Trends in atomic radius down a group

It is fairly obvious that the atoms get bigger as you go down groups. The reason is equally obvious - you are adding extra layers of electrons.

Trends in atomic radius across periods

You have to ignore the noble gas at the end of each period. Because neon and argon don't form bonds, you can only measure their van der Waals radius - a case where the atom is pretty well "unsquashed". All the other atoms are being measured where their atomic radius is being lessened by strong attractions. You aren't comparing like with like if you include the noble gases.

Leaving the noble gases out, atoms get smaller as you go across a period.

If you think about it, the metallic or covalent radius is going to be a measure of the distance from the nucleus to the electrons which make up the bond. (Look back to the left-hand side of the first diagram on this page if you aren't sure, and picture the bonding electrons as being half way between the two nuclei.)

From lithium to fluorine, those electrons are all in the 2-level, being screened by the $1s^2$ electrons. The increasing number of protons in the nucleus as you go across the period pulls the electrons in more tightly. The amount of screening is constant for all of these elements.

In the period from sodium to chlorine, the same thing happens. The size of the a curre comrolled by the 3-level bonding electrons being pulled closer to the nucleus by increasing numbers of period. In each case, screened by the 1- and 2-level electrons.

IONIC RADIUS

Ions aren't the same size of the atoms there or a for compare the sizes of sodium and chloride ions with the sizes of sodium and chlorine atoms.



Positive ions

Positive ions are smaller than the atoms they come from. Sodium is 2,8,1; Na⁺ is 2,8. You've lost a whole layer of electrons, and the remaining 10 electrons are being pulled in by the full force of 11 protons.

Negative ions

Negative ions are bigger than the atoms they come from. Chlorine is 2,8,7; Cl⁻ is 2,8,8. Although the electrons are still all in the 3-level, the extra repulsion produced by the incoming electron causes the atom to expand. There are still only 17 protons, but they are now having to hold 18 electrons.

IONIC STRUCTURES

The structure of a typical ionic solid - sodium chloride

How the ions are arranged in sodium chloride

Sodium chloride is taken as a typical ionic compound. Compounds like this consist of a giant (endlessly repeating) lattice of ions. So sodium chloride (and any other ionic compound) is described as having a giant ionic structure.

You should be clear that giant in this context doesn't just mean very large. It means that you can't state exactly how many ions there are.

There could be billions of sodium ions and chloride ions packed together, or trillions, or whatever - it simply depends how big the crystal is. That is different from, say, a water molecule which always contains exactly 2 hydrogen atoms and one oxygen atom - never more and never less.

A small representative bit of a sodium chloride lattice looks like this:



If you look at the diagram carefully, you will see that the sodium ions and chloride ions alternate with each other in each of the three dimensions.

This diagram is easy enough to draw with a computer, but extremely difficult to draw convincingly by hand. We normally draw an "exploded" version which looks like this:



Why is sodium chloride 6:6-co-ordinated?

The more attraction there is between the positive and negative ions, the more energy is released. The more energy that is released, the more energetically stable the structure becomes.

That means that to gain maximum stability, you need the maximum number of attractions. So why does each ion surround itself with 6 ions of the opposite charge?

That represents the maximum number of chloride ions that you can fit around a central sodium ion before the chloride ions start touching each other. If they start touching, you introduce repulsions into the crystal which makes it less stable.

The physical properties of sodium chloride

Sodium chloride has a high melting and boiling point

There are strong electrostatic attractions between the positive and negative ions, and it takes a lot of heat energy to overcome them. Ionic substances all have high melting and boiling points. Differences between ionic substances will depend on things like:

These variations in first ionisation energy can all be explained in terms of the structures of the atoms involved.

Factors affecting the size of ionisation energy

Ionisation energy is a measure of the energy needed to pull a particular electron away from the attraction of the nucleus. A high value of ionisation energy shows a high attraction between the electron and the nucleus.

