FACTFILE: GCE CHEMISTRY

HALOGENS

Rewarding Learning

Halogens

Students should be able to:

1.8.1 recall the colours of the elements and explain the trends within the Group, limited to physical state at room temperature, melting and boiling points;

1.8.2 compare the solubility and colours of the halogens in water and non-aqueous solvents, for example hexane;

1.8.3 describe the reaction of the halogens with cold dilute and hot concentrated aqueous sodium hydroxide and explain the disproportionation in these reactions;

1.8.4 recall the reaction of chlorine with water to form chloride ions and chlorate(I) ions;

1.8.5 describe the trend in oxidising ability of the halogens down the Group applied to displacement reactions of the halogens with other halide ions in solution;

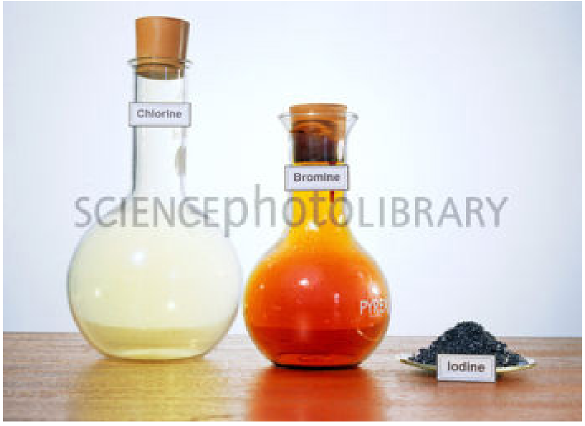
1.8.6 demonstrate understanding of the reaction of solid halides with concentrated sulfuric and phosphoric acid in relation to the relative reducing ability of the hydrogen halides/ halide ions;

1.8.7 compare the advantages and disadvantages of adding chlorine and ozone to drinking water.

The Halogens

The elements of Group VII of the Periodic Table are better known as the halogens. The halogens exist as covalently bonded diatomic molecules (ie F_2, Cl_2, Br_2, I_2). The non-polar molecules have weak van der Waals' forces between them, which increase in strength as the RMM of the molecule increases. This leads to a trend in physical state at room temperature moving from gas to liquid to solid as the Group is descended. Iodine vapour is violet/purple

Halogen	Colour	Physical state	Melting point/°C	Boiling point/°C
Fluorine	Yellow	Gas	-220	-188
Chlorine	Yellow-green/green-yellow/green	Gas	-101	-35
Bromine	Red-brown/ brown-red	Liquid	-7	59
Iodine	Grey-black/ black-grey	Solid	114	183



The halogens have a low solubility in water; they dissolve much more readily in non-polar solvents such as hexane which exhibit the same main intermolecular force, van der Waals' interactions. The halogens are the most reactive non-metals in the Periodic Table. For example, despite chlorine having a low solubility in water, it reacts with it over time producing a mixture of two acids: hydrochloric acid, HCl and chloric(I) acid, HClO which contains chlorate(I) ions.

$$Cl_2(g) + H_2O(l) \rightarrow HCl(aq) + HClO(aq)$$

The above reaction is an example of disproportionation as the chlorine is both oxidised to chloric(I) acid and reduced to hydrochloric acid.

Chlorine is added to drinking water to kill bacteria and make it safer to drink. The use of ozone, O_3, an allotrope of oxygen, is as an alternative to chlorine in water sterilisation.

	Colour in Water
Chlorine water	Green/colourless
Bromine water	Orange/yellow/ brown
Iodine solution (in polar solvents)	Brown/yellow
Iodine solution (in non-polar solvents)	Violet/purple

	advantatges	**disadvantages**
chlorine	• cost effective • Provides residual protection as it is still present in water when it reaches the consumer • More soluble in water	• gives drinking water an unpleasant taste and smell • Chlorine is toxic to humans except in very small doses, care must be taken not to over-chlorinate the water supply • does not kill some microorganisms
ozone	• More effective at killing bacteria • It reacts with natural organic matter far better than chlorine does and removes it from water • The breakdown product is oxygen and there are no residual chemicals left so no smell or taste to the water	• Higher costs • No residual protection against microorganisms • Less soluble in water than chlorine so requires special mixing techniques

Reaction with sodium hydroxide solution

With cold dilute sodium hydroxide solution

Sodium chlorate(I) is formed and a smell of bleach is noted.

