Halogens

What the specification want:
→A description of the following physical properties of the halogens: appearance and physical states at room temperature, volatility, solubility in water and organic solvent.

→ The relative reactivities of the halogens in terms of their ability to gain electrons.

→ The details of the redox changes which take place when chlorine, bromine and iodine react with other halides ions, including observations and half equations.

→The reactions between halides ions (CL-, Br- and I-) and silver ions (Ag+) and ionic equations, the colours of the precipitates and solubility of silver halides in ammonia.

→ The risk associated with the storage and transport of chlorine, uses of chlorine which must be weighed against these risks, including: sterilising water by killing bacteria, bleach.

→Demonstrate and apply knowledge and understanding of:

- The concept of amount of substance in performing calculations involving atom economy;the relationship between atom and economy and the efficient use of atoms in a reaction.
- The preparation of HCL; the preparation of HBR and HI by using the halides and phosphoric acid; the actions of sulfuric acid on chloride, bromides and iodides.
- The properties of the hydrogen halides: different thermal stabilities, similar reaction with ammonia and acidity, different reactions with sulfuric acid.

What are halogens?

Halogens are group 1 on the periodic table. They have seven electrons in their outer shells. They are the most reactive non-metal and none of them are found naturally in the elemental form so they are mostly found in compounds like calcium fluorine or sodium chloride. This means these compounds contain the halide ion F^- and Cl^-.

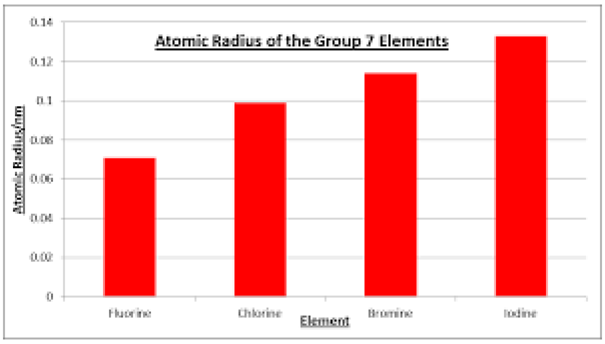
Study tips!

The term halogens is for when we talk about the elements as when we talk about halides it's about the ions or salt. So to differentiate them we change one letter. Halogens will have a **n** for the element: Fluori**ne**,Chlori**ne** ect…. as for the halides it's a **d** for the ions: Fluori**d**e, Chlori**d**e etc...

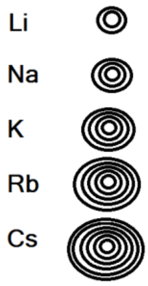
Physical property of halogens:

The atomic radius:

The atomic radius would increase as you go down the groups because the number of the electrons around the nucleus increases which pull the outer electrons far from the nucleus.



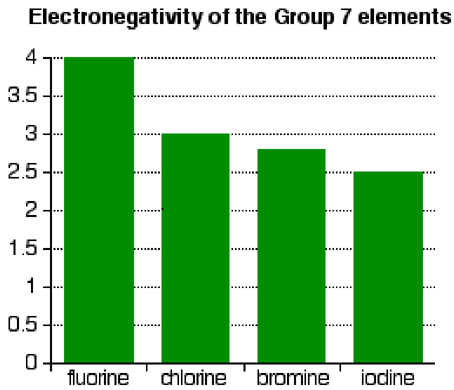
Here you can see the atomic radius is going up as you go down the groups.



Here you can see the number of shell increase as you do down which means the outer shell will be more far apart from the nucleus as you go down the group and makes the atomic radius to increase.

