ELECTRONEGATIVITY

This page explains what electronegativity is, and how and why it varies around the Periodic Table. It looks at the way that electronegativity differences affect bond type and explains what is meant by polar bonds and polar molecules.

If you are interested in electronegativity in an organic chemistry context, you will find a link at the bottom of this page.

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 cesium 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.

\[ \text{A} \quad \bullet \quad \text{B} \]

If the atoms are equally electronegative, both have the same tendency to attract the bonding pair of electrons, and so it will be found on average half way between the two atoms. To get a bond like this, A and B would usually have to be the same atom. You will find this sort of bond in, for example, H₂ or Cl₂ molecules.

Note: It's important to realize that this is an average picture. The electrons are actually in a molecular orbital, and are moving around all the time within that orbital.

This sort of bond could be thought of as being a "pure" covalent bond – where the electrons are shared evenly between the two atoms.

What happens if B is slightly more electronegative than A?
B will attract the electron pair rather more than A does.

\[ \text{\delta^+ A} \quad \bullet \quad \text{\delta^- B} \]

That means that the B end of the bond has more than its fair share of electron density and so becomes slightly negative. At the same time, the A end (rather short of electrons) becomes slightly positive. In the diagram, "\(\delta\)" (read as "delta") means "slightly" - so \(\delta^+\) means "slightly positive".

Defining polar bonds
This is described as a polar bond. A polar bond is a covalent bond in which there is a separation of charge between one end and the other – in other words in which one end is slightly positive and the other slightly negative. Examples include most covalent bonds. The hydrogen-chlorine bond in HCl or the hydrogen-oxygen bonds in water are typical.
What happens if B is a lot more electronegative than A?
In this case, the electron pair is dragged right over to B's end of the bond. To all intents and purposes, A has lost control of its electron, and B has complete control over both electrons. Ions have been formed.

```
+      |
A --- B
```

A "spectrum" of bonds
The implication of all this is that there is no clear-cut division between covalent and ionic bonds. In a pure covalent bond, the electrons are held on average exactly half way between the atoms. In a polar bond, the electrons have been dragged slightly towards one end.

How far does this dragging have to go before the bond counts as ionic? There is no real answer to that. You normally think of sodium chloride as being a typically ionic solid, but even here the sodium hasn't completely lost control of its electron. Because of the properties of sodium chloride, however, we tend to count it as if it were purely ionic.

Note: Don't worry too much about the exact cut-off point between polar covalent bonds and ionic bonds. Our examples will tend to avoid the grey areas – they will be obviously covalent or obviously ionic. You will, however, be expected to realize that those grey areas exist.

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.
- 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 CCl$_4$, each bond is polar.

```
Cl     
\(     \)
     Cl
     Cl
```

Note: Ordinary lines represent bonds in the plane of the paper. Dotted lines represent bonds going away from you into the screen or paper. Wedged lines represent bonds coming out of the screen or paper towards you.
The molecule as a whole, however, isn't polar – in the sense that it doesn't have an end (or a side) which is slightly negative and one which is slightly positive. The whole of the outside of the molecule is somewhat negative, but there is no overall separation of charge from top to bottom, or from left to right.

By contrast, CHCl₃ is polar.

![Diagram of CHCl₃ molecule]

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.

![Electronegativity chart]

Trends in electronegativity across a period

As you go across a period the electronegativity increases. The chart shows electronegativities from sodium to chlorine – you have to ignore argon. It doesn't have an electronegativity, because it doesn't form bonds.

Based on:
Clark, Jim. “chemguide.” 2000. 6 Dec 2001 <http://www.chemguide.co.uk/>
Trends in electronegativity down a group
As you go down a group, electronegativity decreases. (If it increases up to fluorine, it must decrease as you go down.) The chart shows the patterns of electronegativity in Groups 1 and 7.

Explaining the patterns in electronegativity
The attraction that a bonding pair of electrons feels for a particular nucleus depends on:
- the number of protons in the nucleus;
- the distance from the nucleus;
- the amount of screening by inner electrons.

Why does electronegativity increase across a period?
Consider sodium at the beginning of period 3 and chlorine at the end (ignoring the noble gas, argon). Think of sodium chloride as if it were covalently bonded.

![Diagram of NaCl bonding pair](image)

Both sodium and chlorine have their bonding electrons in the 3-level. The electron pair is screened from both nuclei by the 1s, 2s and 2p electrons, but the chlorine nucleus has 6 more protons in it. It is no wonder the electron pair gets dragged so far towards the chlorine that ions are formed.

Electronegativity increases across a period because the number of charges on the nucleus increases. That attracts the bonding pair of electrons more strongly.

Why does electronegativity fall as you go down a group?
Think of hydrogen fluoride and hydrogen chloride.

![Diagram of HF and HCl bonding pairs](image)

The bonding pair is shielded from the fluorine's nucleus only by the 1s² electrons. In the chlorine case it is shielded by all the 1s² 2s² 2p⁶ electrons.

