

## PERIODICITY – GROUPS II AND VII, PERIOD 3

### Group I and Group II Elements

All Group I and II elements are metals. Group I metals are called alkali metals and Group II metals are known as alkaline earth metals.

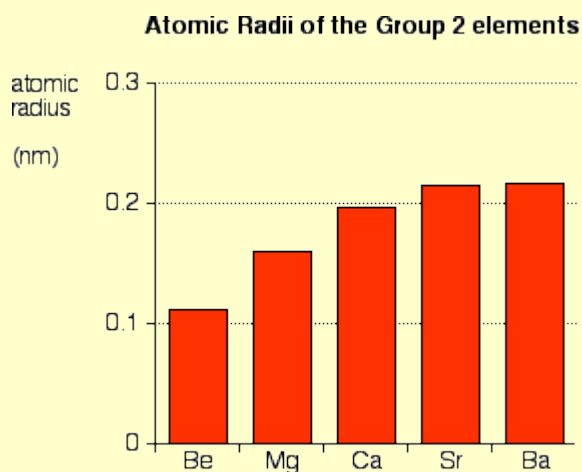
The metals in Group II show a variation in physical and chemical properties as the group is descended. Recall the following properties:

- Metals are solids with giant crystal lattices.
- Metals usually have high melting and boiling points.
- Metals have large atomic radii.
- Metals tend to have high densities.
- Metals tend to lose electrons easily.
- Metals react chemically with non-metals to form ionic compounds.

### Trends of Group II Elements

1. *Atomic radius increases going down group II.*

Trends in Atomic Radius



You can see that the atomic radius increases as you go down the Group. Notice that beryllium has a particularly small atom compared with the rest of the Group.

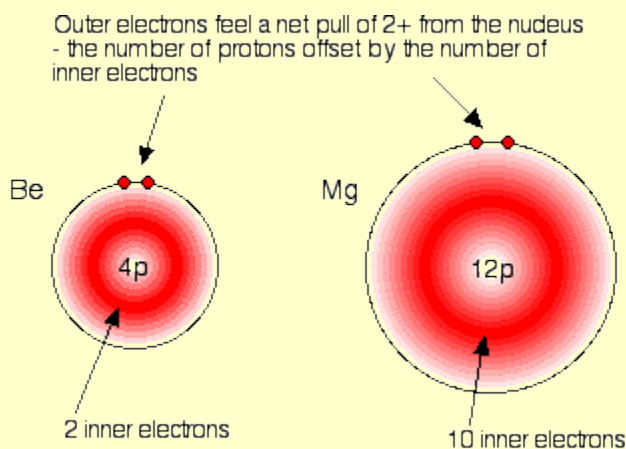
The radius of an atom is governed by

- the number of layers of electrons around the nucleus
- the pull the outer electrons feel from the nucleus.

Compare:

Beryllium	2, 2
Magnesium	2, 8, 2
Calcium	2, 8, 8, 2
Strontium	2, 8, 18, 8, 2
Barium	2, 8, 18, 18, 8, 2

In each case, the two outer electrons feel a net pull of 2+ from the nucleus. The positive charge on the nucleus is cut down by the negativeness of the inner electrons.

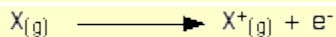


This is equally true for all the other atoms in Group 2.

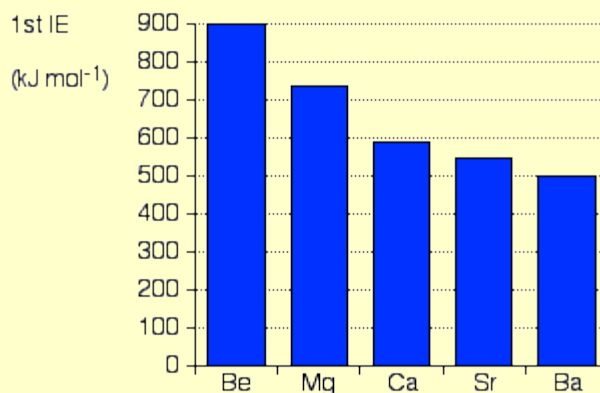
The only factor which is going to affect the size of the atom is therefore the number of layers of inner electrons which have to be fitted in around the atom. Obviously, the more layers of electrons you have, the more space they will take up - electrons repel each other. That means that the atoms are bound to get bigger as you go down the Group.

