Discovering chemistry

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Head of Intellectual Property, The Open University

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Introduction and guidance

Introduction and guidance

This free badged course, *Discovering chemistry*, is eight sessions in length with approximately three hours' study time for each session.

Chemistry lies at the centre of our modern life, playing a part in areas as diverse as the development of new drugs and materials, analysing our environment through to more mundane activities such as washing your clothes and making your tea. But to truly understand the role chemistry plays you need to have a sound grasp of a number of fundamental principles.

This course introduces you to some of these concepts, beginning with the idea that everything that you can see is made of building blocks called atoms. This leads on to a look at the chemical elements and how they are arranged in the periodic table, enabling chemists to rationalise patterns in their chemical and physical behaviour.

Next you will consider chemical reactions, specifically how atoms combine with other atoms to form molecules, and how molecules combine with other atoms or molecules to form bigger molecules. You will meet simple (tried and tested) theories to explain the bonding in molecules and how their shapes may be explained, and indeed predicted. And in a wider sense you'll be looking at why reactions happen at all and how fast they go.

This is also a beginner's level course in the language of the chemist; you'll learn about symbols, formulas and how chemical equations which represent reactions are constructed. Finally you will see how chemists count atoms and molecules, essential for making up solutions of a known concentration in order to carry out a reaction, or performing a chemical analysis.

After studying this course you should be able to:

- explain what is meant by isotopes, atomic numbers and mass numbers of the atoms of chemical elements
- indicate ways in which the chemical periodicity represented by the periodic table is reflected in the electronic structure of atoms
- explain how the molecular structure of chemical compounds is linked to their macroscopic properties
- understand ionic, covalent and metallic bonding
- construct balanced chemical equations for reactions
- use the Lewis structures of some simple chemical substances to illustrate the ideas of the octet rule, the electron-pair bond, and rationalise the three-dimensional structure of molecules
- select a set of organic molecules, each of which contains the same functional group, and use its reactions to show why the functional group concept is useful
- understand the use of the mole as a measure of the amount of a substance

- appreciate various facets of chemical reactions, why they occur and how fast they go, and the role of catalysts.

Moving around the course

In the ‘Summary’ at the end of each session, you will find a link to the next session. If at any time you want to return to the start of the course, click on ‘Course content’. From here you can navigate to any part of the course. Alternatively, use the week links at the top of every page of the course.

It’s also good practice, if you access a link from within a course page (including links to quizzes), to open it in a new window or tab. That way you can easily return to where you’ve come from without having to use the back button in your browser. You can do this by holding down the ‘CTRL’ key (or CMD on a Mac) and left clicking the mouse button; or right click and ‘open link in new tab’.

What is a badged course?

While studying *Discovering chemistry* you have the option to work towards gaining a digital badge.

Badged courses are a key part of The Open University's mission *to promote the educational well-being of the community* . The courses also provide another way of helping you to progress from informal to formal learning.

To complete a course you need to be able to find about 24 hours of study time, over a period of about eight weeks. However, it is possible to study them at any time, and at a pace to suit you.

Badged courses are all available on The Open University's OpenLearn website and do not cost anything to study. They differ from Open University courses because you do not receive support from a tutor. But you do get useful feedback from the interactive quizzes.

What is a badge?

Digital badges are a new way of demonstrating online that you have gained a skill. Schools, colleges and universities are working with employers and other organisations to develop open badges that help learners gain recognition for their skills, and support employers to identify the right candidate for a job.

Badges demonstrate your work and achievement on the course. You can share your achievement with friends, family and employers, and on social media. Badges are a great motivator, helping you to reach the end of the course. Gaining a badge often boosts confidence in the skills and abilities that underpin successful study. So, completing this course should encourage you to think about taking other courses.

Getting a badge is straightforward! Here's what you have to do:

- read each session of the course
- score 50% or more in the two badge quizzes in Week 4 and Week 8.

For all the quizzes, you can have three attempts at most of the questions (for true or false type questions you usually get only one attempt). If you get the answer right first time you will get more marks than for a correct answer the second or third time. Therefore, please be aware that for the two badge quizzes it is possible to get all the questions right but not score 50% and be eligible for the badge on that attempt. If one of your answers is incorrect you will often receive helpful feedback and suggestions about how to work out the correct answer.

For the badge quizzes, if you're not successful in getting 50% the first time, after 24 hours you can attempt the whole quiz, and come back as many times as you like.

Please note that quiz questions using drag and drop do not work on a mobile device. Instead, you should use a tablet or desktop.

We hope that as many people as possible will gain an Open University badge – so you should see getting a badge as an opportunity to reflect on what you have learned rather than as a test.

If you need more guidance on getting a badge and what you can do with it, take a look at the OpenLearn FAQs. When you gain your badge you will receive an email to notify you and you will be able to view and manage all your badges in My OpenLearn within 24 hours of completing the criteria to gain a badge.

Get started with Session 1 .

Session 1: Atoms – the building blocks of matter

Introduction

Atoms are the basic building blocks of all the substances around you, rather like letters are used to construct words and hence a language. And a look 'inside' an atom is perhaps your best starting point when studying chemistry for the first time. As you will learn from this course, it's the components of the atom that are crucial to understanding how substances behave in chemical reactions, and the behaviour of particles on the atomic (and sub-atomic) scale is often not what you would expect.

Learning Outcomes

After studying Session 1 you should be able to:

- describe the structure of atoms in terms of protons, neutrons and electrons
- understand what is meant by a chemical element and how they are arranged in the periodic table
- explain what is meant by atomic number and relative atomic mass of a chemical element
- appreciate the impact of quantum mechanics on understanding how electrons are arranged in atoms.

1 Atoms

The idea that everything that you can see is an assembly of tiny particles called **atoms** is chemistry's greatest contribution to science.

But this isn't a new idea.

In fact an early proposal came from the Greek philosopher Democritus (460 – 370BC), often known as the 'laughing philosopher' as he was always keen to promote the importance of being cheerful, although other accounts suggest he was laughing *at* and ridiculing the misfortunes of others and refer to him as the 'mocker'.

Democritus proposed that no matter how many times you cut something in half, and half again, and half again, eventually you will reach a point when you cannot divide it up any further. This led him to propose that everything is built up from tiny individual particles. In fact atom in Greek translates as ‘not’ and ‘cut’. Democritus along with another philosopher of the time Epicurus (340-270BC) believed in a world made of tiny, hard atoms in endless motion.

It wasn’t until the 19th century, and the work of English chemist, physicist and meteorologist John Dalton that atoms became part of modern science; even in 1900 there were eminent scientists who did not believe that atoms are real. However, between 1900 and 1920 phenomena as varied as the motion of pollen grains in water, diffusion in liquids, radioactivity and the diffraction of X-rays by crystals, all gave similar values for the *sizes* of atoms. The merging of evidence from such different directions pretty much destroyed any serious opposition to the existence of atoms.

The final nail in the coffin of the doubters was the emergence of instruments capable of producing images of atoms and molecules. This was realised in the 1980s, with the invention of the Scanning Tunnelling Microscope (STM). Importantly, atomic sizes measured using this technique agreed with those obtained from the earlier experiments.

Figure 1 shows a ring of 48 iron atoms on a copper surface observed by STM.

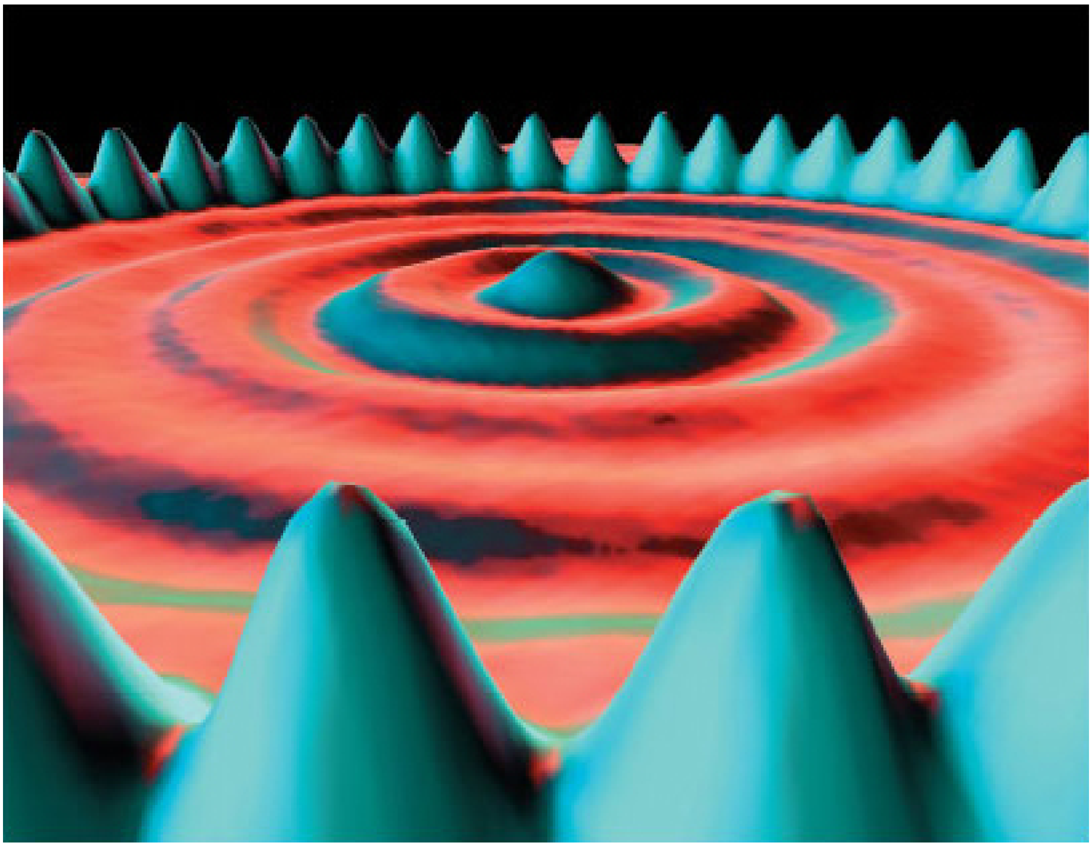


Figure 1 An image of iron atoms on a copper surface observed by STM

Maybe not what you thought an atom might look like, but the wavelike crests and troughs may be explained with reference to quantum mechanics and the wave-like properties of electrons, a topic you will touch on later in this module.

So, you’ve seen that atoms are so small they need sophisticated microscopes in order to ‘see’ them.

But how small they?

As a rough indication, the diameters of atoms range between 1×10^{-10} to 5×10^{-10}m

However, despite being originally thought to be indivisible, atoms *are* built up from a number of smaller components.

If you look inside the atom you will find at its centre the **nucleus**, this is positively charged and contains nearly all of its mass. Around the nucleus move much tinier negatively charged particles called *electrons.* The positive charge of the nucleus is balanced by the negative charge of the electrons, so overall an atom carries no electrical charge. The electrons themselves circle huge distances from the nucleus, moving at speeds close to the speed of light.

So, in fact most of an atom is empty space!

Returning to the nucleus, its positive charge is provided by positively charged particles called *protons*. These are very tightly packed in the nucleus, and your immediate thought might be they would repel one another. However, although we won't go into details here, there exists a force which holds the nucleus together – a sort of atomic 'superglue' ensuring this doesn't happen.

The number of protons in its nucleus, is used to define a unique **atomic number** for each atom.

For an atom, how is atomic number related to the number of electrons?

Answer

As atoms are neutral, the number of positive charges has to equal the number of negative charges, so the number of electrons = number of protons. Thus atomic number must also equal the number of electrons.

So far, you have focussed on the submicroscopic, invisible (to the naked eye) world of an atom.

How does this translate into something you can actually see?

This question will be answered in the next section.

1.1 Chemical elements

The basic form of matter, containing only atoms of the same atomic number, and which cannot be chemically broken down into simpler substances is a **chemical element**.

Chemists have given each element a name and a symbol. This is the same as that given to the atoms it contains. As you will see on working through this module, some elements have an upper-case letter as their chemical symbol (e.g. hydrogen, H) and others have an upper-case letter followed by a lowercase letter (e.g. helium He).

Consider the simplest element hydrogen, this has been given the symbol H.

So the H represents *both* the element hydrogen *and* the atoms of hydrogen.

Taking this a step further, hydrogen has an atomic number of one indicating there is one proton in the nucleus, and one electron in orbit around it.

The atomic number of the element lithium is 3, How many protons are in the nucleus, and how many electrons are orbiting the nucleus?

Answer

There are 3 protons, and given the atom is an uncharged (neutral) species this charge must be balanced by 3 electrons.

The elements may solids, liquids or gases at room temperature, and some examples, together with their chemical symbols are shown in Figure 2.

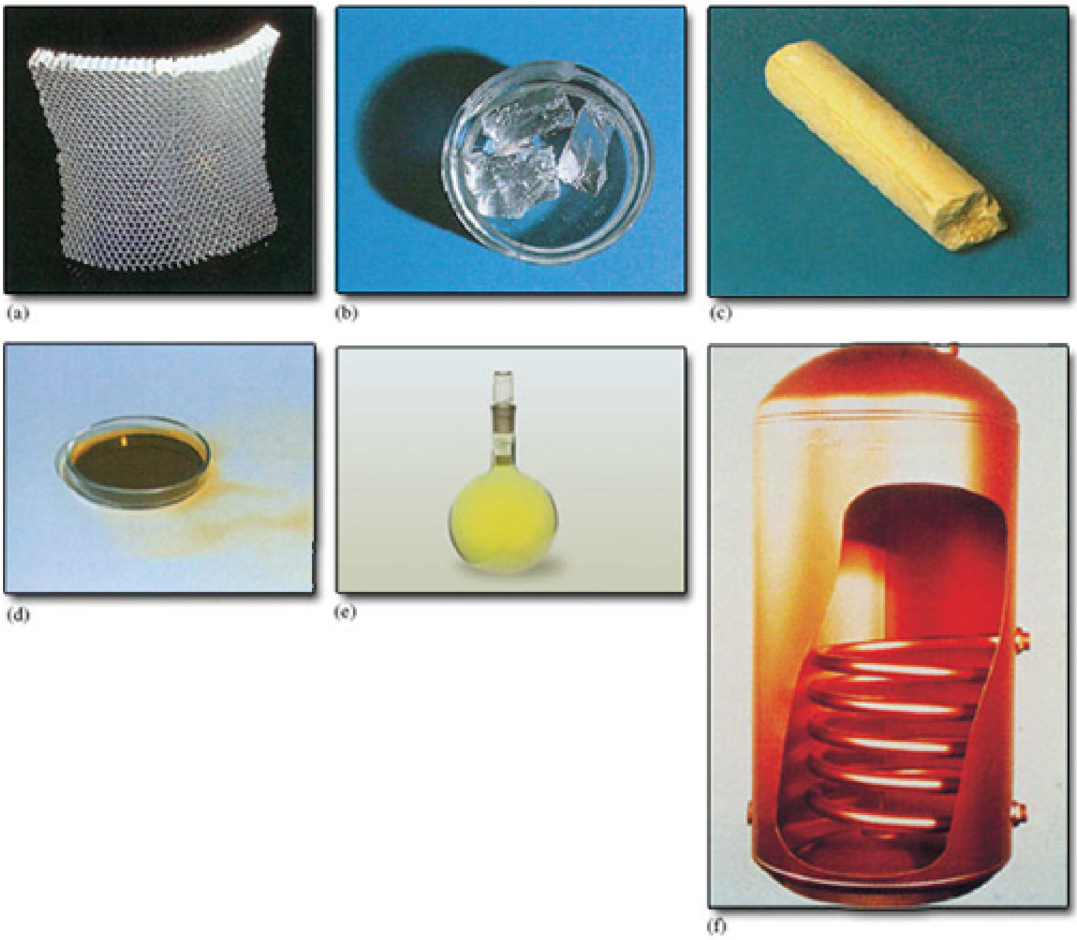


Figure 2 Some chemical elements (a) aluminium, (b) sodium, (c) sulfur, (d) bromine, (e) chlorine, (f) copper. Note that sodium is extremely reactive and as shown here, it is kept under oil to prevent reaction with air or water

What is the state of matter of each of the elements shown in Figure 1.2?