In each case there is a net pull from the centre of the fluorine or chlorine of +7. But fluorine has the bonding pair in the 2-level rather than the 3-level as it is in chlorine. If it is closer to the nucleus, the attraction is greater.

Based on:
Clark, Jim. “chemguide.” 2000. 6 Dec 2001 <http://www.chemguide.co.uk/>
As you go down a group, electronegativity decreases because the bonding pair of electrons is increasingly distant from the attraction of the nucleus.

**The polarizing ability of positive ions**

*What do we mean by "polarizing ability"?*

In the discussion so far, we've thought of ions as arising from highly distorted covalent bonds. You can also think of it the other way round.

Solid aluminum chloride is covalent. Imagine instead that it was ionic. It would contain Al\(^{3+}\) and Cl\(^-\) ions.

The aluminum ion is very small and is packed with three positive charges – the "charge density" is therefore very high. That will have a considerable effect on any nearby electrons.

![Diagram](image)

In the case of aluminum chloride, the electron pairs are dragged back towards the aluminum to such an extent that the bonds becomes covalent.

**Factors affecting polarizing ability**

Positive ions can have the effect of polarizing (electrically distorting) nearby negative ions. The polarizing ability depends on the charge density in the positive ion.

Polarizing ability increases as the positive ion gets smaller and the number of charges gets larger.

As a negative ion gets bigger, it becomes easier to polarize. For example, in an iodide ion, I\(^-\), the outer electrons are in the 5-level – relatively distant from the nucleus.

A positive ion would be more effective in attracting a pair of electrons from an iodide ion than the corresponding electrons in, say, a fluoride ion where they are much closer to the nucleus. Aluminum iodide is covalent because the electron pair is easily dragged away from the iodide ion. On the other hand, aluminum fluoride is ionic because the aluminum ion can't polarize the small fluoride ion sufficiently to form a covalent bond.
Specific examples

What happens if two atoms of equal electronegativity bond together?
The most obvious example of this is the bond between two carbon atoms. Both atoms will attract the bonding pair to exactly the same extent. That means that on average the electron pair will be found half way between the two nuclei, and you could draw a picture of the bond like this:

It is important to realize that this is an average picture. The electrons are actually in a sigma orbital, and are moving constantly within that orbital.

Help! A sigma orbital is a molecular orbital formed by end-to-end overlap between two atomic orbitals.

The carbon-fluorine bond
Fluorine is much more electronegative than carbon. The actual values on the Pauling scale are

<table>
<thead>
<tr>
<th></th>
<th>Carbon</th>
<th>Fluorine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

That means that fluorine attracts the bonding pair much more strongly than carbon does. The bond - on average - will look like this:

Why is fluorine more electronegative than carbon?
A simple dots-and-crosses diagram of a C-F bond is perfectly adequate to explain it.

The bonding pair is in the second energy level of both carbon and fluorine, so in the absence of any other effect, the distance of the pair from both nuclei would be the same.

The electron pair is shielded from the full force of both nuclei by the 1s electrons – again there is nothing to pull it closer to one atom than the other.

BUT, the fluorine nucleus has 9 protons whereas the carbon nucleus has only 6.

Allowing for the shielding effect of the 1s electrons, the bonding pair feels a net pull of about 4+ from the carbon, but about 7+ from the fluorine. It is this extra nuclear charge which pulls the bonding pair (on average) closer to the fluorine than the carbon.
Help! You have to imagine what the bonding pair "sees" if it looks in towards the nucleus. In the carbon case, it sees 6 positive protons, and 2 negative electrons. That means that there will be a net pull from the carbon of about 4+. The shielding wouldn't actually be quite as high as 2-, because the 1s electrons spend some of their time on the far side of the carbon nucleus – and so aren't always between the bonding pair and the nucleus.

Incidentally, thinking about electrons looking towards the nucleus may be helpful in picturing what is going on, but avoid using terms like this in exams.

The carbon-chlorine bond
The electronegativities are:

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>2.5</td>
</tr>
<tr>
<td>Chlorine</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The bonding pair of electrons will be dragged towards the chlorine but not as much as in the fluorine case. Chlorine isn't as electronegative as fluorine.

Why isn't chlorine as electronegative as fluorine?
Chlorine is a bigger atom than fluorine.
fluorine: 1s² 2s² 2pₓ² 2pᵧ² 2p𝑧¹
chlorine: 1s² 2s² 2pₓ² 2pᵧ² 2p𝑧² 3s² 3pₓ² 3pᵧ² 3p𝑧¹

In the chlorine case, the bonding pair will be shielded by all the 1-level and 2-level electrons. The 17 protons on the nucleus will be shielded by a total of 10 electrons, giving a net pull from the chlorine of about 7+.

That is the same as the pull from the fluorine, but with chlorine the bonding pair starts off further away from the nucleus because it is in the 3-level. Since it is further away, it feels the pull from the nucleus less strongly.

