

[A First Year blog on Melting and Boiling Points: Part 1, 2nd February 2019](#)

(This is a **revision** blog. It is merely a *summary* of some of the things that you need to know. *Everything in this blog can be found in the First Year, Foundation Chemistry Book.*)

This blog will be divided into the following Sections

Part 1 An examination of what happens when things Melt and Boil.

Part 2 An explanation of the forces that hold (i) solid substances and (ii) liquid substances together viz. Hydrogen bonds, and the three forces of attraction known collectively as van der Waals’/and London (after Fritz London) forces of attraction. In general these are

A Hydrogen bonds, and

B1 Permanent dipole to Permanent dipole forces of attraction

B2 Permanent Dipole to Induced dipole forces of attraction, and

B3 Temporary/Momentary/Instantaneous dipole to Induced dipole forces of attraction.

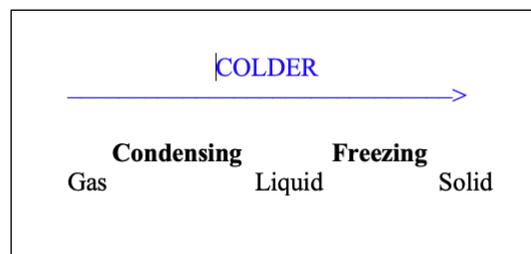
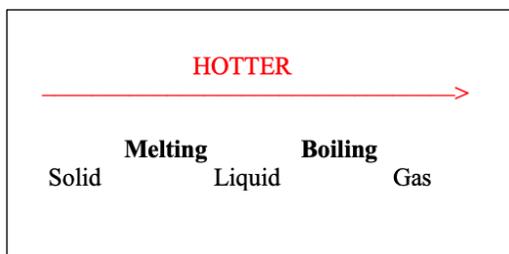
Part 3 An explanation of the above forces.

Part 4 An examination of the forces required to break these bonds (including the sort of questions that are asked in the ‘A’ Level exams requiring candidates to explain the Melting and Boiling temperatures of different substances).

Different forces hold different substances together, and in order to understand what happens in melting and boiling, one must first understand the forces that hold different substances together (because different amounts of energy are required to break differing forces). However, we must talk first about the **processes** involved in the melting and boiling of (A) Metallic substances (B) Ionic substances, and (C) Molecular substances.

There are four common “states” that a substance can have viz. solid (s), liquid (l), gaseous (g), and aqueous (aq). *A plasma contains ionised gas, but plasmas are not part of the UK ‘A’ Level Syllabus.*

In the action of **melting**, a substance becomes converted from a solid to a liquid, and during **boiling** a substance moves from the liquid state to the gaseous state. Some substances such as Iodine and Carbon Dioxide make the transition from a solid straight to the gaseous state without passing through the liquid state. This process is called “**sublimation**” (and the transition back from gas to solid is called “**deposition**”).



The transition from one state to another is a physical change. **No chemical change occurs.** The transition from *ice* H₂O (s) to *liquid water* H₂O (l) is a **physical** and not a chemical change. The transition from *liquid water* H₂O (l) to *steam* H₂O (g) is also a **physical** and not a chemical change. **The substance, Water, remains chemically unchanged throughout both of these processes.**

States of substances

Different substances can exist in different physical states or in different physical *phases* and the two things are not quite the same. (The difference is explained below).

Water can exist as the liquid that runs out of your tap when you wash your hands, or it can exist as the steam that comes out of the spout of your kettle when you make yourself a cup of tea, or it can exist as the ice on a puddle of water in winter, and these are the three most common states viz. Liquid **(l)**, Gas **(g)**, and Solid **(s)**; but, there is one additional very important state in Chemistry, and that is that of something **dissolved in water**. This is called the “Aqueous” **(aq)** state. Its name comes from the Latin word for Water viz. “aqua” – and in English “**(aq)**” could also stand for the adjective “Aquated”. If a substance is dissolved in something other than Water, then the state is not called “(aq)”. It is a *solution*.

The four common States in Chemistry are thus

Liquid	(l)
Gas/gaseous	(g)
Solid	(s)
Aqueous/Aquated	(aq)

In Chemistry, the state in which something is being used can be very important¹ and it is therefore sometimes convenient *and at other times vitally important* to write down the state of the substance that is being used. For example when you were doing GCSE Chemistry you learnt that when you add Hydrochloric Acid² to solid Calcium Carbonate, then the two substances will react together to form Water, Carbon Dioxide and Calcium Chloride. The reaction is written as follows



and you can see that here we have specified the states in which the substances above are being used/being formed.

