11.1 GROUP 17

Some reactions of the halide ions

Learning outcomes

Candidates should be able to:

1 describe the relative reactivity of halide ions as reducing agents

2 describe and explain the reactions of halide ions with:

(a) aqueous silver ions followed by aqueous ammonia (the formation and formula of the $[Ag(NH_3)_2]^+$ complex is not required)

(b) concentrated sulfuric acid, to include balanced chemical equations

Reactivity of halide ions as reducing agents

The halide ions are increasingly effective as reducing agents going down Group 17.

1. A solution of aqueous bromide ions, $Br^-(aq)$, is added to separate samples of $Cl_2(aq)$ and $I_2(aq)$. Describe what is observed in each reaction. Explain your answer in terms of the relative reactivity of these elements as oxidising agents.

observation on addition to $Cl_2(aq)$

.....

.....

observation on addition to $I_2(aq)$

…….....

.....

explanation

.....

.....

.....

..... [3]

Reactions of halide ions aqueous silver ions

We can identify the halide ions, $Cl^-(aq)$, $Br^-(aq)$ and $I^-(aq)$, by using simple chemical tests. If an unknown compound is dissolved in dilute nitric acid and silver nitrate solution is added, a precipitate will form if the unknown solution contains halide ions. The precipitate will be silver chloride (AgCl), silver bromide (AgBr) or silver iodide (AgI) (see Figure 12.4).

These precipitates are similar in colour. We can then use a further test to help us distinguish one precipitate from another. We can add ammonia solution – dilute ammonia solution followed by concentrated ammonia solution – to verify the result. The results of the tests are shown in Table 12.5.

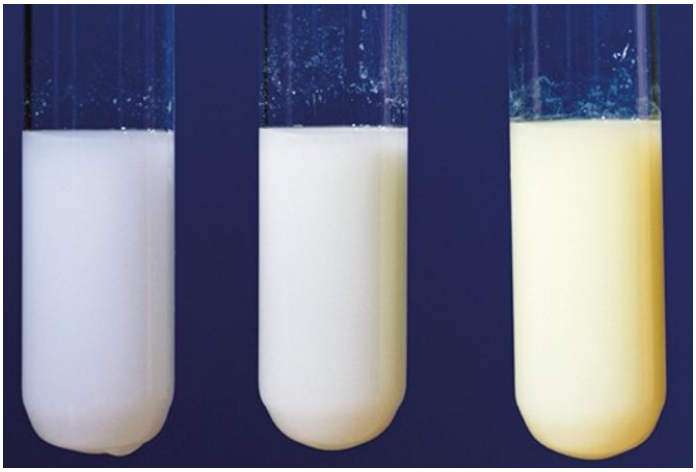
The general equation for the precipitation reaction with silver nitrate solution is:

$AgNO_3(aq) + X^-(aq) \rightarrow AgX(s) + NO_3^-(aq)$

where X^- represents the halide ion.

The nitrate ions can be left out to produce the ionic equation. They are called 'spectator ions', i.e. ions that do not get involved in the reaction:

The ammonia can form complex ions that are soluble in water when added to:
silver chloride, as it forms soluble complex ions with **dilute** ammonia
silver bromide, as it forms soluble complex ions with **concentrated** ammonia.
Silver iodide precipitate does not dissolve on adding dilute or concentrated ammonia solution.



Halide ion	Colour of silver halide precipitate on addition of silver nitrate solution	Effect on precipitate of adding dilute ammonia solution	Effect on precipitate of adding concentrated ammonia solution
chloride, Cl-(aq)	white	dissolves	dissolves
bromide, Br-(aq)	cream	remains insoluble	dissolves
iodide, I-(aq)	pale yellow	remains insoluble	remains insoluble

2. Describe fully what is observed when $AgNO_3(aq)$ is added to the aqueous solution of the chloride of sodium, followed by dilute $NH_3(aq)$. [2]

3. The Group 17 elements form soluble halides with sodium. Describe what is seen when dilute $AgNO_3(aq)$ is added to NaBr(aq) followed by aqueous ammonia. [2]

4. A sample of aqueous calcium halide, $CaX_2(aq)$, contains either chloride, bromide or iodide ions. Complete Table 2.1 to describe a two-step process that could be used to identify the halide ion present. [3]

step	method	observation with $CaCl_2$	observation with $CaBr_2$	observation with CaI_2
step **1**				
step **2**				

