Chapter 6

Topic 6 - Halogens and redox

The halogens are in group 7 of the periodic table. They are also found in trace amounts in the human body. This topic allows us to probe some ideas we already have about periodicity and trends in reactivity. Chemistry is strongly related to electronic structure, and as these elements have very similar electronic structures we can see trends emerging in the way they behave. Try to write the electronic configurations of the halogens in $s\ p\ d$ notation. That should keep you busy. . .

Astatine is radioactive with a relatively short half-life, so you are unlikely to be asked questions about it, but should be able to predict its physical properties (state, appearance) and chemistry from the trends in the rest of the group.

6.1 Physical properties

The physical properties of the halogens show definite periodic trends. At the top of the group they are gases, bromine is a liquid with a low boiling point, iodine is a solid which easily sublimes, and astatine is a solid (if you can get hold of some for long enough!). The reason for this is that as the elements get larger the forces of attraction between molecules get stronger. The colours of the elements get darker as you descend the group.

6.2 Displacement reactions

In order to provide experimental evidence for the relative reactivities of the halogens it is possible perform displacement reactions. These follow the same pattern as reactions used to establish the reactivity series of the metals. *A more reactive halogen will displace a less reactive one from a solution of its ions.* These are done as solution reactions, so there is no need to use chlorine gas. Chlorine water (pale yellow / green), bromine water (orange) and iodine in potassium iodide (dark brown) are the solutions used. To emphasise the colour changes, the results of the aqueous reactions are shaken with hexane. The halogens dissolve better in hexane than in water, so the colours are more pronounced. This is the principle behind **solvent extraction** as shown in experiment 6.1.

You should be able to write ionic equations for the reactions between chlorine and bromide ions, bromine and iodide ions, and chlorine and iodide ions. Do this in the space below, and remember the state symbols.

You should now try to split these ionic equations into **half reactions** where the individual species are shown in reactions with electrons. This should stress which species are being oxidised and which are being reduced (see section 6.2 in the text book if you haven't a clue what this means).

6.3 Oxidation numbers

The course puts a lot of emphasis on the use of oxidation numbers. These give us a way of classifying compounds and tracking the changes which occur during reactions. You should be able to assign oxidation numbers to any species you choose, and do not be afraid to give a fractional value!

- What is the oxidation number of Na in Na?
- What is the oxidation number of Na in NaCl?
- What is the oxidation number of Na in Na^+?
- What is the oxidation number of S in $SO_4{}^{2-}$?
- What is the oxidation number of O in OH^-?

Stock notation is the name given to formulae such as copper (I) oxide for Cu_2O. If water of crystallisation is present the names become slightly cumbersome. $CuSO_4.5H_2O$ is called copper (II) sulphate-5-water for instance.

It is possible to use oxidation numbers, and changes in them, to balance equations. The sum of changes in oxidation number must be zero. When you have balanced an equation to make sure this is so, you can then insert any more numbers which are required to balance the amount of stuff on either side. Sometimes these get a bit complicated and involved, and it is worth working clearly and checking your answer when you think you have finished.

The commonest oxidation state of the halogens is probably -1, followed closely by 0. There are also +1 and +5. Many of the compounds which contain +5 oxidation state halogens are oxidising agents.

It would be very useful to draw a web of the reactions to interconvert oxidation states of halogens

6.4 Oxidation number -1

6.4.1 Hydrogen halides

You have prepared the hydrogen halides by reaction of the appropriate salt and concentrated phosphoric acid. Why is concentrated sulphuric acid not used? White

fumes of the hydrogen halide are produced. This will react with fumes of concentrated ammonia to produce what visible product? A test tube of these gases inverted in a trough of water will show what visible change? It is hard to test the stability

of the gases towards heat - getting a hot enough thing to poke into the tube is difficult! However, the HCl should be unreactive towards heat, the HBr may react but is unlikely to, and the HI should produce a purple vapour and black solid (iodine). This experiment is a good way to demonstrate the trend of variation in bond energy down the group. What is this trend?

6.4.2 Silver halides

The reaction between silver nitrate solution and potassium chloride, bromide or iodide solutions produces *precipitates* which are white, pale yellow / cream and yellow. The silver chloride is more soluble in concentrated ammonia than the bromide, the iodide is insoluble. The ammonia forms a soluble complex with the silver ions with the formula $Ag(NH_3)_2{}^+$. There is a photochemical reaction of the halides which shows that in light the chloride and bromide darken, but the iodide does not.

6.5 Oxidation number 0

The halogens react with alkalis. You could observe this by watching their colours disappear during reactions. You should be able to write equations of the type below - add the state symbols.

$$\mathrm{Cl_2} + 2\ \mathrm{NaOH} \longrightarrow \mathrm{NaCl} + \mathrm{NaClO} + \mathrm{H_2O} \tag{6.1}$$

What happens to the oxidation state of chlorine in this reaction? What sort of reaction is it? Re-write the equation as an ionic equation.

6.6 Oxidation number +1

The sodium chlorate(I) (or sodium hypochlorite) formed in reaction 6.1 is a bleaching agent. It decomposes to produce sodium chloride and oxygen. Write an equation for this.

The halates(I) will react with Fe^{2+} ions in a redox reaction. Can you write an equation for this solution reaction?

6.7 Oxidation number +5

What are the names of $KClO_3$, $KBrO_3$ and KIO_3?

6.8 Percentage purity

The percentage purity of a substance tells a chemist how good they were at preparing a compound! In this chapter you did an assessed practical to determine the percentage purity of potassium iodate(V). The technique involves titrating with an appropriate substance. In this case the solution used for titration is sodium thiosulphate. You should be able to rewrite the equation below as an ionic equation.

$$2\ Na_2S_2O_3(aq) + I_2(aq) \longrightarrow 2\ NaI + Na_2S_4O_6(aq) \tag{6.2}$$

The progress of the reaction should be studied optically by halting the flow of liquid into the test aliquot when the absorption of visible light begins to diminish.

What colour change should you see?

The calculation is simple but has many stages. Work out how much thiosulphate reacted, work out how much iodine this thiosulphate reacted with, work out how much iodate produced this iodine, calculate the mass of iodate you started with overall and work out the percentage purity by dividing this last amount by the mass of crude potassium iodate(V) you started with. Balance the equation below

$$\mathrm{IO_3^-(aq)} + \mathrm{I^-(aq)} + \mathrm{H^+} \longrightarrow \mathrm{I_2(aq)} + \mathrm{H_2O(l)} \tag{6.3}$$

6.9 Other points to note

An important concept in the chapter does not relate to the halogens at all really. In experiment 6.8a the difference in the solubilities of two substances are used to extract one from solution. A saturated solution is made in boiling water. Both substances are dissolved. As the solution cools, one of substances becomes nearly insoluble, while the solubility of the other remains high. Gentle cooling allows the less soluble product to fall out of solution, while the other stays dissolved. In this way the two are separated (the cooled mixture is passed through a Buchner funnel under suction).