Answer

Aluminium, sodium, sulfur and copper are solids. Bromine is a liquid and chlorine is a gas.

So at this point you have a picture of the basic structure of an atom, however there is one further subatomic particle to consider. This will be introduced in the next section.

1.2 Introducing the neutron

So far you know that inside the nucleus are protons.

But there are further particles that can reside there; these have the same mass as protons but carry no charge. They are called **neutrons**.

Why is the word ‘can’ used above? Which atom does not contain any neutrons in its nucleus?

Answer

Hydrogen. You’ll recall this has an atomic number of one. So its nucleus can *only* contain one proton.

The relative charges and relative masses of electrons, protons and neutrons are shown in Table 1. Notice how tiny electrons are compared to protons and neutrons.

Table 1 A comparison of the relative charge, and relative mass of electrons, protons and neutrons

Subatomic particle	Relative charge	Relative mass
Electron	-1	$^{1}/_{1836}$
Proton	+1	1
Neutron	0	1

So in addition to an atomic number, atoms are also defined by their mass, or more precisely what is know as their **mass number**, where.

Mass number = number of protons + number of neutrons.

And elements can be represented as follows:

Where A is the mass number and Z the atomic number.

Looking again at hydrogen (Z=1); adding in the mass number(A), its chemical symbol now becomes indicating its atoms contain one proton and one electron.

1.3 Isotopes

You will recall, way back in the nineteenth century, John Dalton popularised the idea of matter being composed of atoms. More specifically he proposed that the atoms of each element are identical, especially in mass.

The discovery of **isotopes** meant this description, whilst fine up to a point, doesn’t tell the whole story.

All atoms of the same element have identical atomic numbers. But sometimes the number of neutrons in the nucleus can vary for a particular element. This means you can have atoms of the same element with different mass numbers.

Atoms having identical numbers of protons but different numbers of neutrons are called **isotopes.**

Let's have another look at hydrogen.

You’ve seen hydrogen represented as , but there are also two isotopes of hydrogen which contain neutrons. These are deuterium having one proton and one neutron, and tritium with 1 proton plus two neutrons.

These have the chemical symbols: deuterium and tritium,

The key point to remember is because elements are defined by the number of protons not the number of neutrons even though they are isotopes they are still hydrogen atoms.

Bearing this in mind let's now look at a 'bigger atom' and its isotopes.

If you take a lump of copper, all of its atoms have atomic number 29 meaning all their nuclei contain 29 protons (and 29 orbiting electrons).

However you will find some with 29 protons and 34 neutrons, and others with 29 protons and 36 neutrons in the nucleus, i.e. there are two isotopes (Figure 3).

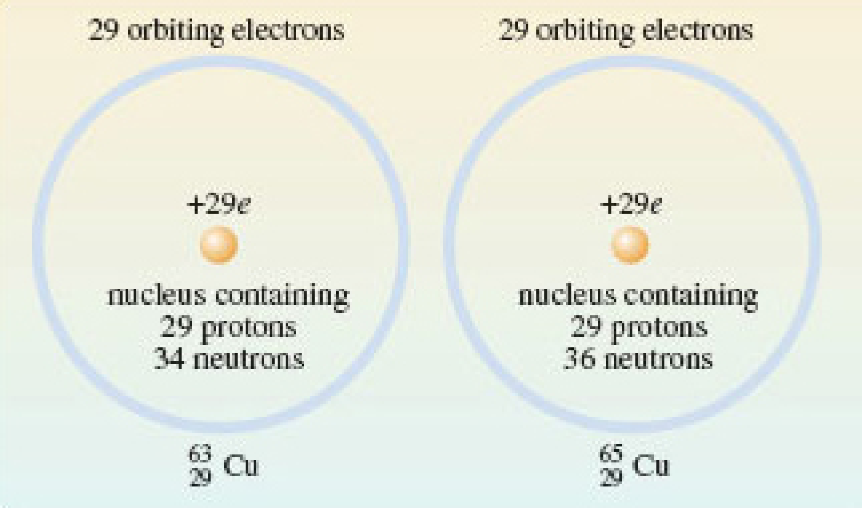


Figure 3 The distribution of protons, neutrons and electrons in the atoms of the two isotopes of copper

To reiterate, even though they have different numbers of neutrons, both of the atoms in Figure 3 are still copper.

Account for the mass numbers of the two copper isotopes shown in Figure 2.

Answer

Adding up the protons and neutrons we get: 29 + 34 = 63 and 29 + 36 = 65.

As shown in Figure 3, the two isotopes are written, and .

And just to clarify things further, the chemical symbol for one of the isotopes (the lighter one) is broken down into its components in Figure 4.

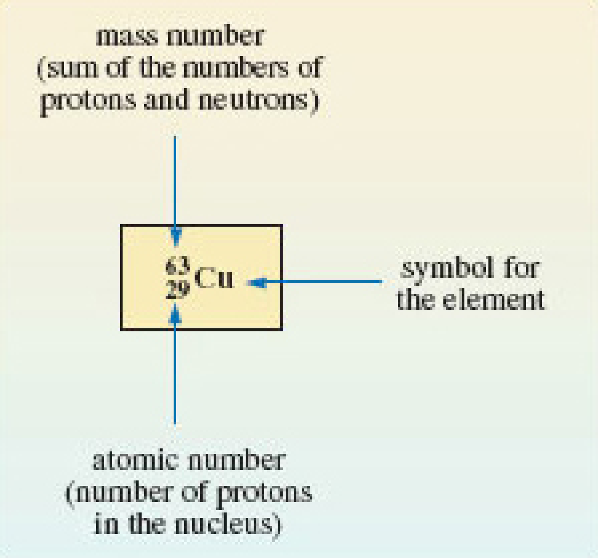


Figure 4 Symbol showing the number of neutrons, protons and electrons in one of the isotopes of copper

1.4 Relative atomic mass

Now you have been introduced to the concept of an isotope it is possible to address one of the key challenges facing a chemist.

Because you are working in the submicroscopic world and the actual masses of the important particles involved are incredibly small it's not really practical to use conventional mass units like grams.

To address this problem a standard is required. This is the carbon-12 isotope.

How many protons and neutrons does contain?

Answer

Six protons and six neutrons.

Atomic mass is expressed in terms of so-called **atomic mass units (amu)**.

Where 1 amu = 1.661 x 10^{-24} g

This number is equal to one twelfth of the mass of an atom of carbon-12.

Every element is assigned an atomic mass, which is its mass relative to that of one twelfth of the mass of an atom of carbon-12. Or to put it slightly differently, the number of times the mass of an atom of an element is heavier than one-twelfth of the mass of carbon-12.

All atomic masses are quoted relative to this value, and not surprisingly are referred to as the **relative atomic mass** of an element.

Later in this course you'll be looking in detail at the periodic table – an arrangement of the elements (in symbol form) on the basis of their atomic numbers and which highlights the physical and chemical patterns and relationships between them. Generally published tables also include relative atomic masses.

An atom of magnesium weighs twice as much as an atom of carbon. Without looking at a periodic table (!) what is its relative atomic mass?

Answer

24

Consider again copper, if you look it up on a periodic table you'll find its relative atomic mass is quoted as 63.5.

But what does this figure represent? How can you have half a proton or half a neutron?

The answer is, you can't.

In fact this is an average value, and what the number represents is the relative abundance of each isotope, in other words how much there is of each one in a sample of the element concerned.

Sticking with copper for the moment; the atoms of natural copper are about 70% and 30% . So, the relative atomic mass of natural copper (63.5) lies between 63 and 65, but closer to 63 because that is the relative atomic mass of the more abundant isotope.

Chlorine has two naturally occurring isotopes, ^{35}Cl and ^{37}Cl. On average, out of every four chlorine atoms you will find three are ^{35}Cl and one is ^{37}Cl. What is the average relative atomic mass of a chlorine atom?

Answer

$(^{3}/_{4} \text{ X } 35) + (^{1}/_{4} \text{ X } 37) = 35.5$

To summarise then, the relative atomic mass of an element is the weighted average of the masses of its isotopes relative to one twelfth of the mass of an atom of carbon-12.

1.5 Ions

Now let's look at electrical charges associated with atoms.

Why is an atom neutral?

Answer

The number of positively protons in the nucleus is balanced by the number of negatively charged electrons orbiting it.

However electrically charged versions of atoms do exist – these are **ions.** And as you'll see later, molecules can also form ions.

Take, for example an atom of lithium.

When it forms compounds (Session 2), lithium exists as lithium ions, represented by Li^+.

These are positively charged species formed by the removal of an electron from the lithium atom. Taking away an electron means there is an overall positive charge on the species as the positive charge of the nucleus is now greater than the negative charge due to the electrons.

Does the mass number change on forming Li^+?

Answer

No the composition of the nucleus is unchanged, you are just taking away an electron – remember these are located outside the nucleus.

These positively charged ions are referred to as **cations**.

However elements can also form negative ions known as **anions**, where electrons have been *added* to the neutral atom, giving and extra negative charge. For example chlorine (Cl) forms the so-called chloride anion (Cl^-), and oxygen (O) forms the oxide anion (O^{2-}). In the latter case two electrons have been added to the oxygen atom to give an overall 2- charge.

1.5.1 Using ions to explore atomic structure

Introducing you to ions at this point provides an opportunity to look back at section 1.1 and revisit that rather remarkable statement about the structure of an atom; ‘an atom is mainly empty space’.

Around 1910, Ernest Rutherford, a physicist working at the University of Manchester carried out an experiment where he fired positively charged helium ions (known as alpha particles) through sheets of gold foil approximately 10 000 atoms thick. Most of the particles passed straight through, with at most only a small deflection. However there were occasional instances of alpha particles rebounding right back from whence they came.

How does this observation support the picture of the atom described in section 1.1?

Answer

Remember that alpha particles are positively charged; any deflection would be due to interaction with other positive charges. The beams that occasionally bounced back suggest there is a concentrated centre of positive charge – the nucleus. And as most alpha particles passed through the foil, this supports the idea that ‘an atom is mainly empty space’.

1.6 Models of the atom

Following his ground breaking experiment with alpha particles, Rutherford painted a picture of an atom being rather like a minute model of the earth orbiting the Sun, with electrons orbiting the atomic nucleus.

However, if electrons really did orbit the nucleus like planets, then they would in fact be constantly accelerating. Any charged object undergoing an acceleration would continuously emit electromagnetic radiation and lose energy. As a result, an electron orbiting in this way would rapidly spiral into the nucleus as its electrical energy reduced.

Clearly, this doesn’t happen, so electrons cannot really be simply orbiting the nucleus.

Consequently this model didn’t remain in vogue for too long.

By the 1920’s a branch of physics known as of quantum mechanics began to stamp its mark on the world of the chemist.

In a nutshell, quantum mechanics relates to the theory of matter on extremely small scales, and tells us that electrons in atoms cannot have well defined orbits but must be described in terms of *probabilities*.

Regions of space within an atom where electrons are highly likely to be found are known as **orbitals.**

So to reiterate this key point; quantum theory tells you that you can't say exactly where an electron in an atom will be at any particular moment, you can only speak about the probability of finding an electron at a particular point.

Figure 5 is a depiction of an electron in a hydrogen atom; the areas where the dots are closer together are those where the electron is more likely to be found, and overall this region of space is spherical.

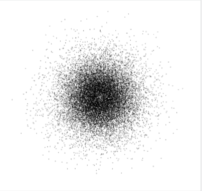


Figure 5 A representation of an electron in a hydrogen atom

So taking all the dots together, representing all the possible positions of the electron, you get a kind of 'fuzzy cloud' surrounding the nucleus.

1.7 Electronic structure of an atom

In chemical reactions, atoms form bonds to other atoms or may change partners. You know electrons are on the outside of atoms, so the expectation would be that contact and connection between atoms is likely to take place through their electrons, and in particular those furthest away from the nucleus.

As a first step towards understanding bond formation, and hence how and why chemical reactions take place, you need to have a basic grasp of how electrons are arranged in atoms.

This is the topic of the next section.

1.7.1 Energy levels in atoms

In this section you will start to look at *how* electrons are arranged in atoms.

Recall electrons are arranged around the nucleus in regions of space where the probability of finding them is relatively high, and where over an extended period, they spend most of their time.

These regions of space are known as **shells**, and you can think of them as the main energy levels of an atom.

Shells are numbered 1, 2, 3 etc. starting from 1, which has the lowest energy and is nearest the nucleus. This number is called the **principal quantum number**, and is given the symbol *n*.

But that's not the end of the story.

With the exception of the lowest energy level (*n*=1), shells are divided into sub-shells (or sub-levels of energy), and each sub-shell is specified by a second quantum number *l*. This is also known as the orbital quantum number, or the angular momentum quantum number.

So how are *n* and *l* related?

For each shell of principle quantum number *n*, *l* can take integer values from zero up to (*n*-1).

How many subshells are there in a shell having principle quantum number 3? Assign an l value to each sub-shell.

Answer

There are 3, which take values l= 0, 1 and 2.

An alternative way of specifying sub-shells uses letters in place of the quantum number *l.*

The following letters are used:

- s for subshells with *l*=0
- p for subshells with *l*=1
- d for subshells with *l*=2
- f for subshells with *l*=3

So in the previous question, the 3 sub-shells in the *n* = 3 energy level are: 3s, 3p and 3d.

What sub-shells are found in the shell having principal quantum number, *n* = 4?

Answer

4s, 4p, 4d and 4f.

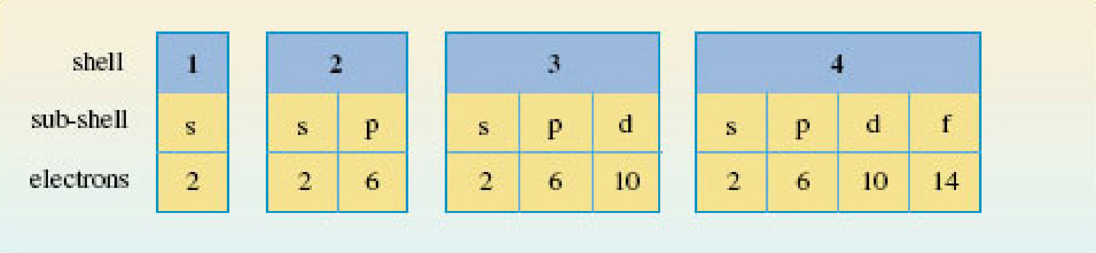
Now, up to this point electrons, haven't been considered.

Electrons, the number of which is indicated by the atomic number of the atom concerned, occupy the energy levels of an atom.

But which shells and therefore subshells do they go into, and how many go into each?

There is in fact an upper limit on the number of electrons that each kind of sub-shell can hold. For s, p, d and f sub-shells, there can be no more than 2, 6, 10 and 14 electrons respectively.

This, together with the other 'rules' you've met so far are summarised in Figure 6.



shell	1	2		3			4			
sub-shell	s	s	p	s	p	d	s	p	d	f
electrons	2	2	6	2	6	10	2	6	10	14

Figure 6 The sub-shells in the shells of principal quantum numbers 1-4, and the maximum number of electrons that each type of sub-shell can hold

1.8 Electronic configurations of atoms

So up to this point, you know that an atom consists of energy levels called shells and these shells are divided into subshells in which electrons are located. The arrangement of electrons in the shells and sub-shells of an atom is called its electronic configuration.

This may sound a little obscure so far, but by looking at a few specific examples the picture becomes clearer.

Let’s go back to hydrogen once again.

How many electrons are found in the hydrogen atom?

Answer

One

So the question is; into what sub-shell does this electron go?

The answer is pretty intuitive – it goes into the lowest available energy level.

The lowest energy shell is defined by the principal quantum number $n = 1$, and this contains an s sub-shell (only). So *that’s* where the single electron in hydrogen goes.

This is denoted $1s^1$, where 1 represents the main energy level (the shell) and s is the subshell. The superscript ^{1} represents the single electron occupying this energy level.

But what about more complicated atoms, i.e. those with greater atomic numbers than one? This is covered in the next section.

1.8.1 Electronic configurations of multi-electron atoms.

Electronic configurations can be assigned to nearly all atoms using the diagram shown in Figure 7.