1. The addition of aqueous silver nitrate to aqueous barium chloride produces a white precipitate which dissolves in an excess of dilute aqueous ammonia to form a colourless solution.
   The addition of an excess of dilute nitric acid to the colourless solution produces a white precipitate, Z.
   What is Z?
   A AgCl B $BaCl_2$ C Ba(NO3)2 D NH4NO3

2. Compound Q dissolves in water. Q(aq) does not react with dilute sulfuric acid.
Q(aq) forms a precipitate when aqueous silver nitrate is added. This precipitate is partially soluble in aqueous ammonia.
What could be compound Q?
A barium bromide
B barium iodide
C magnesium bromide
D magnesium iodide

3. A powder is known to be either a single sodium halide or a mixture of two sodium halides.
A sample of the powder was dissolved in water.
Aqueous silver nitrate was added, and a pale-yellow precipitate was formed. When concentrated aqueous ammonia was then added, this precipitate partly dissolved leaving a darker yellow precipitate.
What could the powder be?
A sodium bromide only
B sodium iodide only
C a mixture of sodium chloride and sodium bromide
D a mixture of sodium chloride and sodium iodide

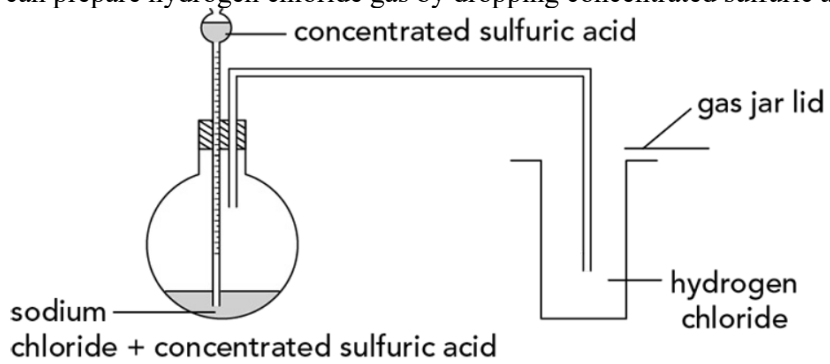
4. The colours of the silver halides AgCl, AgBr and AgI differ.
The solubilities of these halides in aqueous ammonia also differ.
Which row is correct?

1	colour of AgBr	silver halide that is most soluble in $NH_3(aq)$
A	cream	AgCl
B	cream	AgI
C	yellow	AgCl
D	yellow	AgI

Concentrated sulfuric acid concentrated sulfuric acid

Compounds that contain Cl^-, Br^- or I^- ions will react with concentrated sulfuric acid. All of these reactions produce one or more toxic gases.

We can prepare hydrogen chloride gas by dropping concentrated sulfuric acid slowly onto crystals of sodium chloride:



The reaction that takes place is:
$NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$
The hydrogen chloride (HCl) gas produced is visible as white fumes. However, we cannot use the same reaction to prepare samples of pure hydrogen bromide or hydrogen iodide. We saw in Section 12.2 how it gets increasingly easy to decompose the hydrogen halides going down the group. When the hydrogen halides decompose into their elements, the halide part of the molecule in HBr and HI is oxidised. Concentrated sulfuric acid is a relatively strong oxidising agent. It is not strong enough to oxidise HCl, but concentrated sulfuric acid will oxidise and decompose HBr and HI. So, any HBr or HI formed in the reaction between sodium bromide, or sodium iodide, and concentrated sulfuric acid undergoes further oxidation.
With sodium **bromide,** hydrogen bromide is produced in the initial reaction:
$NaBr(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HBr(g)$

This is followed by oxidation of HBr(g). The sulfuric acid itself is reduced to sulfur dioxide gas as it oxidises the HBr formed:

$2HBr(g) + H_2SO_4(l) \rightarrow Br_2(g) + SO_2(g) + 2H_2O(l)$

A reddish brown gas is seen. This is the element bromine, Br_2.