The size of that attraction will be governed by:

The charge on the nucleus.

The more protons there are in the nucleus, the more positively charged the nucleus is, and the more strongly electrons are attracted to it.

The distance of the electron from the nucleus.

Attraction falls off very rapidly with distance. An electron close to the nucleus will be much more strongly attracted than one further away.

The number of electrons between the outer electrons and the nucleus. Consider a sodium atom, with the electronic structure 2,8,1. (There's no reasonable of the can't use this notation if it's useful!)

If the outer electron looks in towards the nucleus, it doesn't chucleus sharply netween it and the nucleus there are the two layers of electrons in the first and second levers. The 11 protons in the st dium shucleus have their effect cut down by the 10 inner electrons. The outer electron therefore only feels a net pull of approximately 1+ from the centre. This lessening of the pull of the nucleus by inner elegrons is known as espeeding or shielding.

Whether the electron is on its own in an urbital or paired with another electron.

Two electrons in the same orbital experience a bit of repulsion from each other. This offsets the attraction of the nucleus, so that paired electrons are removed rather more easily than you might expect.

Explaining the pattern in the first few elements

Hydrogen has an electronic structure of $1s^1$. It is a very small atom, and the single electron is close to the nucleus and therefore strongly attracted. There are no electrons screening it from the nucleus and so the ionisation energy is high (1310 kJ mol⁻¹).

Helium has a structure $1s^2$. The electron is being removed from the same orbital as in hydrogen's case. It is close to the nucleus and unscreened. The value of the ionisation energy (2370 kJ mol⁻¹) is much higher than hydrogen, because the nucleus now has 2 protons attracting the electrons instead of 1.

Lithium is $1s^22s^1$. Its outer electron is in the second energy level, much more distant from the nucleus. You might argue that that would be offset by the additional proton in the nucleus, but the electron doesn't feel the full pull of the nucleus - it is screened by the $1s^2$ electrons.

In period 3, the trend is exactly the same. This time, all the electrons being removed are in the third level and are screened by the 1s²2s²2p⁶ electrons. They all have the same sort of environment, but there is an increasing nuclear charge.

Why the drop between groups 2 and 3 (Be-B and Mg-Al)?

The explanation lies with the structures of boron and aluminium. The outer electron is removed more easily from these atoms than the general trend in their period would suggest.

Be	$1s^{2}2s^{2}$	$1 \text{ st I.E.} = 900 \text{ kJ mol}^{-1}$
В	$1s^{2}2s^{2}2p_{x}^{1}$	1st I.E. = 799 kJ mol ⁻¹

You might expect the boron value to be more than the beryllium value because of the extra proton. Offsetting that is the fact that boron's outer electron is in a 2p orbital rather than a 2s. 2p orbitals have a slightly higher energy than the 2s orbital, and the electron is, on average, to be found further from the nucleus. This has two effects.

- The increased distance results in a reduced attraction and so a reduced ionisation energy. •
- The 2p orbital is screened not only by the $1s^2$ electrons but, to some extent, by the $2s^2$ electrons as well. That also • reduces the pull from the nucleus and so lowers the ionisation energy.

The explanation for the drop between magnesium and aluminium is the same, except that every hing is happening at the 3level rather than the 2-level. Mg $1s^22s^22p^63s^2$ 1st I.E. = 736 kJ mol⁻¹ Al $1s^22s^22p^63s^23p_x^1$ 1st I.E. = 577 k/md⁻¹ The 3p electron in aluminium is slightly more distant from the nucleus than the 3s, and partially screened by the $3s^2$ electrons as well as the innumelections. Both of the factor of the effect of the extra proton. The 3p electron in alumining is slightly more di as well as the innucel chons. Both of the slight fiset the effect of the extra proton.

Why the drop between groups 5 and 6 (N-O and P-S)?

Once again, you might expect the ionisation energy of the group 6 element to be higher than that of group 5 because of the extra proton. What is offsetting it this time?

