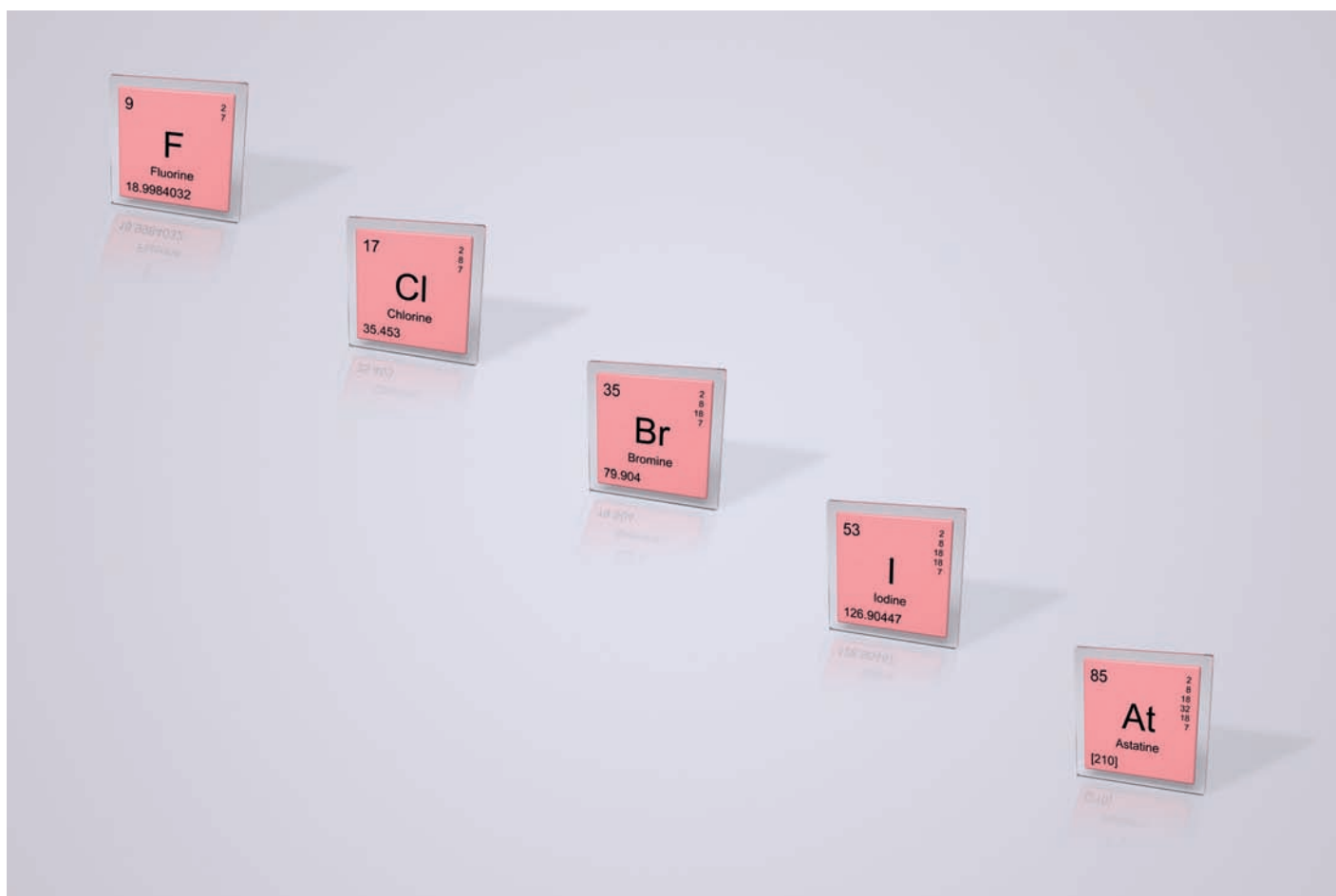


Halogens

Student Notes



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Activity 1: Silver halides

Insoluble silver halides form as precipitates when solutions of silver salts are added to solutions containing halide ions.

The silver chloride, bromide and iodide can be distinguished by their colours and their solubility in ammonia solution, providing tests for these halide ions in solution.

The use of silver halides in film photography is illustrated by the effect of light on the precipitates.