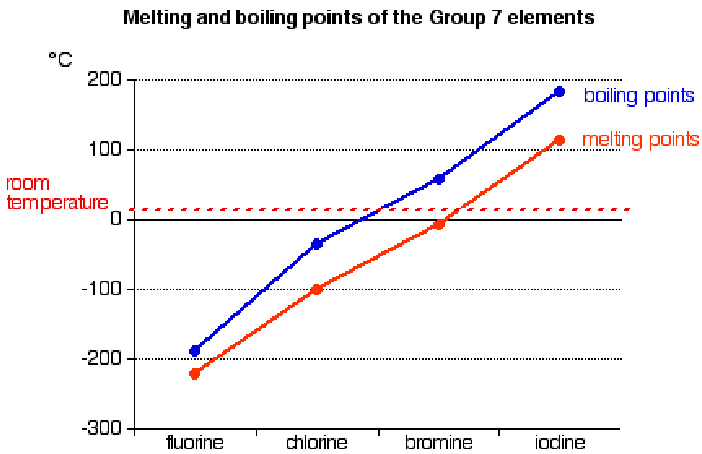
Trend in electronegativity:

It's the measure of the tendency of an atom to attract a bonding pair of electrons. It will go down as you go down the group because there is more shell around the nucleus and the shell is further away.



→Trend in Melting and Boiling point:

The melting and boiling point will rise as you go down the group of the halogens. This is because they exist as diatomic molecules and as you go down the group they will get stronger intermolecular force so the more energy needed to break them. At Room Temperature Fluorine and Chlorine will be a gase, Bromine will be a liquid and Iodine a solid.



Solubilities:

Fluorine will react violently with water, so this one is pointless to do any reaction with. Cl, Br and I all dissolve in water but there is no pattern in this. They will as well be less volatile as you go down the group.

Colours of halogens in water:

→ Chlorine gives a pale green colour.
→ Bromine gives a yellow to dark orange-red colour.
→ Iodine gives a brown, orange colour.

Colours of halogens with solvent (Hexane):

They are more soluble in organic solvents than they are in water.This makes as well more district colours so makes it easier to say which halogens are present.
→ Chlorine gives a green colour.
→ Bromine gives an orange colour.
→ Iodine gives a purple colour

Relative reactivity (To gain electrons):

Halogens are strong oxidising agents so this means they can take electrons from another species. They can take electrons from halides which are I-, Br-, Cl- (ions). As you go down the groups they are less reactive as it's easier to transfer electrons. Halogens that are the most reactive are the most dense as well as they have fewer shells, so more dense as you go up the group. Chlorine would therefore be the strongest oxidizing agent. Not fluorine because it's too reactive and reacts too much in water.

Redox when halogen react with halides:

Chlorine with bromide ions:

$$Cl_{2(aq)} + 2Br^{-}_{(aq)} \rightarrow 2Cl^{-}_{(aq)} + Br_{2(aq)}$$

Now we are going to go through the half equation of both Chlorine and bromide to be able to understand the equation above.

$Cl_{2(aq)} + 2e^{-}_{(aq)} \rightarrow 2cl^{-}_{(aq)}$ ⟵ This equation here show you the Half equation of chlorine. As you can see chlorine gains electrons so is reduced and will give chloride ions. This is an **oxidising agent**. Remember:

Oil Rig: Oxidation is loss, reduction is gain.

Oxidising agent is reduction

Reducing agent is oxidation

$2Br^-_{(aq)} \rightarrow Br_{2(aq)} + 2e^-_{(aq)}$ ← In this equation the same thing happened but we can say the other way around. This time the bromide ions are losing electrons so being oxidised to make bromine. This is a **reducing agent.**

Next you can add the two half equations together **but only if they have the same electrons** like the example above with the $2e^-$.

$$Cl_{2(aq)} + 2e^- + 2br^-_{(aq)} \rightarrow Br_{2(aq)} + 2e^- + 2cl^-_{(aq)}$$

If they do not have the same electrons in both equations then you need to multiply one or both equations to get the same for both. Example:

$Na + e^- \rightarrow Na^-$ so here you would multiply everything by two to get $2e^-$ like this:

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

Next you can see by having the electrons on both sides they can cancel out to give the redox equation we got at the start which show the chlorine is stronger than the bromide ions so will take bromide ion electrons to make itself an chloride ion and makes bromine as he lost his electrons and can't be an ion anymore.

$$Cl_{2(aq)} + 2Br^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2(aq)}$$

<u>If you need more help with the Half-equation and redox equation please go see the appropriate notes for this.</u>

But not all of the halogens will do this if they are not the strongest oxidising from the equation like this one:

$$I_{2(aq)} + 2Br^-_{(aq)} \rightarrow I_{2(aq)} + 2br^-_{(aq)}$$

As you can see here bromide is the strongest oxidising agent than iodine therefore nothing will happen in this equation.