## 2. First Ionisation energy decreases going down group II.

First ionisation energy is the energy needed to remove the most loosely held electron from each of one mole of gaseous atoms to make one mole of singly charged gaseous ions - in other words, for 1 mole of this process:



First Ionisation Energy of the Group 2 elements



Notice that first ionisation energy falls as you go down the group.

Ionisation energy is governed by

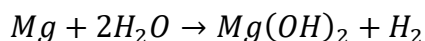
- the charge on the nucleus,
- the amount of screening by the inner electrons,
- the distance between the outer electrons and the nucleus.

As you go down the Group, the increase in nuclear charge is exactly offset by the increase in the number of inner electrons. Just as when we were talking about atomic radius further up this page, in each of the elements in this Group, the outer electrons feel a net attraction of 2+ from the centre.

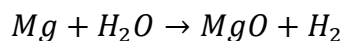
However, as you go down the Group, the distance between the nucleus and the outer electrons increases and so they become easier to remove - the ionisation energy falls.

3. *Reaction with cold water increases going down the group.*

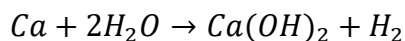
Magnesium reacts very slowly with cold water because the magnesium hydroxide which is formed is insoluble.



Magnesium will react more vigorously in hot water, where it forms magnesium oxide and hydrogen.

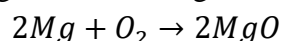


Calcium reacts readily with cold water to form calcium hydroxide and hydrogen.

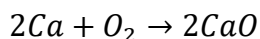


4. *Reaction with oxygen increases going down the group.*

Magnesium reacts readily with oxygen to form magnesium oxide.

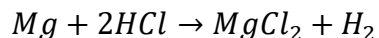


Calcium reacts more readily with oxygen to form calcium oxide.

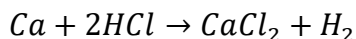


5. *Reaction with hydrochloric acid increases going down the group.*

Magnesium reacts readily with HCl to form magnesium chloride and hydrogen



Calcium reacts more readily with HCl to form calcium chloride and hydrogen.

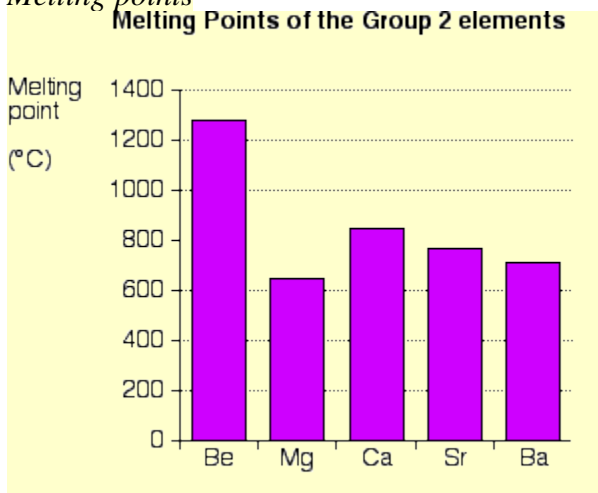


NOTE: The reaction of the metals with dilute acid is generally more vigorous than their reactions with water.

6. *Group II elements have relatively high melting and boiling points.*

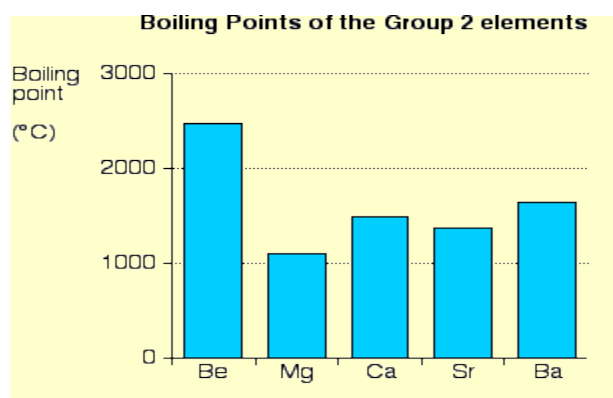
The facts

*Melting points*



You will see that (apart from where the smooth trend is broken by magnesium) the melting point falls as you go down the Group.