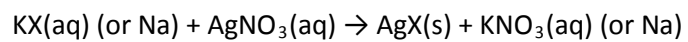
Procedure

You will be provided with 3 potassium (or sodium) halide solutions

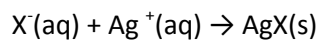
- a Pour about 3 cm³ of each of the halide solutions into separate test-tubes.
- b Add a few drops of silver nitrate solution to the test-tube containing potassium chloride solution. A white precipitate of silver chloride forms.
- c Add a few drops of silver nitrate solution to potassium bromide solution. A cream or off-white coloured precipitate of silver bromide forms.
- d Add a few drops of silver nitrate solution to potassium iodide solution. A yellow precipitate of silver iodide forms.
- e Pour half the contents of the three test-tubes into another three labelled test-tubes.
- f Place one set of three test-tubes in a cupboard and the other set in bright light, such as on a window sill, and leave for 5–10 mins. In bright light, the silver chloride darkens quickly, the silver bromide more slowly, and the silver iodide is not affected at all. Compare with the solutions kept in the dark.
- g–j Use ammonia solution to distinguish between the silver halides.
 - g Prepare fresh samples of the silver halide precipitates as above, a–d.
 - h Slowly add an equal volume of *dilute* ammonia solution to the test-tube containing silver chloride using a teat pipette. Shake well after each addition to mix the contents. The precipitate dissolves, giving a colourless solution.
 - i Add an equal volume of *dilute* ammonia solution to the test-tube containing silver bromide. Shake to mix. The precipitate does not dissolve. Now add concentrated ammonia solution to almost fill the test-tube, stopper the tube and invert to mix. Most of the precipitate dissolves.
 - j Add an excess of *concentrated* ammonia solution to the test-tube containing silver iodide, stopper and invert to mix. The precipitate does not dissolve.

Notes

These precipitation reactions can be represented by the following equations, where X = Cl, Br or I:



or the general ionic equations:



Activity 2: Reactions of aqueous solutions of the halogens

This activity compares the colours of three halogens in aqueous solution and in a non-polar solvent. These halogens also react to a small extent with water, forming acidic solutions with bleaching properties.

Halogens undergo redox reactions with metal halides in solution, displacing less reactive halogens from their compounds. These displacement reactions are used to establish an order of reactivity down Group 7 of the Periodic Table.

Procedure

HEALTH & SAFETY: Wear eye protection

The halogens in water and a hydrocarbon solvent

a Pour about 2 cm³ of each of the aqueous halogen solutions into separate test-tubes. Add equal volumes of hydrocarbon solvent to each tube, stopper the tube and, holding your thumb over the bung, shake the mixture by inverting the test-tube a few times.

b Allow the two layers to settle. Observe and record the colour of each layer. It may be necessary to shake the test-tubes again to transfer more of the halogen from the water to the hydrocarbon layer.

c What does this tell you about the solubility of the halogens in the different solvents. What is the difference between the solvents.

Acidic and bleaching properties of halogen solutions

a Place a piece of Universal Indicator paper on a white tile. Transfer a drop of chlorine water onto the paper using a glass rod. Observe and record the colour(s) of the paper. Explain what you see – think about the species present.

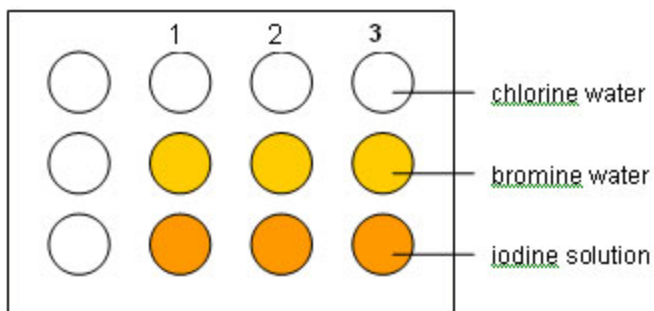
b Wipe the glass rod and the tile clean with a paper towel or tissue. Place a fresh piece of indicator paper on the tile and transfer a drop of bromine water onto it using the glass rod. Observe the colour of the paper.

c Repeat **b**, using the iodine solution.

d Is there a common theme or are there differences between the halogens.