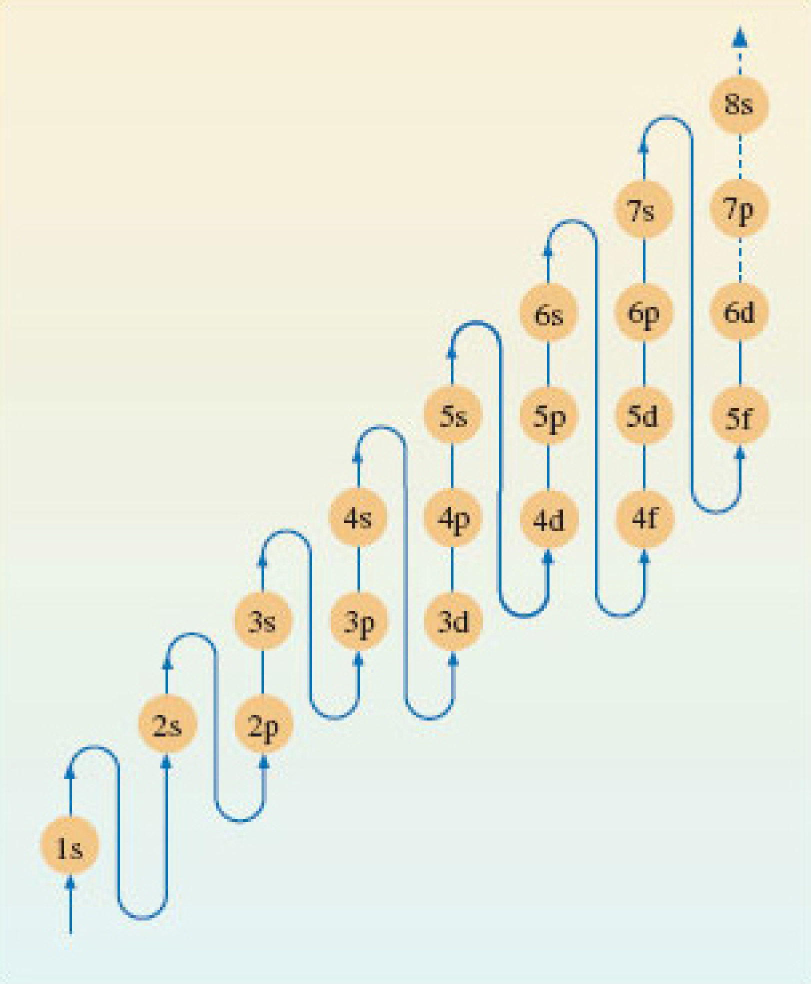


Figure 7 A pathway showing the order in which the sub-shells should be filled when writing out the electronic configurations of atoms

Consider fluorine, this has an atomic number of 9, which means there are 9 electrons to fit into the subshells shown in Figure 7.

Bearing in mind the maximum number of electrons a sub-shell can hold (shown in Figure 6), the electrons in a fluorine atom will be arranged as follows:

Two electrons will be in the lowest energy 1s subshell.

Two electrons will be in the higher energy 2s subshell.

This leaves another five electrons which occupy the 2p subshell.

So using the notation introduced earlier, the electronic configuration for fluorine may be written:

$1s^2\ 2s^2\ 2p^5$.

Now have a go at the following examples (remember you'll need to refer back to Figure 7).

What are the electronic configurations of lithium (atomic number 3), silicon (atomic number 14) and potassium (atomic number 19)?

Answer

Lithium: $1s^2\ 2s^1$

Silicon: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

Potassium: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

You probably noticed a quirk in the expected order of energy level filling which became apparent when you got to potassium. The 4s sub-shell is at lower energy than the 3d subshell. So this means the 4s shell fills with electrons before the 3d.

Try the following example which also highlights this point.

What is the electronic configuration of titanium (atomic number 22)?

Answer

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$

For a bit more practice have a go at the following examples:

What are the electronic configurations of the following elements (these are the ones shown in Figure 1)?

(a) aluminium (atomic number 13), (b) sodium (atomic number 11), and copper (atomic number 29).

Answer

Al: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$

Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^9$

1.9 Exciting electrons

It is important to point out the electronic configurations you've looked at so far correspond to the lowest energy state of the atom (what's known as the **ground state**).

However it is possible to input energy into atoms, (and indeed molecules) and raise electrons to higher energy orbitals (in which case the atom is in an **excited state**) This is the basis of the area of chemistry known as **spectroscopy**, which in its many forms is used to probe the structure of substances and analyse the composition of materials (e.g. measuring the concentration of the metals in drinking water).

Under the right circumstances all atoms will absorb and emit energy, and when that energy falls within the spectrum of visible light then colours are observed.

This is demonstrated in the following clip.

Video content is not available in this format.

Video: Flame colours of metals.

What is the origin of the colours when solutions of metal ions in alcohol were sprayed into the flame of a gas burner?

Answer

The heat of the flame excites electrons in the metal ions to higher energy levels, when they drop back down light having wavelengths characteristic of the specific metal ion is emitted.

1.10 More about atomic orbitals

Up to this point you've considered electrons as being arranged in a series of shells and sub-shells.

These sub shells can be described as specific locations within an energy level (shell) where there is a high probability of finding an electron.

Does this seem familiar?

Hopefully so, these are the **atomic orbitals** introduced in section 1.5, i.e. regions in space where there is a high probability of finding an electron.

A representation of an s-orbital and a p orbital are shown in Figure 8.

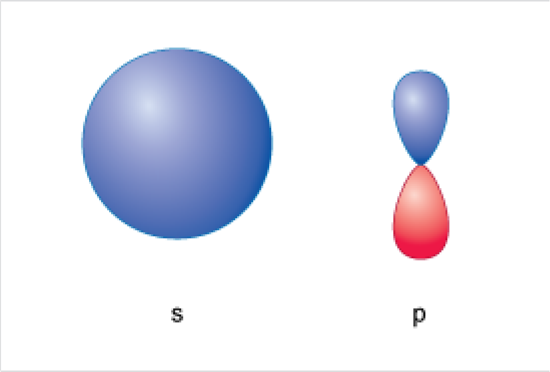


Figure 8 Representation of an s and a p orbital

So this means each shell will have at least one orbital associated with it.

Using this idea, let's now try and build up a more detailed picture of the atom.

Starting at lowest energy shell (n = 1), closest to the nucleus you will find a 1s orbital – this is spherical.

At higher energy, and further from the nucleus in the n=2 shell, you will find two kinds of orbital 2s and 2p. The 2s is also spherical as per the 1s but is (rather obviously) labelled 2 to represent the higher energy shell, and the larger radius than the 1s.

Moving to the n = 3 shell you find d-orbitals, and in the n=4 shell f-orbitals appear, these won't be considered here.

1.10.1 Filling atomic orbitals with electrons

At this point you should have some feel for how electrons arranged in atoms, and current descriptions draw upon the rather intangible field of quantum mechanics.

What is meant by an atomic orbital?

Answer

An atomic orbital describes an allowed distribution in space, about the nucleus where there is a high probability of finding an electron

But how are electrons arranged within each subshell; how many electrons will each orbital contain?

Consider the formula for the sub-shell electron capacities, which is 2(2*l* + 1), *l* being the orbital quantum number.

The factor (2*l* + 1) tells you the number of atomic orbitals in the sub-shell.

How many atomic orbitals are there in an s sub-shell, and how many in a p subshell?

Answer

For an s sub-shell l=0, so (2l + 1) = 1. An s sub-shell contains one orbital.For a p sub-shell l=1, so (2l + 1) = 3. A p sub-shell contains three orbitals.

So looking at the atom as a whole, the lowest energy level (*n*=1) contains one s-orbital only. However, moving to the next highest shell (*n*=2) you will find one s-orbital (the 2s) and a set of three 2p orbitals.

What orbitals would you expect to find in the n=3 shell?

Answer

A 3s orbital, a set of three 3p orbitals and a set of five 3d orbitals.

But how many electrons can occupy an individual orbital?

It turns out that each orbital can contain up to two electrons.

So now Figure 6, section 1.7.1 starts to become clear. The bottom row (labelled ‘electrons’) , is simply showing you the total number of electrons in each subshell assuming each orbital will hold a maximum of two.

How many electrons are required to completely fill a p-sub-shell?

Answer

As *l* =1 for a sub-shell, the factor (2*l* + 1) tells you that it contains three atomic orbitals. Each of the three orbitals can accommodate up to two electrons with opposed spins. So a p sub-shell can contain a maximum of 2 × 3 = 6 electrons.

The final piece of the jigsaw, when building up a picture of how electrons occupy the energy levels of atoms is connected to a property of the electron called **spin**. You will be looking at this in the next section.

1.10.2 Spinning electrons

Electrons can be pictured as spinning in two directions (clockwise and anticlockwise), and when an atomic orbital contains its maximum complement of two electrons, those two electrons must always have opposite spins (one clockwise and the other anticlockwise).

This is depicted in Figure 9.

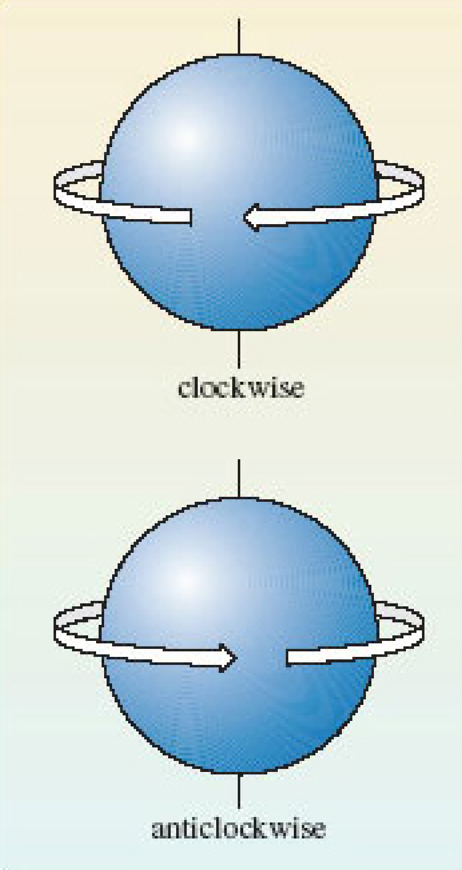


Figure 9 The two directions of electron spin

Strictly speaking this is not an accurate description, remember quantum mechanics tells you electrons are not found at specific points in space and must be described in terms of probability.

So they are not the spinning balls of charge shown here. However this representation *does* provide a useful model of how electrons occupy orbitals, and you will be using this in the next section.

1.11. Putting electrons in boxes

At this point think back to what you know about an s sub-shell.

How many electrons are in a fully occupied s sub-shell?

Answer

As an s sub-shell contains one orbital, this means that it can contain up to two electrons.

Two such electrons with opposed spins are said to be *paired* and are conveniently represented in a so called **box diagram**.

Given a full atomic orbital can contain up to two electrons with opposing spins. This may be simply represented by writing one electron as an upward-pointing half-headed arrow, and the other as a downward pointing half-headed arrow.

And each orbital is drawn as a box into which these half-headed arrows are drawn.

For example, the helium atom has the electronic configuration $1s^2$. As the 1s sub-shell contains just one orbital, this can be depicted by a single box containing the two electrons (Figure 10).

Figure 10 Electron in box depiction of a helium atom

Now consider the box diagram for nitrogen.

What is the electronic configuration of the nitrogen atom?

Answer

$1s^2 2s^2 2p^3$

The 1s and 2s sub-shells contain one orbital each, and the 2p sub-shell contains three. The box diagram that must be filled therefore takes the form shown in Figure 11:

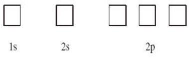


Figure 11 Box depiction of atomic orbitals

So how do the three 2p electrons fill the 2p sub-shell?

There are several possibilities, but the one you want is the **ground-state** arrangement, the state of lowest energy.

There is a simple rule, called **Hund's rule**, which tells you that within any sub-shell, there will be the maximum number of electrons with spins of the same sense.

Because electrons in the same box must have opposed spins, they must, as far as possible, go into different boxes with spins of the same sense, or, as it is usually termed, with **parallel spins**. In this case there are three 2p electrons and three boxes, so each box can take one electron with the same spin, and this is the preferred arrangement according to Hund's rule. The final result for the nitrogen atom is therefore (Figure 12):

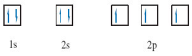


Figure 12 Electron in box depiction of a nitrogen atom

The oxygen atom has atomic number 8. Draw a box diagram for oxygen.

Answer

As there are four 2p electrons and only three 2p boxes, the fourth 2p electron cannot have a spin parallel to the other three. It must go into a box that is already occupied by one electron with opposite spin (Figure 13):

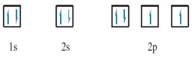


Figure 13 Electron in box depiction of an oxygen atom

2 The periodic table

Ever since chemists were aware that a large number of elements exist, attempts have been made to arrange them in ways that show similarities between them – a classification system. This ultimately led to one of the cornerstones of modern chemistry – the periodic table.

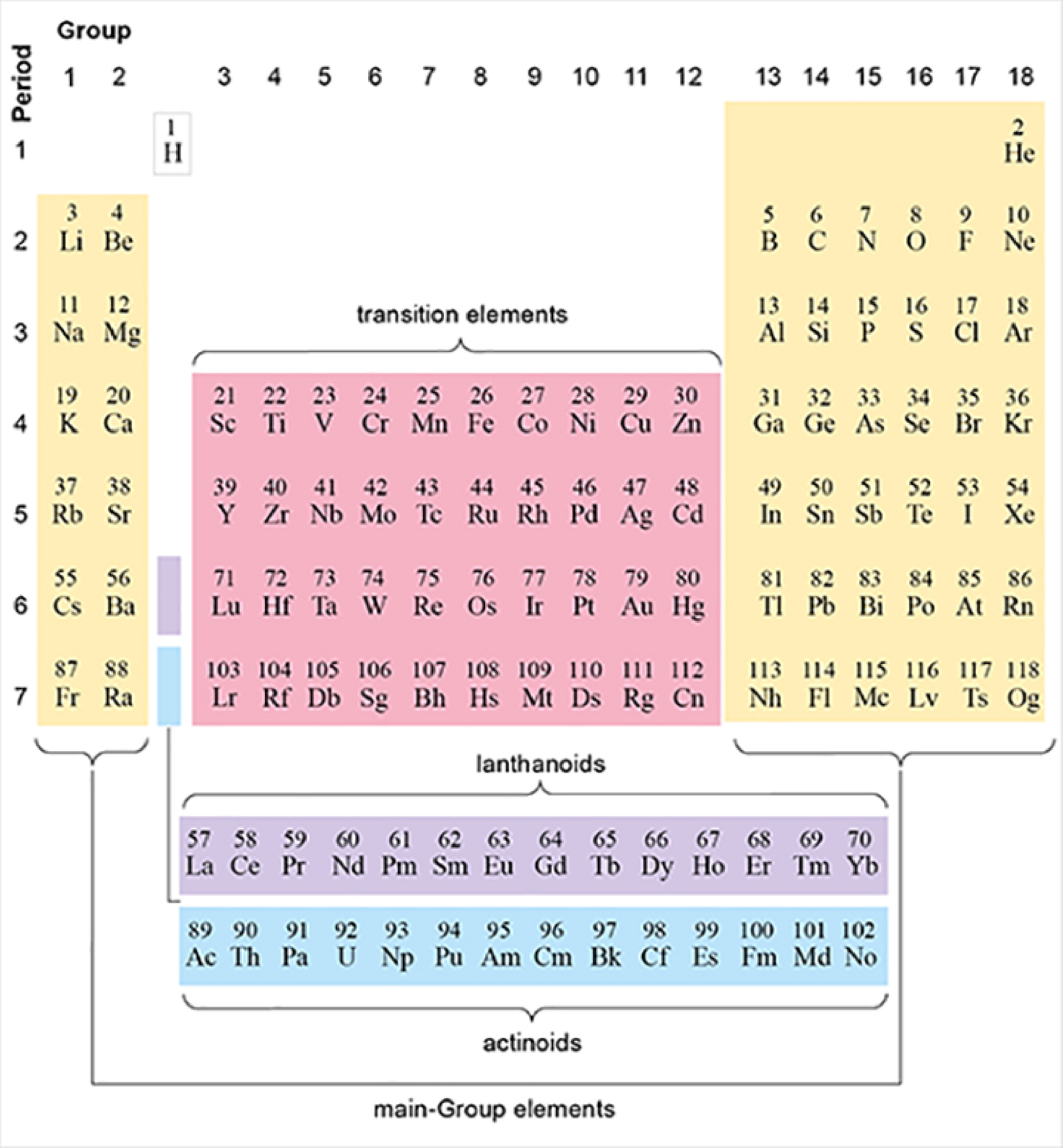
2.1 Chemical periodicity

The chemistry of the elements is extremely varied. But amidst this variety there are patterns, and the best known and most useful is chemical periodicity: if the elements are laid out in order of atomic number, similar elements occur at regular intervals.

