9 STRUCTURE & BONDING

9.1 REVISION

It is assumed that you know the following:
- the solar system model for the structure of the atom
- what atoms try to do to become stable
- how atoms form ionic bonds
- how atoms form covalent bonds
- difference in properties of ionic and covalent compounds

9.2 IS THE ATOM REALLY LIKE THE SOLAR SYSTEM?

In one word, no! Bohr’s model of the atom is very simple, easy to visualise and explain basic atomic behaviour nicely. Unfortunately, the physicists found that it didn’t fit their mathematical models at all well, and they came up with something that works slightly better with their models, but is almost entirely incomprehensible to normal people. This is known as quantum mechanics.

The picture you need for the purposes of understanding how the atom works will be an improved solar system model, which uses some of the quantum mechanical ideas, without descending into the swamp of incomprehensibility. Table 9.1 summarises the Bohr model and the improved version.

<table>
<thead>
<tr>
<th><strong>Bohr’s model</strong></th>
<th><strong>Improved model</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>The electrons circle around the nucleus, which contains protons and neutrons</td>
<td>No change</td>
</tr>
<tr>
<td>The electrons are found at different distances form the nucleus called electrons shells</td>
<td>Basically the same, except they are called energy levels</td>
</tr>
<tr>
<td>There are seven electron shells, labelled K, L, M etc, one for each row of the periodic table</td>
<td>There are seven levels labelled 1-7, but all but the first have sub-levels, or orbitals (s, p, d, f etc), eg 1s, 2p, 3d</td>
</tr>
<tr>
<td>The shells are of fixed energy values and electrons can only exist in these shells</td>
<td>The same, as applied to the orbitals</td>
</tr>
<tr>
<td>The shells can hold a maximum number of electrons: 2, 8, 18, 32 etc</td>
<td>The orbitals can hold a maximum number of electrons: 2 in s, 6 in p, 10 in d, 14 in f</td>
</tr>
<tr>
<td>In the normal stable atom, electrons fill from the lowest shell outwards</td>
<td>In the normal stable atom, electrons fill from the lowest orbital outwards (see Figure 9.1)</td>
</tr>
<tr>
<td>Atoms don’t like to have partly filled shells and will try to empty or fill them</td>
<td>Atoms don’t like to have partly filled orbitals and will try to empty or fill them</td>
</tr>
</tbody>
</table>

You might think very little is different between the two models, other than increasing the number of orbits around the nuclear “sun”. The full quantum mechanical model is much more complex, one of the major changes being that the electrons do not simply circle around the nucleus, but are free to move in three dimensions within certain “probability” volumes.
The critical idea for you is that the sub-orbitals are of fixed energy values, and that electrons can only exist in one of these energy levels. They have some ability to move between levels (see section 9.3), and a certain fixed, exact and constant amount of energy will be lost or gained, depending on the transition. Different elements have different energy levels, but for a given element, all the atoms have the same levels, regardless of temperature. However, if the atom changes from neutral and unbound to charged or bonded, the energy levels change. Thus, a single hydrogen atom has different energy level to a hydrogen atom in a H₂ molecule, and to a H⁺ ion in solution.

![Figure 9.1](image.png)

**Figure 9.1 Sub-orbitals and order of filling (each box can take 1 electron)**

Notice that the 3d sub-orbital is filled after the 4s. Look at the periodic table, and you will notice how there are groups of 2 (groups 1A and 2A), 6 (groups 3A-8A), 10 (the transition metal rows) and 14 (the separate rows of lanthanides).

**Practice Questions**

1. Identify what sub-orbitals are being newly filled for all the elements up to zinc.
2. Extend Figure 9.1, based on the shape of the periodic table.

Electron configurations are a summary of which sub-orbitals the electrons in an atom are located in. This can be in the form of a diagram like Figure 9.1, with a marker in each filled box, or in written form, where the number of electrons in a sub-orbital are indicated as a superscript, such as 1s².

**Example**

*Write the electron configuration for fluorine and fluoride.*

Fluorine has an atomic number of 9, so a neutral atom has 9 electrons, and 1⁻ ion 10 electrons.

