A First Year blog on Melting and Boiling Points: Part 4, 23rd 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 Book*.)

In this blog on Melting and Boiling, in

Part 1 We talked about what happens when things Melt and Boil.

Part 2 We looked at 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 We looked at these forces in greater detail, and now in

Part 4 Let us look at Periods 2 and 3 in the Periodic Table, and at the sort of questions that are asked in the 'A' Level exams requiring candidates to explain the Melting and Boiling temperatures (Melting and Boiling Points) of different substances.

A) Differences in the Periodic Table in Melting Points and Boiling Points

Melting refers to the process whereby a substance, when it *melts,* goes from the solid state (s) to the liquid state (l), whereas **Boiling** refers to the process whereby a substance, when it *boils,* goes from the liquid state (l) to the gaseous state (g)[1], and the amount of energy that it takes to convert a substance from the solid state to the liquid state, and from the liquid state to the gaseous state will depend entirely on the strength of the bonds that are within the substance – and we then need to examine the strength of the bonds inside substances composed of differing elements.

The length of a bond determines how strong it is, and the shorter a bond the stronger it is – and in order to analyse the strength of differing bonds, we must first determine the nature of the bond that is being examined i.e. how many bonds there are in the substance/how short or how long they are/and what type of bond they are (i.e. whether they are metallic, electrovalent, covalent bonds or inter-molecular forces of attraction).

There are extremely strong bonds in pieces of metal/and also in ionic substances/and also in **intra**-molecular covalently bonded substances, therefore it must follow that it will require a large amount of energy in order to break all these bonds. It is this that causes metals (and ionic substances) to have high melting and boiling points – but this does not necessarily apply to molecular substances.

- **Giant** or **macro-molecular** substances that are held together by strong intra-molecular bonds (e.g. diamond and SiO_2) have high MPs/BPs, but
- **simple** molecular substances held together by weak inter-molecular forces have low MPs/BPs. **Inter**-molecular forces of attraction are very weak, therefore simple molecular structures have very low MPs and BPs, and become gases at very low temperatures. *Simple molecular structures are usually gases at room temperature and pressure.*

[1] The difference between boiling and *evaporating* is that in the process of "boiling" (i) bonds are being broken and liquid units/molecules 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 poured 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 gaseous form**, whereas in "evaporation" (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.

A.1) The Melting and Boiling Points of Metals

Every metal ion in a piece of metal has an interest in ALL (not just one or two or three or four or five) but ALL of the huge pool of electrons possessed by that piece of metal! Every positively charged metal ion in a piece of metal exerts a force of attraction on every, on EVERY single one of the negatively charged electrons in the huge pool of delocalised electrons in the piece of metal (and vice versa) because these bonds are non-directional or omni-directional bonds[2]. However, the further away that an electron is from a nucleus the smaller will be the force of attraction be because of the $\frac{1}{\text{distance}^2}$ effect.

The Melting and Boiling points of metals are related to the Group/the Period in which the element resides.

The following factors are involved

More bonds : The more electrons that there are in the pool of delocalised electrons the more bonds there will be, and *the more bonds that there are then the greater will be the amount of energy required* to break those bonds and to melt and subsequently to boil the piece of metal. It is but a short stride to move from there to seeing that since Group III metals delocalise three electrons per atom then there will be more metallic bonds in a piece of Group III metal than there are in a piece of Group II metal, and that a piece of a Group II metal will have more metallic bonds in it than a Group I metal.

Shorter bonds with regard to any one Period : In the table showing atomic radii (on the next page) you can see that atomic *radii decrease in going from left to right across the Periodic Table*, and if shorter bonds are stronger than longer bonds, then pieces of *metal* made from an element to the right of another metal element in any Period of the table will be stronger than a piece of metal made from a metal element to the left of it in the Periodic Table – and thus the metal on the right in any given Period will (all other things being equal) have a higher melting point than the metal element on the left.

Shorter bonds with regard to differing Periods : Equally, *atomic radii increase going downwards in a Group* in the Periodic Table[3] therefore pieces of metal made from elements lower in the Periodic Table will have longer/weaker bonds and thus have lower Melting and Boiling points.