So who first spotted these relationships?

A number of scientists could claim a share of the credit, but the name you'll most often hear in this regard is Dmitri Mendeleev, the nineteenth century Russian chemist. His ground breaking work led to the construction of the periodic table as we know it today.

Essentially the periodic table is a graphic representation of the patterns in the physical and chemical behaviour of the elements. In fact there are various versions, one of which is shown in Figure 14.



Period	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1			1 H																2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Figure 14 The periodic table

Looking closely at Figure 14 you can see the elements are listed by their atomic numbers, shown here above each symbol. They are arranged in horizontal rows called periods and vertical columns called groups.

The table can also be neatly divided up into blocks of elements, again this is shown in Figure 14 where the transition elements, lanthanoides, actinoides and typical elements are highlighted in different colours.

Chemical periodicity is apparent from the appearance of similar elements in the same group, which are often given specific names. For example, the alkali metals appear in the first column on the left of the Table, and the noble gases in the last column on the right.

To illustrate this point further you will look in more detail at these particular groups in the next section.

2.1.1 The alkali metals and the noble gases.

The alkali metals are the elements lithium, sodium, potassium, rubidium, caesium and francium. They are grouped together because they all behave similarly (except with different ferocity) and together form Group 1 of the periodic table.

They are all in fact very soft metals that can be cut with a knife and have relatively low melting temperatures. They do not occur naturally because they react readily with air and moisture and so need to be stored under oil.

One of the signature reactions of alkali metals is their reaction with water in the following video.

Video content is not available in this format.

How does the reactivity with water vary on going from lithium to caesium?

Answer

The reaction becomes progressively more vigorous (and spectacular).

At the opposite end of the scale are the noble gases.

These are found in the last column on the right of the periodic table, and are present in the atmosphere in small amounts:

- 0.934% argon
- 0.0018% neon
- 0.00052% helium
- 0.00011% krypton
- 0.000009% xenon

The noble gases are all characterised by being extremely unreactive (in fact they are often called the inert gases). This is illustrated in the following video clip.

Video content is not available in this format.

Video: noble gases

2.2 Allotropes

Different solid forms of the same element are called **allotropes** (or polymorphs).

Carbon, sulfur and phosphorous are examples of elements that form a number of allotropes.

Let’s focus on carbon.

Diamond is an allotrope of carbon. The arrangement of its atoms is shown in Figure 15; for each atom are four surrounding carbon atoms at the corners of a regular tetrahedron, and the C—C distance is 154 pm.

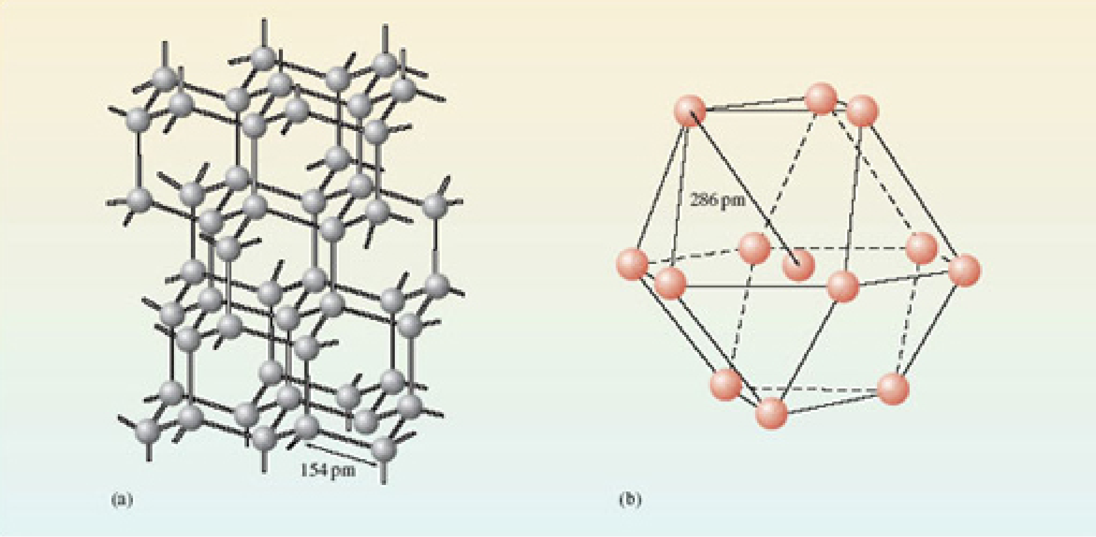


Figure 15 The structure of diamond. Note here distances are reported in picometeres (pm), where 1pm ≡ 10^{-12}m

Figure 16 shows the structure of graphite, the form of carbon used in pencil leads. In this allotrope, there are regular hexagons of carbon atoms arranged in parallel sheets. Within the sheets, the C—C distance is only 142 pm, but the shortest distances between the sheets is 340 pm.

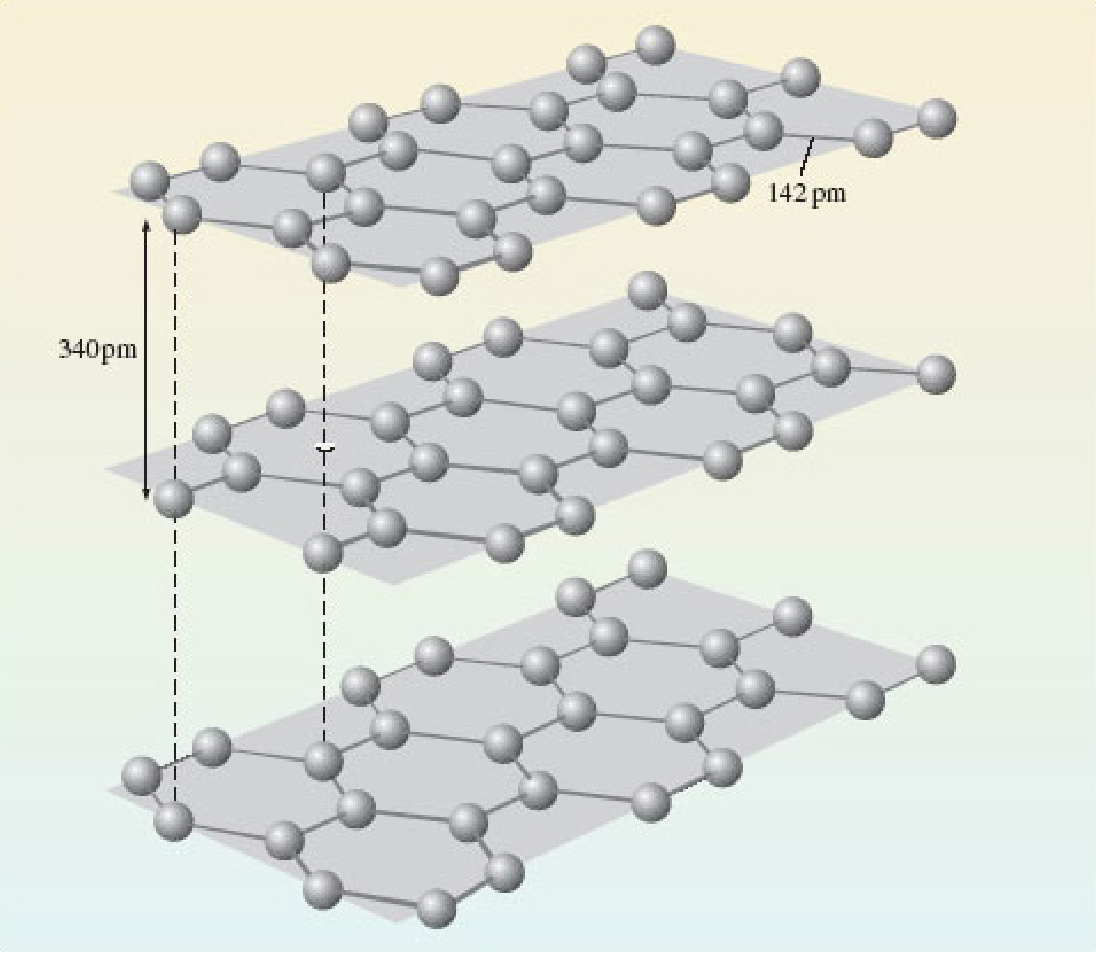


Figure 16 The structure of graphite

In 1985 Robert Curl, Harry Kroto and Richard Smalley discovered a further form of carbon. This is known as buckminsterfullerene and its structure is shown in Figure 17.

There are sixty carbons in its structure.

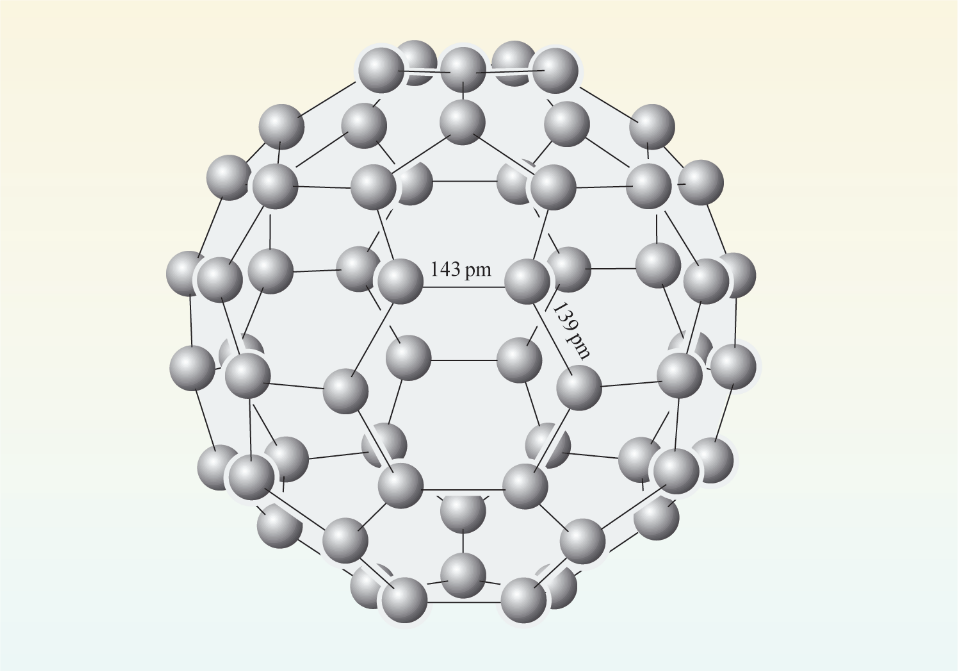


Figure 17 The structure of buckminsterfullerene C_{60}.

Describe the arrangement of the carbon atoms in C_{60}.

Answer

The atoms are arranged in pentagons and hexagons. In fact there are twelve pentagons and twenty hexagons, and the structure resembles a football – hence the frequently used term buckyball.

There is in fact a bigger family of fullerenes comprising cage-like molecules (such as C_{60}) and tube fullerenes called nanotubes.

In addition to carbon, other elements that exist as allotropes include, phosphorus, sulfur and tin . At this point take a look at the following video which shows you the allotropes of sulfur and how they can be interconverted.

Video content is not available in this format.

Video: Sulfur and its allotropes.

3 Electronic configurations revisited

Earlier you looked at the way electrons are arranged in the orbitals of atoms; there are two further features which will be introduced here to set you up for when you examine the way atoms link (bond) together to form molecules later in this module.

Consider for example sodium ^{11}Na. What is the electronic configuration of this atom?

Answer

$1s^2\ 2s^2\ 2p^6\ 3s^1$

In atoms it is the outer electrons, known as **valence electrons** which get involved in bonding. The outermost shell is often referred to as the **valence shell**.

In the case of sodium the 3s electron is the valence electron.

The remaining electrons (those which don't get involved in bonding) are known as **core electrons**. In the case of sodium these are the $1s^2\ 2s^2\ 2p^6$ electrons.

What element has the $1s^2\ 2s^2\ 2p^6$ electronic configuration?

Answer

Neon

So in fact for sodium, the core electrons correspond to the electronic configuration of the preceding noble gas neon. This may be represented as [Ne] and the electronic configuration of sodium may be simplified to [Ne] $3s^1$.

So now you have a sort of shorthand method of writing out electronic configurations.

Have a go at the following examples.

Using the shorthand notation described above, write the electronic configurations of the following elements, carbon (^{6}C), aluminium (^{13}Al) and potassium (^{19}K).

Answer

Carbon: [He] $2s^2\ 2p^2$, aluminium: [Ne] $3s^2\ 3p^1$, potassium: [Ar] $4s^1$

What is the similarity in terms of electronic structure, between sodium and potassium?

Answer

They both have a single electron in the valence shell, in an s-subshell.

In fact the answer to the above question applies to all the elements in the Group 1- all the alkali metals have a single valence electron. However as you go down the group the principle quantum number (n) of the outer shell increases. So you can write the general valance electronic configuration as ns^1.

Moving along to Group 2, the valence electrons are given by ns^2. Starting from the top, beryllium will be $2s^2$, magnesium will be $3s^2$, calcium will be $4s^2$ and so on.

What is the valence electronic configuration of oxygen, phosphorus and bromine?

Oxygen: $2s^2\ 2p^4$ phosphorus $3s^2\ 3p^3$ bromine: $4s^2\ 4p^5$

So to reiterate the key point; it is the valence electrons that are involved in bond formation during chemical reactions, and you will look at the nature of chemical bonding in electronic terms later in the course. But before this, in the next session you will be looking at the way atoms combine to form molecules and the huge richness and variety of chemical compounds.

4 This session’s quiz

Check what you’ve learned by taking the end-of-session quiz.

Session 1 quiz

Open the quiz in a new window or tab (by holding ctrl [or cmd on a Mac] when you click the link), then return here when you have done it.

Summary of session 1

1. All matter is made up of tiny particles called atoms which are composed of a central positively charged nucleus surrounded by negatively charged electrons.
2. The nucleus comprises positively charged protons and neutrons carrying no charge. The masses of protons and neutrons are the same, but the mass of electrons is negligible in comparison. The number of protons must equal the number of electrons, where there is an imbalance the species are referred to as ions.
3. The number of protons in the nucleus is the atomic number of an atom, and a substance made up of atoms of the same atomic number is an element.
4. Atoms of the same element that differ only in the number of neutrons they contain are known as isotopes. They have different atomic masses to other isotopes of the same element.
5. Electrons are not located in a precise orbits around the nucleus, rather in regions of space where there is a high probability of finding them – these are atomic orbitals.
6. Electrons in atoms are labelled by a unique set of quantum numbers.
7. The arrangement of electrons in the atomic orbitals of an atom is known as its electronic configuration. The outermost electrons which are involved in chemical bonding are known as valence electrons. The remainder are the core electrons.
8. In the periodic table, elements are arranged into horizontal rows called periods and vertical columns called groups. Patterns in the chemical and physical properties of the elements is revealed by the appearance of similar elements in the same Group.
9. Different solid forms of the same element are known as allotropes.

Session 2: Chemical compounds

1 From elements to compounds

Atoms of different elements can combine in a seemingly infinite variety of ways to form chemical compounds. Each one can be represented by a formula that shows how many atoms of each element there are in the compound.

Some examples of compounds and their constituent elements are given in Table 1.

Table 1 The constituent elements of some selected chemical compounds.

Compound	Constituent elements	Compound	Constituent elements
sodium chloride	sodium, chlorine	calcium carbonate	calcium, carbon, oxygen
Water	hydrogen, oxygen	carbon dioxide	carbon, oxygen
sulfur dioxide	sulfur, oxygen	iron oxide	iron, oxygen
sulfuric acid	hydrogen, sulfur, oxygen	sodium hydroxide	Sodium, oxygen and hydrogen.