F: \(1s^2 \ 2s^2 \ 2p^5\)

F⁻: \(1s^2 \ 2s^2 \ 2p^6\)
PRACTICE QUESTION
3. Write electron configurations for the following atoms or ions:
   - sodium
   - sodium 1+
   - chlorine
   - chloride 1-
   - calcium
   - calcium 2+
   - iron

9.3 An Introduction To Spectroscopy

So sodium, for example, which has 11 electrons, fills the first level (1s orbital) with two electrons, the second (2s and 2p orbitals) with 8 and the final electron is in the third level (3s).

The electron in level 3 has more energy than the eight in level 2, which have more than the two in level 1. When the atom has all its electrons in the lowest levels possible (as with sodium above), it is said to be in the **ground state** – the normal state and the lowest energy possible (as shown in Figure 9.2).

![Figure 9.2: The sodium atom in the ground state](image)

If enough energy is applied to the sodium atom, one of the electrons can jump up to a higher level as long as there is space. So the 3s electron could jump up to the empty 3p orbital (as shown in Figure 9.3). This is known as **absorption**, and the atom is no longer in the ground state, but through the absorption of energy has reached an **excited state**.

![Figure 9.3: The sodium atom in an excited state](image)
The amount of energy required to lift an electron from sub-orbital 3s to 3p is quite unique for sodium atoms, and different to the energy required to cause a shift from level 2p to level 3s. The energy can be supplied in the form of heat, electricity or light.

An atom in an excited state does not stay there for long (fractions of a microsecond in fact), and falls back to the ground state, as the electron in the “wrong” level returns to where it came from, as shown in Figure 9.4. When it does so, the extra energy it absorbed in jumping up a level is released again, normally in the form of light. This is known as emission. The yellow-orange streetlights work by this process, since they contain sodium vapour and are electrically powered.

A measurement of the energy absorbed or emitted can be plotted, and gives information about the type of atom present, and its concentration. This graph of intensity (number of electrons jumping) against energy (height of jump) is called a spectrum, as shown in Figure 9.5. Each different chemical substance has a different spectrum. This field of spectroscopy is the most important area of chemical analysis, and you will learn much more about it next semester.
9.4 ELECTRONEGATIVITY

You are aware of the different ‘appetite’ of elements for electrons to make them stable: metals, such as sodium, want to get rid of them, the halogens desperately need them. A measure of the need of elements for electrons is called electronegativity. Elements with a need to gain electrons to become stable have higher electronegativity values than those wishing to lose electrons.

If we concentrate on only the main-group elements, the general trend is for an increase in electronegativity from left to right (but not including the inert gases), but decreasing down a group. Thus, fluorine is the most electronegative element, and caesium the least. Table 9.3 lists electronegativity values for some of the main-group elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>EN</th>
<th>Element</th>
<th>EN</th>
<th>Element</th>
<th>EN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>2.20</td>
<td>Oxygen</td>
<td>3.44</td>
<td>Phosphorus</td>
<td>2.19</td>
</tr>
<tr>
<td>Lithium</td>
<td>0.98</td>
<td>Fluorine</td>
<td>3.98</td>
<td>Sulfur</td>
<td>2.58</td>
</tr>
<tr>
<td>Boron</td>
<td>2.04</td>
<td>Sodium</td>
<td>0.93</td>
<td>Chlorine</td>
<td>3.16</td>
</tr>
<tr>
<td>Carbon</td>
<td>2.55</td>
<td>Magnesium</td>
<td>1.31</td>
<td>Bromine</td>
<td>2.96</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.04</td>
<td>Silicon</td>
<td>1.90</td>
<td>Iodine</td>
<td>2.66</td>
</tr>
</tbody>
</table>

The actual electronegativity values are not important to us; what is significant is the relative values for two elements in a bond. The greater the difference, the more unevenly shared the electrons, and vice versa. The extreme is an ionic bond, where one atom is very hungry for electrons and the other is a willing supplier. However, this isn’t telling us anything we didn’t know already: metals form ionic bonds with non-metals.

What electronegativity values tells us is that all covalent bonds are not the same. Until now, we have described a covalent bond as each atom putting one electron into the bond, and sharing equally in the pair. A simple picture would be an inflated balloon with the atoms at either end. However, if one of the atoms has a stronger pull on the electrons (because of a higher electronegativity), the balloon gets ‘squeezed’ so that this atom has more than its share. Figure 9.6 illustrates this point.

