Chem Factsheet

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Van der Waals Forces

This Factsheet is designed to explain what is generally meant by the phrase "Van der Waals Forces" and how these forces account for the physical properties of many substances.

Johannes van der Waals
1837 - 1923

There is a certain amount of confusion over exactly what a Van der Waals force is. Some books may use the term loosely to cover all intermolecular forces (forces **between** molecules!), even hydrogen bonds, though this is rare.

Strictly speaking Van der Waals forces cover permanent dipole-permanent dipole forces and some texts may refer to these as "**strong** Van der Waals forces". However, for the purposes of most A-level syllabuses, Van der Waals forces applies to the weakest of intermolecular forces – the forces that might otherwise be referred to as induced dipole-induced dipole forces or London Dispersion Forces.

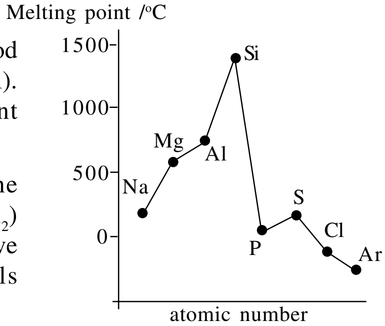
What will an examination require you to know?

In general, it is important to recall that ionic substances exist in lattices with very strong electrostatic forces holding each ion in place. Most of these must be broken for the substance to melt and all must be broken for it to boil. Hence, a great deal of energy and a high temperature is usually required. Differences are accounted for by variations in the sizes and charges of ions.

Metals also exist in lattices, though the arrangement is much looser. Many metals also have very high melting points. Differences are accounted for by variations in sizes and charges of the metal ions, and the number of delocalised electrons.

Note:
High melting points in Period 3 for the metals (Na, Mg, Al). Also for the giant covalent lattice (Si).

Low melting points for the simple molecules (P_4, S_8, Cl_2) & atomic Ar – all of which have only weak Van der Waals forces.



However, when we come to study covalent elements and compounds the situation seems less straightforward.

Element	Melting Point. (/K)
Sulphur	392
Carbon (graphite)	4000
Iodine	387
Silicon	1680

The most important idea to recall for examinations is that some non-metal elements exist as simple molecules and some as giant covalent lattices.

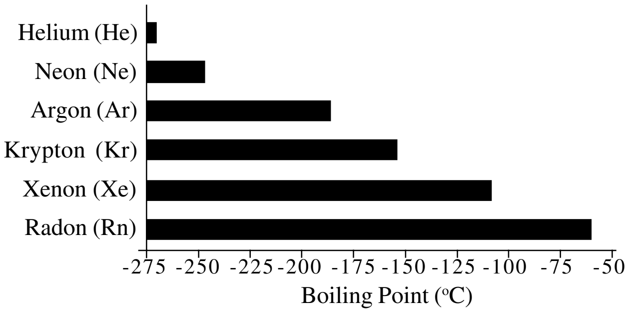
In the table above, both graphite and silicon are giant covalent lattices and so have melting points as high or higher than most metals due the number of very strong covalent bonds that would have to be overcome before they melt.

Iodine (I_2) and sulphur (S_8), however, are simple molecules. The covalent bonds between the atoms in these molecules are of a similar strength as carbon-carbon bonds but the melting point is much lower because only the forces that attract one S_8 molecule to another S_8 molecule must be overcome to melt, not the "internal" covalent bonds. These intermolecular forces are very weak Van der Waals forces and so the melting point is much lower.

What causes Van der Waals Forces?

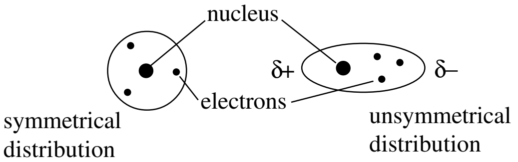
The very simplest elements to consider are the noble gases (Group 0) as they exist as individual atoms. Their outer shells are complete and so there is very little tendency for them to bond to each other ionically or covalently. There cannot be a permanent dipole in a single atom and so there seems to be no way in which one atom can attract another. This explains why they are all gases but does not explain how it's possible to condense them. What forces hold the atoms to each other in the liquid state?

Element	Atomic Number	Atomic Mass	Boiling Point (/°C)
Helium	2	4	-269
Neon	10	20	-246
Argon	18	40	-186
Krypton	36	84	-152
Xenon	54	131	-108



In 1930 American Physicist ***Fritz London*** noted the relationship between the size (and mass) of these elements and their boiling points.

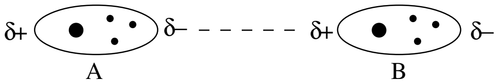
He suggested that the attractions needed for the liquid form to exist must come from perturbations in the electron distribution and hence the electron density around the nucleus.



In other words, the electrons around the nucleus (which are on average symmetrically distributed over time) are able to move. This may lead them to spontaneously (just for a moment) take up an unsymmetrical distribution, causing an imbalance in the charge – or an ***instantaneous dipole***.

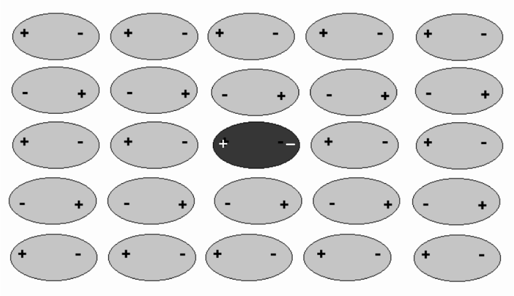
Suppose one side of the atom has a slight surplus of electrons at one such moment in time. Hence, it will have a partial negative charge (or δ-). The opposite side will have a slight lack of electrons and consequently a partial positive charge (or δ+).

Such a spontaneous dipole may induce an opposite dipole in neighbours providing they are close enough. The δ- side repelling electrons in a neighbour to induce a δ+, the δ+ side attracting electrons in a neighbour to induce a δ-.



The spontaneous dipole in atom A has a surplus of negative charge to the right (δ-), repelling away electrons in atom B, inducing a δ+. Atoms A and B will momentarily attract each other (– – – – – –) via the opposite δ- and δ- charges.

Not only will these two atoms attract each other but the affected neighbour will then induce further dipoles in more distant neighbours and these forces may be enough to condense the substance, even a noble gas, providing that there is insufficient heat energy available (i.e. temperature low enough) to overcome these Van der Waals (or London Dispersion) forces..



An instantaneous dipole in one atom may induce dipoles in neighbours, forming a regular lattice arrangement.

An examination question may well expect you to be able to use diagrams to explain how such induced dipoles come about. It is likely to also expect you to explain why the boiling points of noble gases increase as we move down Group 0.

The Strength of Van der Waals forces

Noble gases are monoatomic elements. They have relatively few electrons to move and so any spontaneous dipole will be very small. The smaller the atom (eg He), the fewer the electrons. Also the smaller the atom the closer to the nucleus and less shielded the outer (valence) electrons will be. This means the electrons are less free to move and so the smaller the atom the weaker any spontaneous dipole. This will induce correspondingly weaker dipoles in neighbours and result in very weak Van der Waals forces and low melting / boiling points.

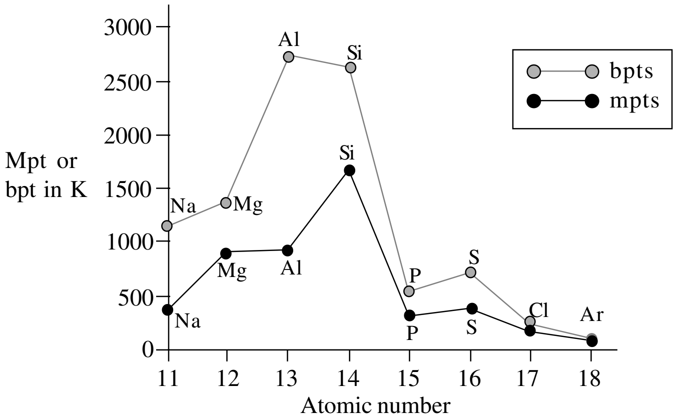
Equally, the larger the atom (eg Xenon), the more electrons it will have in more distant and more shielded orbitals. Spontaneous dipoles can be larger and induce larger forces in their neighbours. Melting and boiling points will be correspondingly higher.

In single atoms induced dipolar forces may be as weak as 0.05 kJ/mol but similar forces exist between large molecules and their strength will rise considerably. It would expected that you could account for the varying boiling points of molecules within oil fractions. Whereas the LPG fraction has very weak forces from molecules containing only a few carbon atoms and so is a gas. Molecules in Bitumen may contain 60 or more carbon atoms. This allows for much larger Van der Waals forces and so Bitumen is a thick liquid or even a solid at room temperature.

Periodicity

A common A level question is to account for melting points across a period.

