Chapter 4

Bonding

The discussion of bonding in the IB can be very satisfying as it is thorough and involves many new and interesting concepts. Of course, this can make it hard too. We break down our bonding concepts into four distinct areas: ionic, covalent, metallic and intermolecular. For each type we consider how the bonds make the atoms in substances stick together (microscopic) and the properties that these interactions give the substance (macroscopic). Many of the concepts should be familiar from GCSE but make sure that you are willing to expand on what you already know and can interpret results in a more flexible manner.

4.1 What is a bond?

What is a bond? What are we actually talking about when we consider bonding? I would say that a bond is a strong favourable electronic interaction between two atoms. Where does this interaction come from? The nuclei in all atoms are positively charged. Putting electrons between a pair of nuclei can make a bond if the attraction between the positive nuclei and the negative electrons outweighs the unfavourable repulsion between the nuclei and between the electrons (covalent). Having opposite charges on atoms (ions) will result in electrostatic attractions between them and these too can hold atoms together (ionic). In metals the situation is like a hybrid of the two just mentioned: electrons are held between atoms, but the atoms are actually positively charged.

4.2 Ionic bonding

Ionic bonding occurs between ions. Ions form as a result of a large difference in the electronegativity of two atoms - one atom is really electronegative and good at forming something negative, the other is terrible at holding onto electrons and so loses (at least) one electron and forms a positive ion. The ions are then held together by strong electrostatic interactions between them. You should be able to predict what ions are formed from what elements based on their positions in the periodic table.

4.3 Covalent bonding

Covalent bonding involves sharing pairs of electrons. The bond is held together by attraction between the nuclei and the electrons in between them. Covalent bonding is normally found in compounds in which the difference in electronegativity of the atoms is small. (The atoms themselves are almost always non-metals, and therefore they have high electronegativity values.) We know two types of covalent bond: σ and π bonds. These look like atomic s and p orbitals respectively if viewed down the internuclear axis (a line drawn between the centres of the two nuclei).

4.3.1 Polarity of bonds

Bonds can be between atoms which are different. If the atoms have a reasonable difference in their electronegativities we can imagine that the electrons in the bond are held closer to the more electronegative of the two. In such a case there will be an uneven distribution of negative charge in the bond, leaving the more electronegative element with a $\delta-$ charge and the other $\delta+$. The bond is described as being polar. For instance, the bond between hydrogen and chlorine in HCl is polar: $\underset{\delta+}{\mathrm{H}}-\underset{\delta-}{\mathrm{Cl}}$

4.3.2 Polarity of molecules

If a molecule is to be polar then it must contain at least one polar bond and the centres of positive and negative charge must not coincide. We can only work out the polarity of a molecule if we know something about its shape, which we'll consider a bit later on. We looked at polar molecules when we saw jets of liquids being deflected by charged rods - some were deflected (the polar ones) some were not.

4.3.3 How big a difference in electronegativity?

We say that a 'large enough' difference in electronegativity between atoms will result in an ionic bond. A lower difference will result in a polar covalent bond, and zero difference results in a good old-fashioned covalent bond. What are the numbers?

Electronegativity is an arbitrary unitless scale and it would be pretty pointless to assign numbers to what the difference in electronegativities should be. The electronegativities of common non-metals in covalent bonds are considered to range from the high to the really high:

$$\text{B \& Si} < \text{P \& H} < \text{C \& S \& I} < \text{Br} < \text{Cl \& N} < \text{O} < \text{F}$$

Any difference that you are asked to consider will normally be large. Note that C and H are very close in electronegativity, as this has implications for organic chemistry.

4.4 Shapes of molecules

Consideration of molecular shape is probably quite a new idea to you. We can use valence shell electron pair repulsion (VSEPR) theory to explain the shapes of molecules. There are a few questions to ask and things to consider when considering how to work out what shape a particular species is:

- How many regions of high electron density are there around the central atom?
- How many of these are bonding electrons, and how many are non-bonding?
- Areas of electron density try to get as far away from each other as possible but $\cdots$
- Lone pairs repel more than bonding electrons.

Classic examples are the hydrides of C, N and O (CH_4, NH_3, H_2O). All of these have four regions of electron density around the central atom. To a first approximation these will be arranged tetrahedrally. In CH_4 this is the end of the story - the H−C−H bond angle is 109.5°.

In NH_3 there is a lone pair of electrons on the N. This repels the electrons in the bonds more than the bonding electron pairs repel each other, so the H−N−H bond angle is reduced from that in the tetrahedron to 107°. The shape is described as a trigonal pyramid.

In H_2O there are two lone pairs of electrons on the O. These repel the bonding electron pairs even more, reducing the H−O−H bond angle to about 104°. The shape is described as non-linear, bent, angular or v-shaped.

Other common shapes of molecules (and ions) include octahedral (6 regions of negative charge), trigonal bipyramidal (5 regions of negative charge), trigonal planar (three regions of negative charge) and linear (2 regions of negative charge).