With sodium **iodide,** the sulfuric acid is reduced to several sulfur products as it oxidises the hydrogen iodide formed to different extents. The products of the oxidation of HI are sulfur dioxide, sulfur and hydrogen sulfide, as shown in the reactions below:

$NaI(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HI(g)$

followed by oxidation of HI(g):

$2HI(g) + H_2SO_4(l) \rightarrow I_2(g) + SO_2(g) + 2H_2O(l)$

and:

$6HI(g) + H_2SO_4(l) \rightarrow 3I_2(g) + S(s) + 4H_2O(l)$

and:

$8HI(g) + H_2SO_4(l) \rightarrow 4I_2(g) + H_2S(g) + 4H_2O(l)$

Several observations can be made here:
sulfur is seen as a yellow solid
hydrogen sulfide has a strong smell of bad eggs
iodine is produced as a violet / purple vapour.

5. The halide ions react easily with concentrated H_2SO_4.
The main sulfur-containing product of each reaction is shown in the table.

halide ion	Cl^-	Br^-	I^-
main sulfur-containing product of reaction with concentrated H_2SO_4	HSO_4^-	SO_2	H_2S
oxidation number of sulfur			

(i) Complete the table to show the oxidation number of sulfur in each of the sulfur-containing products. [1]

(ii) Explain why different sulfur-containing products are produced when each of these halide ions reacts with concentrated H_2SO_4. [1]

6. Hydrogen chloride gas is made in the laboratory by adding concentrated sulfuric acid to potassium chloride.

(i) Construct an equation for this reaction. [1]

(ii) Explain why hydrogen iodide is **not** prepared by adding concentrated sulfuric acid to sodium iodide. [2]

7. HCl(g) is prepared by adding NaCl(s) to concentrated H_2SO_4.
HI(g) is **not** prepared by adding NaI(s) to concentrated H_2SO_4 because the HI(g) produced also reacts with concentrated H_2SO_4.

(i) Identify the type of reaction that occurs when NaI(s) reacts with concentrated H_2SO_4 to form HI(g). [1]

(ii) Write an equation for the reaction of H**I**(g) and concentrated H_2SO_4. [1]

(iii) Explain why H**I**(g) reacts with concentrated H_2SO_4 whereas HCl does not. [1]

8. NaC*l* reacts with concentrated H_2SO_4 to form HC*l* and $NaHSO_4$. Explain the difference between the reactions of concentrated H_2SO_4 with NaC*l* and with NaI. Your answer should refer to the role of the sulfuric acid in each reaction. [3]

9. Concentrated sulfuric acid is added to separate samples containing equal amounts of NaC*l* , NaBr and NaI. All three samples initially react to produce the hydrogen halide.

(i) Write an equation to describe the acid–base reaction that occurs when concentrated sulfuric acid reacts with NaBr. [1]

(ii) Deduce which sodium halide, NaC*l* , NaBr or NaI, produces the largest percentage yield of hydrogen halide when concentrated sulfuric acid is added. Explain your answer by considering the relative reactivity of the halide ions as reducing agents. [3]

5. Which statement about Group 17 elements and compounds is correct?
   A Sodium chloride produces chlorine when reacted with concentrated sulfuric acid.
   B Sodium chloride produces chlorine when reacted with bromine.
   C Sodium bromide produces bromine when reacted with concentrated sulfuric acid.
   D Sodium bromide produces bromine when reacted with iodine in aqueous potassium iodide.

6. The solids sodium chloride and sodium iodide both react with concentrated sulfuric acid at room temperature.
   With NaCl, the products are $NaHSO_4$ and HCl .
   With NaI, the products are $NaHSO_4$, HI, I_2, SO_2, H_2O, S and H_2S.
   What is the explanation for this difference in products?
   A Chloride ions will displace iodine from the solution.
   B Hydrogen chloride is more volatile than hydrogen iodide.
   C Iodide ions are better reducing agents than chloride ions.
   D Sulfuric acid is able to act as a dehydrating agent with NaI.

7. A solid sodium halide, NaX, is reacted with concentrated sulfuric acid. The lowest oxidation state of sulfur in the products is +4.
Halogen Y_2 is less volatile than halogen X_2.
What are the identities of sodium halide NaX and halogen Y_2?

	sodium halide NaX	halogen Y_2
A	sodium bromide	chlorine
B	sodium bromide	bromide
C	Sodium iodide	Bromine
D	Sodium iodide	astatine

8. In a series of nine experiments, to test the reactivity of the halogens, an aqueous solution of each halogen is added to an equal volume of an aqueous solution containing halide ions, as shown in the table.