**FIGURE 9.6 The balloon analogy for covalent bonds**

How does an uneven share of the electrons affect the atoms? To consider this, we have to view the electrons in the bond, not as individual units, but as contributing to a volume (ie. the balloon) containing a 2− charge. That volume can be divided in any way. In Figure 9.6(a), the even sharing of the electrons means that each atom has a 1− charge as its share, which is equal to the 1− charge it put into the bond.
In Figure 9.6(b), the atom on the right (which has the higher EN) has more of the volume and therefore, slightly more than half the $2-$ charge. It has gained a small amount of negative charge in the formation of the bond, while the other atom has lost some, and therefore, gains a slight positive charge. This is known as a polar covalent bond, because of the slight $+ \text{ and } -$ charges or poles in the bond. The other bond (in (a)) is known as a non-polar covalent bond. In general, a difference of at least 1 in EN values indicates a polar bond.

It should be made very clear that the $+ \text{ and } -$ charges in polar covalent bonds are not full charges, like they are in ionic bonds. The distribution of the electrons is not even between the two atoms; atom A might have the ‘equivalent’ of 1.1 electrons and atom B the other 0.9 — though it must be said that these fractions of electrons are not real, but just a way of picturing what is happening. A polar covalent bond in a structural formula will often have the symbols $\delta^+$ and $\delta^-$ to clearly distinguish it from an ionic bond ($\delta$ is frequently used in science to symbolise ‘a small amount of’).

**EXAMPLE**

What type of covalent bonds would form between the following pairs of atoms?

(a) carbon and hydrogen  
(b) oxygen and hydrogen  
(c) oxygen and oxygen

(a) Carbon has an EN of 2.55 and hydrogen 2.2: a difference of 0.35. This is relatively small, and the bond is generally considered to be non-polar.

(b) Oxygen has an EN of 3.44: now the difference is 1.24. This is quite significant, and the bond is polar.

(c) Bonds between atoms of the same element must be non-polar, because the EN values are the same.

**PRACTICE QUESTIONS**

5. Which of the following covalent bonds is considered polar?  
   (a) C=C  (b) C=O  (c) C—N  (d) N—O  (e) C—F

6. Which of the elements listed in Table 9.2 would form a polar covalent bond with hydrogen?

### 9.6 INTERMOLECULAR FORCES

Intermolecular forces (or bonds) are those between molecules. They affect the physical properties of the substance: melting and boiling points, density, solubility, etc. The stronger the intermolecular forces are, the higher these values will be because the molecules are held together more strongly.

Ionic and covalent network compounds do not really have individual molecules. The forces that hold the atoms together also hold the ‘molecules’ together. This gives these types of substances very high melting and boiling points, relatively high densities (though not as high as metals) and in the case of networks, very limited solubility.

In this section, the effect of intermolecular forces on the physical properties of ‘true’ molecular compounds — covalent molecular compounds — will be described. In this type of compound, there are the strong covalent bonds within the molecules, holding the atoms together, and relatively weak forces between the molecules, as shown in Figure 9.7.
Covalent intramolecular bonds

Weak intermolecular force

**FIGURE 9.7** *Intra- and intermolecular bonds in covalent molecules*

What causes these intermolecular forces in covalent molecules? In the previous section, we saw that certain covalent bonds developed small positive and negative charges. The most significant intermolecular forces are simply caused by attraction between atoms in different molecules with opposite δ+ and δ− charges. The greater the difference in EN values between atoms in a covalent bond, the greater the charge build-up and the stronger the intermolecular force as a result. Figure 9.8 shows the intermolecular forces in water.

The forces between the slightly positive atoms (eg. hydrogen) and slightly negative atoms (eg. oxygen) are called **dipole attraction**. Because, in water, they are particularly strong, and involve hydrogen as one of the atoms, they are given a special name — **hydrogen bonds**. They occur in compounds where hydrogen is attached to a strongly electronegative element, that is F, Cl, N and O. Hydrogen bonds are the strongest of the intermolecular forces.

![Dipole attraction between methanal molecules](image)

**FIGURE 9.8** *Intermolecular forces in water*

Dipole attractions between other polar covalent bonds are not as strong as hydrogen bonds. Figure 9.9 shows dipole attractions between molecules of methanal.

![Dipole attraction between methanal molecules](image)

**FIGURE 9.9** *Dipole attraction between methanal molecules*

*Molecules without polar covalent bonds exhibit very weak intermolecular forces*, known as **dispersion forces**. It is somewhat difficult to explain why any attraction should occur between molecules, such as methane, and we won’t attempt to do so here.