You can see therefore why it is that **textbooks say that the amount of energy needed to melt a piece of a metal will depend on the Group and the Period to which the metal belongs.**[4]

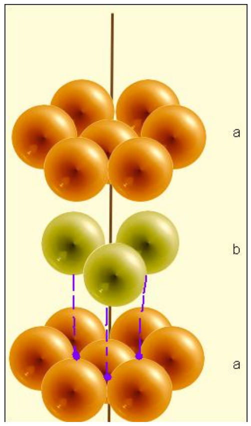
There is one other very important factor that affects the Melting and Boiling Points of Metals, and that is to do with how metallic ions in a piece of metal are packed on top of and around each other – but the subject of Packing is very complicated and needs the actual physical handling of something like billiard balls stacked on top of each other to be understood properly. Luckily, therefore, you do not need to know anything about Packing at 'A' Level.

---

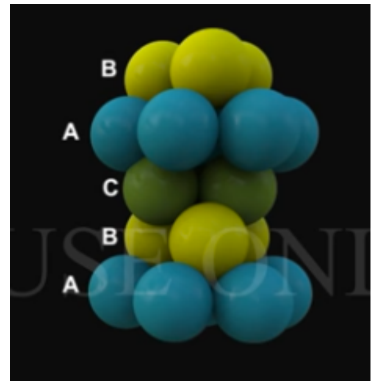
[2] The force of attraction diminishes by [$\frac{1}{\text{distance}^2}$] and, clearly, the further away that a metal ion and an electron are from each other, the very much less will that force of attraction be – **but that does not stop every ion and every electron from being attracted to each other!**

[3] As the Principal Quantum Energy Level goes from n=1 to n=2 to n=3 and so on.

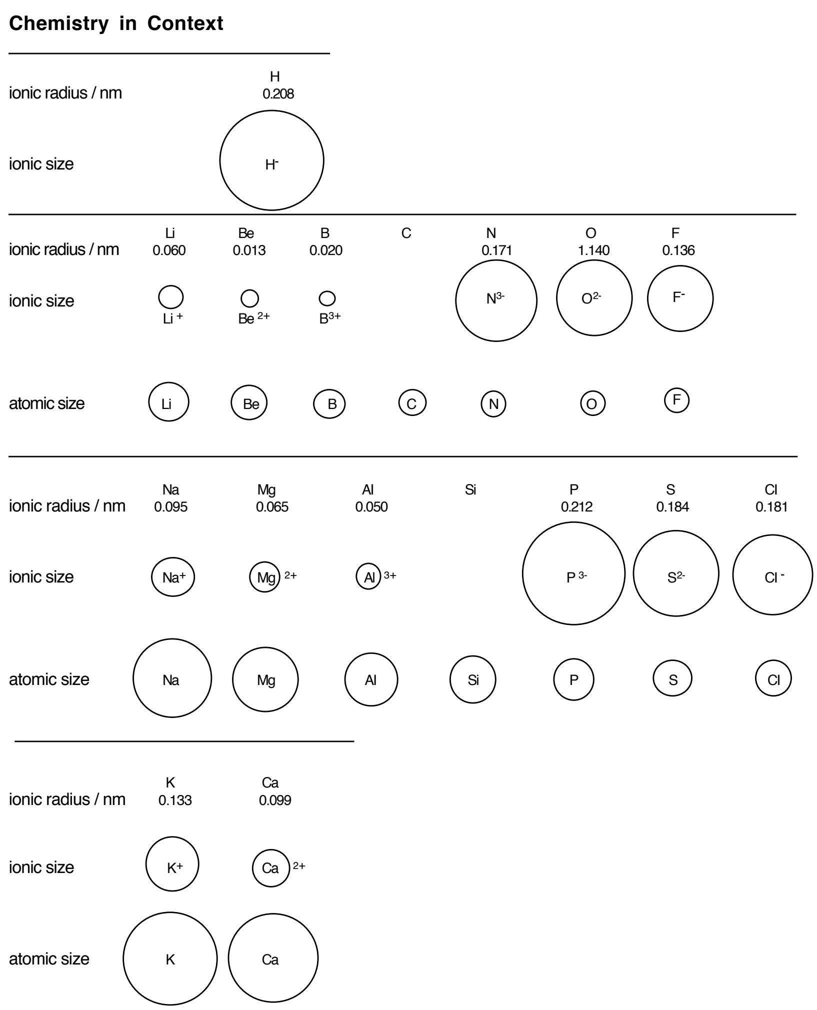
[4] Actually, it is more complicated than this when it comes to Transition Metals/etc, but I want to concentrate only on the principles that are involved.