Ν	$1s^22s^22p_x^{1}2p_y^{1}2p_z^{1}$	$1 \text{ st I.E.} = 1400 \text{ kJ mol}^{-1}$
0	$1s^22s^22p_x^22p_y^12p_z^1$	$1 \text{ st I.E.} = 1310 \text{ kJ mol}^{-1}$

The screening is identical (from the $1s^2$ and, to some extent, from the $2s^2$ electrons), and the electron is being removed from an identical orbital.

The difference is that in the oxygen case the electron being removed is one of the $2p_x^2$ pair. The repulsion between the two electrons in the same orbital means that the electron is easier to remove than it would otherwise be.

The drop in ionisation energy at sulphur is accounted for in the same way.

Trends in ionisation energy down a group

As you go down a group in the Periodic Table ionisation energies generally fall. You have already seen evidence of this in the fact that the ionisation energies in period 3 are all less than those in period 2.

Taking Group 1 as a typical example:

Why is the sodium value less than that of lithium?

There are 11 protons in a sodium atom but only 3 in a lithium atom, so the nuclear charge is much greater. You might have expected a much larger ionisation energy in sodium, but offsetting the nuclear charge is a greater distance from the nucleus and more screening.

Li $1s^22s^1$ 1st I.E. = 519 kJ mol⁻¹ Na $1s^22s^22p^63s^1$ 1st I.E. = 494 kJ mol⁻¹





Lithium's outer electron is in the second level, and only has the $1s^2$ electrons to screen it. The $2s^1$ electron feels the pull of 3 protons screened by 2 electrons - a net pull from the centre of 1+.

The sodium's outer electron is in the third level, and is screened from the 11 proton Ω , the ducleus by a total of 10 inner electrons. The 3s¹ electron also feels a net pull of 1+ from the centrer of the extra Ω m other words, the effect of the extra protons is compensated for by the effect of the extra screening electrons. The only factor left is the extra distance between the outer electron and the nucleus in sodium's case. That Ω were the ionisation energy.

Similar explanations hold as you way in the rest of this group or, indeed, any other group. Ionisation energies and reactivity

The lower the ionisation energy, the more easily this change happens:

X(g) ----- X+(g) + e

You can explain the increase in reactivity of the Group 1 metals (Li, Na, K, Rb, Cs) as you go down the group in terms of the fall in ionisation energy. Whatever these metals react with, they have to form positive ions in the process, and so the lower the ionisation energy, the more easily those ions will form.

The danger with this approach is that the formation of the positive ion is only one stage in a multi-step process.

For example, you wouldn't be starting with gaseous atoms; nor would you end up with gaseous positive ions you would end up with ions in a solid or in solution. The energy changes in these processes also vary from element to element. Ideally you need to consider the whole picture and not just one small part of it.



electron affinity) because the energy released in other steps in its reactions more than makes up for the lower amount of energy released as electron affinity. Second electron affinity

You are only ever likely to meet this with respect to the group 6 elements oxygen and sulphur which both form 2- ions.

Defining second electron affinity

The second electron affinity is the energy required to add an electron to each ion in 1 mole of gaseous 1- ions to produce 1 mole of gaseous 2- ions.

This is more easily seen in symbol terms.

X⁻(a) + e⁻ → X²⁻(a)

It is the energy needed to carry out this change per mole of X⁻.

Why is energy needed to do this?

You are forcing an electron into an already negative ion. It's not going to go in willingly!



ELECTRONEGATIVITY

What is electronegativity Definition

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned a value of 4.0, and values range down to caesium and francium which are the least electronegative at 0.7.

What happens if two atoms of equal electronegativity bond together?

Consider a bond between two atoms, A and B. Each atom may be forming other bonds as well as the one shown - but these are irrelevant to the argument.