Colours of halogens with halides:

Halide / Halogen	Cl^-	Br^-	I^-
Cl_2	no reaction, stay colourless	There will be a reaction, it will turn yellow.	There will be a reaction, it will turn brown.
Br_2	no reaction, will stay yellow	no reaction, will stay yellow	There will be a reaction and will turn orange

I_2	no reaction, stay brown	no reaction, stay brown	no reaction, stay brown

You can sometimes see this as well: $KI+Cl_2$ which will still give a colour to be brown but the colours change can be still difficult to detect and with an organic solvent the colours can be more distinct. the upper layer will be the organic solvent.
These two videos are very interesting if you want to see the reaction happening with halogens and halides:https://www.youtube.com/watch?v=HW2jRyQ3dzo
And the same thing but this time with cyclohexane as well:https://www.youtube.com/watch?v=MC8kEpWMSkk

The reaction between halides ions and silver ions or silver nitrate:

Silver halides are precipitated (Precipitate are two solution mixes and a solid is formed) when a solution of silver ions is added to a solution containing chloride,bromide or iodide. The general equation is:

$$Ag^{+}_{(aq)} + X^{-}_{(aq)} \rightarrow AgX_{(s)}$$

We can add as well some ammonia to the reaction to be able to see the solubility of the halide as it can be hard to distinguish between the colours.

→ Silver ions with chloride will give a white precipitate and will be soluble with dilute ammonia.
→ Silver ions with Bromide will give us a cream precipitate and will be soluble with concentrated ammonia.
→ Silver ions with iodide will give a yellow precipitate and will be insoluble in ammonia even concentrated.

If you add instead silver nitrate this will give the same thing even with ammonia.

This video can show you the experience for this:https://www.youtube.com/watch?v=La2KXjOh5vU

The risks and benefits of using chlorine:

Chlorine is very dangerous even in small doses. Chlorine can be detectable by the smell at 1ppm so very easy to smell. At this small dose you can still get irritation in the eyes, skin and respiratory system. If you have a bigger concentration than this is even more dangerous as it will react in your lungs to form hydrochloric acid HCL, which will affect the lungs tissue and essentially causes drowning as liquid floods the lungs.

Some of the use and benefits of chlorine is that we can use it for water treatment where it is added to the water to kill the bacteria and other pathogens. Because of this in the early twentieth there was a decline in the number of deaths from typhoid. Chlorine is also used in household bleach products, to kill bacteria on surfaces or to remove stains from clothing. The bleach is an oxidising agent, removes stains by breaking bonds in coloured chemicals to form colourless products.

Transporting chlorine:

Even if you have some chlorine prepared on site at the chemical plant requiring chlorine, there is still some chlorine that needs to be transported. Chlorine can be transported by road or rail in specially designed pressurised tank containers.In some countries like the UK you will find a warming plate (Figure1). This plate will be attached to the tank during the transport and if there is an accident this gives us information about the action needed

.