$Cl_2(g) + 2NaOH(aq) \rightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$

With hot concentrated sodium hydroxide solution

The chlorine is oxidised further, to an oxidation state of +5 in sodium chlorate(V):

$3Cl_2(g) + 6NaOH(aq) \rightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$

Ionic equation: $3Cl_2(g) + 6OH^-(aq) \rightarrow 5\,Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$

Bromine will produce sodium bromate(I) in a reaction at 0 °C.
Iodine will produce sodium iodate(I) at 0 °C but it will decompose rapidly

Displacement reactions

The trend in reactivity of the halogens can be illustrated by observing their effectiveness as oxidising agents. The oxidising power of a halogen is a measure of the strength with which a halogen atom can gain an electron. The halogens decrease in reactivity down the Group as their oxidising ability decreasing. This is due to the increase in atomic radius and shielding which results in a decreased attraction between the incoming electron and the atomic nucleus.

The decrease in reactivity as the Group is descended can be demonstrated by displacement reactions of aqueous halides using Cl_2, Br_2 and I_2.

Word equation: chlorine + sodium bromide → sodium chloride + bromine

Symbol equation: $Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2$

Ionic equation: $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$

Observation: the solution changes from colourless (NaBr) to orange (due to aqueous bromine)

Word equation: chlorine + potassium iodide → iodine + potassium chloride

Ionic equation: $Cl_2 + 2KI \rightarrow I_2 + 2KCl$

$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$

Observation: the solution changes from colourless (NaI) to brown (due to aqueous iodine)

Bromine oxidises iodide only:

Ionic equation: $Br_2 + 2I^- \rightarrow I_2 + 2Br^-$

Observation: the solution changes from colourless (NaI) to brown (due to aqueous iodine)
Iodine does not oxidise chloride or bromide.

Halide ions as reducing agents

The halide ions can act as reducing agents and the trend can be demonstrated in the reaction between solid halide salts and concentrated sulfuric acid. The strength of the reducing power of the HALIDE IONS INCREASES down the group.

Both sodium fluoride and sodium chloride react with concentrated sulfuric acid to form the respective hydrogen halides, hydrogen fluoride and hydrogen chloride. These gases are observed as steamy/misty fumes.

$NaF(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HF(g)$

$NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$

These reactions are classed as acid-base reactions; HF or HCl are not sufficiently strong reducing agents to reduce the sulfuric acid and so no redox reactions take place.

Bromide ions are stronger reducing agents than chloride and fluoride and after the initial acid-base reaction the bromide ions reduce the sulfur in H_2SO_4 from an oxidation state of +6 to +4 in sulfur dioxide, SO_2.

$NaBr(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HBr(g)$
acid–base reaction

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

Observations include: misty/steamy fumes of HBr, red-brown vapour of Br_2

Iodide ions are the strongest halide reducing agents. They can reduce the sulfur in H_2SO_4 from an oxidation state of +6 to +4 in SO_2, to 0 in S and -2 in H_2S. In addition to the acid-base reaction, there are three possible redox reactions:

$NaI(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HI(g)$
acid–base reaction

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

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

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

Observations include: steamy /misty fumes of HI, grey-black solid on sides of test-tube and purple/violet vapour of iodine, the yellow solid sulfur and H_2S, a gas with a rotten egg smell.

Only the acid-base reaction occurs with halide salts and concentrated phosphoric acid as phosphoric acid does not act as an oxidising agent.