For some of the examples in this table, you may be thinking (not unreasonably) that the link between the compound and what elements it is made from is not clear.

A fair point.

However the structure and origin of the names and formulas of compounds will be the focus of this session’s study, which together with an introduction to chemical bonding and the useful concept of valency, should go a long way to addressing this point, and giving you a fundamental understanding of the nature of chemical compounds in general.

1.1 Introducing chemical compounds

To start your exploration of the way elements combine to form compounds, let’s look at a simple example.

When sodium (a metal) and chlorine (a gas) are brought into contact, they react vigorously, and white crystals of sodium chloride are formed.

In these crystals, there are equal numbers of sodium and chlorine atoms; that is, the sodium and chlorine atoms are combined in the simple ratio 1:1.

But this doesn’t tell the whole story.

- ■ In session 1, you met charged versions of atoms; what are they called?
- □ These are ions (positively charged ions are called cations and negatively charged ions are called anions).

Sodium chloride is an example of what is known as an ionic compound, meaning the component atoms are present in the form of their ions; so to be absolutely precise it is sodium cations (Na^+) and chloride anions (Cl^-) that are present in a 1:1 ratio.

So the **chemical formula** for sodium chloride is NaCl.

Compounds are also formed with their component ions in other ratios.

For example chlorine and magnesium react to form a compound where there are two chloride anions for every magnesium cation. So the formula for magnesium chloride is $MgCl_2$. You'll notice the subscript 2 represents the fact there are two chlorine atoms in the formula. In fact if you were really pedantic you could write the formula as Mg_1Cl_2, but the subscript 1 is always left out, (likewise NaCl is never written as Na_1Cl_1).

Finally, in both these cases, and indeed ionic solids in general, the total charge of the cations equals the total charge of the anions and the compound is electrically neutral.

- ■ Look again at the formula for magnesium chloride; what is the charge on the magnesium cation?
- □ In $MgCl_2$, because you have two Cl^- ions per magnesium ion, the cation must be Mg^{2+} to ensure the compound is electrically neutral.

So far in this introduction to chemical compounds you have met examples of substances made up of ions.

But this isn't always the case.

Instead substances may be made of molecules – this is the topic of the next section.

1.2 Molecular substances

Imagine a chemist handed you a glass stoppered flask containing what appeared to a yellow gas and told you that this was chlorine. You might initially be a little worried recalling that chlorine is extremely toxic, but given you now know about atoms and have been introduced to the sub microscopic world of chemistry you might start to think about what's going on at this scale.

What actually is chlorine?

Knowing that chlorine has the symbol Cl, your first thought might (quite reasonably) be that chlorine gas is composed of single atoms.

But this isn't the case.

Chlorine gas actually consists of chlorine atoms joined together in pairs to form **molecules**.

These have the formula Cl_2.

And rather confusingly both the atoms and the molecules are referred to by chemists as chlorine.

A gas, like chlorine, occupies much more space than a solid or liquid, so the distance between the molecules is comparatively large. At normal temperatures pressures, and measuring distances in picometeres (pm), where $1pm \equiv 10^{-12}m$, the distance between chlorine molecules averages about 3500pm. This is compared with a distance of only

198pm separating the chlorine atoms in the actual Cl_2 molecules, and is illustrated in Figure 1(a), where the green/grey spheres represents chlorine atoms.

In other words the distance between the atoms in the chlorine molecule is small compared with the average distance between the molecules in a jar of chlorine gas. This disparity is less extreme, but still evident in liquid bromine and solid iodine, which are in the same group of the periodic table as chlorine.

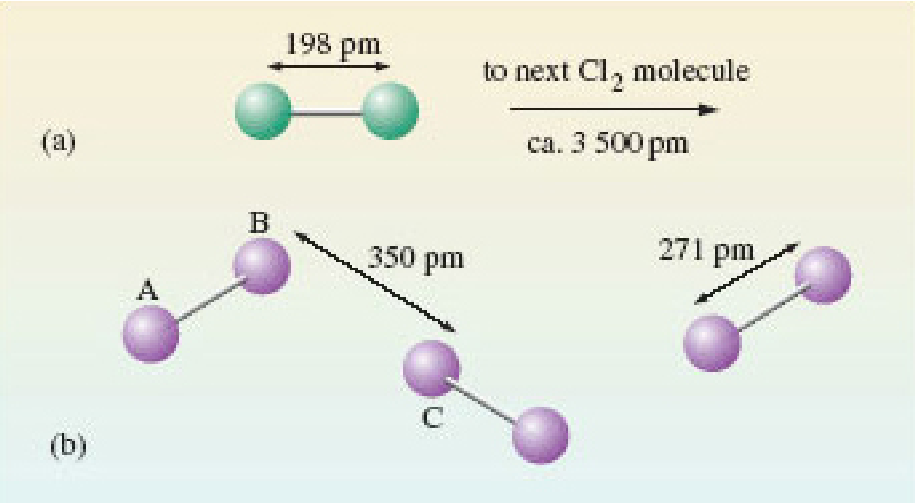


Figure 1 Representations of (a) a chlorine molecule. (b) iodine molecules

Turning now to iodine – a solid at room temperature.

The positions of atoms in solids may be worked out using a technique called X-ray crystallography, the results of which ae shown for iodine in Figure 1b.

I_2 molecules (labelled AB) which can be identified through their separation by a distance of 271 pm. These molecules are separated by longer distances of at least 350 pm (BC)

So the iodine atoms can be grouped into pairs; and the logical conclusion is that (like chlorine) solid iodine consists of I_2 molecules.

Similar reasoning can be used to identify molecules in chemical compounds.

Take for example carbon dioxide (CO_2).

At room temperature carbon dioxide is a gas containing CO_2 molecules, but on cooling it becomes a solid (“dry-ice”).

In dry ice each carbon atom has two oxygen atom neighbours at a distance of 116pm – these atoms are arranged in a straight line. The next nearest atom is another oxygen at 311pm. So here is the evidence that solid carbon dioxide contains linear CO_2 molecules, with the atom sequence O-C-O. This is shown in Figure 2. Note the colour coding of the spheres. Molecule BAC is in the plane of the paper; the other four molecules shown are not.

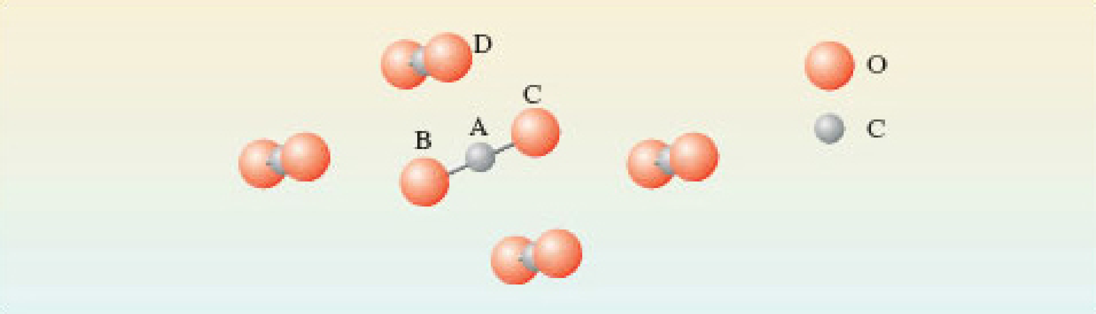


Figure 2 A representation of solid carbon dioxide, 'dry ice'

Dry ice has some interesting properties – some of these are illustrated in the following video.

Video content is not available in this format.
The properties of carbon dioxide.

2 Molecular and empirical formulas

Cl_2, Br_2, I_2 and CO_2 are called **molecular formulas**.

They tell us how the atoms are grouped together in the molecules from which the substance is built up.

Suggest why Cl_2, Br_2, $I_2$and CO_2 are referred to as *molecular substances*?

Provide your answer...

Answer

They have structures which allow discrete molecules to be picked out.

Now let's throw in a slight complication.

Take a look at the following video, which shows aluminium combining with the halogen elements in a chemical reaction.

Video content is not available in this format.

Video 1: Reaction of aluminium and the halogens

- Describe the reaction of aluminium with bromine – state your observations in a single sentence.
- In amongst your observations you will most probably have noted that aluminium (a solid) was mixed with liquid bromine. There was a short interval before the reaction got going, but when it did it was pretty spectacular (flames and smoke were produced). It's perhaps worth adding here, that not all chemical reactions are quite so dramatic!

The product of this reaction is a white solid called aluminium bromide, which consists of three bromine atoms for every aluminium atom.

- What chemical formula would you expect for aluminium bromide?
- $AlBr_3$ The subscript three following bromine indicates the Al: Br ratio is 1:3. Remember a subscript 1 after the Al is taken as read and never shown in a formula.

Actually this is an unfair question, because if you examine the crystal structure of solid aluminium bromide you'll find it is actually made up of Al_2Br_6 molecules (Figure 3). The two aluminium atoms, and four of the bromine atoms at the ends of the molecule, lie in the same plane (at right-angles to the plane of the paper). The two bromines that bridge the aluminium's lie above and below this plane.

But, note the ratio of Al to Br is still 1:3.

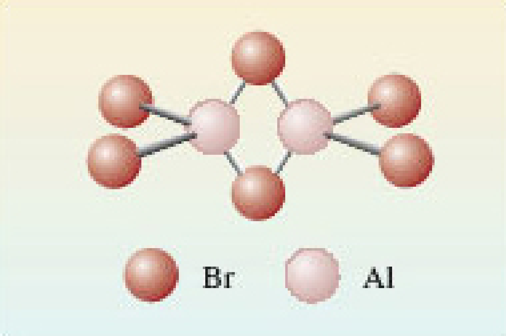


Figure 3 The structure of the Al_2Br_6 molecule

This can be explained if you consider $AlBr_3$ to be the simplest ratio of the elements present in the substance – this is known as the **empirical formula**.

- Do these molecules have the same empirical formula as the solid in which they are found?
- *Yes*; the molecular formula is Al_2Br_6 but in both the molecules and the solid, the ratio of aluminium atoms to bromine atoms is 1:3.

As is the case here the empirical formula need not necessarily be the same as the molecular formula, the latter shows the *actual* number of atoms in one molecule of a compound.

2.1 Some further examples of molecular substances

The element carbon forms a vast range of compounds, often in combination with hydrogen, nitrogen, oxygen and other elements such as sulfur and phosphorus.

This whole area of the subject is referred to as organic chemistry.

Organic compounds are almost entirely molecular, common examples are methane, glucose, ethanol and vinegar (acetic acid).

This point is illustrated in Figure 4, which shows the grouping of the atoms in the molecules of two important organic compounds.

Figure 4a shows the structure of aspirin, the best-known painkiller, and a precautionary treatment of heart conditions. The molecule in Figure 4b is RDX, a military high explosive.

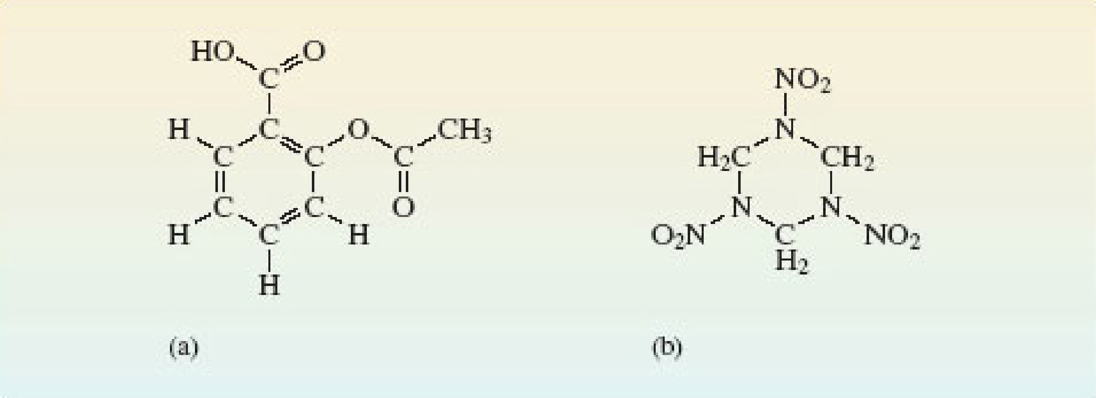


Figure 4 Molecules of: (a) acetylsalicylic acid (aspirin); (b) 1,3,5-trinitroperhydro-1,3,5-triazine, also known as RDX (Research Department Explosive) or cyclonite

Don’t worry about the names used for organic compounds either here or elsewhere in this course. Where such compounds are discussed, you will only be looking at differences in the *structure* of their molecules; just view the names as labels.

Let’s now return to where we started and look in a bit more detail at compounds that can be described as non-molecular.

2.2 Non-molecular substances

Non-molecular substances defy attempts to pick out discrete molecules from their structures.

You have already met sodium chloride (NaCl) earlier in this module – this is common table salt.

■ What chemical entities make up NaCl?

□ Sodium cations (Na^+) and chloride anions (Cl^-)

But how are these ions arranged to form a crystal of sodium chloride?

This is built up from tiny cubes shown in Figure 5 consisting of sodium cations (Na^+) and chloride anions (Cl^-)

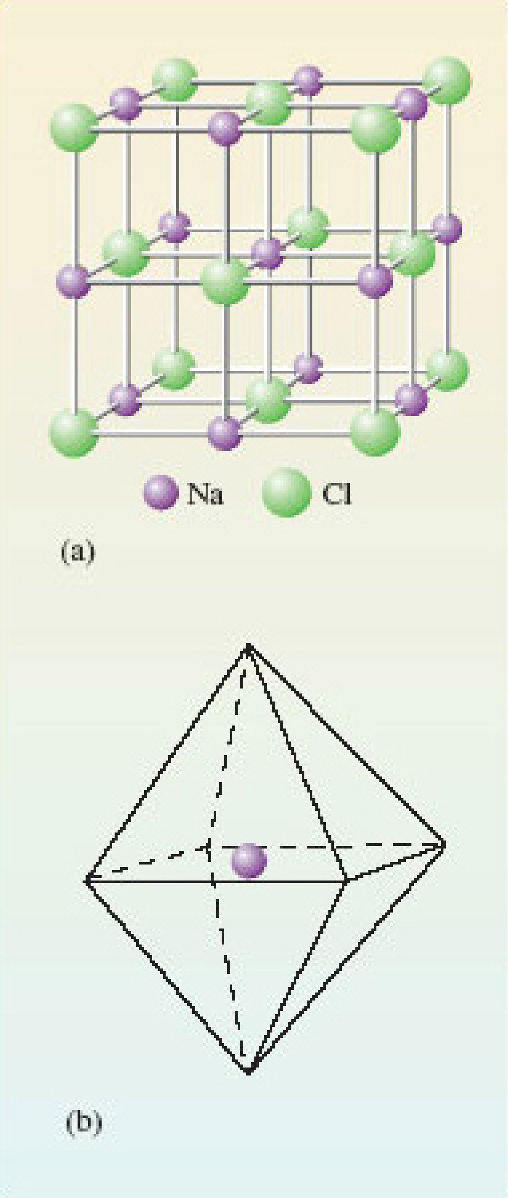


Figure 5 (a) Structure of common salt or sodium chloride; (b) a regular octahedron whose corners represent the positions of the chloride anions around each sodium cation

Look first at the sodium at the centre of the cube. The six chloride anions lie at the corners of a regular octahedron Figure 5(b).

The formula NaCl is an empirical formula; so it is telling you that in sodium chloride there are equal numbers of sodiums and chlorines. This condition is automatically fulfilled by joining many of the cubes shown in Figure 5(a) through their faces.

But, Figure 5 provides no evidence that NaCl is the *molecular formula* of sodium chloride. In fact quite the opposite.

■ Suggest why this is the case?

□ The six chloride ions around the sodium cation all lie equal distances away – remember this is a regular octahedron. There are no grounds for singling out just one chloride ion, coupling it with a sodium cation and calling the result an NaCl molecule.

So as there is no evidence of discrete NaCl molecules in the solid; NaCl is a *non-molecular* compound, and the concept of a “molecular formula” is not appropriate.

