Ri Christmas Lectures® 2012: The Modern Alchemist

Teaching Resource - Group 7(17) The Halogens

Overview:

This resource contains information regarding Group 7(17) of the Periodic Table - The Halogens. Included is an overview of the elements that make up the group, and their structure, general reactivity, and specific examples of their reactions. The resource is supported by links to useful materials, and video clips from the 2012 Christmas Lectures®.

What Are the Halogens?

The Halogens are group 7 (or in a long form periodic table, 17) of the periodic table. The name 'Halogen' literally means 'salt-former' (why will become clear during the resource).

- Fluorine
    - Fluorine is a very pale yellow, strongly smelling, highly toxic, gas. Fluorine is one of the most respected (or feared) elements among chemists, and will react with almost every element in the periodic table (except Helium, Neon, and Argon).
- Chlorine
    - Chlorine as a pale green, strongly smelling, highly toxic, gas. Chlorine finds use as a disinfectant for drinking water, as well as its compounds being used in swimming pools, and as part of the popular cleaning agent bleach.
- Bromine
    - Bromine is a dark red, low boiling (toxic) liquid. At room temperature, bromine is in equilibrium with its gas, meaning if it is kept in a sealed container, the vapour should be visible. Bromine is found in seawater, and its compounds have found use in pharmaceuticals, camera film, and insecticides.
- Iodine
    - Iodine is a silvery grey solid at room temperature, existing as individual crystals with defined faces (although it is usually supplied as powder). Iodine does not pass through a liquid phase under normal atmospheric pressure; instead it 'sublimes', turning straight from the solid into the gaseous phase. Iodine vapour has a strong purple colour, and if iodine crystals are heated gently, this can easily be seen (although the vapour is poisonous and choking, therefore inhalation should be avoided).

- Astatine
    - Astatine is highly radioactive, with the longest lived isotope having a half-life of 8 hours (See Teaching Resource - Radioactivity at the RSC Learn Chemistry Website for more information on Radioactivity). Due to its radioactivity and rarity, Astatine has very few uses. Its appearance is believed to be that of a dark (possibly black) solid.
- Ununseptium
    - Ununseptium is a relatively new addition to the Halogens, and was only reported in 2010. However, the existence of Ununseptium has yet to be confirmed by IUPAC (the governing body of international Chemistry). Despite this, it is believed that Ununseptium would be a highly radioactive metallic element.

Structure & Trends:

There are several interesting trends and similarities between the Halogens, these are better explained with consideration of the elements side by side. Some useful information about each halogen is provided in the table below.

Halogen	Electronic Configuration	Atomic Radius (pm)	Electronegativity (Pauling Scale)	First Ionisation Energy ($kJ\ mol^{-1}$)
Fluorine	[He] $2s^2$, $2p^5$	71	4.0	1681.045
Chlorine	[Ne]$3s^2$, $3p^5$	99	3.0	1251.185
Bromine	[Ar] $3d^{10}$, $4s^2$, $4p^5$	114	2.8	1139.858
Iodine	[Kr] $4d^{10}$, $5s^2$, $5p^5$	133	2.5	1008.393
Astatine	[Xe] $4f^{14}$, $5d^{10}$, $6s^2$, $6p^5$	150	2.2	930.118
Ununseptium	[Rn] $5f^{14}$, $6d^{10}$, $7s^2$, $7p^5$	Unknown	Unknown	Unknown

- Electronic Structure

  The Group 7 elements (the Halogens) are similar in that they all have seven outer electrons. This is just short of a full outer compliment of 8 (or 18 for periods 4 and 5, or 32 for periods 6 and 7). Therefore, the outermost electrons in any given halogen are contained within an np^7 configuration, where n is the appropriate energy level.

  Note, that if electron configurations are not considered, i.e. for GCSE students, then it is sufficient to know that each halogen contains 7 electrons in its outermost electron shell (as is suggested by the group number, 7).

- Atomic Radius

  As you go down the elements that make up group 7, you see that the atomic radii increase. Although extra protons are being added to the nucleus, each extra period adds a new electronic energy level (shell) to the atom which is fully populated. These shells reduce the attractive force from the nucleus that the outermost electrons experience, allowing them to move further from the nucleus, thus increasing the atomic radius. This effect is known as electronic 'shielding' and comes about due to differences in orbital penetration (more information is available here[1], although this is of a higher level than is required by the curriculum).