Lithium iodide, on the other hand, would be described as being "ionic with some covalent character". In this case, the pair of electrons hasn't moved entirely over to the iodine end of the bond. Lithium iodide, for example, dissolves in organic solvents like ethanol - not something which ionic substances normally do.

Summary

- No electronegativity difference between two atoms leads to a pure non-polar covalent bond.
- A small electronegativity difference leads to a polar covalent bond. \Box A large electronegativity

difference leads to an ionic bond. Polar bonds and polar molecules

In a simple molecule like HCl, if the bond is polar, so also is the whole molecule. What about more complicated molecules?

In CCl₄, each bond is polar.



The hydrogen at the top of the molecule is less electronegative than carbon and so is slightly positive. This means that the molecule now has a slightly positive "top" and a slightly negative "bottom", and so is overall a polar molecule.

A polar molecule will need to be "lop-sided" in some way.

Patterns of electronegativity in the Periodic Table

The most electronegative element is fluorine. If you remember that fact, everything becomes easy, because electronegativity must always increase towards fluorine in the Periodic Table.

Note: This simplification ignores the noble gases. Historically this is because they were believed not to form bonds - and if they don't form bonds, they can't have an electronegativity value. Even now that we know that some of them do form bonds, data sources still don't quote electronegativity values for them.

Explaining the increase in atomic radius

The radius of an atom is governed by

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

Compare lithium and sodium:

Li $1s^22s^1$ Na $1s^22s^22p^63s^1$



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.

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

Trends in First Ionisation Energy

First ionisation energy is the energy needed to remove the more loos ary held electron from each of one mole of gaseous atoms to make one mole of singly charges g soous ions - in other words, for 1 mole of this process:

First Ionisation Energy of the Group 1 elements



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

Explaining the decrease in first ionisation energy

Ionisation energy is governed by

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

Li	red
Na	strong persistent orange
Κ	lilac (pink)
Rb	red (reddish-violet)
Cs	blue? violet? (see below)
Ca	orange-red
Sr	red
Ba	pale green
Cu	blue-green (often with white flashes)
Pb	greyish-white

The colours in the table are just a guide. Almost everybody sees and describes colours differently, For example, the word "red" has been used several times to describe colours which can be quite different from each other. Other people use words like "carmine" or "crimson" or "scarlet",

REACTIONS OF THE GROUP 1 ELEMENTS WITH OXYGEN AND CHLORINE

General These are all very reactive metals and have to be stored out of to motion air to prevent their oxidation. Reactivity increases as you go down the Group as you go down the Group.

Depending on how far down the From e are formed when the metals burn (details below). Reaction with oxygen is not the leaction with air. note dramatic version

Lithium is unique in the Group because it also reacts with the nitrogen in the air to form lithium nitride (again, see below).

Details for the individual metals Lithium

Lithium burns with a strongly red-tinged flame if heated in air. It reacts with oxygen in the air to give white lithium oxide. With pure oxygen, the flame would simply be more intense.

4Li + O2 ------ 2Li2O

For the record, it also reacts with the nitrogen in the air to give lithium nitride. Lithium is the only element in this Group to form a nitride in this way.

6Li + N₂ ------ 2Li₃N

Sodium

Small pieces of sodium burn in air with often little more than an orange glow. Using larger amounts of sodium or burning it in oxygen gives a strong orange flame. You get a white solid mixture of sodium oxide and sodium peroxide.

The equation for the formation of the simple oxide is just like the lithium one.

You are probably familiar with the reaction between magnesium and dilute sulphuric acid to give lots of hydrogen and a colourless solution of *magnesium sulphate*. Notice that you get a solution, not a precipitate. The magnesium sulphate is obviously soluble.

You may also remember that *barium sulphate* is formed as a white precipitate during the test for sulphate ions in solution. The ready formation of a precipitate shows that the barium sulphate must be pretty insoluble. In fact, 1 litre of water will only dissolve about 2 mg of barium sulphate at room temperature.