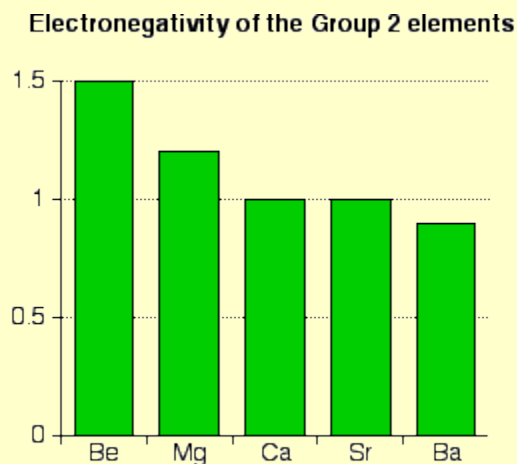
*Boiling points*



You will see that there is no obvious pattern in boiling points. It would be quite wrong to suggest that there is any trend here whatsoever.

7. *Electronegativity values are generally low, and show a slight decrease down the group.*

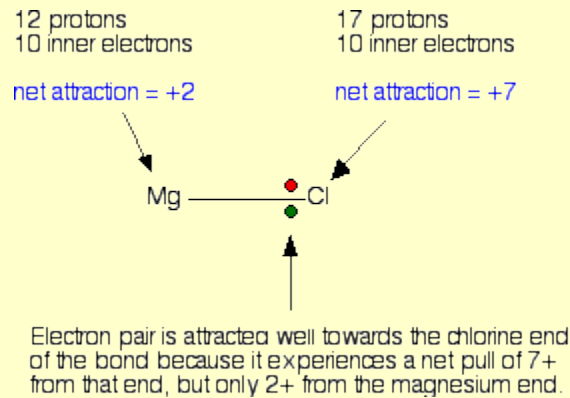
Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is given an electronegativity of 4.0.



All of these elements have a low electronegativity. (Remember that the most electronegative element, fluorine, has an electronegativity of 4.0.) Notice that electronegativity falls as you go down the Group. The atoms become less and less good at attracting bonding pairs of electrons.

Explaining the decrease in electronegativity

Imagine a bond between a magnesium atom and a chlorine atom. Think of it to start with as a covalent bond - a pair of shared electrons. The electron pair will be dragged towards the chlorine end because there is a much greater net pull from the chlorine nucleus than from the magnesium one.

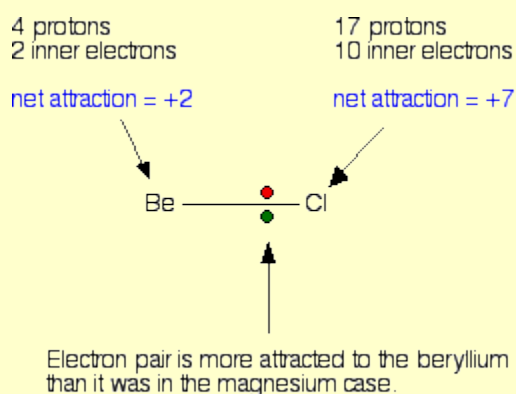


The electron pair ends up so close to the chlorine that there is essentially a transfer of an electron to the chlorine - ions are formed.

The large pull from the chlorine nucleus is why chlorine is much more electronegative than magnesium is.

Now compare this with the beryllium-chlorine bond.

The net pull from each end of the bond is the same as before, but you have to remember that the beryllium atom is smaller than a magnesium atom. That means that the electron pair is going to be closer to the net 2+ charge from the beryllium end, and so more strongly attracted to it.



In this case, the electron pair doesn't get attracted close enough to the chlorine for an ionic bond to be formed. Because of its small size, beryllium forms covalent bonds, not ionic ones. The attraction between the beryllium nucleus and a bonding pair is always too great for ions to be formed.

### Summarising the trend down the Group

As the metal atoms get bigger, any bonding pair gets further and further away from the metal nucleus, and so is less strongly attracted towards it. In other words, as you go down the Group, the elements become less electronegative.

As you go down the Group, the bonds formed between these elements and other things such as chlorine become more and more ionic. The bonding pair is increasingly attracted away from the Group 2 element towards the chlorine (or whatever).