- Electronegativity and Ionisation Energies

  Electronegativity refers to the ability of a nucleus to attract the electrons in a chemical bond. Fluorine is the most electronegative element in the Periodic Table. The most commonly used measurement of electronegativity is the Pauling scale (as seen in the table above).

  As can be seen from the table above, the electronegativity of the Halogens decreases as you descend the group. This is due to the increased shielding effect of the extra electron shell which is added with each new period. This decreases the attractive effect of the nucleus on the outermost electrons, thus decreasing the amount of energy required to remove an electron.

  As can also be seen from the table above, the ionisation energies of the halogens decrease down the group. This is a practical manifestation of the decreased electronegativity and increased shielding effects as you descend group 7. This combination of effects makes it easier to remove an outer electron, thus decreasing the ionisation energy.

Reactivity:

As the halogens have seven outer electrons, they will react strongly in order to gain one more electron; this allows them to have a full compliment of eight outer electrons, and achieve a Noble Gas like electronic configuration.

- Molecular Structure

  Due to the desire to gain an extra electron, the halogens in their elemental state exist as diatomic molecules joined by a single covalent bond. This in effect allows them to complete their outer energy level by 'sharing' a pair of electrons.

- Displacement Reactions - Reactions with Metal Halides

  Due to the differences in electronegativity as you move down group 7, the higher halogens are stronger oxidising agents (they are more electronegative) - meaning they are able to oxidise the lower halogens.

  This property allows displacement reactions to take place between a halogen and a metal halide; where a more reactive halogen will displace a less reactive halogen.

  These reactions allow the order of reactivity within group 7 to be established fluorine > chlorine > bromine > iodine. Astatine and Ununseptium are (for obvious reasons) not tested using this method.

  Therefore, chlorine will oxidise bromide from sodium bromide, therefore being reduced itself, forming bromine, and sodium chloride.

[1] ChemWiki, UC Davis, http://chemwiki.ucdavis.edu/

$$Cl_2 + 2NaBr \rightarrow Br_2 + 2NaCl$$

Chlorine is reduced to Chloride (Cl^-), Bromide (Br^-) is oxidised to Bromine

Chlorine is acting as an oxidising agent, Bromide is acting as a reducing agent

Video Clip - Displacement Reactions

In this clip from the 2012 Christmas Lectures®, Dr Peter Wothers demonstrates how a more reactive halogen can displace one of the less reactive members of group 7 - with the aid of some water from the Dead Sea.

The Halogens - Displacement of Bromide

Running Time - 1 min 58 secs

A practical exercise for students demonstrating the order of reactivity of the halogens is available from the Nuffield Foundation here[2].

- Reactions with the Alkali Metals:

  The name 'halogen' literally means 'salt-former' and the halogens do indeed form salts when reacted with the Group 1 elements - the Alkali Metals (See Teaching Resource Group 1 - The Alkali Metals at the RSC Learn Chemistry Website).

  When a halogen is introduced to an alkali metal (for example chlorine being introduced to sodium) the halogen will oxidise the alkali metal, taking one electron and forming a metal cation (a positively charged ion). When the halogen does this, it gains one electron - it is reduced - to form a halide anion (a negatively charged ion).

  This process can be demonstrated using the following equation, where M is the alkali metal, and X is the halogen:

$$2M + X_2 \rightarrow 2MX$$

  We can also show redox half equations for this process:

$$2M \rightarrow 2M^+ + 2e^-$$

$$X_2 + 2e^- \rightarrow 2X^-$$

  The products from these reactions are ionic salts. They are held together by electrostatic interactions, and form regular structures called a crystal lattice.

  These reactions are generally very favourable, as they allow both the Alkali metal, and the Halogen to alter their electronic configuration to that of a Noble gas, both having full outer electronic energy levels (shells).

[2] Practical Chemistry, Nuffield Foundation, http://www.nuffieldfoundation.org/practical-chemistry/

Video Clip - Salt forming Reaction of Chlorine and Fluorine

In this clip from the 2012 Christmas Lectures®, Dr Peter Wothers demonstrates how Chlorine and Sodium - both highly reactive and dangerous elements - react to form normal table salt; and with the help of Prof. Eric Hope form the University of Leicester, Peter demonstrates the reaction between the most reactive Alkali metal, and the most reactive Halogen.

The Halogens - Salt Forming Reactions

Running Time - 6 mins 35 secs

View the full 2012 Ri Christmas Lectures® - The Modern Alchemist, along with behind the scenes footage, and related content, at the Ri Channel[3].

[3] Ri Channel, www.richannel.org