Solubility of halides

The halides of the alkaline earth metals, MX₂, are easily isolated and the anhydrous salts can be obtained by heating the hydrated salts and are essentially ionic. The halides of Mg and Ca readily absorb and are soluble in water. The solubility of the halide decreases on descending the group because the hydration enthalpies decrease faster than the lattice enthalpies do. The solubilities of the fluorides of group 2 follow the opposite trend however. This is because the very small size of the fluoride ions means that in the solid state the much larger M²⁺ ions are more and more in contact with each other as their size increases causing a faster lowering of the lattice energies

Solubility of the carbonates

lotesale.co.uk The carbonates tend to become less soluble

None of the carbonates is anything Augnesium carbonate is soluble to the extent of about 0.02 g per 100 g

The trend to lower solubility is, however, broken at the bottom of the Group. Barium carbonate is slightly more soluble than strontium sulphate.

There are no simple examples which might help you to remember the carbonate trend.

THERMAL STABILITY OF THE GROUP 2 CARBONATES AND NITRATES

The effect of heat on the Group 2 carbonates

All the carbonates in this Group undergo thermal decomposition to give the metal oxide and carbon dioxide. Thermal decomposition is the term given to splitting up a compound by heating it.

If "X" represents any one of the elements:

XCO3(s) - XO(s) + CO2(a)

As you go down the Group, the carbonates have to be heated more strongly before they will decompose.

The carbonates become more stable to heat as you go down the Group.

The effect of heat on the Group 2 nitrates

The structure of the carbonate ion

If you worked out the structure of a carbonate ion using "dots-and-crosses" or some similar method, you would probably come up with:

This shows two single carbon-oxygen bonds and one double one, with two of the oxygens each carrying a negative charge. Unfortunately, in real carbonate ions all the bonds are identical, and the charges are spread out over the whole ion - although concentrated on the oxygen atoms. We say that the charges are *delocalised*.

This is a rather more complicated version of the bonding you might have come across in benzene or in ions like ethanoate. For the purposes of this topic, you don't need to understand how this bonding has come about.

The next diagram shows the delocalised electrons. The shading is intended to show that there is a greater chance of finding them around the oxygen atoms than near the carbon.



Polarising the carbonate ion

Now imagine what happens when this ion is placed next to a positive ion. The past of ion attracts the delocalised electrons in the carbonate ion towards itself. The carbonate ion becomes places at the delocalised electrons in the carbonate ion towards itself.



If this is heated, the carbon dioxide breaks free to leave the metal oxide.

How much you need to heat the carbonate before that happens depends on how polarised the ion was. if it is highly polarised, you need less heat than if it is only slightly polarised.

The smaller the positive ion is, the higher the charge density, and the greater effect it will have on the carbonate ion. As the positive ions get bigger as you go down the Group, they have less effect on the carbonate ions near them. To compensate for that, you have to heat the compound more in order to persuade the carbon dioxide to break free and leave the metal oxide.

In other words, as you go down the Group, the carbonates become more thermally stable.

What about the nitrates?

The argument is exactly the same here. The small positive ions at the top of the Group polarise the nitrate ions more than the larger positive ions at the bottom. Drawing diagrams to show this happening is much more difficult because the process has interactions involving more than one nitrate ion.

Explaining the trend in terms of the energetics of the process

Looking at the enthalpy changes

If you calculate the enthalpy changes for the decomposition of the various carbonates, you find that all the changes are quite strongly endothermic. That implies that the reactions are likely to have to be heated constantly to make them happen.

The calculated enthalpy changes (in kJ mol⁻¹) are given in the table. Figures to calculate the beryllium carbonate value weren't available. Remember that the reaction we are talking about is:

XCO _{3(s}	3) ———		XO ₍₃₎ +	CO _{2(g)}
MgCO ₃		+11'	7	
CaCO ₃	+178			
SrCO ₃	+235			

BaCO₃

You can see that the reactions become more endothermic as you go down the Group. That's entirely what you would expect as the carbonates become more thermally stable. You have to supply increasing amounts of heat energy to make them otesale.co. decompose.