**PRACTICE QUESTION**

7. What type of intermolecular forces would occur in (a) HCl and (b) ethane?
Effect On Melting And Boiling Points
What effect do the different types of intermolecular forces have on the physical properties of covalent molecules? Because even hydrogen bonds are much, much weaker than ionic or covalent bonds, it doesn’t take much energy (heat) to ‘unstick the glue’ between the molecules. Therefore, the melting and boiling points of covalent molecules are much lower than ionic, metallic or covalent network substances.

Within the class of covalent molecules, those with hydrogen bonds will have the highest melting and boiling points and densities. One other point that needs to be made when comparing physical properties is that the formula weight of a compound should be taken into account. The heavier the molecule, the denser it will be and the more heat is required to melt and boil it.

EXAMPLES
1. Explain why water has a boiling point almost 300°C higher than oxygen gas.

Water has hydrogen bonds which are much stronger. The bond in oxygen gas (O=O) is non-polar, because both atoms have the same electronegativity. It requires much more heat to break the hydrogen bonds in water than the weak dispersion forces in oxygen, even though oxygen is heavier (32 compared to 18).

2. Arrange the following organic molecules in order of increasing boiling point: methanol, ethanol, ethane, methanal.

The formula weights for methanol (32), ethane (28) and methanal (30) are similar, but ethanol (46) is higher.

\[
\begin{align*}
\text{Methanol} & \quad \text{Ethanol} & \quad \text{Ethane} & \quad \text{Methanal} \\
\end{align*}
\]

The structural formulae above for the four compounds shows that only ethane has no polar bonds. It, therefore, must have the lowest boiling point. Of the others, the polar bond in methanol and ethanol is the OH bond, which allows for hydrogen bonding. The C=O bond in methanal allows dipole attraction, but is weaker than that in the other two. Methanal will have the second lowest boiling point. Methanol will be next highest, and ethanol the highest because its intermolecular forces are as strong as methanol and it is heavier.

Order (with actual b.p. in °C given): ethane (–89), methanal (–21), methanol (61), ethanol (78).

PRACTICE QUESTIONS
8. Water and ammonia both have hydrogen bonds between the molecules. Why does water have a higher boiling point?
9. How would you expect the boiling point of HF to compare with that of water and ammonia?
10. Why does hydrogen peroxide (H₂O₂) have a higher boiling point than water?
11. Explain the boiling point trend in the simple organic compounds, propanol (97°C), propanal (–21°C) and butane (–89°C).
Effect On Solubility

The golden rule for predicting the solubility of compounds in solvents is ‘like dissolves like’: compounds dissolve in solvents with similar types of bonds. Thus, compounds with polar or ionic bonds dissolve in solvents with polar bonds — (there are no ionic liquids), while compounds without polar bonds dissolve in non-polar solvents. Table 9.4 classifies some important solvents by their polarity.

TABLE 9.4 Classification of solvents by polarity

<table>
<thead>
<tr>
<th>Polarity</th>
<th>Common solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very high</td>
<td>water</td>
</tr>
<tr>
<td>Moderate</td>
<td>methanol, ethanol, propanone (acetone)</td>
</tr>
<tr>
<td>Low (or non-polar)</td>
<td>hexane, trichloromethane (chloroform)</td>
</tr>
</tbody>
</table>

EXAMPLES

1. Explain why sodium chloride and ethanol both dissolve in water, but ethane doesn’t.

   Water contains polar covalent bonds, which will have an attraction for the ions in sodium chloride, and the polar OH bond in ethanol. Ethane, without polar bonds is not attracted to the water.

2. Predict the most suitable solvent (from water, ethanol and hexane) for calcium chloride, methanal and butane.

   Calcium chloride (ionic): water
   Methanal (polar covalent): water or ethanol
   Butane (non-polar): hexane

PRACTICE QUESTIONS

12. Why does carbon dioxide dissolve in water, but nitrogen does not.
13. Which would be more soluble in water — ammonia or methane?
14. What would be a suitable solvent for naphthalene, which is a compound containing only C-H and C-C bonds?

WHAT YOU NEED TO BE ABLE TO DO

- describe the improved model of the structure of the atom
- write electron configurations for elements up to atomic number 36
- define the terms ground state and excited state
- using diagrams, explain absorption and emission of energy by atoms
- define electronegativity
- predict the polarity of bonds
- describe different types of intermolecular forces
- predict physical properties on the basis of intermolecular forces