Halogen solution	halide solution		
	sodium chloride (aq)	sodium bromide (aq)	sodium iodide (aq)
chlorine (aq) bromine (aq) iodine (aq)	experiment 1 experiment 4 experiment 7	experiment 2 experiment 5 experiment 8	experiment 3 experiment 6 experiment 9

The nine resulting mixtures are then shaken separately with an equal volume of hexane. The nine tubes are left to stand so that the aqueous and organic solvents separate into layers.
How many test-tubes contain a purple upper hexane layer?
A 1 **B** 2 **C** 3 **D** 5

10. Calcium chlorate(**I**), $Ca(C|O)_2$, is used as an alternative to sodium chlorate(**I**), NaC|O, in some household products.
The chlorate(**I**) ion is formed when cold aqueous sodium hydroxide reacts with chlorine. Write an ionic equation for this reaction. State symbols are **not** required. [1]

11. When K**I**(aq) is added to $CuSO_4$(aq) the blue-coloured solution turns brown and a white precipitate of Cu**I**(s) is seen.
The reaction between copper ions and iodide forms only two products.
(i) Complete the equation for this reaction.

.....Cu^{2+} + ...**I**– →.....Cu**I** + ... [1]

(ii) Identify the oxidising agent in this reaction. Explain your answer in terms of electron transfer. [1]

12. 1cm^3 of $MgCl_2$(aq) is placed in a test-tube. A few drops of $AgNO_3$(aq) are added, followed by1cm^3 of dilute NH_3(aq).
State in full what is observed in this experiment. [2]

13. When 1cm^3 of $MgCl_2$(aq) is added to 1cm^3 of Br_2(aq) in a test-tube, the solution remains orange. Explain this observation. [1]

9. Powder P is a mixture containing two of AgC*l*, AgBr or AgI.
P is shaken with dilute aqueous ammonia. A yellow solid, Q, remains.
The mixture is filtered and Q is washed and dried. The filtrate is collected and treated with aqueous nitric acid to produce a white precipitate, R, which is filtered off, washed and dried.
Q and R are warmed separately with concentrated sulfuric acid, H_2SO_4.
Which observations are made?

	R + concentrated H_2SO_4	Q + concentrated H_2SO_4
A	violet fumes	orange fumes
B	violet fumes	steamy fumes
C	steamy fumes	violet fumes
D	orange fumes	steamy fumes

10. J dissolves in water to give an aqueous solution K.
K gives a dense white precipitate when aqueous silver nitrate is added.
When heated with aqueous potassium hydroxide, K gives off a gas that turns moist universal indicator paper blue.
What is J?
A **ammonium chloride**
B **ammonium sulfate**
C **sodium chloride**
D **sodium hydroxide**

11. When concentrated sulfuric acid is added to solid sodium bromide, bromine gas is produced, along with a number of other products. However, when concentrated sulfuric acid is added to solid sodium chloride, only hydrogen chloride and sodium hydrogensulfate are produced.
What is the reason for this difference?
A Bromine is less volatile than chlorine.
B Hydrochloric acid is a weak acid.
C Sulfuric acid is **not** an oxidising agent.
D The bromide ion is a stronger reducing agent than the chloride ion.

14. The Group 17 elements form soluble halides with sodium.
Describe what is seen when dilute $AgNO_3(aq)$ is added to NaBr(aq) followed by aqueous ammonia. [1]

15. NaCl reacts with concentrated H_2SO_4 to form HCl and $NaHSO_4$.
When NaBr reacts with concentrated H_2SO_4, the products include Br_2 and SO_2.
Identify the type(s) of reaction that occur in each case by completing Table 3.1.
Explain the difference in these reactions. [3]

reactants	type(s) of reaction
NaCl and concentrated H_2SO_4	
NaBr and concentrated H_2SO_4	

16. Which statement relating to the elements in Group 17 and their compounds is correct?
A Bromine will reduce KI to form iodine.
B Iodide ions react to form a white precipitate when added to silver nitrate solution.
C Bromide ions react to form a white precipitate when added to silver nitrate solution.
D Chlorine reacts with hydrogen to form a colourless gas.

17. A Group 2 metal combines with bromine to form a crystalline solid, **M**Br_2. Excess aqueous $AgNO_3$ is added to a solution of **M**Br_2 and a precipitate forms. The mixture is filtered. The precipitate is dried and the mass of the precipitate is recorded.
(a) State the formula and colour of the precipitate. [2]

(b) Complete the equation to represent the reaction between **M**Br_2 and $AgNO_3$.