Cubic Close (abab) Packing
Source : UCD

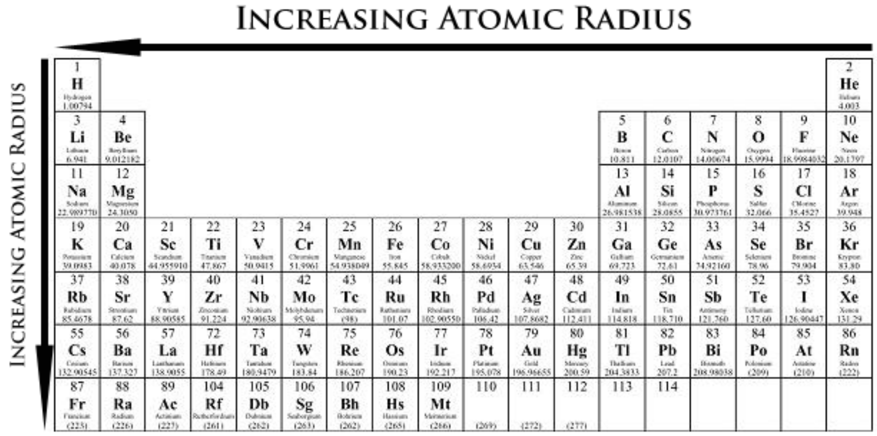


Hexagonal Close (abcabc) Packing
Source: https://www.youtube.com/watch?v=7TdNbg3Kt2c



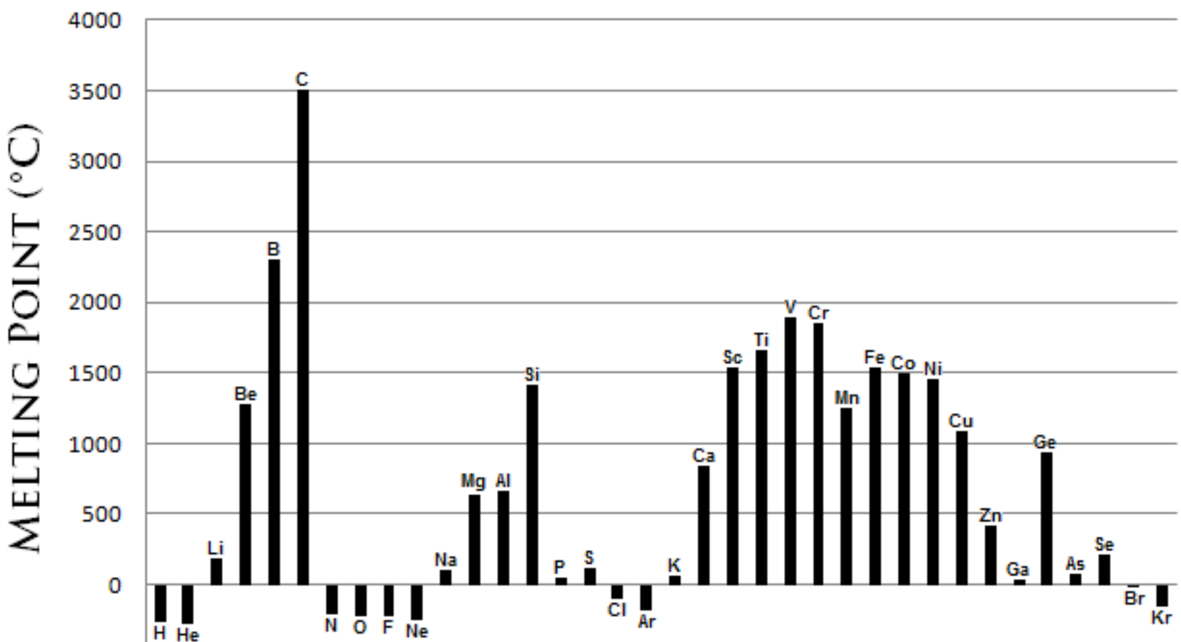
Atomic radii decrease as you go from left to right across a Period. This happens because the increasing number of protons draws the electron cloud closer and closer to the nucleus of the atom.

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



Source : University of California, Davis

The result of all those different factors gives the following MPs.



Source : University of California, Davis

A2) <u>The Melting and Boiling Points of Non-metal Elements that have simple molecular structures</u>

The high Melting and Boiling Points of Metals are entirely related to the fact that every piece of metal has strong omni-directional metallic bonding holding the piece of metal together.