8. There is a general increase in density from calcium to barium.

The numbers of protons and neutrons in the nuclei of the atoms increase down the group, and so the masses of the atoms increase as well. This contributes to their increasing density, because

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

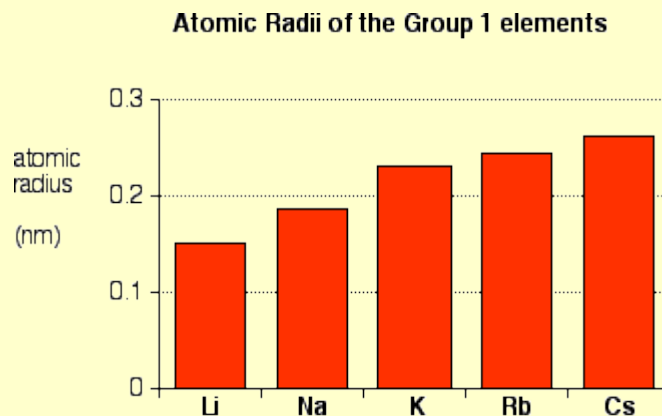
Thus, we can conclude that the metallic character increases down Group II. This means that barium is more metallic than strontium, which, in turn, is more metallic than calcium, and so on. This trend of increased metallic character down the group is general for all the groups.

### Trends of Group I Elements

Like typical metals, the elements of Group I are solids at room temperature, and have low electronegativity. However, they do not show all of the typical physical properties of metals. Here are some of the differences in physical properties:

- They are soft and can be easily cut with a knife
- They have relatively low densities

#### 1. Trends in Atomic Radius



You can see that the atomic radius increases as you go down the Group.

The radius of an atom is governed by

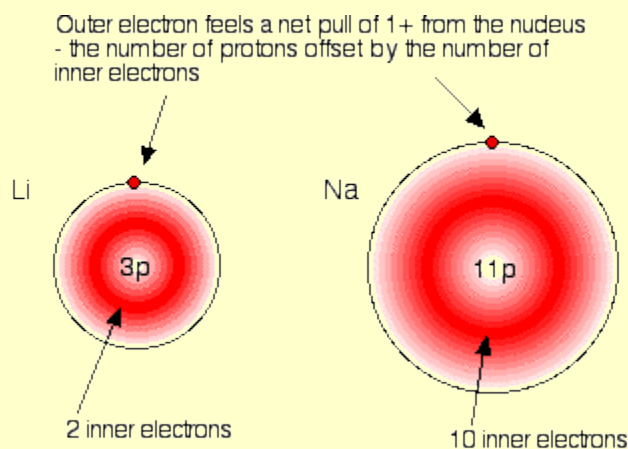
- the number of layers of electrons around the nucleus
- the pull the outer electrons feel from the nucleus.

Compare:

Lithium	2, 1
Sodium	2, 8, 1
Potassium	2, 8, 8, 1

In each case, the outer electron feels a net pull of  $1+$  from the nucleus. The positive charge on

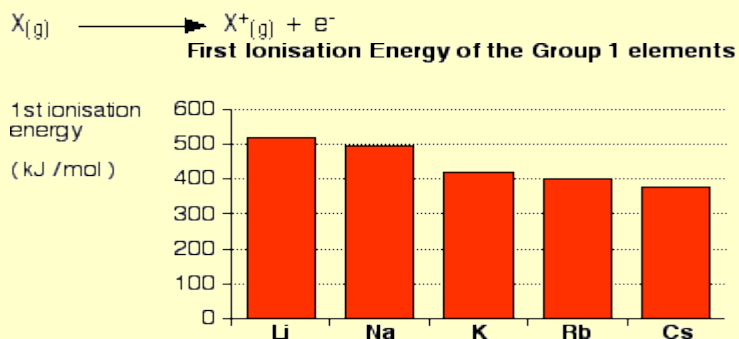
the nucleus is cut down by the negativeness of the inner electrons.



This is equally true for all the other atoms in Group 1. The only factor which is going to affect the size of the atom is therefore the number of layers of inner electrons which have to be fitted in around the atom. Obviously, the more layers of electrons you have, the more space they will take up - electrons repel each other. That means that the atoms are bound to get bigger as you go down the Group.