2.3 Comparing ‘dry ice’ with sand

Earlier, you saw that carbon dioxide may be viewed as a molecular substance. The element below carbon in the periodic table is silicon.

And silicon also forms a compound with oxygen having a 1:2 ratio of the component atoms in its formula.

This is silicon dioxide – SiO_2 – also known as silica, and is the main component of sand, but at this point the key thing to note is that it has the same ratio of atoms in its empirical formula as carbon dioxide.

But here’s the difference.

In solid carbon dioxide, two of the oxygen atoms around each carbon were much closer than others, so a CO_2 molecule may be clearly identified.

Now consider silica (Figure 6).

■ What atoms, and how many atoms surround each silicon atom in SiO_2?

□ Silicon is surrounded by four oxygen atoms.

A better description would be to say; each silicon atom sits at the centre of a tetrahedron of oxygen atoms: and as shown in Figure 6 they are all at the same distance (162pm).

There is *no* evidence of discrete SiO_2 molecules.

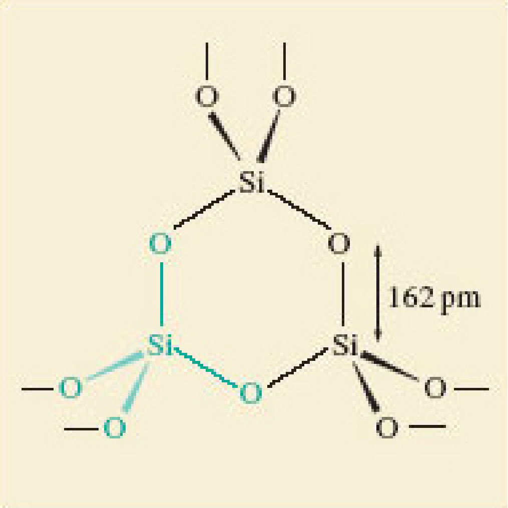


Figure 6 The structure of silica, SiO_2, in the form of quartz. One SiO_4 tetrahedron is highlighted in green

2.4 Extended structures

In session 1, you looked at the diamond and graphite allotropes of carbon, these will be revisited here, together with the metal aluminium.

Figure 7 shows the environment of each atom in diamond and metallic aluminium.

- Are these substances molecular or non-molecular?
- Both substances are non-molecular.

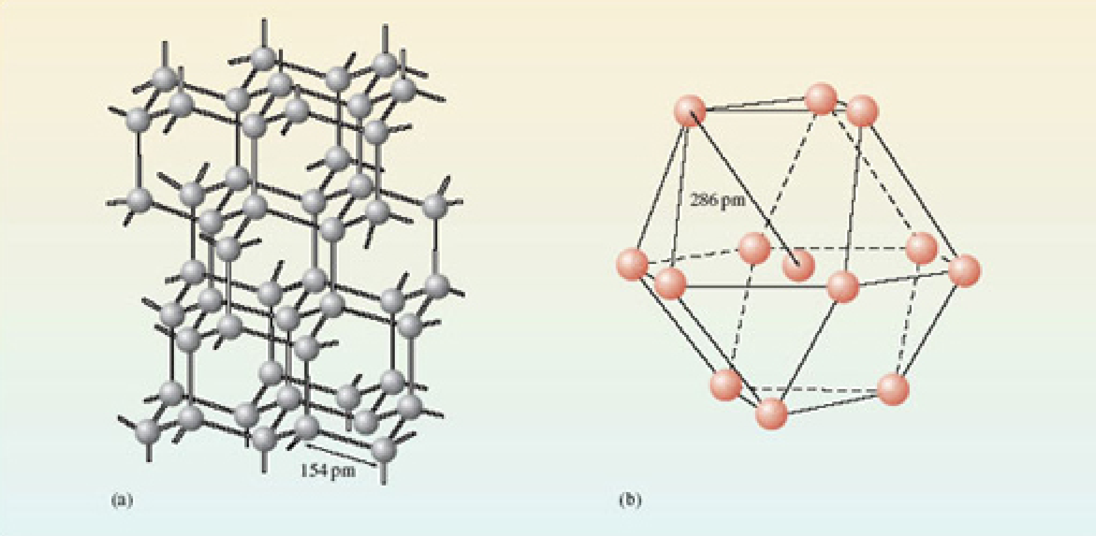


Figure 7 The environment of each atom in (a) the diamond form of the element carbon; (b) aluminium

- Looking at diamond (Figure 7a), describe the environment around each carbon atom.
- There are four surrounding carbon atoms at the corners of a tetrahedron, and as shown in the figure the C-C distance is 154pm.

In aluminium (Figure 7b) each atom has twelve surrounding aluminium atoms, and the Al-Al distance is 286pm.

The key point is, there is no justification for dividing the structure up into molecules containing two or more atoms. The individual units shown here extend throughout a crystal of the substance, and its formula will vary with crystal size.

For this reason the term **extended structure** is used to describe non-molecular substances of this type.

In Figure 7 (a and b), the extension is in three dimensions, but it may sometimes occur in one or two.

Sticking with carbon, let’s look again at one of its other allotropes – graphite (Figure 8).

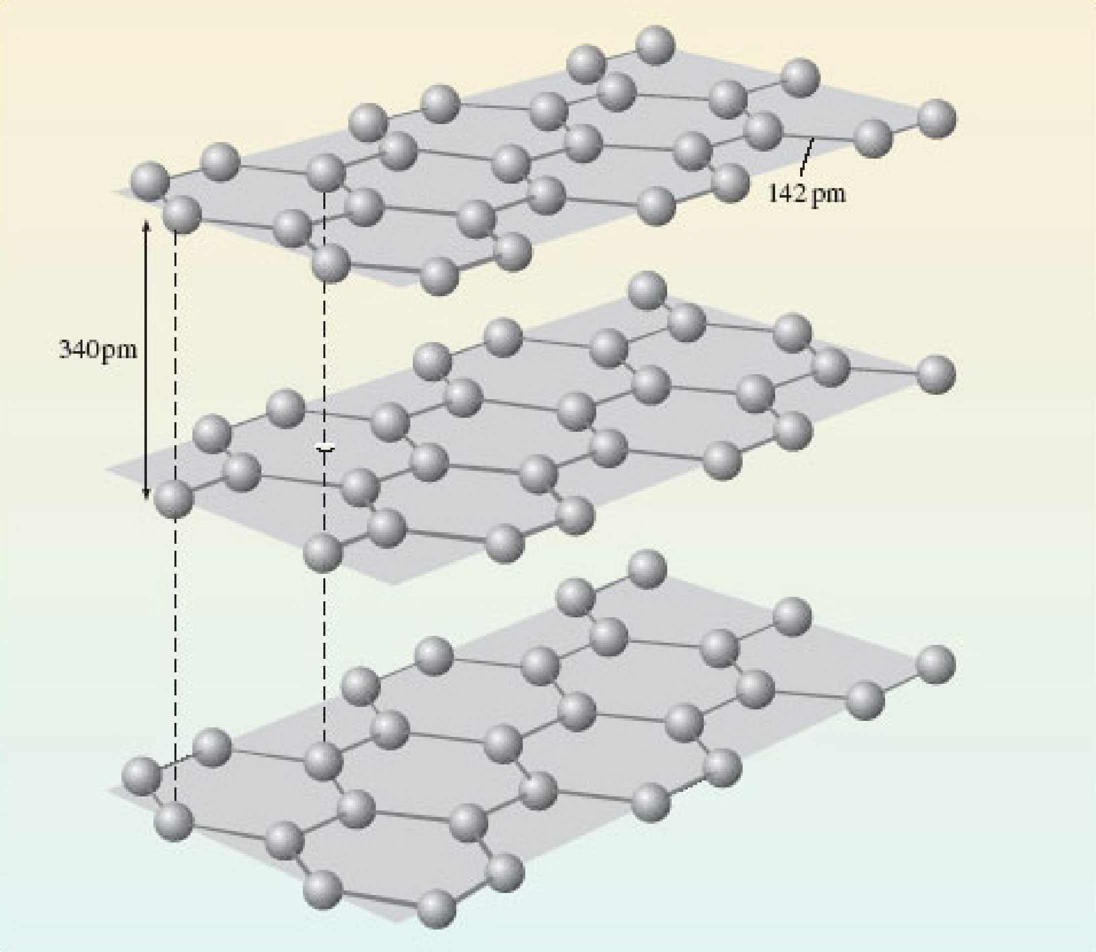


Figure 8 The structure of graphite

- Describe the environment around each carbon atom in graphite.
- Each carbon is surrounded by three others, and the atoms form regular hexagons, arranged in parallel sheets. Within the sheets, the C-C distance is 142pm, whereas the shortest distance between the sheets is 340pm.

So graphite is an extended structure, but this time the extension is in two dimensions.

Although not considered here substances do exist which may be described as one dimensional structures.

2.5 Binding forces in molecular and non-molecular substances

Now let’s start to think a little about chemical bonding.

As you will see in Session 3 of this module, elementary bonding theories imply that materials as different as salt, iodine and aluminium are held together by different types of chemical bond, although as you’ll see these all arise from a balance of forces acting between positively charged nuclei and negatively charged electrons.

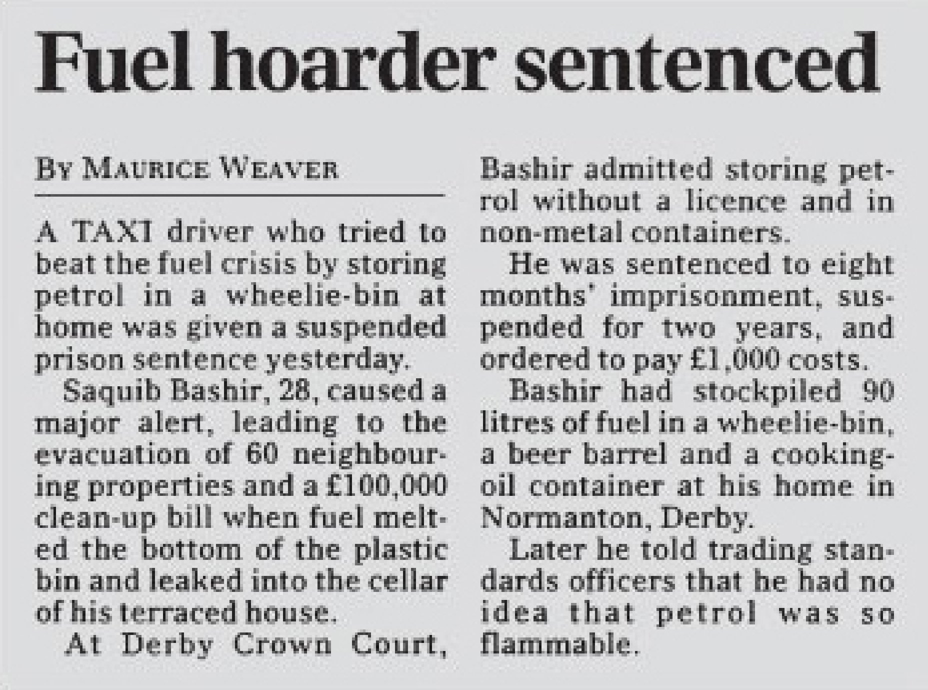
As these forces are stronger at shorter distances, in solid iodine (Figure 1b), the short distances between the pairs of atoms (I_2 molecules) suggest that the forces holding these atoms together are strong. But, the longer distance between different pairs (molecules) tells us that the forces acting *between* one I_2 molecule and another are much weaker. Now, iodine melts at only 114^{o}C, and boils at 185^{o}C.

■ Why does iodine have low melting and boiling temperatures?

□ In solid iodine, different I_2 molecules are held together by weak forces, so only a little thermal energy is needed to separate them and create first a liquid, and then a gas. Both liquid and gaseous iodine also contain I_2 molecules. To melt and then boil iodine it is not necessary to break up the I_2 molecules themselves.

This also explains another property of iodine: it dissolves fairly easily in an organic solvent like petrol. This is telling you the solid crystal falls apart and individual I_2 molecules drift off into solution.

As organic compounds are molecular, they too, often dissolve in petrol. For example organic polymers you meet in everyday life although having unusually large molecules, being molecular this could cause problems! An example is illustrated in Figure 9.



Fuel hoarder sentenced

By Maurice Weaver

A TAXI driver who tried to beat the fuel crisis by storing petrol in a wheelie-bin at home was given a suspended prison sentence yesterday.

Saquib Bashir, 28, caused a major alert, leading to the evacuation of 60 neighbouring properties and a £100,000 clean-up bill when fuel melted the bottom of the plastic bin and leaked into the cellar of his terraced house.

At Derby Crown Court, Bashir admitted storing petrol without a licence and in non-metal containers.

He was sentenced to eight months' imprisonment, suspended for two years, and ordered to pay £1,000 costs.

Bashir had stockpiled 90 litres of fuel in a wheelie-bin, a beer barrel and a cooking-oil container at his home in Normanton, Derby.

Later he told trading standards officers that he had no idea that petrol was so flammable.

Figure 9. From the *Daily Telegraph,* 6 April 2001 (note the erroneous use of 'melt' for 'dissolve' in this extract)

By contrast, in salt, silica or aluminium (all non-molecular), the bonding is more evenly distributed through the crystal, and there are no points of weakness where discrete molecules can be prised apart.

So the melting and boiling temperatures of non-molecular substances tend to be greater than those of molecular ones. Salt, silica and aluminium, for example, melt at 801^{o}C, 1713^{o}C and 660^{o}C, respectively.

3 Another look at the language of chemistry

So now you have had a look at how atoms join together to form larger structures which can be described as either molecular or non-molecular. These have been elements (e.g. carbon and aluminium) and compounds (e.g sodium chloride and silica).

From now on the focus will be on compounds and specifically, how chemists use a shorthand notation to represent them.

In fact by now you might have got the impression that chemists speak a language of their own – and this is true – it's the language of formulas and equations. With regular use this tends to become second nature but a little effort in coming to terms with these representations can open the door to so much.

The word 'formula' has a Latin origin meaning 'form' or 'shape'. The plural is formulae and you will often come across this. However, this module uses the form that is becoming increasingly common: formulas.

You've seen several examples of chemical formulas in the preceding sections, now's the time to explore in a bit more detail what the formula of a compound actually tells you.

3.1 Interpreting chemical formulas

Many people, even if they have no chemistry background whatsoever will tell you the formula of water is H_2O.

But what does this really mean?

In essence it is like all chemical formulas – a representation of the chemical compound – a type of shorthand notation.

A molecule of water is made up of an oxygen atom to which is attached two hydrogen atoms. The oxygen atom is in the middle.

In Figure 10 the water is represented in two different ways – these are depictions of the water molecule commonly used by chemists.

The first (Figure 10a) is a space-filling view. It shows the space occupied by the clouds of electrons surrounding the atoms in the molecule.

- ■ Why is the central oxygen atom larger than the hydrogen atoms?
- □ Hydrogen has just one electron whereas oxygen has eight, so the space occupied by the electrons in oxygen, and hence the size of the atom is much larger.

The second view (Figure 10 b) is called a ball-and-stick model. It is perhaps less 'realistic' but has the major advantage that the relative positions of the centres of the atoms in the water molecule can be seen more easily. It also represents the geometry of the molecule. The angle between the three atoms in the water molecule is about 104°. This is called the **bond angle**.

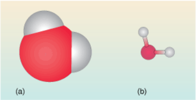


Figure 10 (a) Space-filling model of a water molecule. (b) Ball-and-stick model of a water molecule

So in the formula (H_2O), the atoms of the molecule are represented by their chemical symbols: H for hydrogen and O for oxygen. As you saw earlier, the subscript 2 indicates that there are two hydrogen atoms in the formula. So a subscript applies to whatever element comes immediately before the subscript. And where there is no subscript shown there is assumed to be a subscript 1. So in the formula H_2O for water, two hydrogen atoms and one oxygen atom are represented.

Formulas don't have to include subscripts, for example carbon monoxide CO where there is simply one carbon atom bonded to one oxygen atom.

A more complex formula is that of calcium nitrate, $Ca(NO_3)_2$. This is an ionic solid and the components are Ca^{2+} and NO_3^-.

Breaking the formula down – ignoring the charges for the moment.

There is no subscript following Ca, so the assumption is that there is just one calcium represented in the formula.