The table above shows the Melting Points of the first 36 elements, and from it you will see that Metal elements have high Melting Points but that, in contrast, those Non-Metal elements that have **simple molecular structures** have low Boiling Points – and, indeed, at 0˚C/273K most of the Non-Metal elements are gases.[5] The reason for this is very simple viz. **Non-Metal elements that have simple molecular structures have very weak inter-molecular forces of attraction (such as Hydrogen bonds and vdW forces) holding them together.**

I showed you this table in an earlier blog, and I show it to you again now

Type of bond/force of attraction	**Energy required to break the bond/the force of attraction (but can vary enormously)**
Covalent and electrovalent bonds	Many hundreds and sometimes even thousands of kJ mol^{-1}
Hydrogen "bonds"	about 10-50 kJ mol^{-1}
Permanent dipole to Permanent dipole	about 5 kJ mol^{-1}
Permanent dipole to Induced dipole	about 3 kJ mol^{-1}
Instantaneous dipole to Induced dipole	about 1 kJ mol^{-1}

and you can see that compared to *covalent* and *electrovalent* bonds, *Hydrogen bonds* are weak, and that *vdW forces* are even weaker still. It is thus no surprise that the Melting and Boiling Points of elements that have simple molecular structures are very low indeed.

A3) The Melting and Boiling Points of elements that have giant/macromolecular structures

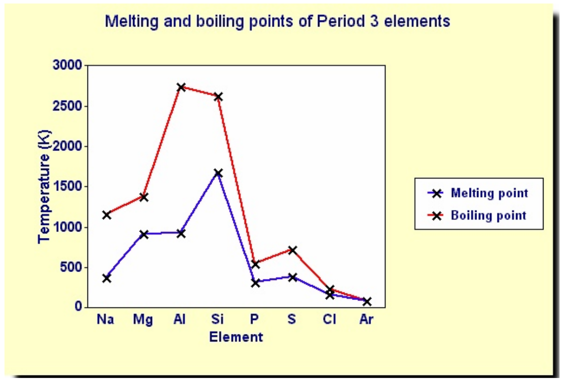
Pieces of metal are held together by very strong omni-directional metallic bonds, and those elements that have simple molecular structures are held together by very weak inter-molecular bonds – but those elements that have **giant** or **macromolecular** structures are held together by very strong *covalent* bonds, and thus they have very high Melting and Boiling Points.

The thing that you then need to know is which Non-Metal elements have giant/macromolecular structures and which have simple molecular structures, and then we will have covered Melting Points and Boiling Points in more than sufficient depth for 'A' Level purposes, and **you just have to learn the following table off by heart.**

Group	I	II	III	IV		V	VI	VII	VIII
Period 2									
Element	Li	Be	B	C (graphite)	C (diamond)	N	O	F	Ne
Structure	**M**	**M**	**GM**	**GM**	**GM**	**SM**	**SM**	**SM**	**SM**
Period 3									
Element	Na	Mg	Al	Si		P_4	S_8	Cl	Ar
Structure	**M**	**M**	**M**	**GM/Md**		**SM**	**SM**	**SM**	**SM**

M = Metallic Structure ***GM = Giant Molecular*** ***Md = Metalloid*** ***SM = Simple Molecular Structure***

[5] 0˚C is a temperature that relates entirely to the Earth and has no importance whatsoever to any other part of the Universe. It is important to human beings because life forms on earth are totally dependent on Water, but there is no *'a priori'* reason for believing that other life forms must have evolved around this need for Water. For example, if you can obtain a copy of Professor Fred Hoyle's excellent "The Black Cloud", then you ought to read it. If you have had (as I had in my youth) a very restricted intellectual upbringing because of religious factors, then it will broaden your intellectual horizons. (If you have never encountered the Latin phrase *'a priori'* before, then in this context it means 'beforehand'/'before you study the relevant facts'.)



Source: creative-chemistry.org

Anything that has a giant molecular structure is held together by __strong__ covalent bonds.[6] If therefore, in the exams, you are asked why the giant molecular substance XYZ (e.g. Diamond) has a *high* MP/BP, then the answer that you give must state that "the substance is held together by nothing but strong covalent bonds", and if you are asked why the simple molecular substance ABC (e.g. P_4/S_8/Cl_2) has a relatively *low* MP/BP, then the answer you give must be that "the **molecules** of the substance are held together by nothing but weak inter-molecular forces of attraction".