Equally, if the reactants had involved Silver and one of the products had been Silver Chloride, then we would have put “(s)” after the Silver Chloride, and this would have been made it very clear that the Silver Chloride is a solid (and even though it is an ionic ‘salt’, it is one of the ionic ‘salts’ that is *not* soluble in Water) – therefore it was being formed as a precipitate.³

Phases

All that I want to say about phases is that two different substances can have the same state (e.g. “liquid”) but if when they are mixed together they still separate out from each other and then remain distinct from each other (i.e. one floats on top of the other) then the two substances are in different **phases**. We will need this distinction when we come to talk about

- i) Electrochemistry (where we will talk about “phase boundaries”), and we will also encounter this in
- ii) Organic Chemistry when we talk about immiscible liquids (and “immiscible” means that even if two liquids are mixed together they will still separate out and remain distinct from each other).

¹ For example, the amount of heat involved in doing something to a given mass of water will depend critically on whether the water is in liquid, solid or gaseous form.

² **An acid is a substance that dissociates protons.** HCl(g) is a molecular substance and **it is NOT acidic until it comes into contact with water** and forms HCl(aq) at which time it then becomes an ionic substance when the H⁺(aq) and Cl⁻(aq) species are formed. Until the H⁺(aq) species is formed, HCl (g) i.e. Hydrogen Chloride gas is NOT an acid because in that state/phase it cannot dissociate protons!

³ The English word “Precipitate” comes from the Latin verb “precipitare” ‘to throw out’. Therefore in Chemistry a precipitate is something that is being thrown out of the solution i.e. it is no longer dissolved in the solution but is being thrown out/precipitated out of the solution as a solid.

Evaporation

The difference between boiling and *evaporating* is that in the process of “boiling” (i) bonds are being broken and liquid ionic units in ionic substances or liquid molecules in molecular substances are being converted into gas **right throughout the whole structure of the liquid** and *not just at the surface of the liquid*, and (ii) irrespective of how much energy is being injected into the liquid, **the temperature of the whole liquid substance remains constant at the Boiling Point of the liquid until every single unit/molecule of the substance has been converted into its gaseous form.**

In “evaporation” however (a) it is only specific **localised** bonds that are being broken and this happens **only at the surface of the liquid** and thus (b) the temperature of the liquid has absolutely nothing whatsoever to do with the Boiling Point of the liquid. The energy needed in evaporation is miniscule compared to the energy needed in boiling. In fact, in the evaporation associated with the drying of washing on a clothes line, virtually all the energy used is provided by the kinetic energy possessed by the molecules of the wind that collide with the molecules of water on the surface of the damp clothes.

What then are the bonds or the forces of attraction that are being broken?

Let us now spend some time talking about the different forces that hold things together.

If any two entities remain bound together as one entity, then there MUST be some sort of force of attraction that binds those two entities together! At ‘A’ Level we talk about three sorts of bonds, and four types of weak forces of attraction.

- A) Metallic bonds
- B) Ionic or electrovalent bonds
- C) Molecular or Covalent bonds, and
- D) **Inter**-molecular forces of attraction (which even though they are often called “bonds”, are strictly speaking **not** ‘bonds’ at all but just weak ‘forces of attraction’) viz.
 - a) Hydrogen bonds (which are not really “bonds”), and
 - b) three types of van der Waals’/London forces of attraction

I will **not** talk about Johannes Diderik van der Waals and Fritz Wolfgang London here, but both of the two gentlemen were Nobel Laureates (i.e. they were awarded Nobel prizes for their contributions to science). Another Nobel Laureate, Peter Debye, made a notable contribution in this field and I do not know why his contribution is overlooked. In this blog I shall use the name “Waals/London/Debye” (WLD) to refer to these forces of attraction.

Please take careful note of the difference between an **intra**-molecular bond and an **inter**-molecular force of attraction. “Intra” means “within” and “inter” means “**between**”. (The way that you can remember the difference is that **INTER**-city trains run **between** cities.)

