(\text{s})$  is **soluble in both dilute and concentrated  $\text{NH}_3(\text{aq})$** .

For  $\text{AgBr}$ :

The formation of diamminesilver(I) complex in dilute aqueous ammonia is **not sufficient to cause the ionic product of  $\text{AgBr}$  to fall below its  $K_{\text{sp}}$  value**. However, with concentrated aqueous ammonia, the formation of diamminesilver(I) complex is **sufficient to decrease the  $[\text{Ag}^+]$ , thus causing the ionic product of  $\text{AgBr}$  to fall below its  $K_{\text{sp}}$  value**. This explains why  $\text{AgBr}(\text{s})$  is soluble in concentrated  $\text{NH}_3(\text{aq})$  but insoluble in dilute  $\text{NH}_3(\text{aq})$ .

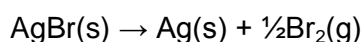
For  $\text{AgI}$ :

The formation of diamminesilver(I) complex in both dilute and concentrated aqueous ammonia is **not sufficient to cause the ionic product of  $\text{AgI}$  to fall below its  $K_{\text{sp}}$  value** (as the  $K_{\text{sp}}$  value of  $\text{AgI}$  is extremely low). Therefore,  $\text{AgI}(\text{s})$  is insoluble in both dilute and concentrated  $\text{NH}_3(\text{aq})$ .

### 3.2 Photochemical reaction of silver halide

	<b>Cl<sup>-</sup>(aq)</b>	<b>Br<sup>-</sup>(aq)</b>	<b>I<sup>-</sup>(aq)</b>
AgNO <sub>3</sub> (aq)	White ppt of AgCl	Cream ppt of AgBr	Yellow ppt of AgI
Effect of sunlight on AgX	White ppt of AgCl turns purple-grey	Cream ppt of AgBr turns green-yellow	no effect

Colour changes which occur when AgCl and AgBr are exposed to sunlight result from the conversion of these silver halides to silver and halogen.



The photochemical change involving AgBr plays an essential part in black and white photography. Photographic plates and films contain silver bromide. This decomposes to silver on exposure to light. When the photograph is developed, the plate/film is treated with 'hypo' (sodium thiosulfate solution). This removes the excess AgBr as a soluble complex  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ , and the silver remains on the plate/film as an opaque shadow.

#### **Quick Check 3 [N2012/II/3(b)]**

(a) When HCl(aq) is added to AgNO<sub>3</sub>(aq), what will be seen in the container

(i) immediately

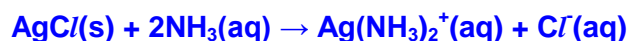
**White precipitate of AgCl will be observed.**

(ii) after one hour in daylight?

**White precipitate turns purple-grey.**

(b) How do you confirm that the original precipitate was AgCl by adding a single reagent to it? Describe what you would see and give an equation with state symbol for the reaction that occurs with the reagent you have chosen.

**To the precipitate, add dilute NH<sub>3</sub>(aq). If AgCl is present, it will dissolve.**



### 3.3 Reaction of halide ions with concentrated sulfuric acid

Concentrated H<sub>2</sub>SO<sub>4</sub> reacts with **solid** sodium halides to form hydrogen halides.



As concentrated H<sub>2</sub>SO<sub>4</sub> is also an oxidising agent, it may oxidise the HX(g) produced, depending on the reducing power of the X<sup>-</sup> ion.



**Ease of oxidation of HX:  $HI > HBr > HCl$  ( $HCl$  is not oxidised by conc.  $H_2SO_4$ )**

**Reducing power of halides:  $I^- > Br^- > Cl^- > F^-$**

$\therefore$  HI can reduce  $H_2SO_4$  (oxidation state of S = +6) to mainly  $H_2S$  (oxidation state of S = -2) and itself oxidised to  $I_2$  readily.