Displacement reactions

a Using a plastic pipette put two drops of chlorine solution in each of three dimples in the spotting tile, as shown below. In the same way and using a clean plastic pipette for each solution, add bromine water, and iodine solution to the spotting tile.



b Add two drops of potassium chloride solution to each of the three dimples in column 1 of the tile. Observe and record any colour changes that take place.

c Add two drops of potassium bromide solution to each of the three dimples in column 2 of the tile. Observe and record any colour changes that take place.

d Add two drops of potassium iodide solution to each of the three dimples in column 3 of the tile. Observe and record any colour changes that take place.

e For reactions in which bromine or iodine are suspected to have formed, the reaction could be repeated with 2 cm³ of each solution in a test tube, and hexane could then be added to confirm the presence of bromine or iodine.

f Decide upon a series of reactivity for Group 7.

Activity 4: Acidic and bleaching properties of halogen solutions

These halogens also react to a small extent with water, forming acidic solutions with bleaching properties.

Procedure

Wear eye protection

- a) Place a piece of Universal Indicator paper on a white tile. Transfer a drop of chlorine water onto the paper using a glass rod. Observe and record the colour of the paper.
- b) Wipe the glass rod and the tile clean with a paper towel or tissue. Place a fresh piece of indicator paper on the tile and transfer a drop of bromine water onto it using the glass rod. Observe the colour of the paper.
- c) Repeat b, using the iodine solution.

Results

1. Using the results of the experiment with chlorine water explain your observations.
2. Compare the results for all the solutions and explain the differences.

Activity 5: Which bleach is the most cost effective?

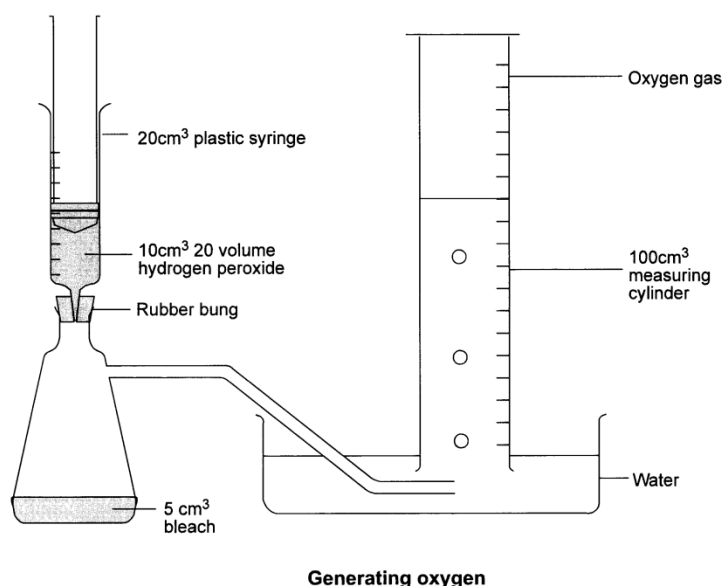
You are the scientist working for a consumer magazine. This month they are investigating chlorine-containing bleaches. Different domestic bleaches contain different amounts of chlorine. This is not necessarily reflected in the price. This practical will help to determine which is the most cost effective product. Excess hydrogen peroxide is added to household bleach and the volume of oxygen produced is measured. The concentration of sodium chlorate(I) in the bleach can be calculated.

The procedure

Use the pipette to measure 5 cm^3 of household bleach into the flask and replace the bung. Fill the syringe with 10 cm^3 of 20 volume hydrogen peroxide and fit its nozzle into the rubber bung. Fill the measuring cylinder with water. Squirt the peroxide into the bleach. The solutions will react and oxygen will be given off and collected in the measuring cylinder. Shake to ensure complete mixing and take a reading of the volume of the gas collected when gas has stopped being given off.

Repeat for each bleach.

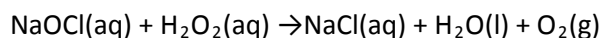
Calculate the percentage of sodium chlorate(I) in the bleach.



Write a report for the 'Consumer Watch-dog' magazine, giving the results, explaining the methodology of the tests and ultimately which is the most cost effective bleach.