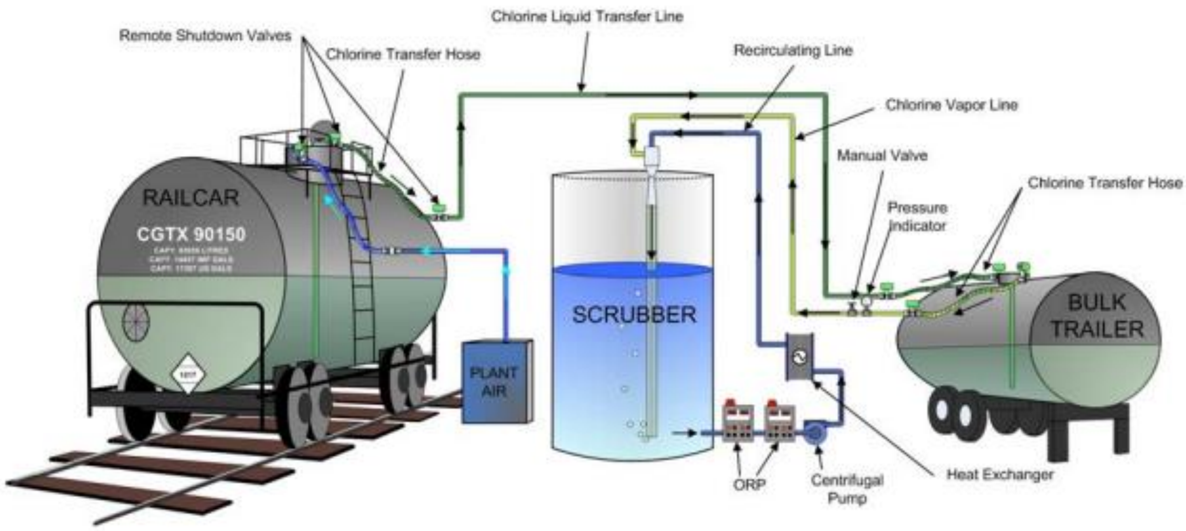
(Figure 1)

The chlorine is transported as a liquidas more chlorine can be stored in a fixed volume as a liquid under pressure than as a gas. If the tank gets too high in temperature or pressure then there are devices designed to vent the tank and release some of the chlorine gas as it is better to release a bit of chlorine gas than have a catastrophic explosion in case of a tank failure. The tank will normally be made of steel. The instead of the tank needs to be dry as chlorine will react with water to produce corrosive acid.The tank has as well a cylindrical, protective housing at the top. This is where all the loading and unloading is done at the top of the tank with is another safety feature of the tank as if there is an excess flow valve, which is designed to close automatically if the angle valve which regulates the discharge of chlorine is broken or sheared off in case of an accident in transport. It is activated if the discharge of liquid chlorine at the exit port exceeds some predetermined value.

Unloading and storing chlorine:

When chlorine is transferred on delivery from the rail tanker to a bulk trailer on site, a scrubber unit ensures that the air being displaced from the trailer has any chlorine removed from it. The scrubber has sodium hydroxide solution that reacts with the chlorine to produce sodium chlorate(I)-bleach that can be sold.

Chem Masterpiece



Chlorine can be transported and then stored in cylinders.workers at the chemical plant meet regulations regarding handling the cylinders by carefully moving the cylinders using a hoist to avoid damage to the outside. One method they use for checking stored cylinders is to take a stick with cloth soaked with concentrated ammonia solution over the end of the cylinder. if the cylinder is leaking then a wide cloud of ammonium chloride will be seen.

Iodine-Thiosulfate titrations:

Iodine-Thiosulfate titrations can be used to determine the concentration of sodium chlorate in bleach. We need to know how different concentrations will be used for different bleach. Chlorine reacts with sodium hydroxide to make sodium chlorate(I), $NaClO$. A solution of about 12% $NaClO$ by mass is used in some water purifying to kiss bacteria. A solution of about 5% is used in household bleach products.

Iodine-Thiosulfate titrations involve redox reactions. They are used to find the concentration of a chemical that is a strong enough oxidising agent to oxidise iodine ions. For bleach excess of iodine ions is added to the chlorate(I) ions which for this redox reaction:

$$ClO^- + 2I^- \rightarrow I_2 + Cl^- + H_2O$$

The iodine produce can be titrated using thiosulfate ions $S_2O_3^{2-}$ in the following reaction:

$$2\ S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\ I^-$$

At the end point of the titration can be clearly identified by adding starch solution. The end point is determined when the final trace of blue/black colour is no longer visible.