Most solids adopt a giant lattice structure. The structure of the lattice can vary quite considerably (based on how the atoms or ions or molecules are “packed” together), but luckily you do not need to know anything about “packing” at ‘A’ Level.

Up to this point, most of what I have said has been GCSE material, but I have used non-GCSE language and couched it all in the sort of language that you need to use and to understand now that you have got to ‘A’ Level.

Let us therefore start talking ‘A’ Level Chemistry; and, please remember that all this is just **revision** – you need to have read the whole of the First Year Foundation Book in order to understand even something as simple as Melting and Boiling (and please remember also that ‘A’ Level Chemistry is a big step up from GCSE stuff)!

A) Metallic bonds

Metallic bonds are (or they result from) the omni-directional electrostatic forces of attraction that positively charged metal ions in a piece of metal exert upon the negatively charged sea of delocalised electrons surrounding the positive ions.

A piece of a metal element (such as lead/zinc/copper/etc) consists of a large number of atoms of the element whose electrons have been delocalised thus creating positively charged ions of the metal, and every single positively charged metal ion exerts a force of attraction upon every single negatively charged delocalised electron in the piece of metal (and vice versa) – and thus metallic bonds are **non-directional** or **omni-directional** bonds. *[Clearly, the further away that a metal ion and an electron are from each other the smaller will the force of attraction be! The force of attraction is proportional to $\frac{1}{\text{distance}^2}$.]*

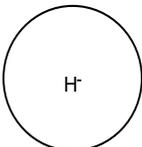
The overall force of attraction involved in metallic bonding will depend on a number of factors such as
A) the size of the charge on the metal ion involved (e.g. Group II metallic ions will have a larger charge than Group I metals, and Group III metallic ions will have a larger charge than Group II metals, and
B) the physical size of the metal ion will also be a factor because

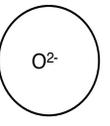
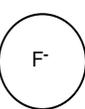
- B.1) as you go across a Period, **the number of protons increases**, therefore the pull of the protons in the nucleus gets larger and larger, and the electron cloud gets pulled closer and closer to the nucleus and the size of the **metallic ionic radius therefore decreases as you go across a Period**, and
- B.2) as you go down a Group the shells and sub-shells are located further and further away from the nucleus of the ion therefore the size of the $1 \div (\text{distance})^2$ effect becomes smaller and smaller and the pull on the electron cloud gets less and less.

These effects can be seen in the table on the next page.

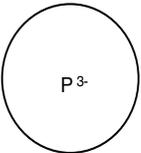
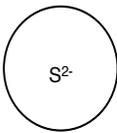
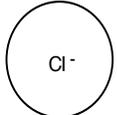
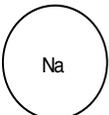
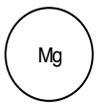
NB Strictly speaking, I should here talk to you about “**Charge Density**” (i.e. the amount of charge divided by the volume of space in which that charge is contained), but this blog is going to be a long one anyway, and I do not want to make things more complicated than they will be in this blog. (I will talk to you about Charge Density in a later blog when we talk about “Thermal Decomposition” – this being one of the last topics to be tackled in First Year ‘A’ Level Chemistry.)

Chemistry in Context

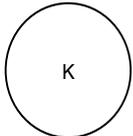
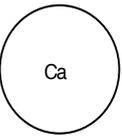
ionic radius / nm	H 0.208
ionic size	

ionic radius / nm	Li 0.060	Be 0.013	B 0.020	C	N 0.171	O 1.140	F 0.136
ionic size							
atomic size							

Atomic radii decrease as you go from left to right across a Period. This happens because the increasing number of protons draws the electron cloud closer and closer to the nucleus of the atom.

ionic radius / nm	Na 0.095	Mg 0.065	Al 0.050	Si	P 0.212	S 0.184	Cl 0.181
ionic size							
atomic size							

Ionic radii get larger as you go down a Group because the shells and sub-shells get further and further away from the nucleus.

ionic radius / nm	K 0.133	Ca 0.099
ionic size		
atomic size		

Radii of the most stable ions for some of the first 20 elements in the periodic table.

