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.

Lesson organisation

This series of simple experiments illustrates some of the chemical properties of the halogens following an introduction to the physical properties of the Group 7 elements. It can be done as a demonstration or as a class experiment.

Investigating the solubility of the halogens in a non-polar solvent can be left out, or only shown as a demonstration.

If the activity is done as a demonstration it should take around 15 minutes. If it is done as a class experiment you should allow 30 minutes.

Apparatus and chemicals

Eye protection

One demonstration or one group of students requires:
Test-tube rack, to hold 10 test-tubes
Test-tubes, 10
Cork or rubber bungs to fit, 4
Plastic dropping pipettes, 6
White spotting tile
White tile
Glass rod
Paper towel or tissue
Universal Indicator paper (about 2 cm strips), 3

About 10 cm³ of each of the following halogen solutions in stoppered test-tubes (see notes 1 and 2):
- Chlorine water, 0.1% (w/v) (The gas is Toxic, Irritant, Dangerous for the environment but the solution is Low Hazard)
- Bromine water, 0.3% (w/v) (Toxic, Irritant, Dangerous for the environment at this concentration)
- Iodine solution, 0.5% (w/v) (Dangerous for the environment at this concentration)

Half a test-tube of each of the following solutions (see note 3):
- Potassium (or sodium) chloride solution, about 0.1 mol dm⁻³ (Low hazard)
- Potassium (or sodium) bromide solution, about 0.1 mol dm⁻³ (Low hazard)
- Potassium (or sodium) iodide solution, about 0.1 mol dm⁻³ (Low hazard)

Optional:
- Cyclohexane (Highly flammable, Harmful, Danger for the Environment) or other suitable non-polar solvent, about 10 cm³ (see note 1)
Technical notes

Chlorine water (Chlorine gas escapes, which is Toxic, Irritant, Dangerous for the environment but the solution is Low Hazard at the concentration used) Refer to CLEAPSS® Hazcard 22B, Recipe card 28
Bromine water (Toxic, Irritant, Dangerous for the environment at concentration used) Refer to CLEAPSS® Hazcard 15B, Recipe card 28
Iodine solution (Dangerous to the environment at concentration used) Refer to CLEAPSS® Hazcard 54, Recipe card 39
Potassium chloride solution (Low hazard) Refer to CLEAPSS® Hazcard 47B, Recipe card 51
Sodium chloride solution (Low hazard) Refer to CLEAPSS® Hazcard 47B, Recipe card 63
Potassium iodide solution (Low hazard) Refer to CLEAPSS® Hazcard 47B, Recipe card 55
Cyclohexane (Highly flammable, Harmful, Danger for the Environment) Refer to CLEAPSS® Hazcard 45B

1. Each group of students should be supplied with stoppered test-tubes containing about 10 cm³ of each of the aqueous solutions of the halogens and one of cyclohexane (optional).
2. The halogen solutions can be diluted further to minimise the amount of chlorine or bromine fumes given off but should not be so dilute that their distinctive colours are not clearly visible in the test-tubes (a white background may be needed for chlorine water).
3. The concentration of the potassium (or sodium) iodide should be adjusted so that it gives a light brown solution on adding the chlorine water. If these reagents are too concentrated, a black precipitate of iodine often results instead of a brown solution.
4. At the end of the experiments all mixtures and solutions should be returned to a suitable waste container in a fume cupboard for safe disposal.
5. It is essential for the acidity test that the chlorine water is just that. Some samples of ‘chlorine water’ that can be purchased from suppliers are actually chlorine in sodium hydroxide solution: this can give unexpected results in the test for pH.

Procedure

HEALTH & SAFETY: Wear eye protection

The halogens in water and a hydrocarbon solvent (optional)

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.

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 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.
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 (Optional) 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.

Teaching notes

A results table similar to the one below could be used for the recording of results. It has been completed with expected observations.

<table>
<thead>
<tr>
<th>Colour after shaking with hydrocarbon solvent</th>
<th>Effect on indicator paper</th>
<th>Reaction with potassium chloride solution</th>
<th>Reaction with potassium bromide solution</th>
<th>Reaction with potassium iodide solution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chlorine water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aqueous layer: pale yellow-green</td>
<td></td>
<td>Turns red, then rapidly bleaches white</td>
<td>No reaction</td>
<td>Yellow-orange colour of bromine appears</td>
</tr>
<tr>
<td>Hydrocarbon layer: colourless</td>
<td></td>
<td></td>
<td></td>
<td>Brown colour of iodine appears</td>
</tr>
<tr>
<td><strong>Bromine water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aqueous layer: yellow-orange</td>
<td></td>
<td>Turns red, then slowly bleaches white</td>
<td>No reaction</td>
<td>No reaction</td>
</tr>
<tr>
<td>Hydrocarbon layer: colourless</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Iodine solution</strong></td>
<td>Paper stained brown</td>
<td>No reaction</td>
<td>No reaction</td>
<td>No reaction</td>
</tr>
<tr>
<td>Aqueous layer: brown to colourless</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrocarbon layer: colourless</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>chlorine water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>bromine water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>iodine solution</strong></td>
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</tr>
</tbody>
</table>
The halogens are more soluble in the hydrocarbon and move to this top layer, when shaken with a hydrocarbon solvent. For chlorine and bromine the colour does not change. You might need a white background to see the colour of the chlorine solution. However, for iodine there is a colour change, from brown in water to purple in the hydrocarbon layer.

Where no displacement reaction takes place between a halogen solution and a halide solution, it may be that some lightening in the colour of the solution is observed and this can be explained by the effect of dilution.

Take care to limit students' exposure to chlorine and bromine water fumes. Some students with respiratory problems can show an allergic reaction to chlorine, the onset of which may be delayed.

Iodine is the least soluble of the halogens in water. It is more soluble in potassium iodide solution, so the 'iodine solution' here is actually iodine in potassium iodide solution.

Draw the students' attention to the similarity between the colour of iodine vapour and its colour in a non-polar solvent. Polar water molecules interact with iodine molecules, altering the wavelengths of light they absorb.

All three halogens react with water to produce a strong acid (HX), and a weak acid (HOX), which has bleaching properties and is an oxidising agent.

\[
X_2(aq) + H_2O(l) \rightarrow HX(aq) + HOX(aq)
\]

The extent of reaction decreases down the Group. With iodine it is so small that the acidic and bleaching properties of the solution are not seen in this experiment.

In the displacement reactions chlorine displaces both bromine and iodine from their compounds and bromine displaces iodine – for example:

\[
Cl_2(aq) + 2KI(aq) \rightarrow I_2(aq) + 2KCl(aq)
\]

The order of reactivity is therefore chlorine > bromine > iodine. A more advanced treatment identifies the halogens as oxidising agents, accepting an electron to form halide ions:

\[
Cl_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Cl^-(aq)
\]

Contrary to belief among many students, the reaction has nothing to do with the reactivity of potassium 'grabbing' the chlorine. Potassium is only present here as very unreactive potassium ions in solution!

Reference

This experiment has been reproduced from Practical Chemistry: