Chem Factsheet

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Relating the Properties of Crystal Structures to Structure and Bonding

This topic builds on the work covered in;
Factsheet 05- Bonding
Factsheet 06 – Structure of Elements and Compounds

To succeed in this topic you need to:
Understand what is meant by ionic, covalent and metallic bonding
Understand the different types of intermolecular forces

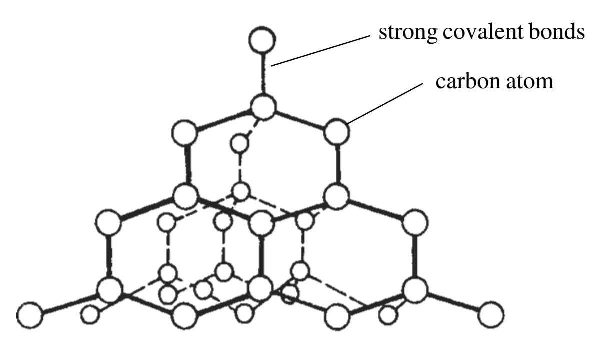
Introduction

All materials are made up from atoms. There are only about 100 kinds of atom in the entire universe. These atoms are the building blocks that make all the plants and animals, solids liquids and gases that we encounter everyday. *Bonding* of atoms in different ways creates various *structural* forms. The bonding and structure determine the appearance of any material but also all its other physical properties.

This Factsheet will concentrate on *crystalline structures* which you are most likely to meet in examination question papers.

You will need to know about the following examples of crystalline structures: diamond, graphite, sodium chloride, ice, iodine and metals.

1) Diamond



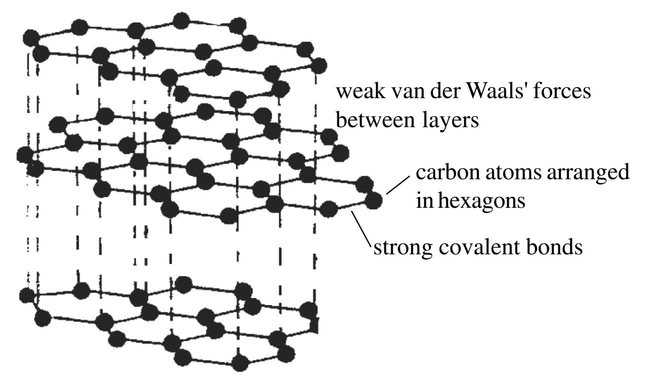
Structure and Bonding
- Giant covalent lattice structure
- Millions of carbon atoms bonded directly or indirectly to each other by strong covalent bonds.
- Every carbon atom forms four covalent bonds by sharing electrons with each of its four nearest neighbours.
- Every carbon atom can be imagined to be at the centre of a regular tetrahedron surrounded by four other carbon atoms whose centres are at the corners of the tetrahedron.

Common errors: Terms such as "ions", free electrons", "molecular" and "intermolecular forces" are NEVER applicable when describing the structure and bonding in diamond.

Relating Properties of Diamond to Structure and Bonding
- Very strong and rigid structure which is very difficult to distort or break because of the 3-dimensional pattern of strong covalent bonds. In fact, diamond is the hardest natural material known.
- Very high melting point (3823K) because a lot of energy is needed to break the strong covalent bonds. In order to reach the liquid state *most* of the covalent bonds would need to be broken.
- Does not conduct electricity because all the electrons are held tightly in the bonds between the atoms and are not free to move.

Note: Silicon can also exist in the same crystalline structure as diamond. It is not as hard as diamond because the covalent bonds are longer and therefore weaker. Silicon has a high melting point but it is only 1683K.

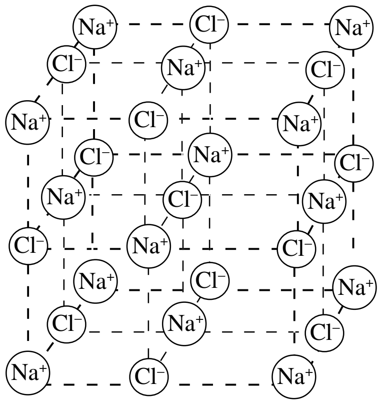
2) Graphite



Structure and Bonding
- Layers of carbon atoms arranged in hexagons joined together by strong covalent bonds.
- Each carbon uses 3 out of 4 outer electrons to bond covalently to three others.
- Fourth electrons from each atom are delocalised throughout the layer of C atoms.
- Weak van der Waals' forces hold the layers together.

Relating Properties of Graphite to Structure and Bonding
- Conducts electricity very well because the delocalised electrons are free to move throughout the layers.
- High melting point (3925K) because, in order to melt graphite, it is not sufficient to loosen one layer from another by breaking the Van der Waal forces. To achieve melting it is necessary break much of the strong covalent bonding throughout the whole structure.
- Soft, slippery texture and can be used as a lubricant because the weak Van der Waal forces are easily overcome allowing the layers to slide over each other like cards in a pack of playing cards.

3) Sodium chloride



dashed lines are not physical bonds

Structure and Bonding

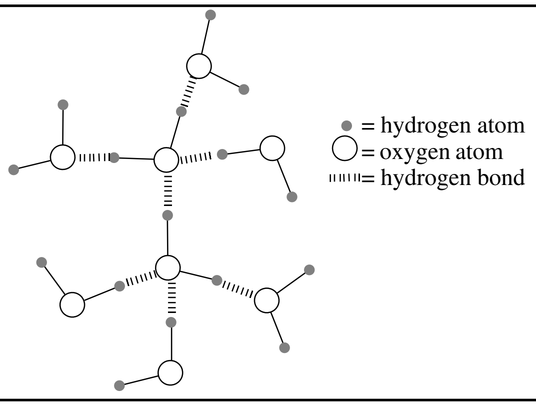
- Giant ionically bonded lattice.
- Electrons have been transferred from the sodium atoms to form sodium ions.
- Electrons have been transferred to the chlorine atoms to form chloride ions.
- The sodium ions carry a positive charge; Na^+ (cation).
- The chloride ions carry a negative charge; Cl^- (anion).
- Each positive sodium ion is surrounded by 6 chloride ions and vice versa.
- Overall, the ions are arranged to form a cubic crystal with cations and anions alternating along any edge of the cube
- The oppositely charged ions are held together by strong electrostatic forces of attraction.
- The net electrical force binding the ions together is described as ionic bonding.

Note: "*an* ionic bond" is a meaningless term because, unlike the atoms involved in a covalent bond, each cation attracts every anion and vice versa. "*Ionic bonding*" describes the *net* attractive forces between the ions.

Relating Properties of Sodium Chloride to Structure and Bonding

- High melting point, because a lot of energy is needed to overcome the strong electrostatic forces between the cations and anions.
- Soluble in water because, when the positive and negative ions attract polar water molecules, sufficient energy is released to break the ionic bonding forces.
- Conducts when molten or in solution because the ions are then free to move.
- Brittle because any stress will cause the crystal to cleave along planes parallel to the face of the crystal cube.

4) Ice



Structure and Bonding

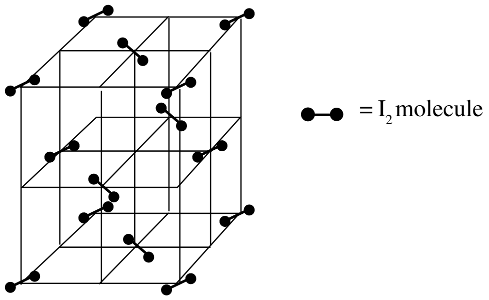
- Covalently bonded molecules, H-O-H.
- Simple molecules in hydrogen bonded crystal structure.
- Hydrogen bonds between neighbouring H_2O molecules. These are caused by the very highly electronegative oxygen atom which attracts most of the electron cloud away from the hydrogen atom. A hydrogen bond is then the electrostatic attraction between the δ+ hydrogen atoms in one molecule and a lone pair on the oxygen atom in a neighbouring molecule.
- Two hydrogen bonds per water molecule maintain the crystal structure below 273K.

Relating Properties of Ice to Structure and Bonding

- Relatively high melting point, 273K for such a small molecule because the relatively strong hydrogen bonds need to be broken.
- Less dense than water because the long hydrogen bonds in ice hold the water molecules further apart than in the liquid. Thus the same mass occurs in a larger volume.
- Remains solid below 273K because the hydrogen bonds are strong enough to resist the thermal vibrations of the water molecules
- Fairly easily crushed because the crystal will sheer where it is hydrogen bonded.
- Non-conducting because no free electrons or ions exist in ice. The molecules are polar but neutral overall.

Note: The physical properties of such molecular crystals are controlled by the inter-molecular forces not the intra-molecular covalent bonds. The latter remain intact during melting, crushing etc.

5) Iodine



Structure and Bonding

- Covalently bonded molecules, I-I.
- Simple non-polar molecules in crystal structure.
- Van der Waal forces between neighbouring I_2 molecules maintain the crystal structure at room temperature.

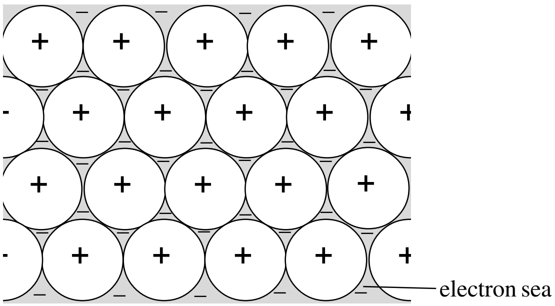
Relating Properties of Iodine to Structure and Bonding

- Low melting point, 387K, because relatively little energy is needed to break the weak Van der Waal intermolecular forces.
- Non-conducting because no free electrons or ions exist in the crystal. The I_2 molecules are neutral overall.

Note: Again, the physical properties of such molecular crystals are controlled by the inter-molecular forces not the intra-molecular covalent bonds.

Note: Van der Waals' forces increase with increasing size of the molecules. This is why, at room temperature, chlorine is a gas, bromine is a liquid but iodine is a crystalline solid.

6) Metals



Structure and Bonding

- Strong metallic bonding.
- Giant lattice structure of cations (+) surrounded by a 'sea of delocalised electrons'.
- The free, delocalised electrons come from the outer or valence shell of each atom.
- Metallic bonding is the net attraction between the cations and the delocalised electrons. The electrons are the 'glue' which hold the metal ions in place.
- The metal lattice is usually close packed.

Relating Properties of Metals to Structure and Bonding

- High melting points (usually) because the strong metallic bonding requires a large amount of energy to be weakened to the point where the cation are free to move.
- The free delocalised electrons make all metals very good conductors of electricity in both solid and liquid state.
- Metals are malleable and ductile (not brittle) because the layers of cations can slip over each other without cleaving because the delocalised electrons maintain the bonding between layers.
- High density due to the close packing resulting from the strong metallic bonding and the spherical shape of the ions.

Practice Questions

There are many different approaches for examination bodies to test your understanding of crystalline structures.

They may provide information of the physical properties of relevant materials and then ask how this links in with the crystalline structures of those materials.

1. The table below shows some values of melting points and some heat energies needed for melting.

Substance	I_2	NaCl	Carbon (graphite)
Melting point / °C	114	801	Sublimes at 3652
Heat energy for melting / kJmol^{-1}	7.9	28.9	——-

   (a) Name three types of forces between molecules.
   (b) Describe the bonding between the atoms and between the molecules in a crystal of iodine.
   (c) An iodine crystal is said to have what crystal type?
   (d) To melt iodine crystals requires heat energy. Why is this energy needed?
   (e) Sodium chloride crystals are held together by what bonds?
   (f) A sodium chloride crystal is said to have what crystal type?
   (g) To melt one mole of sodium chloride requires a lot of energy. Explain why.
   (h) The heat energy needed to vaporise one mole of sodium chloride, (171kJmol–1), is almost 6 times greater than the heat energy required to melt one mole of sodium chloride.Why should this be so?
   (i) Why do you think graphite remains as a solid at very high temperatures? Answer in terms of the structure and bonding of graphite.

Another approach is to talk about bonds and then link it in with the physical properties of contrasting substances.

2. Graphite and iodine crystals both contain covalent bonds. However the physical properties of their crystals could hardly be more different. Compare their melting points and their electrical conductivities and say how these differences can be explained by referring to their bonding and structures.

Next a question comparing the structure of contrasting substances and relating these with the physical properties.

3. Crystals of sodium chloride melt at 801°C and diamond melts at 3554°C. Compare their structures and explain why the melting point of diamond is so high.

Here is a question comparing diamond and iodine. This time looking at similarities in bonding but contrasting the differences in their structure and properties.

4. Diamond and iodine are both crystalline solids at 25 °C. What type of bonding do they have in common, and what is the difference in their structures. How does the difference in their structures account for their different melting points.

Some questions may simply ask you to recall information and be able to draw labelled diagrams.

5. Draw labelled diagrams to illustrate the structure and type of bonding found in (a) Graphite and (b) Sodium chloride

Some questions might approach the subject via electrical conductivity.

6. How can the electrical conductivities of sodium chloride, diamond and graphite be explained by looking at their structure and bonding.

7. Aluminium it conducts electricity very well. Explain why this is so by describing its bonding and crystalline structure.