## 2. Trends in First Ionisation Energy

First ionisation energy is the energy needed to remove the most loosely held electron from each of one mole of gaseous atoms to make one mole of singly charged gaseous ions - in other words, for 1 mole of this process:



Notice that first ionisation energy falls as you go down the group.

Ionisation energy is governed by

- the charge on the nucleus,
- the amount of screening by the inner electrons,

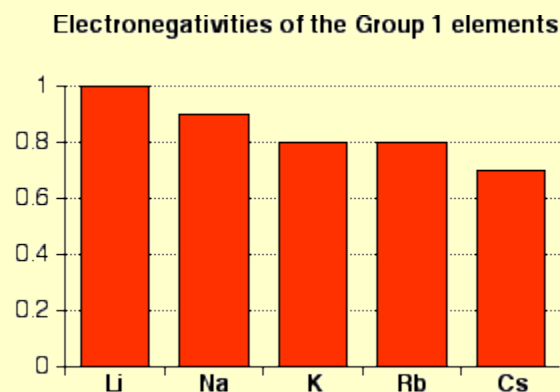


- the distance between the outer electrons and the nucleus.

As you go down the Group, the increase in nuclear charge is exactly offset by the increase in the number of inner electrons. Just as when we were talking about atomic radius further up this page, in each of the elements in this Group, the outer electrons feel a net attraction of  $1+$  from the centre.

However, as you go down the Group, the distance between the nucleus and the outer electrons increases and so they become easier to remove - the ionisation energy falls.

### 3. Trends in Electronegativity

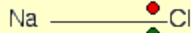


All of these elements have a very low electronegativity. (Remember that the most electronegative element, fluorine, has an electronegativity of 4.0.) Notice that electronegativity falls as you go down the Group. The atoms become less and less good at attracting bonding pairs of electrons.

Imagine a bond between a sodium atom and a chlorine atom. Think of it to start with as a covalent bond - a pair of shared electrons. The electron pair will be dragged towards the chlorine because there is a much greater net pull from the chlorine nucleus than from the sodium one.

11 protons  
10 inner electrons  
net attraction = +1

17 protons  
10 inner electrons  
net attraction = +7



Electron pair is attracted well towards the chlorine end of the bond because it experiences a net pull of 7+ from that end, but only 1+ from the sodium end.

The electron pair ends up so close to the chlorine that there is essentially a transfer of an electron to the chlorine - ions are formed.

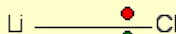
The large pull from the chlorine nucleus is why chlorine is much more electronegative than sodium is.

Now compare this with the lithium-chlorine bond.

The net pull from each end of the bond is the same as before, but you have to remember that the lithium atom is smaller than a sodium atom. That means that the electron pair is going to be closer to the net 1+ charge from the lithium end, and so more strongly attracted to it.

3 protons  
2 inner electrons  
net attraction = +1

17 protons  
10 inner electrons  
net attraction = +7



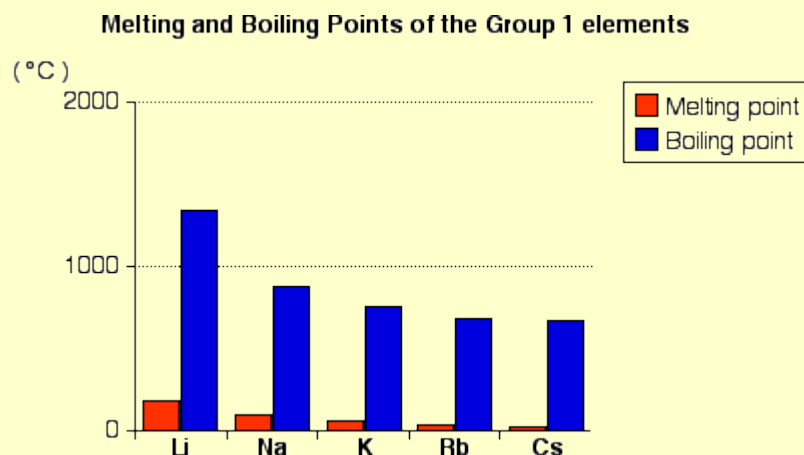
Electron pair is more attracted to the smaller lithium than it was in the sodium case.