Polar bonds
Think about the carbon-fluorine bond again. Because the bonding pair is pulled towards the fluorine end of the bond, that end is left rather more negative than it would otherwise be. The carbon end is left rather short of electrons and so becomes slightly positive.

\[ \delta^+ \quad \delta^- \]

The symbols \( \delta^+ \) and \( \delta^- \) mean "slightly positive" and "slightly negative." You read \( \delta^+ \) as "delta plus" or "delta positive".

We describe a bond having one end slightly positive and the other end slightly negative as being *polar.*
Some important examples of polar bonds
Hydrogen bromide (and other hydrogen halides)

\[
\begin{array}{c}
\text{H} \\
\text{Br}
\end{array}
\]

\(\delta^+\) \hspace{1cm} \(\delta^-\)

Bromine (and the other halogens) are all more electronegative than hydrogen, and so all the hydrogen halides have polar bonds with the hydrogen end slightly positive and the halogen end slightly negative.

**Help! Halogen:** a member of group VII of the Periodic Table – fluorine, chlorine, bromine and iodine.

**Halide:** a compound of one of these – e.g. hydrogen chloride, hydrogen bromide, etc.

The polarity of these molecules is important in their reactions.

**The carbon-bromine bond in compounds**
Bromine is more electronegative than carbon and so the bond is polarized in the way that we have already described with C-F and C-Cl.

\[
\begin{array}{c}
\text{C} \\
\text{Br}
\end{array}
\]

\(\delta^+\) \hspace{1cm} \(\delta^-\)

The polarity of the carbon-halogen bonds is important in reactions.

**The carbon-oxygen double bond, the carbonyl group**
**The simple view of the bonding in carbon-oxygen double bonds**
The very electronegative oxygen atom pulls both bonding pairs towards itself – in the sigma bond and the pi bond. That leaves the oxygen fairly negative and the carbon fairly positive.

\[
\begin{array}{c}
\text{C} \\
\text{O}
\end{array}
\]

\(\delta^+\) \hspace{1cm} \(\delta^-\)

Where the carbon-oxygen double bond, C=O, occurs in organic compounds it is called a *carbonyl group*. The simplest compound containing this group is methanal.

We are going to look at the bonding in methanal, but it would equally apply to any other compound containing C=O. The interesting thing is the nature of the carbon-oxygen double bond - not what it's attached to.
An orbital view of the bonding in carbon-oxygen double bonds

*The carbon atom*

Just as in ethene, the carbon atom is joined to three other atoms. The carbon's electrons rearrange themselves, and promotion and hybridizations give sp\(^2\) hybrid orbitals.

Promotion gives:

\[
\begin{array}{c}
\text{promotion} \\
\begin{array}{c}
2s \\
\text{promotion} \\
2p_x \\
\text{promotion} \\
2p_y \\
\text{promotion} \\
2p_z
\end{array}
\end{array}
\rightarrow
\begin{array}{c}
\begin{array}{c}
2s \\
\text{promotion} \\
2p_x \\
\text{promotion} \\
2p_y \\
\text{promotion} \\
2p_z
\end{array}
\end{array}
\]

Hybridization of the 2s orbital and two of the 2p orbitals means that the carbon atom now looks like the diagram on the right.

Three sp\(^2\) hybrid orbitals are formed and these arrange themselves as far apart in space as they can – at 120° to each other. The remaining p orbital is at right angles to them.

This is exactly the same as in ethene.

*The oxygen atom*

Oxygen's electronic structure is \(1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1\).

The 1s electrons are too deep inside the atom to be concerned with the bonding and so we'll ignore them from now on. Hybridization occurs in the oxygen as well. It is easier to see this using "electrons-in-boxes".

This time two of the sp\(^2\) hybrid orbitals contain lone pairs of electrons.

Help! A "lone pair" of electrons is a pair of electrons at the bonding level which isn't being used to bond on to another atom.

The carbon atom and oxygen atom then bond in much the same way as the two carbons do in ethene. In the next diagram, we are assuming that the carbon will also bond to two hydrogens to make methanal – but it could equally well bond to anything else.

Based on:
Clark, Jim. "chemguide. 2000. 6 Dec 2001 <http://www.chemguide.co.uk/>
End-to-end overlap between the atomic orbitals that are pointing towards each other produce sigma bonds.

Notice that the p orbitals are overlapping sideways.

This sideways overlap produces a pi bond. So just like C=C, C=O is made up of a sigma bond and a pi bond.

Does that mean that the bonding is exactly the same as in ethene? No! The distribution of electrons in the pi bond is heavily distorted towards the oxygen end of the bond, because oxygen is much more electronegative than carbon.

This distortion in the pi bond causes major differences in the reactions of compounds containing carbon-oxygen double bonds like methanal compared with compounds containing carbon-carbon double bonds like ethene.