When it comes to the oxides of the Period 3 elements, it will be up to you to know that
- metal oxides are **__ionic__** and they therefore have high MPs/BPs, whereas
- some non-metal oxides such as SiO_2 are **__giant molecular__** substances (just like Diamond) and form just one huge molecule therefore they have high MPs/BPs, whereas
- others (such as SO_2 and SO_3) are **__simple molecular__** structures and thus have relatively low MPs/BPs, and in between
- there are **__big multiple molecule__** structures (e.g. polymers) held together by vdW forces of attraction but the molecules are so large (therefore their electron clouds are very large and their Momentary Dipoles are therefore very large) that the inter-molecular force of attraction is much larger than normal and they therefore have higher MPs/BPs than simple molecular structures.

Through experimentation, man has found that different substances boil at different temperatures.[7] He therefore needed to understand why this is so – because if he could not understand this phenomenon, then he could easily put the wrong sort of liquid into the radiator of his car (and it would constantly be boiling!), or he could put the wrong sort of substance into the cooling system of his refrigerators, and (because it would not change from the liquid state to the gaseous state, and thus not absorb heat from the refrigerator in order to be able to do so) it would never be able to keep his food cold.

The stuff that we have talked about in the last four blogs is thus not part of an airy-fairy exercise just to see how good your brain is. It is about **reality**, and in the exam, the way that the examiners might test your understanding of this reality is to ask you to place in the order of their boiling points three *liquid* substances e.g. Tetrachloromethane (CCl_4), Hydrochloric Acid (HCl), and Water (H_2O), and they would ask you to give an explanation for your answer, and your answer should look like this *(and please remember that a Hydrogen bond is the closest thing here to a real bond, and that inter-molecular vdW forces of attraction are NOT bonds but are just weak forces of attraction)*.

---

[6] Carbon is a highly flammable substance and thus, after leaving University, when I first started visiting industrial operations which had massive furnaces in them, I was stunned (indeed "gob-smacked"!) to discover that some of them had furnaces lined with blocks of **Carbon** (called Carbon Refractory Lining blocks). The blocks of Carbon never caught fire because there was no oxygen in the furnace, and the reason that the furnaces were lined with blocks of carbon was that Carbon has a very high melting point (and high chemical resistance).

[7] When a liquid "evaporates" then the *phase* or the *state* of the molecules of the liquid **at the *__surface__* of the liquid** change from the liquid phase or state to the gaseous phase or state; but, when a liquid "boils", then **__ALL__ the molecules of the liquid (no matter where in the liquid they may be)** undergo the change from the liquid phase or state to the gaseous phase or state. THAT is the difference between evaporation and boiling (and why boiling is accompanied by such vigorous movement inside the liquid)!

***Main* force of attraction possessed by the molecules of the following substances**

SUBSTANCE	Hydrogen bonds	PD to PD	MD to Induced D
Water (l)	√		
Hydrogen chloride (l)		√	
Tetrachloromethane (l)			√

The order, in terms of the boiling points (from the highest boiling point to the lowest) is

1) H_2O
2) HCl, and
3) CCl_4

and the reason for this is that when a molecular substance boils, then all its inter-molecular bonds break and the liquid is transformed from its liquid state into its gaseous state.

In general

- Hydrogen bonds are the strongest of the above three stated forces of attraction, therefore more energy is required to break them than is required to break the others, therefore they will break only at a higher temperature than the others, and
- Permanent dipole to Permanent dipole forces of attraction are not as strong as Hydrogen bonds therefore less energy is required to break such forces of attraction, therefore they will break at a lower temperature than Hydrogen bonds, and
- Momentary or Instantaneous dipole to Induced dipole forces of attraction are not as strong as Permanent dipole to Permanent dipole forces of attraction therefore less energy is required to break such forces of attraction, therefore they will break at an even lower temperature.

In the exam you will NOT have the time to give lengthy explanations. **All that the examiners want you to do is to identify the type of bonding in each substance**.

However, one of the three substances that I have given you here does not have a boiling point that is governed entirely by the principles that I have covered so far. Let me just tell you that there are at least two other rules (viz. number of electrons and packing) that govern MPs and BPs. The first one of these is that since the inter-molecular force of attraction is determined by partial separation of charge, then the greater the number of electrons that there are in the molecules concerned, the larger will be the partial separation of charge and the greater the inter-molecular force of attraction.