However the unit '$(NO_3)_2$', needs a little unravelling.

There are three oxygen atoms and one nitrogen atom N (no written subscript so assumed to be 1) in the NO_3 unit.

The subscript 2 indicates there are two of everything that comes before it. In other words what's inside the brackets is doubled up – there are two (NO_3) units for every calcium.

To summarise, the formula represents one calcium atom, two nitrogen atoms and six oxygen atoms. The reason for writing $Ca(NO_3)_2$ rather than CaN_2O_6 is that, in the compound calcium nitrate, each one of the two nitrogen atoms is attached to three oxygen atoms.

Thus the chemical formula can convey some structural information too.

■ In terms of the ions involved, can you suggest *why* the contents of the brackets are multiplied by 2?

□ Calcium nitrate itself (has to be) un-charged, and looking at its components, the calcium cations have a charge of +2 and the nitrate group has a charge of -1, so you need two of the latter for every calcium cation to satisfy this condition.

Now you have a feel for what formulas represent, let's now have a look at *why* compounds have specific formulas.

3.2 Valency – the combining power of an atom

Elements have a tendency to form compounds with other elements in fixed ratios.

It is almost as though atoms have a set number of 'hooks' that can be used to link to other atoms. Of course, there are no actual hooks and the bonds between atoms are formed from their valence electrons.

Let's look at a simple example.

Carbon forms many compounds with hydrogen and their formulas are consistent with carbon having four ‘hooks’.

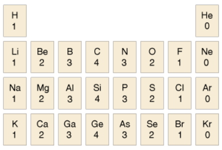
- ■ How many valence electrons does carbon have?
- □ The electronic configuration of the carbon atom is $1s^2 2s^2 2p^2$. So, in the valence shell (in this case corresponding to the principal quantum number 2), there are four electrons. Here the number of valence electrons corresponds directly to the number of ‘hooks’.

Here the number of valence electrons corresponds directly to the number of hooks, the link is not always so simple, as you will see.

The simplest compound of carbon and hydrogen is the gas methane, CH_4: a formula that would be obtained if it were assumed that carbon had four ‘hooks’ and hydrogen had one. Similarly the chlorine atom also has one ‘hook’, so the prediction for the formula of the compound from carbon and chlorine is CCl_4.

This tendency for atoms to behave as though they have a specific number of ‘hooks’ is known as **valency,** and is sometimes referred to as the combining power of an atom (or a group of atoms).

The usual valency values of some elements are shown in Table 2. You should note the pattern here compares with the layout of the periodic table.



H 1							He 0
Li 1	Be 2	B 3	C 4	N 3	O 2	F 1	Ne 0
Na 1	Mg 2	Al 3	Si 4	P 3	S 2	Cl 1	Ar 0
K 1	Ca 2	Ga 3	Ge 4	As 3	Se 2	Br 1	Kr 0

Table 2 Valency of some more common elements

3.3 Valency and predicting formulas in ionic compounds

In ionic compounds, valency gives an indication of the charge an ion formed from a particular element will carry.

Take for example, magnesium, Mg, this has a valency of two and tends to form ions carrying two positive charges, Mg^{2+}. Note that the valency does not indicate whether an ion will carry a positive or negative charge: oxygen, O, also has a valency of two, and forms negative ions, O^{2-}.

However, you *can* predict whether an atom will form negative or positive ions from its position in the Periodic Table: elements to the left (metals) will tend to form positive ions; those on the right (non-metals) will tend to form negative ions. And recall when oppositely charged ions combine to form compounds, there must be the same number of positive and negative charges, so that the compound carries no overall charge.

Thus, when $Mg^{2+}$and O^{2-} combine to form the ionic compound magnesium oxide, there have to be equal numbers of magnesium cations and oxide anions.

Magnesium oxide has the formula MgO.

This reveals another corner chemists cut when writing formulas. Note that charges do not appear in the chemical formulas of compounds: you don’t write $Mg^{2+}O^{2-}$).

Similarly, when magnesium cations, Mg^{2+}, combine with chloride anions, Cl^{-}, there must be twice as many chloride anions as magnesium cations in order for the charges to balance each other. The chemical formula of magnesium chloride is $MgCl_2$.

■ Using Table 2 predict the ions that will be formed from the following atoms: K, Ca, Al, S, F and Br.

□ K^+, Ca^{2+}, Al^{3+}, S^{2-}, F^- and Br^-

■ Give the formulas of the compounds that will be formed when calcium forms an ionic compound with fluorine..

□ Calcium has a valency of 2, so you are dealing with Ca^{2+} cations. Fluorine has a valency of 1, so forms F^- anions, thus an electrically neutral ionic compound will be CaF_2.

■ In the case of oxygen you have O^{2-} anions, what is the formula of the oxide it will form with aluminium?

□ This is a bit more involved. Remember you need to form an electrically neutral compound.So given you have Al^{3+} ions, you have to multiply Al by two and O by three. The formula will be Al_2O_3.

Now here's another (slight) complication.

Ionic compounds can also contain molecules which bear charges, and these units are charged either positively or negatively. These are often referred to as ionic groups. One example is the nitrate group (NO_3^-) which you have met already.

■ In a single sentence describe the structure of the nitrate anion.

□ A molecule carrying a single negative charge, consisting of three oxygen atoms covalently bound to a nitrogen atom.

Table 3 gives the formulas and charges on some other ionic groups.

Table 3 Some common ionic groups

Charge	Name and formula
+1	ammonium NH_4^+
-1	hydroxide, OH^-
	nitrate, NO_3^-
-2	sulfate, SO_4^{2-}
	carbonate, CO_3^{2-}

■ Give the formulas of the ionic compounds that comprise the following pairs of ions:

i. sodium and hydroxide
ii. potassium and nitrate
iii. ammonium and nitrate

☐

i. NaOH
ii. KNO_3, note here, as there is only one nitrate group, the brackets around the NO_3 unit tend to be left out.
iii. NH_4NO_3, as above, this could reasonably be written $(NH_4)(NO_3)$, but again as these ionic groups combine in a 1:1 ratio the brackets are omitted.

!Warning! not supportedSo far you have seen how valency may be used to rationalise the formulas of compounds, but as was alluded to above to really get to grips with how (and why) compounds form you need to consider the electrons on atoms that get involved in bonding. This is the focus of the next session.

4 This session’s quiz

Check what you’ve learned by taking the end-of-session quiz.

Session 2 quiz

Open the quiz in a new window or tab (by holding ctrl [or cmd on a Mac] when you click the link), then return here when you have done it.

Summary of session 2

- Chemical compounds are combinations of the atoms of two or more chemical elements. The empirical formula of a compound tells us the ratio in which the atoms of its elements are combined.
- Molecular substances have structures from which discrete molecules can be picked out by using interatomic distance as a criterion; non-molecular substances do not. The formula of these discrete molecules is called the molecular formula. Most molecular compounds contain just one type of molecule, which then has the same empirical formula as the compound. Most organic compounds are molecular substances.
- Molecular substances usually have lower melting and boiling temperatures than non-molecular ones. They also tend to dissolve more easily in organic solvents such as petrol.
- The valency of an atom can be described as the number of ‘hooks’ each atom has which it can use to attach to other atoms.
- In ionic compounds valency gives an indication of the charge on cations and anions (or ionic groups).

Session 3: Chemical bonding

Introduction

So far in this course you have seen a number of examples of atoms being joined together in some form, this may be to form molecules or extended structures or ionic solids. But what is the 'glue' holding the atoms together?

One thing you *do* know is that electrons are involved; specifically the outer (or valence) electrons of atoms, and this is the starting point to enable you to look more closely at the nature of the chemical bond.

Learning Outcomes

After studying Session 3 you should be able to:

- understand the common themes running through ionic, covalent and metallic descriptions of chemical bonding
- understand how the concept of electronegativity and its variation over the periodic table can be used to rationalise the nature of the bonding in substances
- appreciate how chemical substances can be described (and classified) in terms of structure and bond type.

1 Fundamental ideas behind the chemical bond

Simple theories of chemical bonding are based on the idea of the electron-pair bond, and the extent to which a pair of valence electrons is shared between the atoms that are bonded together.

Note – the key word here is extent – you'll see why this is later.

In addition there is also an assumption that the electronic structures of noble gas atoms (group 18) are especially stable (you looked at the extreme stability of these gases in session 1) and that many elements 'try to' attain these configurations when forming compounds.

This is referred to as the **octet rule**.

- ■ What is the outer (valence) electronic configuration of the noble gases?
- □ This can be represented as ns^2np^6, where n is the principle quantum number. Remember all the orbitals with the same value of n are said to be in the same shell, the point here is – the outer shell contains eight electrons (an octet), and is full.

These ideas were the brainchild of American chemist G.N. Lewis and will be considered in the next section.

2 Lewis structures – a starting point

The theories of shared electron pairs in chemical bonding developed by G.N. Lewis may be found in a classic paper; *The atom and the molecule* published in the Journal of the American Chemical Society in 1916.

To illustrate this approach let's look at two examples.

- ■ Are the following compounds molecular or non-molecular? Chlorine (Cl_2) and sodium chloride (NaCl).
- □ Chlorine (Cl_2) is a molecular compound – it is made up of discrete Cl_2 molecules.

  Sodium chloride (NaCl) a non-molecular compound, is made up of Na^+ and Cl^- ions.

Starting with Cl_2, how do two chlorine atoms form a bond to make a chlorine molecule?

You will look at simple bonding theory applied to chlorine in the next section.

2.1 Chlorine (Cl_2)

Before considering how two chlorine atoms form a chemical bond you need to consider the appropriate valence electrons.

- ■ How many valence electrons does chlorine have?
- □ The electronic configuration of chlorine is: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. Alternatively this can be written [Ne] $3s^2\ 3p^5$ in other words the core electrons are $1s^2\ 2s^2\ 2p^6$ corresponding to the electronic configuration of the noble gas neon. Thus the valence electrons are $3s^2\ 3p^5$ i.e. there are seven.

Because chlorine has an electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$, all it needs is a single electron to give it 8 electrons in its outer shell, and thus the electronic configuration of argon.

- ■ Suggest how chlorine could acquire this extra electron?
- □ It could share an electron with another atom, or one electron could be transferred to it from another atom.

In chlorine an electron pair is shared between the two atoms in Cl_2.

This is called **covalent bonding**.

So by sharing electrons through covalent bond formation, atoms are able to fill their valence shell and so attain a noble gas configuration.

2.2 Sodium chloride

Sodium chloride is an ionic compound, and this tells you when forming bonds electron loss and gain to form ions must be involved.

Sodium has the electronic configuration, $1s^2\ 2s^2\ 2p^6\ 3s^1$ (or [Ne] $3s^1$) so it has one valence electron. It can acquire a filled outer shell by transferring its outer electron to the chlorine atoms.

And you know, adding one electron to a chlorine atom will give it a noble gas configuration.

- ■ How will the charges on sodium and chlorine be changed by this transfer of an electron?
- □ Remember electrons are negatively charged, so if sodium is losing an electron it must become a positively charged ion – it forms a cation. Likewise when chlorine gains an electron it will become negatively charged – an anion.

So the transfer of the electron to chlorine in NaCl produces ions, each of which can exist independently of any one partner. As they are oppositely charged there will be an attraction between them – this attraction is the ionic bond.

In sodium chloride, each ion is surrounded by as many ions of opposite charge as space allows. In this case the number is six (Figure 1).

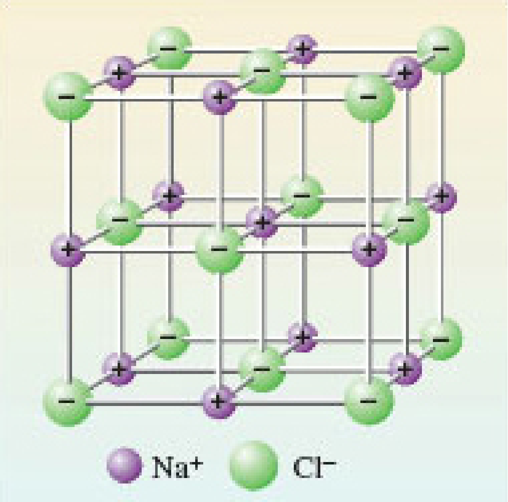


Figure 1 An ionic picture of solid sodium chloride – an assembly of Na^+ and Cl^- ions

It is worth making the point here that although this is the way ionic bonding is usually taught, and has stood the test of time, it is rather an unrealistic situation in practice, rather is a convenient 'thought experiment'.

Yes – you can pass chlorine gas over sodium and a reaction will take place to form sodium chloride. But generally speaking you don't get sodium atoms and chlorine atoms interacting together and electron transfer occurring as described above. A much more likely process is for ionic compounds form from solutions in water in which the ions are already present and crystallise out of solution when water is evaporated.

However – this apart – the basic definition of the ionic bond still stands – that is the electrostatic attraction between cations and anions.

2.3 Ionic and covalent compounds – a comparison

of properties

Consider a crystal of sodium chloride.

As a consequence of the strong attractive forces existing between the closely packed ions of opposite charge, the sodium chloride structure is not easily broken down: it has a high melting temperature and does not dissolve in organic solvents like the liquid hydrocarbons found in petrol. When it does melt, or dissolve in water, the ions separate and the resulting ionic fluid conducts electricity.

Figure 2 shows a simple experimental set-up to show molten sodium chloride (or indeed a solution of sodium chloride in water) conducts electricity. A battery is connected to two metal rods. The electrode attached to the negative terminal of the power source is called the cathode, and the anode is the electrode connected to the positive terminal.

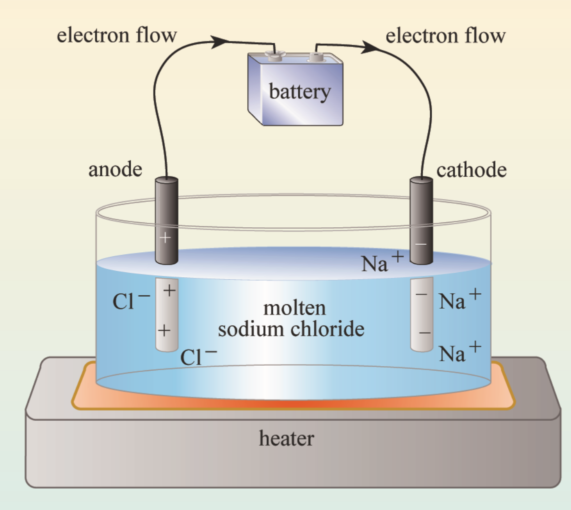


Figure 2 An experiment to demonstrate the electrical conducting properties of molten sodium chloride

Turning now to Cl_2.

Here the bonding can be maintained only if the atoms stay together in pairs, so it gives rise to a molecular substance; as you saw earlier elemental chlorine consists of discrete Cl_2 molecules with only weak forces acting between them. It is a gas at room temperature, and dissolves easily in liquid hydrocarbons, including petrol.

- Would you expect a solution of chlorine in a hydrocarbon to conduct electricity?
- No, because it contains no ions.

2.4 Sketching the Lewis structures for Cl_2 and NaCl

The description of the bonding in Cl_2 molecules and the ionic solid NaCl, in the previous sections took a lot of words.

However there is a way of doing this, very concisely, using simple diagrams, the chemical symbols you met earlier and “dots and crosses” to represent valence electrons.

Here’s how it works.

Figure 3(a) below shows the **Lewis structure** for the Cl_2 molecule. The valence electrons are grouped in pairs, to reflect the pairing of electrons you've previously seen for atomic orbitals.

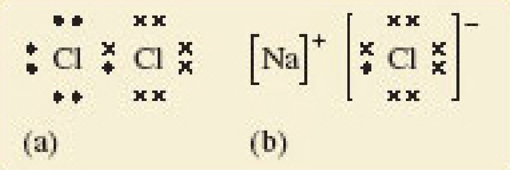


Figure 3 Lewis structures for (a) Cl_2 and (b) the ions in solid NaCl

The shared pair is shown as a dot and a cross in the centre. The remaining electrons in the valance shell of each atom are distributed in pairs, so taking the shared electrons into account there are eight electrons around each chlorine atom in the molecule. Note that the use of a dot or a cross is just to indicate where a particular electron originates, they are purely symbols. There's no difference between an electron represented by a cross and one allocated a dot.