Melting points and boiling points for Period 3



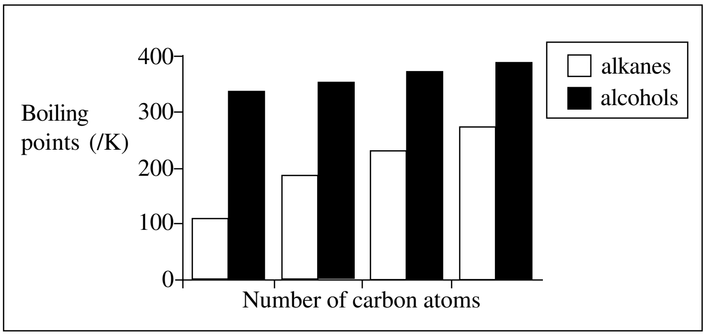
We have already accounted for the high melting points of the first four elements and the much lower melting points of the next four. But you could be expected to account for the differences between the melting/boiling points of these last four, non-metallic elements.

Simply comparing their atomic masses will not explain the variations here.

However, when you account for the total mass of their molecules (P_4 =124 S_8 =256 Cl_2 =71 Ar=40), it is clear that the higher the molecular mass the high the melting point will be due to stronger Van der Waals forces because larger molecules have more electrons to create stronger instantaneous dipoles.

Adding different forces

Boiling points of alcohols comapred with alkanes

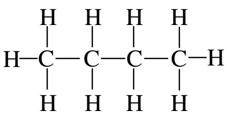


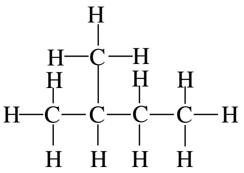
You will frequently be asked to account for the differences between the boiling or melting points of substances with similar numbers of carbon atoms. It is important to realise that all molecules experience Van der Waals forces, even if they also experience stronger forces at the same time.

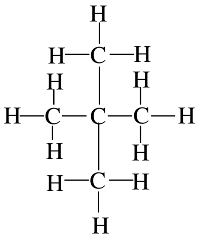
As you can see from the bar-chart, alkanes have much lower boiling points than their equivalent alcohol. This is because alcohols can hydrogen bond. However, increasing the number of carbon atoms does not increase the number of hydrogen bonds possible, so the increase in boiling point must still be largely accounted for by the increase in Van der Waals due to increased molecular mass and consequent increased number of electrons.

Molecular shape and Van der Waals

Pentane, methylbutane and dimethylpropane are all alkanes with the same molecular formula and mass – they are structural isomers of each other.


Pentane


Methylbutane


Dimethylpropane

Their boiling points are 36, 28, and 9.5°C respectively. Since none has a permanent dipole and all have the same mass there must be another factor changing their boiling points. In this case, it would be their ability to pack close to each other.

Although we can assume that the Van der Waals forces are similar, straight chain molecules such as pentane can line up more closely and more branched isomers cannot. Therefore the Van der Waals forces in methylbutane, and even more so in dimethyl propane which has more branches, act over a longer distance and are weakened as a result, leading to less energy being required to overcome them.

Practice Questions

Question	Total marks	Mark-scheme
Explain why fluorine and chlorine are gases at RTP, while bromine is a liquid and iodine is a solid	4	• Stronger intermolecular forces (in Bromine and Iodine) -1 • Require more energy to overcome (to make the substance boil or melt) -1 • Only Van der waals forces (as there is no permanent dipole) -1 • Larger moles down group 7 produced larger instantaneous dipole -1
Why do fluorine (F_2) and argon (Ar) have similar boiling points (85 K and 87 K) even though fluorine is a diatomic molecule?	1	• Similar molecular mass (Mr F_2 = 38, Ar =40). Similar number of polarisable electrons
Predict the trend in melting points of the first four alkenes and explain this in terms of forces	5	• Melting points will rise from ethene to pentene -1 • Due to increasing intermolecular forces -1 • Which require more energy to overcome. -1 • Van der waals forces (-1) increase with molecular mass (-1)
Diatomic oxygen (O_2) molecules have no permanent dipole. Explain how the molecules can be attracted to each other.	3	• Electrons may move spontaneously creating an imbalance of charge. • δ- charge (where there are excess electrons) induces a ä+ charge in neighbouring molecules • These attractions are called Van der Waals forces.
How might a polar molecule such as HCl attract a non-polar molecule such as Br_2	2	• δ+ H will attract electrons in bromine molecule, inducing a δ- charge. or • δ- Cl will repel electrons in bromine molecule, inducing a δ+ charge. -1 • Opposite charged dipoles will then attract each other -1
The petroleum industry often reforms alkanes to make branched structures which have the same energy content as their straight-chain counterparts but are more volatile. Why are they more volatile and why is this useful?	4	• Branched chains cannot pack together very tightly. -1 • This means their Van der waals forces hold them to their neighbours less tightly. -1 • Less energy is needed to break these forces (making them more volatile). -1 • More volatile fuels vapourise more easily and so are more easily ignited. -1

Acknowledgements: *This Factsheet was researched and written by Paul Swainson.*
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