Chapter 7

Topic 7 - Covalent bonds

This topic covers the type of bonding which holds the atoms in molecules together. Many ideas fall within its boundaries, including the shapes of molecules, the dative covalent bond, electronegativity and degree of ionic character, bond energies, rates of reaction, equilibrium and le Chatelier's principle. This wide-ranging nature should exemplify, but can actually disguise the key points. These are

- Covalent bonds hold atoms together by sharing pairs of negatively charged electrons between positively charged nuclei
- Different nuclei have different abilities to hold on to negative charge
- Breaking covalent bonds requires an energy input to a system
- Making covalent bonds releases energy from a system to its surroundings

7.1 Dots, crosses and shapes

You should be able to draw dot and cross diagrams from GCSE work. In the Nuffield course you only need to draw outer electrons and there is no need for 'rings' around the atoms. Try to draw ethanol and carbon dioxide in the space below to satisfy yourself that you can do this.

Electrons are negatively charged and repel one another. In a molecule such as methane the four pairs of bonding electrons get as far away as possible from each other - a tetrahedral arrangement is found (bond angle is 109.5°). The shape of ammonia is not planar however, as there is a **lone pair** (non-bonded pair of electrons) on the nitrogen atom. This pair of electrons repels bonding electrons more strongly than bonding pairs of electrons repel one another. Hence the three N-H bonds are squeezed slightly closer together than they would be in a tetrahedron (bond angle is 107.5°). You should be able to explain the shapes and bond angles of water and hydrogen chloride in similar detail.

The larger repulsion by lone pairs can be explained by considering where these electrons are likely to be found. They will be closer to the nucleus of the atom than pairs of electrons in a bond, and will be 'squashed' against it, thus occupying more space.

When we consider multiple bonds, which are especially important in organic chemistry, we are introduced to the terms 'pi bond' and 'sigma bond'. You only need to know that the sigma bond is symmetrical about the axis joining the two nuclei and the pi bond is not, as it consists of two electron clouds. We will learn more about the properties of sigma and pi bonds in the next topic.

The next section on covalent bonds emphasises that covalent bonds can be very strong. The structures of carbon and graphite are discussed. Each are giant structures, but the way the atoms are bonded together contributes to their very different physical properties. You should be able to explain the difference in electrical conductivity in terms of delocalised electrons.

The final section considers dative covalency. A dative covalent bond is one in which both of the electrons shared between two atoms are provided by only one atom. This is an important piece of chemistry which explains the formation of the ammonium and oxonium ions. Draw dot and cross diagrams of these below.

7.2 Electronegativity

Electronegativity is the power of an atom in a molecule to attract electrons to itself. This is an important definition, as it is not to do with the ability of an isolated atom to attract electrons (which is the electron affinity). There are a few scales of electronegativity, and it is only wise to use numerical values if you know how they were obtained. For the most part they are obtained from thermodynamic data, which are either average values and therefore not entirely applicable to a particular instance, or which are hard to measure and unreliable. What you should concern yourself with at the moment is a study of the trends in electronegativity.

The use of electronegativity at the moment is limited to a discussion of the nature of bonds. A bond between two atoms with a large difference in electronegativity is likely to be ionic, whereas a bond between atoms with similar electronegativities is likely to be covalent. You should be able to explain why certain bonds are more polarised than others, and this is simply done by comparing the electronegativities of the atoms present. Remember that the elements at the top right of the periodic table are much more electronegative than those at the bottom left. A difference in electronegativity is seldom the sole reason for something happening in chemistry, so do not use it as an answer to everything!

Do you think that most bonds have a degree of covalent character and a degree of ionic character?

7.3 Bond energies

What is the definition of standard enthalpy of combustion, symbol $\Delta H_c^\ominus$?

The first experiment in this section introduces the idea of burning a homologous series of alcohols and working out the differences between successive ΔH_c values. Each alcohol differs by a single -CH_2- unit and there is a consistent difference between successive values. This implies that the energy associated with breaking a set number of particular types of bonds and then making a set number of particular types of bonds releases a particular amount of energy - the energies of bonds are specific. An obvious extension to this is calculating the energies of individual bonds.

We see that multiple bonds are shorter than single bonds (between the same atoms) and that they have higher bond energies.

7.3.1 Rates of reaction

You should be able to describe the formation of a transition state, the effect of a catalyst and draw a energy profile for a reaction showing the activation energy. This is a powerful tool for describing reactions and explaining observations. Draw a diagram below. Remember that increasing temperature increases the rate of reaction by increasing the proportion of particles with sufficient activation energy. **A cata-**

lyst acts by providing an alternative route (or mechanism) for a reaction which has a lower activation energy (and a different transition state). This last point is important - the catalyst does not lower the activation energy of the reaction.

7.4 Reversible reactions

Reactions do not always go to completion. Some are reversible, and in the solution and gas phases reversible reactions often have both the forward and reverse reactions occurring simultaneously. If the rate of the forward reaction is the same as the rate of the reverse reaction then a **dynamic equilibrium** is established. The manufacture of ammonia by the Haber process is an example of a dynamic equilibrium. The overall concentrations of reactants and products are constant, even though individual particles are reacting in one direction or the other.

7.4.1 Le Chatelier's principle

This states that **if the conditions under which an equilibrium exists are changed, the position of equilibrium shifts to counteract the change**. This is a very useful way of being able to predict what will happen to a reaction if the conditions are changed. Remember that a catalyst does not affect the position of equilibrium, it merely alters the speed at which equilibrium is attained.