.....**M**Br_2 + ...$AgNO_3$ → ..... [1]

(c) A 0.250g sample of pure **M**Br_2 contains 8.415×10^{-4}mol **M**Br_2. Calculate the relative formula mass, $\mathbf{M}_r$, of **M**Br_2. Use this to identify **M**. Show your working.

$\mathbf{M}_r$= .....
M = ... [3]

(d) A sample of **M**Br_2 is dissolved in water. Chlorine gas is then bubbled into the solution.
(i) Describe the observations for this reaction. [1]

(ii) Name the type of reaction that occurs when **M**Br_2 reacts with chlorine gas. [1]

(e)Compound **Y** is a pure **insoluble** solid which contains halide ions.
A single reagent is added directly to compound **Y** to determine the halide ion present.
Identify the reagent added. State the observation which would confirm that **Y** contains bromide ions.

reagent .....

observation ..... [2]

18. A student does three tests on separate samples of NaC**l**(aq).
Complete Table 1.2 with the observations the student makes in each test.

Table 1.2

	test	observations
1	addition of a few drops of $Br_2(aq)$	
2	addition of a few drops of concentrated H_2SO_4	
3	addition of a few drops of dilute $AgNO_3(aq)$	

[3]

12. Solid sodium iodide reacts with concentrated sulfuric acid to form more than one product that contains sulfur.
What is the lowest oxidation number of sulfur in these products?
A –2 **B** 0 **C** +4 **D** +6

13. Which statement about Group 17 elements and compounds is correct?
A Sodium chloride produces chlorine when reacted with concentrated sulfuric acid.
B Sodium chloride produces chlorine when reacted with bromine.
C Sodium bromide produces bromine when reacted with concentrated sulfuric acid.
D Sodium bromide produces bromine when reacted with iodine in aqueous potassium iodide.

14. Which statement about the halogens or halide ions is correct?
A Bromide ions react to form a white precipitate when added to silver nitrate solution.
B Bromine does **not** oxidise chloride ions when added to sodium chloride solution.
C Fluorine atoms form cations by accepting electrons when they react.
D Chloride ions are stronger reducing agents than iodide ions.

15. When concentrated sulfuric acid is added to solid sodium chloride, HCl is formed but not Cl_2.
When concentrated sulfuric acid is added to solid sodium iodide, I_2 is formed.
Which statement explains these observations?
B Sulfuric acid is an oxidising agent and chloride ions are more easily oxidised than iodide ions.
A Sulfuric acid is an oxidising agent and iodide ions are more easily oxidised than chloride ions.
C Sulfuric acid is a reducing agent and chloride ions are more easily reduced than iodide ions.
D Sulfuric acid is a reducing agent and iodide ions are more easily reduced than chloride ions.

16. Which statement is correct?
A Hydrogen bromide reduces concentrated sulfuric acid to form sulfur dioxide gas.
B Hydrogen bromide decomposes at a higher temperature than hydrogen chloride.
C When hydrogen bromide gas is shaken with aqueous silver nitrate a yellow precipitate is formed.
D When hydrogen bromide gas is bubbled through aqueous iodine the solution becomes colourless.

17. Which row gives mixtures that both result in the oxidation of a halide ion?

	mixture 1	mixture 2
A	$AgNO_3$(aq) and NaCl(aq)	concentrated H_2SO_4(aq) and HI(aq)
B	Br_2(aq) and NaCl(aq)	concentrated H_2SO_4(aq) and HCl(aq)
C	Cl_2(aq) and NaBr(aq)	$CH_3CHBrCH_3$(l) + NaOH (ethanolic)
D	Br_2(aq) and NaI(aq)	concentrated H_2SO_4(aq) and NaBr(s)

18. The table shows statements about some of the properties of halogens and their compounds and explanations for these properties.
Which row shows a correct statement about the property and a correct explanation for the statement?

	statement	explanation
A	iodine is a solid at room temperature	the I–I bond strength is high
B	the decomposition of hydrogen iodide is more endothermic than the decomposition of hydrogen chloride	chlorine is more reactive than iodine
C	when chlorine is bubbled into aqueous potassium iodide, a purple solution is seen	chlorine is a stronger oxidising agent than iodine
D	when concentrated sulfuric acid is added to solid potassium iodide, a purple vapour is seen	iodide ions are being oxidised to iodine by the sulfuric acid