Explaining the enthalpy changes

+267

(or with Born-Haber cycles) and with Here's where things start to get difficult! If you aren't in ilia with Hess's Law c lattice enthalpies (lattice energies), you aren't row, to understand the next bil. Don't waste your time looking at it.

Using an enthal

You can dig around to find the underlying causes of the increasingly endothermic changes as you go down the Group by drawing an enthalpy cycle involving the lattice enthalpies of the metal carbonates and the metal oxides.

n

Lattice enthalpy is the heat needed to split one mole of crystal in its standard state into its separate gaseous ions. For example, for magnesium oxide, it is the heat needed to carry out 1 mole of this change:

MgO(s) → Mg²⁺(a) + O²(a) LE = +3889 kJ mol⁻¹

The cycle we are interested in looks like this:



You can apply Hess's Law to this, and find two routes which will have an equal enthalpy change because they start and end in the same places.



These values both fall as you go down the Group.

For reasons we will look at shortly, the lattice enthalpies of both the oxides and carbonates fall as you go down the Group. But they don't fall at the same rate.

The oxide lattice enthalpy falls faster than the carbonate one. If you think carefully about what happens to the value of the overall enthalpy change of the decomposition reaction, you will see that it gradually becomes more positive as you go down the Group.

than they usually are. If the solution is hot and concentrated (as it is likely to be if you add water to solid beryllium chloride a very exothermic reaction), chloride ions can remove one or more of these hydrogen ions to produce hydrogen chloride gas. All the other ionic chlorides in Group 2 dissolve in water without any obvious reaction. **The structure of beryllium**

empty orbital

empty orbital

chloride As a gas ...

Beryllium chloride, BeCl₂, is a linear molecule with all three atoms in a straight line. Showing only the outer electrons:

Beryllium chloride is known as an *electron-deficient compound* because it has the two empty orbitals at the bonding level.

As a solid . . .

If it had this same simple structure as a solid, you would expect the melting point to be much lower than it actually is. It is a very small molecule, and so the intermolecular attractions would be expected to be fairly weak.



Why isn't beryllium chloride ionic?

Beryllium has quite a high electronegativity compared with the rest of the Group. That means that it attracts a bonding pair of electrons towards itself more strongly than magnesium and the rest do.

In order for an ionic bond to form, the beryllium has to let go of its electrons. It is too electronegative to do that.

Beryllium forms 4-coordinated complex ions

Some simple background

Although beryllium doesn't normally form simple ions, Be^{2+} , it does form ions in solution. In these, the beryllium ion becomes attached to four water molecules to give a complex ion with the formula $[Be(H_2O)_4]^{2+}$.

That means that it will be fairly easy to convert tin(II) compounds into tin(IV) compounds. This is best shown in the fact that Sn²⁺ ions in solution are good reducing agents.

For example, a solution containing tin(II) ions (for example, tin(II) chloride solution) will reduce a solution of iodine to iodide ions. In the process, the tin(II) ions are oxidised to tin(IV) ions.



Tin(II) ions also reduce iron(III) ions to iron(II) ions. For example, tin(II) chloride solution will reduce iron(III) chloride solution to iron(II) chloride solution. In the process, the tin(II) ions are oxidised to the more stable tin(IV) ions.



Tin(II) ions will also, of course, be easily oxidised by powerful oxidising agents like acid the horassium manganate(VII) solution (potassium permanganate solution). This reaction could be used as a tradition of the concentration of tin(II) ions in a solution.



In organic chemistry, tin and concentrated hydrochloric acid are traditionally used to reduce nitrobenzene to phenylamine (aniline). This reaction involves the tin first being oxidised to tin(II) ions and then further to the preferred tin(IV) ions.