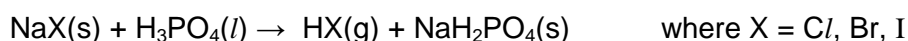
HBr can reduce concentrated  $H_2SO_4$  (oxidation state of S = +6) to  $SO_2$  (oxidation state of S = +4) and itself oxidised to  $Br_2$  in small amounts.

HCl cannot reduce concentrated  $H_2SO_4$ .

	Reaction with concentrated $H_2SO_4$	Observations
NaI(s)	$NaI(s) + H_2SO_4(l) \rightarrow HI(g) + NaHSO_4(s)$ $2HI(g) + H_2SO_4(l) \rightarrow I_2(g) + SO_2(g) + 2H_2O(l)$ <b><math>8HI(g) + H_2SO_4(l) \rightarrow 4I_2(g) + H_2S(g) + 4H_2O(l)</math></b>	(small amount of) White fumes of HI observed. Colourless, pungent gases ( $SO_2$ and $H_2S$ ) evolved. <b>Violet fumes and black solid of <math>I_2</math> formed.</b>
NaBr(s)	$NaBr(s) + H_2SO_4(l) \rightarrow HBr(g) + NaHSO_4(s)$ <b><math>2HBr(g) + H_2SO_4(l) \rightarrow Br_2(g) + SO_2(g) + 2H_2O(l)</math></b>	Some white fumes of HBr observed. Colourless, pungent gas $SO_2$ evolved. <b>Red-brown fumes of <math>Br_2</math> observed.</b>
NaCl(s)	<b><math>NaCl(s) + H_2SO_4(l) \rightarrow HCl(g) + NaHSO_4(s)</math></b>	<b>White fumes of HCl evolved.</b>

How can HBr and HI be synthesised?

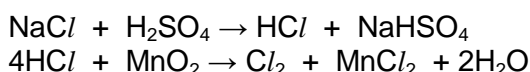
We can make use of a non-volatile acid which is not oxidising, e.g., concentrated phosphoric acid,  $H_3PO_4$ , instead.



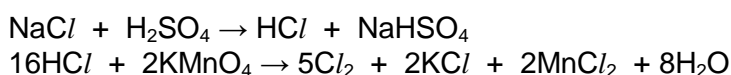
### 3.2.1 Reaction of halides in the presence of concentrated $H_2SO_4$ and $MnO_2$ or $KMnO_4(aq)$

In the presence of stronger oxidising agents (e.g. concentrated  $H_2SO_4$  &  $MnO_2$  /  $KMnO_4(aq)$ ), the halogen  $X_2$  is produced)

#### (a) With concentrated $H_2SO_4$ & $MnO_2(s)$



#### (b) With concentrated $H_2SO_4$ & $KMnO_4(aq)$



As  $\text{KMnO}_4$  is able to oxidise  $\text{HCl}$  to  $\text{Cl}_2$ , that is the reason why  $\text{HCl(aq)}$  is not used to acidify  $\text{KMnO}_4(\text{aq})$ .

In summary,

- Ease of oxidation of  $\text{X}^-$  to  $\text{X}_2$  increases from  $\text{Cl}^-$  to  $\text{I}^-$ .
- When concentrated  $\text{H}_2\text{SO}_4$  is added to solid halides, steamy / white fumes of  $\text{HX(g)}$  is evolved.
- $\text{HBr}$  and  $\text{HI}$  will also be oxidised by concentrated  $\text{H}_2\text{SO}_4$  into  $\text{Br}_2$  and  $\text{I}_2$  respectively. However, concentrated  $\text{H}_2\text{SO}_4$  is not a strong enough oxidising agent to oxidise  $\text{HCl}$  to give  $\text{Cl}_2$ . (Oxidation of  $\text{HCl}$  to give  $\text{Cl}_2$  will only take place if a stronger oxidising agent, e.g.  $\text{MnO}_2$  or  $\text{KMnO}_4$ , is also present.)