Making hydrochloric acid as a co-product:

A large proportion of the hydrochloric acid that is made is a co-product from the chlorination of organic compounds. For example the poly(chloroethene) is the reaction of ethene with chlorine. The 1,2 dichloroethane that is formed undergoes thermal cracking to give chloroethane and hydrogen chloride. The hydrogen chloride can then be converted into hydrochloric acid by passing it through water. A solution of a high concentration can be produced easily as hydrogen chloride is very soluble in water. The hydrogen chlorine gas is made up of covalent molecules and when it is dissolved in water it forms the hydrated ions H+(aq) and Cl-(aq).

Hydrogen halides:

We know that fluorine is the strongest oxidising agent in group 7. fluorine atoms have the greatest tendency to be reduced or gain electrons. In doing so fluorine atoms become fluoride ions and the fluoride ions have a low tendency to lose electrons and turn back into an atom. The fluorine ions are difficult to oxidise and therefore are poor reducing agents.

<u>Sodium fluoride and sodium chloride</u>

They both react in concentrated acid to make hydrogen fluoride and hydrogen chloride gas. In some experiments you will see a white fume of hydrogen chloride as it meets the moist air. Tiny droplets of hydrochloric acid are being made.

$$H_2SO_{4\,(aq)} + NaCl_{(aq)} \rightarrow HCl_{(g)} + NaHSO_{4(aq)}$$

<u>Sodium bromide</u>

It will first react with concentrated sulfuric acid to make hydrogen bromide.

But the bromide ions produced are strong enough reducing agents to reduce the sulfuric acid to sulfur dioxide. so this means adding sulfuric acid to sodium bromide would not be a good way to produce hydrogen gas because it won't be pure. The gas that will be reacted would be a mixture of hydrogen bromide, sulfur dioxide and bromine vapour as the reaction is exothermic.

<u>Sodium iodide</u>

React with sulfuric acid to make hydrogen iodine.

$$H_2SO_{4\,(aq)} + NaI_{(aq)} \rightarrow HI_{(g)} + NaHSO_{4(aq)}$$

But here the iodine is an even stronger reducing agent than bromide from before. so this time the sulfuric acid is reduced further to make hydrogen sulfide gas. With bromide ion, the oxidation state of sulfur decreased by two as with iodide ions the oxidation state decreased by eight. So by adding concentrated sulfuric acid to sodium iodide is not a good idea too, to get hydrogen iodide as it will not be pure. The gas that will be made this time is hydrogen iodide and hydrogen sulfide.

So when we prepare the hydrogen halides in the lab the appropriate sodium halide is used. So to make hydrogen chloride we will use the sodium chloride and concentrated sulfuric acid but for the sodium bromide and iodide we will use concentrated phosphoric acid which will make pure hydrogen bromide or iodide.

Similarities and differences in the properties of hydrogen halides:

The thermal stability

It will decrease as you go down the group 7. Hydrogen iodine is broken down into its elements at a lower temperature compared to hydrogen chloride as the bond strength between the hydrogen and the halogens decrease as you go down the group 7.

When the hydrogen halides are heated in the laboratory, the hydrogen fluoride isn't broken down into the hydrogen and fluorine. Hydrogen chloride isn't broken down into hydrogen and chlorine, for hydrogen bromide some of the bromine gas is made and lastly the hydrogen iodide will make a large amount of purple gaseous iodine when a red hot needle is plunged into hydrogen iodide.

Acidity

In solution, very soluble hydrogen halides are all very acidic apart from hydrogen fluoride which is even more acidic. For HCl, HBr and HI there is almost 100% dissociation.

Reaction with ammonia

All of the hydrogen halides react with ammonia to make salt. If a glass rod dipped in concentrated ammonia solution is placed in the hydrogen halides then a white cloud of ammonium halide will be made. For example:

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$

Reaction with sulfuric acid

The reaction of hydrogen halides with concentrated sulfuric acid are different because the strength of the halides ions increases reducing agents. When we compare the reaction of solid halides with sulfuric acid, the hydrogen fluorine and hydrogen chloride do not react. Hydrogen bromide makes sulfur dioxide and hydrogen iodine makes hydrogen sulfide.