Theory

The active ingredient of household bleach is sodium chlorate(I) (sodium hypochlorite). This reacts with hydrogen peroxide:



So one mole of oxygen is equivalent to one mole (74.5 g) of sodium hypochlorite and the percentage of sodium hypochlorite in the original bleach solution can be calculated as follows:

If the total volume of gas in the measuring cylinder is $V \text{ cm}^3$, then the volume of oxygen produced will be $V-10 \text{ cm}^3$ because the hydrogen peroxide will displace 10 cm^3 of air. At room temperature this is approximately $(V-10)/24\,000$ mole. So 5 cm^3 of bleach solution contained $(V-10)/24\,000$ mole of sodium hypochlorite which is $[(V-10)/24\,000] \times 74.5 \text{ g}$. So in 100 cm^3 of solution there would be $20 \times [(V-10)/24\,000] \times 74.5$, ie $0.062(V-10) \%$ sodium hypochlorite.

So normal household bleach (concentration of less than 5 %) should give a maximum of 90 cm^3 of gas in total. The density of bleach is about 1.2 g cm^{-3} so the w/v percentage could be converted into w/w if required.

Activity 6: Extracting iodine from seaweed

Ribbon seaweeds (sp. laminaria) contain iodine compounds which they obtain by extracting iodide ions from seawater. This iodine can be extracted from the seaweed by heating it in air to an ash, in which the iodine is present as iodide. The iodide is dissolved out of the residue by boiling water, the solution filtered and the iodide oxidised to iodine using hydrogen peroxide. The iodine colours the solution brown at this stage. Isolating the iodine from this solution can be done by solvent extraction, followed by evaporation of the solvent.

Apparatus and chemicals

Each practical will require:

Eye protection

Access to fume cupboard

Beakers (250 cm³), 2

Beaker tongs

Filter funnel

Filter paper

Evaporating basin (75 cm³ or similar)

Separating funnel (100 cm³)

Bunsen burner and tripod

Heat resistant mat

Large tin lid (size to fit across the top of the tripod)

Hydrogen peroxide solution, '20 volume' (about 1.6 mol dm⁻³) (**Irritant** at this concentration), 10 cm³

Cyclohexane (**Highly flammable, Harmful, Dangerous for environment**), about 20 cm³

Distilled or deionised water

Sulfuric acid, 1 mol dm⁻³ (**Irritant** at this concentration), 5 cm³

Kelp or ribbon seaweed (Laminaria)

Procedure

HEALTH & SAFETY: Carry out the first stage in a fume cupboard. Wear eye protection.

a Pile the seaweed up on the tin lid supported on a tripod and begin heating with a strong Bunsen flame. It may have to be added a portion at a time during the heating, given the quantity to be reduced to ash. When all has been turned to ash, about a dessertspoonful of residue will remain.

b Boil the ash with about 20 cm³ of purified water in a beaker, and filter while hot. Collect the clear filtrate in a second beaker and allow to cool.

c Turn off the Bunsen burner.

d Add about 2 cm³ of dilute sulfuric acid to the solution, followed by hydrogen peroxide solution. A deep brown colour of iodine is formed as hydrogen peroxide oxidises the iodide ions present to iodine.

e Transfer the mixture to a separating funnel and add 10 - 20 cm³ of cyclohexane. Stopper the separating funnel, secure it with your thumb, and shake vigorously for about 30 s. With the separating funnel inverted, release any pressure that has built up by opening the tap briefly.

f Clamp the funnel and allow the layers to separate. The cyclohexane will form a layer on top of the aqueous layer, and be coloured purple by the iodine now dissolved in it.

g Run off the lower aqueous layer and discard down the sink with running water.

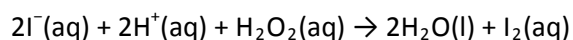
Notes

The seaweed contains a wide range of elements drawn from sea-water by the living algae, giving concentrations in the organism that may be considerably higher than in sea-water itself. In the past, this natural concentration of useful elements, for which there was then no other economic source, gave rise to a large scale 'cottage industry' network around the west coasts of Britain and Ireland, employing thousands in gathering and burning the kelp on the shore. The story of these past times can be used to enliven the waiting times at the different stages of the demonstration – see **Weblinks** below.