Answers

1 (a) Force 1 ....van der Waals'
Force 2 ....dipole –dipole
Force 3 ....hydrogen bonding

Remember:
- ***Not ionic*** *because these are forces between ions not between molecules*
- ***Not covalent*** *as this would be intra-molecular, that is to say within a molecule, not between molecules.*

(b) Covalent between the atoms, I-I
and van der Waals' between the I_2 molecules

Remember:
- *The covalent bonds are intra-molecular between the paired atoms of iodine that make up the iodine molecule.*
- *The van der Waals' forces hold the iodine molecules in position in the crystal of iodine.*

(c) Molecular.

Remember:
- *There are no ions present so it cannot possibly be described as ionic.*
- *Iodine molecules are held in place by intermolecular van der Waals' forces. So it is certainly a molecular crystal type.*

(d) Van der Waals' forces between the molecules must be broken.

Remember:
- *There are no ions in iodine crystals, if you mention them you will lose marks.*
- *If you suggest that covalent bonds between the iodine atoms must be broken you will also lose marks.*

(e) Ionic bonding
(f) Giant ionic lattice structure
(g) Ionic bonding involves very strong electrostatic forces between ions. A large amoun of energy is needed to overcome these forces.
(h) All bonding must be broken rather than weakend.

Remember:
- *When you melt a crystal of sodium chloride you put in energy until the lattice is broken up and the ions are free to move around. But they are still very close to each other. The electrostatic forces are still acting keeping the ions together to form molten sodium chloride. To vaporise the sodium chloride you have to provide a much greater amount of energy to overcome the electrostatic forces and completely separate the sodium and chloride ions.*
- *Do not mention sodium chloride molecules or you will lose marks.*

(i) Giant covalent lattice. The strong covalent bonds need a lot of energy to break them.

2. Iodine sublimes on heating and has a low melting point. Graphite has a very high melting point.

Iodine does not conduct electricity ; graphite does
Iodine has a simple molecular covalent lattice structure.
Molecules consist of two iodine atoms held together by a single covalent bond.
Van der Waals' forces hold the iodine molecules in place in its lattice.
Iodine has a low melting point because the van der Waals' intermolecular forces are weak and require only a small amount of energy to break them.
Iodine has no free electrons or free ions to conduct electricity. Iodine crystals are therefore non-conducting.

Graphite has a giant covalent layer lattice structure with three covalent bonds and one delocalised electron per carbon atom.

Graphite has a very high melting point because many strong covalent bonds need to be broken which takes much energy. Graphite conducts because it has delocalised free electrons.

3. NaCl is a giant ionic lattice structure.

Remember
You lose marks if you use the terms atoms and molecules when describing the sodium chloride lattice structure.

Diamond has a giant covalent lattice structure

Remember
- You will lose marks if you use the term molecular rather than giant.
- You will also lose marks if use the term ionic as there are no carbon ions involved.
- You will lose marks if you mention van der Waals' because you could be confusing the structure of diamond with the structure of iodine or graphite crystals.

Many strong covalent C-C bonds need to be broken if the structure of diamond is to break down. This takes much energy.

Remember.
- *Don't talk about the bonds being weakened they would have to be broken for melting to take place.*
- *If you are certain you can draw the structure of diamond then you can get these ideas across with a diagram.*
- *Don't draw unwanted diagrams which may confuse the issue, for example the structure of graphite.*
- *Again talk only about covalent bonds not van der Waals' or you will lose marks.*

4. Both have covalent bonds BUT the structure of iodine is simple molecular with the iodine molecules (I_2) kept in place in the lattice by weak van der Waals' forces. However, diamond is a giant covalent lattice with each atom bonded to four others in a tetrahedral arrangement.

Iodine melts easily because only weak inter-molecular forces need to be broken whereas, in diamond, many strong covalent bonds would need to be broken so it has a very high melting point.

Remember:
If you go on to draw a diagram make sure it is correct and does not contradict your written answer.

5. See previous notes on these materials.

6. Sodium chloride is a giant ionic lattice. In the solid state the ions are fixed and therefore sodium chloride does not conduct when solid. However it does conduct when aqueous or molten because there are mobile ions in solution or when molten.

Diamond is a giant covalent lattice structure. There are no free electrons or ions so it does not conduct at all.

Graphite is a giant covalent layer lattice structure but it has delocalised electrons and it therefore conducts electricity.

7. The structure is a lattice of positive ions surrounded by a delocalised "sea of electrons". These delocalised electrons (3 per atom) are free to move and responsible for aluminium's very high conductivity.

Remember.
- *Refer to positive ions not nuclei.*
- *Refer to the lattice structure of the metal.*
- *Refer to the ability of the delocalised electrons to move.*

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