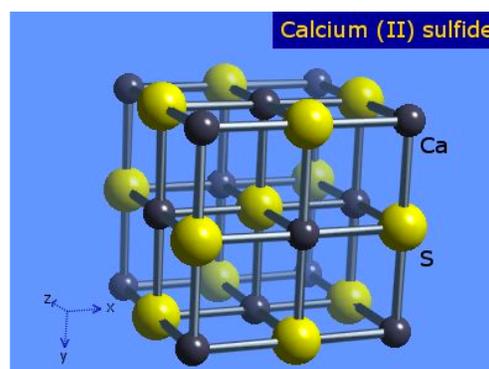
The magnitudes of the ionic radii above are those from Stark & Wallace's data book.

OK, let us now look at ionic bonds.

B) Ionic bonds

An Electrovalent or Ionic bond results from (or is) the omni-directional electrostatic force of attraction between oppositely charged ions (normally in a giant ionic lattice structure). An ionic bond is what binds together just one positively charged ion and one negatively charged ion in just one ionic unit e.g. as in the ions Na^+ and Cl^- in one ionic unit of NaCl, or Mg^{2+} and O^{2-} in MgO – but the definition also applies to whatever number of ionic units there are in an ionic structure.

A cluster of solid (as opposed to liquid or gaseous or aqueous) ionic units of an ionic substance will take the form of a **giant ionic crystal lattice structure**, and it really is important when you are in your lab at school that you go and examine a three dimensional model of something like Sodium Chloride (NaCl) or Magnesium Oxide (MgO) (i) because I am not very good at drawing things on a computer, and (ii) because it is extraordinarily difficult to depict in two dimensions on a piece of paper something that exists in three dimensions. In contrast, a three-dimensional laboratory model can easily portray a three-dimensional structure. The diagrams below come from https://www.webelements.com/compounds/magnesium/magnesium_oxide.html but there are many diagrams of **giant ionic lattice structures** on the web.



The important things to note are that

- the Mg^{2+} ions and the O^{2-} ions alternate, and that therefore
- each ion will have **SIX** oppositely charged ions as its neighbours i.e. four as its neighbours in one plane (*one above, one below, and one on each side of it*), and then one *in front* of it and one *behind* it – giving six oppositely charged neighbouring ions in total.

If you concentrate on the central ions (O^{2-} , S^{2-}) you will see the six neighbours clearly.

The force holding an ionic substance together is the electrostatic force of attraction between oppositely charged particles; and, at GCSE Level you would have been told that a positively charged ion is attracted to a negatively charged ion – and that is absolutely true, but at ‘A’ Level you are required to broaden your horizons somewhat. The reality is that **there is a force of attraction between EVERY ion and every oppositely charged ion in an ionic structure.** (However, the farther apart that the ions are from each other, the smaller will the force of attraction be because of the “ $\frac{1}{\text{distance}^2}$ ” effect.)

Now, the reason that I have pointed this out to you (in both metallic and in ionic bonding) is that every single one of these omni-directional forces of attraction must be broken when a metal or an ionic substance “melts” or “boils” (and thus a largish amount of energy will be consumed).

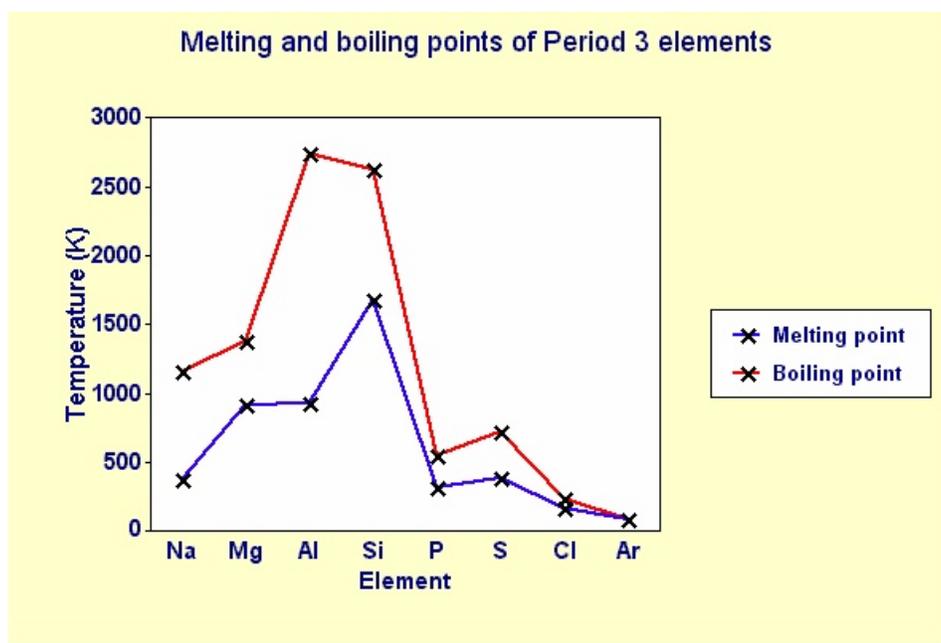
The thing that holds a whole giant ionic lattice crystal structure together is ionic bonding in the case of an ionic substance and metallic bonding in the case of a metal, and it is the electrostatic force of attraction between **each and every** ion and **each and every** *oppositely* charged ion in the whole structure.