In some lithium compounds there is often a degree of covalent bonding that isn't there in the rest of the Group. Lithium iodide, for example, will dissolve in organic solvents - a typical property of covalent compounds. The iodine atom is so large that the pull from the iodine nucleus on the pair of electrons is relatively weak, and so a fully ionic bond isn't formed.

As the metal atoms get bigger, any bonding pair gets further and further away from the metal nucleus, and so is less strongly attracted towards it. In other words, as you go down the Group, the elements become less electronegative.

With the exception of some lithium compounds, these elements all form compounds which we consider as being fully ionic. They are so weakly electronegative that we assume that the electron pair is pulled so far away towards the chlorine (or whatever), that ions are formed.

#### 4. Trends in Melting and Boiling Points



You will see that both the melting points and boiling points fall as you go down the Group.

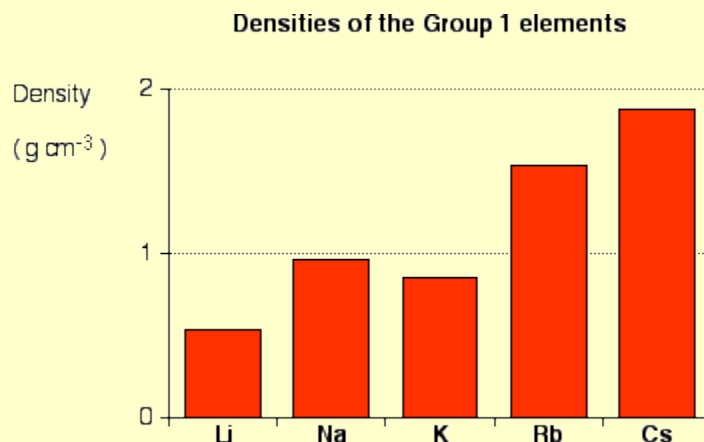
When you melt any of these metals, the metallic bond is weakened enough for the atoms to move around, and is then broken completely when you boil the metal.

The fall in melting and boiling points reflects the fall in the strength of the metallic bond.

The atoms in a metal are held together by the attraction of the nuclei to the delocalised electrons. As the atoms get bigger, the nuclei get further away from these delocalised electrons, and so the attractions fall. That means that the atoms are more easily pulled apart to make a liquid and finally a gas.

In the same way that we have already discussed, each of these atoms has a net pull from the nuclei of  $1+$ . The increased charge on the nucleus as you go down the Group is offset by additional levels of screening electrons. All that matters is the distance between the nucleus and the bonding electrons.

#### 5. Trends in Density



Notice that these are all light metals - and that the first three in the Group are less dense than water (less than 1 g cm<sup>-3</sup>). That means that the first three will float on water, while the other two sink.

The density tends to increase as you go down the Group (apart from the fluctuation at potassium).

It is quite difficult to come up with a simple explanation for this, because the density depends on two factors, both of which are changing as you go down the Group.

All of these metals have their atoms packed in the same way, so all you have to consider is how many atoms you can pack in a given volume, and what the mass of the individual atoms is. How many you can pack depends, of course, on their volume - and their volume, in turn, depends on their atomic radius.

As you go down the Group, the atomic radius increases, and so the volume of the atoms increases as well. That means that you can't pack as many sodium atoms into a given volume as you can lithium atoms.

However, as you go down the Group, the mass of the atoms increases. That means that a particular number of sodium atoms will weigh more than the same number of lithium atoms.

So 1 cm<sup>3</sup> of sodium will contain fewer atoms than the same volume of lithium, but each atom will weigh more. What effect will that have on the density? It is completely impossible to say unless you do some sums.

### **Trends in Group VII – The Halogens**

The atoms of the halogens each contain seven valence electrons. They then share the single unpaired valence electron to form diatomic covalent molecules in which the atoms are held by

strong single covalent bonds. Weak forces then exist between the molecules. Weak intermolecular forces are typical of substances with simple molecular structures.

The halogens therefore:

- Have low melting and boiling points
- Are more soluble in non-polar solvents than in water (which is polar)
- Are non-electrolytes (they do not conduct electricity)
- Exist as gases, volatile liquids or soft solids at room temperature, depending on the relative strengths of the intermolecular forces.