Examples from lead chemistry

With lead, the situation is reversed. This time, the lead(II) oxidation state is the more stable, and there is a strong tendency for lead(IV) compounds to react to give lead(II) compounds.

Lead(IV) chloride, for example, decomposes at room temperature to give lead(II) chloride and chlorine gas:



... and lead(IV) oxide decomposes on heating to give lead(II) oxide and oxygen.



Lead(IV) oxide also reacts with concentrated hydrochloric acid, oxidising some of the chloride ions in the acid to chlorine gas. Once again, the lead is reduced from the +4 to the more stable +2 state.



Trying to explain the trends in oxidation states

There's nothing surprising about the normal Group oxidation state of +4.

All of the elements in the group have the outer electronic structure $ns^2np_x^1np_y^1$, where n varies from 2 (for carbon) to 6 (for lead). The oxidation state of +4 is where all these outer electrons are directly into variation the bonding.

As you get closer to the bottom of the Group, there is an increase optendency for the r² pair not to be used in the bonding. This is often known as the *inert pair effect* - and is dominant in lead chemistry.

However, just giving it a name i C'h ert pair effect" explans o thing. You need to look at two different explanations depending on whet et you are talking about the form of ionic or covalent bonds.

The inert pair effect in the formation of ionic bonds

If the elements in Group 4 form 2+ ions, they will lose the p electrons, leaving the s² pair unused. For example, to form a lead(II) ion, lead will lose the two 6p electrons, but the 6s electrons will be left unchanged - an "inert pair".

You would normally expect ionisation energies to fall as you go down a Group as the electrons get further from the nucleus. That doesn't quite happen in Group 4.

This first chart shows how the total ionisation energy needed to form the 2+ ions varies as you go down the Group. The values are all in kJ mol⁻¹.

So that's how the carbon is organised just before it bonds. Now we need to look at the oxygen.

Oxygen's electronic structure is 1s²2s²2p_x²2p_y¹2p_z¹.

Hybridisation occurs in the oxygen as well. This time, sp^2 hybrids are formed with the s orbital and two of the p orbitals being rearranged to give 3 orbitals of equal energy - leaving a temporarily unaffected p orbital.



This time two of the sp² hybrid orbitals contain lone pairs of electrons.



Then bring them together so that the pale green hybrid orbitals overlap end-to-end to form simple covalent bonds. These are properly called sigma bonds, and are shown as orange in the next diagram.

This brings the various p orbitals close enough together that they overlap sideways.

They are all simple covalent molecules with a typical tetrahedral shape. All of them are liquids at room temperature. (Although at room temperature, lead(IV) chloride will tend to decompose to give lead(II) chloride and chlorine gas - see below.)

Lead(II) chloride, PbCl₂

Lead(II) chloride is a white solid, melting at 501°C. It is very slightly soluble in cold water, but more soluble in hot water. You can think of lead(II) chloride as being mainly ionic in character.

Stability

At the top of Group 4, the most stable oxidation state shown by the elements is +4. This is the oxidation state shown by carbon and silicon in CCl₄ and SiCl₄. These therefore have no tendency to split up to give dichlorides.

However, the relative stability of the +4 oxidation state falls as you go down the Group, and the +2 oxidation state becomes the most stable by the time you get to lead.

Lead(IV) chloride decomposes at room temperature to give the more stable lead(II) chloride and chlorine gas.



Suppose a water molecule is going to react with the carbon tetrachloride. The reaction would have to start by the water molecule's oxygen attaching itself to the carbon atom via the oxygen's lone pair. A chlorine atom would get pushed off the carbon in the process.

There are two problems with this.

First, the chlorines are so bulky and the carbon atom so small, that the oxygen can't easily get at the carbon atom.



... and even if it did, there will be a stage where there is considerable cluttering around that carbon atom before the chlorine atom breaks away completely. There is going to be a lot of repulsion between the various lone pairs on all the atoms surrounding the carbon.