The two principal products were soda ash (sodium carbonate) for the alkali industry in the 18th and early 19th centuries, and iodine in the later nineteenth century. Kelp was also used, and still is, as an excellent fertiliser. Soda ash production from kelp ceased when the chemical industry itself found ways of producing sodium carbonate from sodium chloride, and iodine production from kelp ceased when the extraction of iodine from Chile saltpetre became dominant. In both events, thousands were put out of work, leading to large numbers emigrating from Scotland and Ireland to America and elsewhere. Nowadays, a small-scale industry continues, providing the raw material for expensive kelp-derived health supplements containing several 'essential minerals' including iodine. A typical kelp capsule may contain 0.1% iodine. The main kelp product at present, though, is for alginates used in food and drink, cosmetics and dozens of other everyday products.

Burning the kelp converts the iodine compounds in the kelp into iodide anions. Bromide and chloride ions are also present. The cations in the ash include sodium and potassium, so the leached solution in effect contains sodium and potassium halides.

Adding hydrogen peroxide in acid solution preferentially oxidises the iodide anions to iodine:



Although iodine is sparingly soluble in water, it is much more soluble in the presence of more iodide ions, and the brown colour is due to this effect, though some of the iodine may be present as a dark brown precipitate.

On shaking the aqueous mixture with cyclohexane iodine, being much more soluble in organic solvents than in water, passes mainly into the cyclohexane. The change to a purple colour shows that the iodine is now present as iodine molecules, I₂.

When the cyclohexane evaporates at room temperature, the less volatile iodine is left behind and forms shiny black crystals in the evaporating basin. Solid iodine sublimes, so in time the iodine would also evaporate if not kept in the closed container.

Web Links

There is a wealth of information available on the internet as background to this experiment. Just a small sample of these sites is given below

For biological background on kelp:

<http://www.pznw.co.uk/marine/kelp.html>

For background information on the chemistry of iodine, and its historical discovery:

<http://en.wikipedia.org/wiki/Iodine>

For historical details of kelp-burning communities, try:

<http://www.orkneyjar.com/tradition/kelpburning.htm>

Activity 7: Extension question

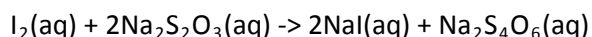
This question is about Iodine Number

This old method for determining the degree of unsaturation in a fat or oil is still used by most students following a food science course. You are asked to process the following experimental results.

Iodine monochloride is used to determine the degree of unsaturation in oils. The iodine monochloride adds rapidly to the carbon-carbon double bonds present. In an experiment, 0.127g of an unsaturated oil was treated with 25.00 cm³ of 0.100 mol dm⁻³ iodine monochloride solution. The mixture was kept in the dark until the reaction was complete. The unreacted iodine monochloride was then treated with an excess of aqueous potassium iodide, forming iodine.

The liberated iodine was found to react with 40.00 cm³ of 0.100 mol dm⁻³ sodium thiosulfate.

- (i) Suggest why it is necessary to keep the mixture of oil and iodine monochloride in the dark. (1)
- (ii) Write an equation for the reaction between iodine monochloride and potassium iodide. (1)
- (iii) Calculate the number of moles of sodium thiosulfate which were used in the titration. (1)
- (iv) Calculate the number of moles of iodine liberated, given that iodine reacts with sodium thiosulfate according to the equation:



Hence calculate the number of moles of unreacted iodine monochloride. (1)

- (v) Calculate the number of moles of iodine monochloride that reacted with the unsaturated oil. (1)

Direct addition of iodine to an unsaturated oil is slower than the addition of iodine monochloride.

However, unsaturation is quoted as the iodine number. The iodine number is the number of grammes of iodine that in theory can be added to 100 g of oil.

- (vi) Calculate the iodine number of this oil, given that one mole of iodine monochloride is equivalent to one mole of iodine molecules. (1)

Glossary

Diatomic	A molecule consisting of two identical atoms.
Displacement	Where a more reactive element displaces a less reactive one from a solution of its salts.
Electronegativity	The ability of an atom to attract the bonding electron pair in a covalent bond.
Oxidation	Loss of electrons.
Precipitate	A solid formed by the reaction of two substances in solution.
Reduction	Gain of electrons.

Royal Society of Chemistry
Education Department

Registered Charity Number: 207890

Burlington House
Piccadilly, London
W1J 0BA, UK
Tel: +44 (0)20 7437 8656
Fax: +44 (0)20 7734 1227

Thomas Graham House
Science Park, Milton Road
Cambridge, CB4 0WF, UK
Tel: +44 (0)1223 420066
Fax: +44 (0)1223 423623

Email: education@rsc.org
www.rsc.org/education

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