The number of electrons in a molecule will be correlated to the Atomic or Proton Number (because there must be as many electrons as there protons in a neutrally charged entity), and Atomic Number is associated with Atomic Mass, and therefore many textbooks use short-hand and say that MPs and BPs are related to the mass of the molecule – and whilst MPs and BPs are related to mass, MPs and BPs are not **caused** by the mass of the molecule.

If I were now to give you the actual BPs of the three substances that we have looked at viz.

SUBSTANCE	Hydrogen bonds	PD to PD	MD to Induced D
Water (l)	+100˚C / 373K		
Hydrogen chloride (l)		-85˚C / 188K	
Tetrachloromethane[8] (l)			+77˚C / 350K

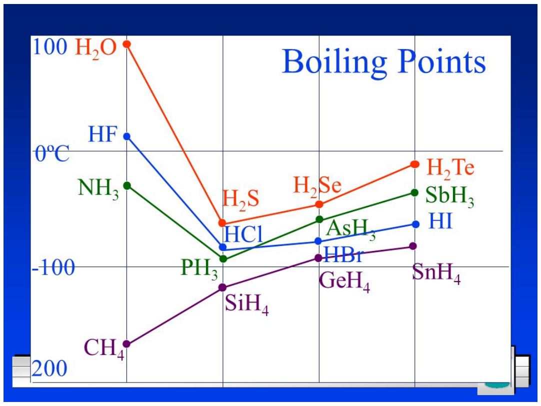
then you would immediately think to yourself "The reason that Tetrachloromethane has a higher BP than Hydrogen Chloride is probably because each molecule of the former has more electrons in it than

[8] The Greek word "tetra" means "four" in English, therefore Tetrachloromethane has four Chlorine atoms in it instead of four Hydrogen atoms (as does Methane).

molecules of the latter, therefore the inter-molecular force of attraction is larger" and you would be absolutely right in your assessment of the situation.

NB In general, in **any** Science 'A' Level exam, the examiners neither expect nor want you to write a lengthy answer to the question that was asked. The people who have to mark exam papers are given stereotypical answers and they can give you marks only according to that schedule. Make the point that you want to make **in as short a time as possible** and then move on. If at all possible, give your answer in bullet points. If the question carries 3 points then you need to give the examiner 3 factors (not 2 and not 4). You do not get extra marks for giving a brilliant answer to a (usually) fairly simple question. You will still get three marks even if you spend 30 minutes belabouring one point. Get on and get all the marks that you can. Modern 'A' Level Science exams **are about quantity and not quality**. There are no marks for brilliant answers. *You get one mark for every point that the examiner's marking scheme allows you to make – no more and no less!* At 'A' Level, exam **technique** is very important indeed when it comes to scoring maximum marks.

In the olden days the examiners used to love to give you something like the following diagram and ask you to explain the differences in the Boiling Points involved.



Source: Unknown (but there are many such charts on the web)

- The topmost line represent the Boiling Points of H_2X compounds in Group VI.
- The next line down represents the BPs of HX compounds in in Group VII.
- The one below it represents the Boiling Points of the XH_3 compounds in Group V, and
- the bottom line represents the BPs of the XH_4 compounds of Group IV

where "X" is an unknown element in each case.

If you look at the extreme left of each line you will see that the molecules are H_2O / HF / and NH_3 , and thus involve precisely the three most electronegative elements in the Periodic Table. Their Boiling Points will thus be higher than the Boiling Points of their counterparts in the same Groups as they are.

However, please now look at the bottom line on the graph, and you will see that CH_4 does not have a higher BP than the other XH_4 substances. This is because **Carbon does not form Hydrogen bonds**, therefore CH_4 does not have a higher Boiling Point than the other XH_4 compounds in that Group.

NB The larger the number of electrons that there are in a molecule, the larger will the electron cloud be and thus the greater will the vdW forces be between molecules – and the greater the inter-molecular force of attraction, the larger will be the resulting amount of energy needed to break such forces of attraction (and the higher will the Boiling Point be).

If it were not for the Hydrogen bonding in Fluorine/Oxygen/and Nitrogen, then the Boiling Points in the Periods in the diagram would rise as each Period is traversed, purely and simply because each successive substance has more electrons in it.