I hope that I have now given you some idea of the power of the ionic bonding inside a giant ionic lattice crystalline structure – and thus **you will now be able to work out for yourself why ionic substances have high Melting Points and high Boiling Points**. It takes an awful lot of energy to break all the bonds between all the oppositely charged ions in an ionic substance, and it is this that causes metallic and ionic substances to have **HIGH** Melting and **HIGH** Boiling Points.

In order to melt an ionic substance, you have to break not just one bond but EVERY SINGLE ionic bond in the substance, and there will be grillions of such bonds – and that is why so much energy is needed for melting and for boiling metallic and ionic substances!

Before we leave ionic substances (and look at molecular substances) let us do one more thing – and that is let us give a name to one important aspect of ionic and metallic bonding.

We have seen that in ionic bonding, the force of attraction of any one ion is not directed solely in one direction i.e. at just one of its neighbouring oppositely charged ions, but it is in fact directed at EVERY oppositely charged ion in the whole giant ionic lattice crystal; and, to underline the fact that the force of ionic attraction is not directed solely in one direction, chemists say that the force of attraction is “*non-directional*”. However, this is a negative description, and I prefer to stress the fact that the ionic force of attraction radiates out in **EVERY** direction, and I myself say that the ionic force of attraction is “*omni-directional*”.⁴ I will say that again. The force of ionic attraction is *omni-directional*, and this is in sharp contrast to intra-molecular forces of attraction which are uni-directional i.e. they are exerted in only one very specific direction.



Source: creative-chemistry.org

OK, that is enough about Metallic and Ionic bonding for the moment. I will return to them in Part 4 of this blog, but let us now look at Molecular bonding.

⁴ In English, the Latin word “*omni*” means “all” or “every”.

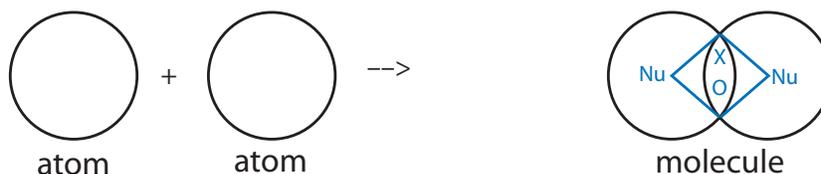
C) Molecular substances

When two (or more) atoms get together and *share* one or more **PAIRS** of electrons, then a molecular substance is formed, and an electrostatic force of attraction then binds the atoms together – because what is happening is that both sets of protons in the bonded nuclei of the atoms in the molecule are holding onto the *shared* pairs of electrons which lie “trapped” between them.

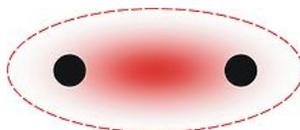
Electrons in atoms occupy *atomic* orbitals, but when two (or more) atoms get together to form a molecule, then they occupy σ and π **molecular** orbitals and not s/p/d/f/etc **atomic** orbitals (and you learnt about this in your very first ‘A’ Level Chemistry lessons).

A Covalent or **intra**-molecular bond is a bond **inside a molecule** and it results from the electrostatic force of attraction that two positively charged nuclei exert upon one or more pairs of **shared** negatively charged electrons. The diagrams below show a molecular σ (sigma) bond where a pair of bonded atoms are sharing the bonded electrons located between them.

The first diagrams below are my attempt to show two atoms locked together in a σ bond, and the one below mine is that by Professor Stephen Lower.



In the diagram above, the positively charged protons in the nuclei (“Nu”) of the two bonded atoms are exerting an electrostatic force of attraction (shown here as “<>”) on the pair of negatively charged bonding electrons “xo”.