$NaCl(s) + H_3PO_4(l) \rightarrow NaH_2PO_4(s) + HCl(g)$

$NaBr(s) + H_3PO_4(l) \rightarrow NaH_2PO_4(s) + HBr(g)$

$NaI(s) + H_3PO_4(l) \rightarrow NaH_2PO_4(s) + HI(g)$

Misty/steamy fumes of the hydrogen halide would be observed in each reaction.

Revision Questions

1 Which one of the following lists the colour of solid iodine and of iodine dissolved in the solvent stated?

	Solid	Water	Hexane
A	grey-black	purple	yellow/brown
B	dark purple	yellow/brown	purple
C	yellow/brown	grey-black	yellow/brown
D	grey-black	yellow/brown	purple

2 An experiment was set up to investigate the displacement reactions of the halogens.

Solutions of sodium halides were prepared and reacted with other halogens.
The results table is shown below.

	sodium iodide (aq)	sodium bromide (aq)	sodium chloride (aq)
iodine solution		X	X
bromine solution			
chlorine solution	✓		

✓ means that a reaction took place

X means that no reaction took place

a) Complete the **three** remaining places in the table. [2]

b) (i) Both bromine and iodine solutions are coloured. Describe the observations which would indicate a reaction took place when aqueous sodium iodide is added to a bromine solution.

....

....

.... [2]

(ii) Write the ionic equation for the reaction between bromine solution and aqueous sodium iodide.

.... [1]

c) (i) Describe what is observed when chlorine solution is added to aqueous sodium bromide.

....

.... [2]

(ii) Write the equation for the reaction between chlorine solution and aqueous sodium bromide.

.... [1]

3 The halogens form Group VII of Periodic Table.

a) The table below gives some of the physical properties of the halogens.

Element	Atomic radius (nm)	Boiling point (^oC)	Electronegativity value	First ionisation energy ($kJmol^{-1}$)
Fluorine	0.133	-187	4.0	1618
Chlorine	0.181	-35	3.0	1256
Bromine	0.196	59	2.8	1143
Iodine	0.219	183	2.0	1009

(i) Explain why the atomic radii of the halogens increase as the Group is descended.

....

.... [1]

(ii) Explain the trend in the boiling points of the halogens.

....

.... [2]

(iii) Explain what is meant by the term **electronegativity**.

....

.... [1]

(iv) Explain the trend in electronegativity values of the halogens.

....

....

.... [2]

(v) Write and equation, including state symbols, for the first ionisation energy of fluorine.

.... [1]

(vi) Explain the trend in the ionisation energy of the halogens.

....

....

.... [2]

b) Chlorine is used to sterilise water.

(i) Write an equation for the reaction of chlorine with water.

.... [1]

(ii) Using changes in oxidation number explain why this is considered to be a disproportionation reaction.

....

....

.... [3]

4 Solid samples of sodium chloride, sodium bromide and sodium iodide can be distinguished using concentrated sulfuric acid.

a) (i) Write an equation for the reaction of sodium chloride with concentrated sulfuric acid.

.... [2]

(ii) Balance the following half-equation for the reduction of concentrated sulfuric acid to form hydrogen sulfide.

$$H_2SO_4 \; + \; H^+ \; + \qquad\qquad \rightarrow \; H_2S \; + \; H_2O$$

[2]

(iii) Combine the reduction half-equation in **(a)(ii)** with the following oxidation half-equation to produce a balanced redox equation.

$$2I^- \rightarrow I_2 + 2e^-$$

.... [2]

(iv) Give **one** observation which indicates the formation of hydrogen sulfide.

.... [1]

(v) Name **two** other reduction products which are formed when concentrated sulfuric acid is added to sodium iodide.

....

....

.... [2]

(vi) Suggest why iodide ions are stronger reducing agents than chloride ions.

....

....

.... [2]

5 Which one of the following increases as Group VII is descended?

A Atomic radius
B Electronegativity
C First ionisation energy
D Reactivity