### *Appearance*

All the halogens are coloured, the colour becoming more intense as the group is descended. Chlorine is a yellow-green gas at room temperature and pressure, while bromine is a deep red liquid (the vapour also deep red). At room temperature, iodine is a black solid with a sheen, which gives off a purple vapour on sublimation.

### *Chemical Reactivity*

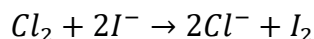
Fluorine is the most reactive non-metal known and its chemistry can be complicated by the fact that it will oxidise many substances, including water. Astatine, the last element in the group, is radioactive, making it unsafe and unsuitable for school laboratory experiments. Astatine is also extremely rare (it is thought that there is less than 25 g in the Earth's crust).

Unlike metals, the reactivity of non-metals depends on their ease of electronegativity. The halogens are highly electronegative and are therefore very reactive. Smaller atoms gain electrons more readily than larger ones, and so the reactivity decreases as the group is descended.

### *The Halogens as Oxidising Agents*

Consider a situation in which one halogen (chlorine, for example) is reacted with the ions of another (iodide, perhaps) from a salt solution.

In the chlorine and iodide ion case, the reaction is as follows:

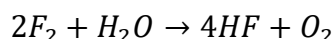


- The iodide ions lose electrons to form iodine molecules. In other words, they are oxidized.
- The chlorine molecules gain electrons to form chloride ions— they are reduced.

This is therefore a redox reaction in which chlorine acts as an oxidizing agent.

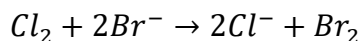
### Fluorine

Fluorine must be excluded from this discussion because its oxidizing abilities are too strong. Fluorine oxidizes water to oxygen, as in the equation below, and so it is impossible to carry out reactions with it in aqueous solution.

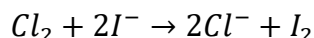


### Chlorine, Bromine and Iodine

In each case, a halogen higher in the group can oxidize the ions of one lower down. For example, chlorine can oxidize bromide ions to bromine:

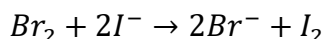


The bromine forms an orange solution. As shown below, chlorine can also oxidize iodide ions to iodine:



The iodine appears either as a red solution if little chlorine is used, or as a dark gray precipitate if the chlorine is in excess.

Bromine can only oxidize iodide ions, and is not a strong enough oxidizing agent to convert chloride ions into chlorine. A red solution of iodine is formed (see the note above) until the bromine is in excess. Then a dark gray precipitate is formed.



Iodine won't oxidize any of the other halide ions, except possibly the extremely radioactive and rare astatide ions.

To summarize

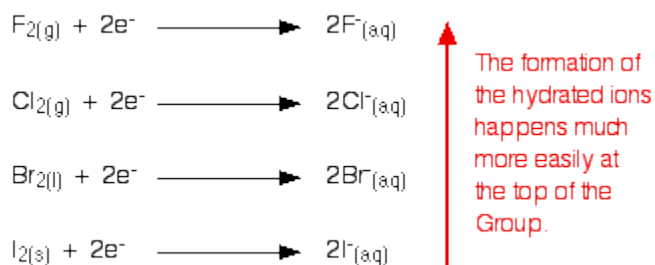
- Oxidation is the loss of electrons. Each of the elements (for example, chlorine) could potentially take electrons from something else and are subsequently ionized (e.g.  $Cl^-$ ). This means that they are all potential oxidizing agents.
- Fluorine is such a powerful oxidizing agent that solution reactions are unfeasible.
- Chlorine has the ability to take electrons from both bromide ions and iodide ions. Bromine and iodine cannot reclaim those electrons from the chloride ions formed.
- This indicates that chlorine is a more powerful oxidizing agent than either bromine or iodine.

- Similarly, bromine is a more powerful oxidizing agent than iodine. Bromine can remove electrons from iodide ions, producing iodine; iodine cannot reclaim those electrons from the resulting bromide ions.

In short, oxidizing ability decreases down the group.

### Explaining the trend

Whenever one of the halogens is involved in oxidizing a species in solution, the halogen ends is reduced to a halide ion associated with water molecules. The following figure illustrates this process:



Down the group, the ease with which these hydrated ions are formed decreases; the halogens become less effective as oxidizing agents, taking electrons from something else less readily.