Source : Stephen Lower, Simon Fraser University

Bonds **INSIDE** or within a molecule are called “**INTRA**-molecular” bonds, and they hold the **atoms** inside a molecule together, and bonds **BETWEEN** molecules are called “**INTER**-molecular” bonds/forces of attraction, and they are what hold **molecules together**.

There are four sorts of inter-molecular bonds/forces of attraction viz.

- a) Hydrogen bonds, and
- b) three forces of attraction which I collectively call WLD (Walls/London/Debye) forces of attraction viz.
 - b1) Permanent dipole to Permanent dipole bonds⁵
 - b2) Permanent dipole to Induced dipole bonds, and
 - b3) Momentary or Temporary or Instantaneous dipole to Induced dipole bonds.

⁵ We will talk about “dipoles” next week, but basically a dipole exists whenever there is a separation of charge (**no matter how small that separation of charge may be**). A total separation of charge would result in **ions** in an ionic substance and not in a *molecular* substance.

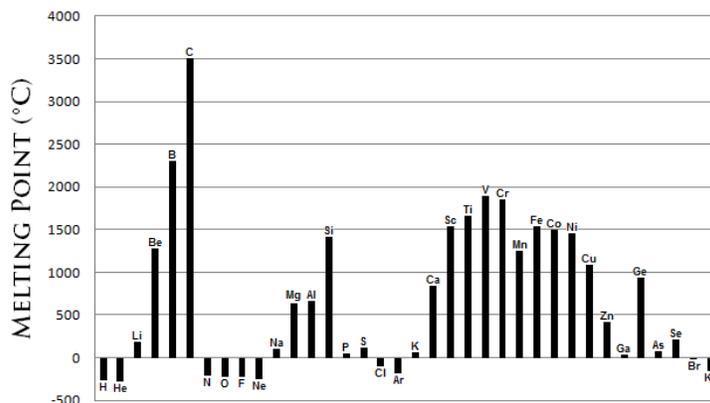
The borderline between different types of bonds

We have already talked about the fact that it would be wrong to regard the difference between molecular and ionic bonding in stark black and white terms. For example, if the two elements participating in a covalent bond have differing electronegativity values, then the more electronegative atom will pull some of the electron cloud of the less electronegative atom towards itself, and the resulting *partial separation of charge*⁶ will create an element of polarity inside the covalent molecule – and **the existence of this dipole (resulting from the partial separation of charge) in the molecule will thus confer an ionic character on the “molecule”** (even though molecules are NOT made up of ions).

Similarly, in an ionic substance such as Na^+Cl^- , the *positively charged* metal cation (Na^+) will attract the electron cloud of its neighbouring *negatively charged (non-metal)* anions (Cl^-) towards itself. To a certain extent therefore, where there was theoretically a total separation of charge (i.e. the entity was totally polarised into positive and negative entities), the transferred electrons now become partly “*shared*”, and since one of the distinguishing features of a covalent bond is the “sharing” of electrons, then **there will be an element of covalency in ALL ionic bonds** (even though ions do NOT form covalent bonds).

Thus, whilst it is possible for a molecular substance to have **no ionic character whatsoever** (e.g. a *diatomic molecule cannot have ANY ionic character at all*), nevertheless it is unusual for an ionic substance to be *totally* free of ALL covalent characteristics!

Let me now show you a graph which shows the temperatures of the Melting Points of the first 36 elements in the Periodic Table. (At ‘A’ Level you are **not** required to know about the elements in the Periodic Table higher than Krypton.)



Source : University of California, Davis

OK, that is a good enough introduction to Melting and Boiling. In it I have told you about some of the very strong forces that hold metallic and ionic substances together, and I have told you a bit about the very strong forces that hold the atoms in molecules together (i.e. **intra**-molecular forces). What I have not told you about is **inter**-molecular forces of attraction, and *in next week's blog that is precisely what I am going to talk about*.

Until next week, could I ask you to look at the diagram above and see what trends you can spot. (Hint: *look diagonally!*)

⁶ i.e. the electron cloud has not separated completely into positive and negative areas – but the hitherto **evenly** distributed electron cloud on a species is now distributed **unevenly** with a slightly larger amount of the electron cloud in one area than in another area thus giving δ^- and δ^+ areas. We will talk about this in greater depth next week.