4.5 Hybridization

We use the idea of hybridization to explain our observations of the bonding in molecules. In methane, CH_4, for example, the C−H bonds are equivalent. How can this be if there are two electrons in the carbon s orbital and two unpaired electrons in two of the p orbitals? Clearly, this can't be the case. The shape would be wrong and the bonds would be of different strengths. We consider that some average, or hybrid, orbitals are formed from the atomic orbitals. These all have the same energy (they are degenerate). There are some rules for hybridization:

- n atomic orbitals must result in the creation of n orbitals
- Hybrids are always formed from the s orbital and at least one of the p orbitals
- Shape gives us a clue as to the type of hybrid orbitals formed

No. of orbitals	Hybridization	Shape about central atom
2	sp	Linear
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral

If we know the shape we can predict the type of hybridization with ease. If we know the type of hybridization it is trivial to work out the shape.

4.6 Metallic bonding

Metallic bonding occurs in metallic elements and in alloys. The IB description of metallic bonding is very similar to that found at GCSE; atoms lose their valence electrons to form a lattice of positive ions surrounded by delocalised electrons. It is the delocalised electrons that give the metallic structures their characteristic properties: malleability, ductility and electrical conductivity.

4.7 Intermolecular forces

There are three main types of intermolecular forces. To be able to talk intelligently about them you should be able to recognise when a substance is molecular - it is no use describing the intermolecular forces in e.g. magnesium oxide because there are no molecules! In order of increasing strength the three types of force are

- van der Waals' forces

- permanent dipole-dipole interactions
- hydrogen bonds

Boiling points and so forth are controlled by the strengths of these *inter*molecular forces. The *intra*molecular forces (covalent bonds) are so strong that they do not control the boiling points of molecular substances. If you write something like 'The boiling point is low because it has weak covalent bonds' then you are doing something wrong.

4.7.1 van der Waals' forces

These are the weakest of the intermolecular forces. This is not to say that they are unimportant. The forces arise as a result of the motion of electrons in molecules. At any instant in time there is a probability that there will be an imbalance in the electron distribution in a molecule - this will leave it with a dipole, although the movement of the electrons will mean that it is short-lived. This small transient dipole can induce a dipole in a neighboring molecule, producing a favorable interaction between the $\delta+$ and $\delta-$ parts of the two molecules.

These interactions are weak because they are short-lived and the imbalance in charge distribution is normally insubstantial. The interactions will get stronger if there are more electrons in the molecule because the chance of significant imbalance in the distribution of the electron cloud is greater.

4.7.2 Permanent dipole-dipole interactions

If a molecule possesses a permanent dipole we essentially have an amplified case of the vdW interaction previously described. Polar molecules are attracted to one another by reasonably weak electrostatic attractions. These attractions result from permanent dipoles which usually have a larger dipole moment and are longer lived than the transient dipoles in vdW interactions, therefore dipole-dipole interactions are generally stronger.

4.7.3 Hydrogen bonding

Hydrogen bonds only occur in special situations. They arise because the nucleus of the hydrogen atom is easily exposed when it is attached to a highly electronegative atom. This atom needs to be N, O or F. The hydrogen atom becomes highly positively polarised - it is almost a proton. This 'proton' can attract a non-bonding pair of electrons from *another* N, O or F, essentially producing a very strong dipole-dipole interaction.

Hydrogen bonding is responsible for the high boiling point of water - without hydrogen bonding the boiling point of H_2O would be about -100 °C. This value is obtained by extrapolating from the boiling points of the other group 6 hydrides - H_2S, H_2Se and H_2Te. Similarly 'anomalous' boiling points are seen in HF and NH_3 but not in CH_4; the first two do have hydrogen bonding, the last does not. Hydrogen bonding also gives ice a very open structure, making it less dense than liquid water. Very few (that I know of) other substances show this strange behaviour.

4.8 Resonance and delocalization

Molecules and ions which contain alternating single and double bonds can form different, but often chemically identical, structures. The electrons in the double bonds can move to the single bonds and then back again. Important examples are ozone, O_3, carbonate, CO_3^{2-} and benzene, C_6H_6. These different structures are called resonance structures as they resonate between two or more forms.

We can imagine an average structure of these resonance structures, and in fact we can explain it in terms of molecular orbitals. The p atomic orbitals of the atoms are not involved in making the 'skeleton' of the molecule, which is formed by the σ bonds. These remaining p orbitals each contain an electron. The orbitals can overlap forming π molecular orbitals in which the electrons are delocalized over all of the electrons involved in the alternating single-double bond system. This is actually energetically more stable than forming distinct single and double bonds and the difference in energy between the two extremes is called the *delocalization energy*. We will meet the idea of delocalization again when we study benzene chemistry.

4.9 Allotropes of carbon

Allotropes are different crystalline forms of an element. Carbon has three main allotropes: graphite, diamond and buckminsterfullerene. In graphite the atoms are arranged in layers of sp^2 hybridized carbon with delocalized p electrons in between the layers. The layers are thus held together by vdW forces which accounts for the ability of the layers to slide over one another with relative ease. The electrons can also move, meaning that the structure can conduct electricity.

Diamond has a giant three-dimensional structure of sp^3 hybrdized carbons. All of the bonds are equal and strong, leading to a very hard substance. There are no delocalized electrons, meaning it does not conduct electricity.

Buckminsterfullerene has sp^2 hybridization like graphite. However, because it forms a structure like a football the arrangement is a distorted trigonal planar one. As in graphite there are delocalized electrons which gives C_{60} the ability to conduct electricity, albeit poorly.