Likewise the ions in sodium chloride have also been represented in this way in Figure 3(b).

The chloride anion has eight outer electrons; recall the chlorine atom has gained an electron to complete its octet. Similarly sodium loses its outer electron to form a cation, so the Lewis structure of the cation has no electrons shown.

In both structures, the formation of a chemical bond involves the production of a new electron pair in the outer shell of chlorine. However, in Cl_2, because the two atoms are identical, the electron pair must be equally shared between the two atoms. In contrast you can view the electron pair as being located on the chloride anion in NaCl.

You will return to this point later, but first a look at a molecule which does not follow the octet rule.

2.5 The hydrogen molecule

Hydrogen, the lightest element, exists as covalently bonded H_2 molecules.

However because of its electronic configuration, the octet rule cannot apply.

- Why is hydrogen an exception to the octet rule?
- Hydrogen has the valence electronic configuration $1s^1$. There is no 1p orbital.

How can hydrogen acquire a stable outer shell configuration?

The closest noble gas is helium, $1s^2$, and it can achieve this by sharing its outer electron with another hydrogen atom to form a covalent bond.

2.6 Chemical bonding – a common theme

Reflecting on what you have learned about bonding so-far, have a go to the following question.

- ■ Ionic and covalent bonding may be thought of as extreme examples of a common process – what is this process?
- ☐ The common process is the formation of an electron-pair bond; in covalent bonding the electron pair is shared between the atoms involved; in ionic bonding it resides on just one of them.

The link between ionic and covalent bonding is highlighted with reference to the concept of *electronegativity*, you will be looking at this in the next section.

3 Electronegativity

The electronegativity of an element is a measure of the power of its atoms to attract electrons *when forming chemical bonds*.

The greater the power to attract electrons, the greater the electronegativity.

Let’s look at how this idea applies to chlorine and sodium chloride.

In the Cl_2 molecule the two identical atoms have an equal ‘appetite’ for electrons: their electronegativities are equal, so the electron pair is shared equally between them.

But this clearly can’t be the case for sodium chloride.

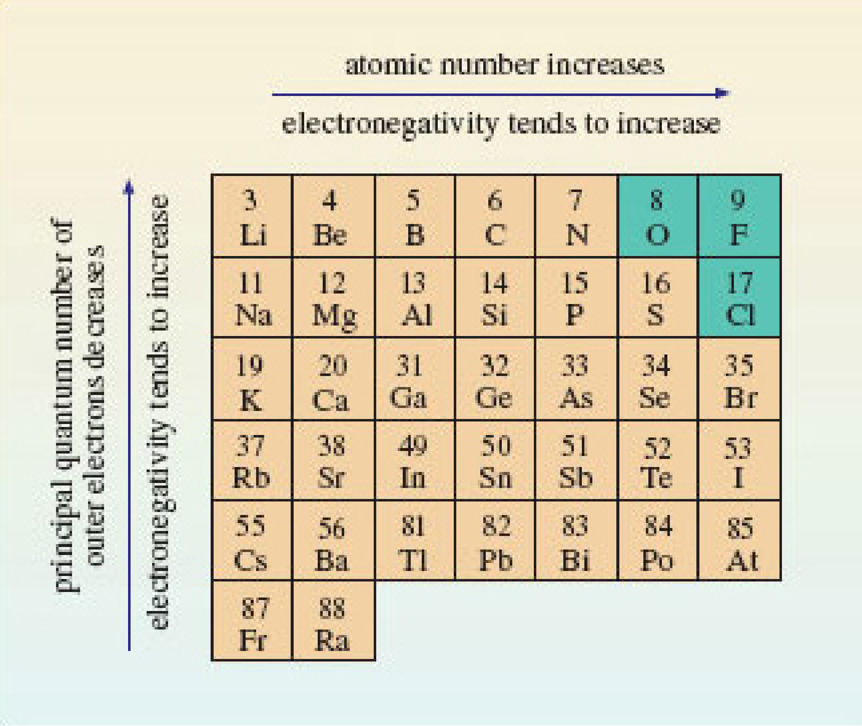
- ■ Which atom is the more electronegative, sodium or chlorine?
- □ As the chlorine atom is acquiring an electron to form an anion, logically you’d expect chlorine to be the more electronegative.

In fact in sodium chloride, the electron pair has been completely taken over by chlorine, which forms a chloride ion.

3.1 Electronegativity and the periodic table

In the last section you considered two elements, which clearly had markedly different electronegativities; chlorine, near the end of period 3, has a greater electronegativity than sodium, at the beginning.

This contrast applies generally: the electronegativities of atoms increases across a period of the periodic table; in addition electronegativities also increase up a group from the bottom to the top. This is illustrated in Figure 4. To keep things simple, only a portion of the periodic table is shown here.



3 Li	4 Be	5 B	6 C	7 N	8 O	9 F
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl
19 K	20 Ca	31 Ga	32 Ge	33 As	34 Se	35 Br
37 Rb	38 Sr	49 In	50 Sn	51 Sb	52 Te	53 I
55 Cs	56 Ba	81 Tl	82 Pb	83 Bi	84 Po	85 At
87 Fr	88 Ra					

Figure 4 Variation in electronegativity over the periodic table

■ Account for the variation in electronegativity shown in Figure 4. (*Hint: think back to what you know about the structure of atoms*).

□ Across a period of the periodic table, the atomic number, or positive charge on the nucleus, increases. This increases the attraction of the outer electrons to the nucleus, so the electronegativity of the elements also increases.

The principle quantum number of the outer electrons decreases from the bottom to the top of the group. This means that they get closer to the positively charged nucleus. The result is, again, that the outer electrons are attracted more strongly, and the electronegativity increases.

■ Suggest why the noble gases have been omitted from Figure 4

□ These are completely unreactive, in fact at normal temperatures helium, neon and argon form no compounds; hence electronegativities are not assigned to them.

So taking everything into account, top of the league table for electronegativity is fluorine, followed by oxygen and chlorine. The three most electronegative elements are shown on a green background in Figure 4.

But how does electronegativity impact on bonding?

This will be considered in the next section.

3.2 Electronegativity and the chemical bond

Let’s go back and think a little more about sodium chloride.

Figure 4, in Section 3.1 confirms that chlorine is much more electronegative than sodium.

Because of this large difference in electronegativity, the electron pair (x●) spends all of its time on chlorine, the charges on sodium and chlorine are +1 and -1 respectively, and NaCl is ionic.

In Cl_2, by contrast, the electronegativity difference between the bound elements is zero; the shared electrons spend equal times on each chlorine atom, both chlorines are uncharged, the substance is molecular and held together by covalent bonding.

Covalently bonded molecular substances such as Cl_2, I_2 and CO_2 are combinations from the right of Figure 4, because, although for these elements the individual electronegativities are large, the electronegativity *differences* between them are small.

These two cases deal with combinations of elements with very different electronegativities from the left and right of Figure 4 (ionic bonding), and with combinations of elements of high but similar electronegativity from the right (covalent bonding). And throughout the discussion so far it has been implied that compounds are *either* ionic or covalent – but this is not necessarily the case.

If you consider the water molecule (H_2O), this consists of two H-O bonds, these may be described as covalent with both atoms contributing one electron to the bond. However, because oxygen is more electronegative than hydrogen, the two electrons in the bond are more likely to be found closer to the oxygen. This unequal distribution of electrons results in what is known as a polar covalent bond; the bonding electrons are skewed towards the oxygen and as a result, in water, oxygen will have a partial negative charge (often represented as ! ! δ-), and hydrogen a partial positive charge (dδ+).

Taking the water molecule as a whole, and noting it has V shape (for reasons which will become clear later in this course), the polar nature of water may be represented by Figure 5.

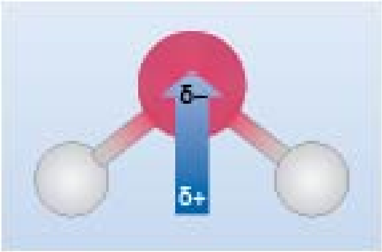


Figure 5 The polarity of the water molecule

The existence of polar bonds is crucial to the unique properties of water – this will not be discussed in detail here, however take a look at the following visual evidence, which you may wish to try for yourself.

- If a plastic pen is rubbed vigorously with a woollen cloth, and held next to a slow, steady stream of water the water is deflected towards it (Figure 6). Suggest why.

Figure 6 Deflection of a stream of water

- The pen becomes electrostatically charged on rubbing, and attracts the oppositely charged end of the water molecules.

This example is simply an illustration of a more general point.

In practice the type of bonding observed depends on the difference in electronegativity between the atoms involved. If the disparity is small then bonds may be described as covalent. As the electronegativity difference increases there is a gradual change through polar covalent, to fully ionic bonding.

Up to this point, the combination of elements of low but similar electronegativity from the left of the periodic table has not been considered.

What might you expect?

The reasoning pursued until now suggests that, in this case, electronegativity differences between atoms will be small, shared electron-pair bonds and covalent substances, possibly of the molecular type are likely.

Actually this isn’t the case as you’ll see next.

4 Bonding in metals

Elements on the far left of the periodic table combine together in a different way to what you've seen so far. They are metals and their bonding is somewhat different.

Two familiar properties of metals make for a good starting point for developing a model of bonding in metals.

i. Metals have a strong tendency to form positive ions. Thus, when sodium reacts with water, and when magnesium and aluminium react with acids, hydrogen gas is evolved and the ions Na^+, Mg^{2+} and Al^{3+}, respectively, are formed.
ii. Metals are good conductors of electricity: when a voltage difference is applied across two points on a piece of metal, there is a movement of electrons between the two points, and an electric current flows.

Let's consider metallic sodium.

- ■ How is a sodium cations formed from a sodium atom?
- □ The Na^+ ion is formed by removing the single outer electron from a sodium atom, it has the shell structure of neon.

The key feature of the bonding in sodium and indeed metals in general is the fact that the electrons so removed are no longer tied to individual metal ions, and are allowed to move freely throughout the entire volume of the metallic substance.

The low electronegativities mean that none of the atoms present will readily *take on* these electrons, either by forming a negative ion, or by accepting a share in electron-pair bonds. Consequently, a pool of free electrons is created which is like hot money: they are passed quickly from hand to hand, and can find no permanent home!

These free electrons, sometimes described as an '**electron gas**', are responsible for the ability of metals to conduct electricity. At the same time, they occupy the space between the positive ions, so their negative charge acts like a binding glue pulling the metal sites together. The **metallic bond** is an attraction between these positive and negative charges.

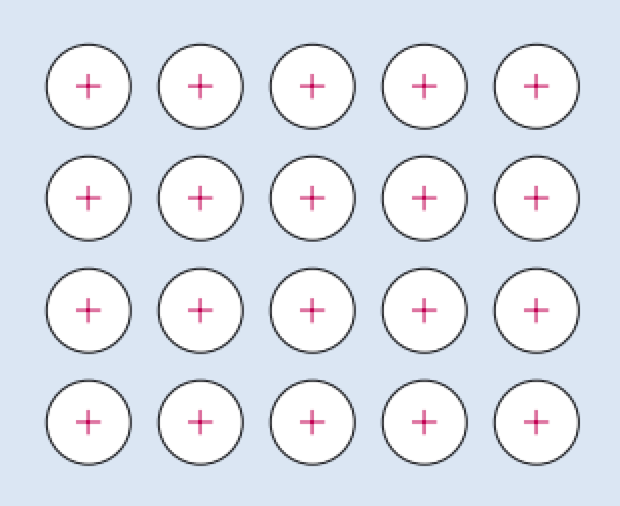


Figure 7 In the electron gas model of metallic bonding for metals and alloys, an array of positive ions is steeped in a pool of negatively charged free electrons (indicated by the

background blue tone)

Now watch the following video which is a modern version of an experiment carried out by the Cornish chemist and inventor Sir Humphrey Davy around 1807. You saw in Session 1 how vigorously the alkali metals such as sodium react with water. However if ammonia gas is cooled below its boiling point, it becomes a very effective liquid solvent. The video shows sodium metal being dissolved in ammonia.

Video content is not available in this format.

- ■ What were your observations when sodium was added to liquid ammonia?
- □ Sodium dissolved to give a blue solution. The blue colour is thought to arise from electrons surrounded by ammonia molecules. On increasing the concentration of sodium a shiny bronze colour was oberved.

4.1 Alloys

To conclude this section on metals, one final point.

So far, consideration has only been given to cases where all the atoms are the same, and a metallic *element* is the result. However, such metallic substances can be formed from two or more elements, and they are then called **alloys**.

One of the earliest examples is bronze, an alloy of copper and tin.

Copper and tin are fairly soft metals, but from about 3000 BC a harder metal was produced by heating mixed ores of copper and tin with charcoal, to form bronze. At the atomic level, copper atoms are mixed with tin atoms, a situation which increases the hardness of the material, and consequently bronze was widely used as blades in daggers, the tips of spears or the heads of axes, where copper or tin alone would have been too soft to use.

5 Cataloguing chemical substances

At this point in the course a useful classification systems for chemical substances has emerged.

As you’ve seen they may be divided into molecular and non-molecular types, largely on the basis of their structures. Then a further division can be made according to the major source of the chemical bonding holding their atoms together. In molecular substances, the bonding is covalent, but in the non-molecular class, it may be covalent, ionic or metallic.

This classification is summarised in Figure 8.

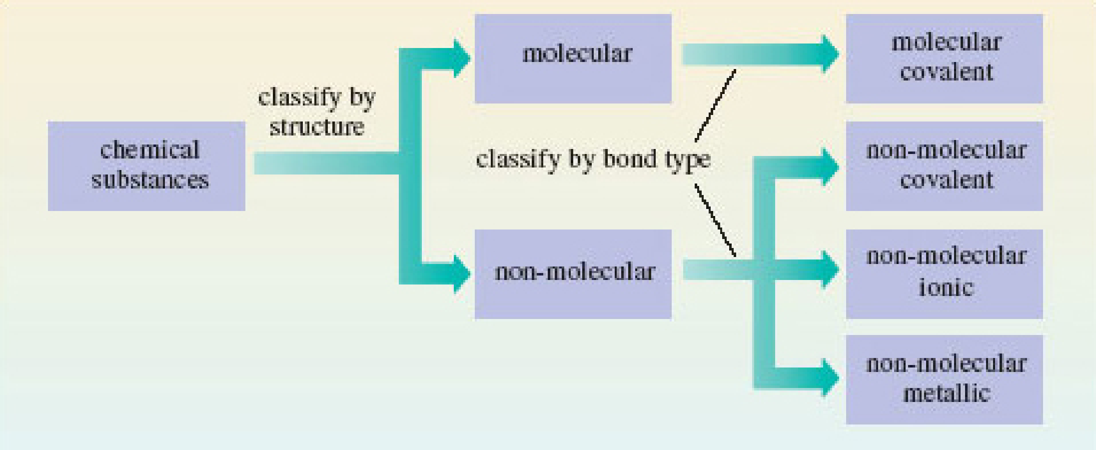


Figure 8 A classification of chemical substances by structure and bond type

- Consider the compounds IBr, $CaCl_2$ and $CaMg_2$. One is ionic, one is covalent, and one is metallic. Identify which is which, and match each compound to one of the descriptions below. In each case, suggest whether the compound is molecular or non-molecular.

  i. White solid that melts at 782°C. It is a poor conductor of electricity in the solid state, but a good one when melted or dissolved in water.
  ii. Brown-black solid that melts at 41°C to give a liquid with low electrical conductivity.
  iii. Silvery-looking solid that melts at 720°C. Whether solid or molten, it is an excellent conductor of electricity.

- CaCl2; (ii) IBr; (iii) CaMg2.

  The properties listed are characteristic of (i) an ionic substance, (ii) a molecular covalent substance, and (iii) a metallic substance. CaCl2 is a combination of elements from the extreme left and extreme right of the periodic table, so the electronegativity difference will be large and CaCl2 will be the ionic compound; such compounds are non-molecular. IBr will be covalent because it is a combination of elements of high electronegativity from the extreme right of the periodic table. CaMg2 will be a metallic alloy because it is a combination of metallic elements with low electronegativity, Such alloys are non-molecular.

So, up to this point you’ve met some elementary ideas about chemical bonding, you’ll be developing these further in the next session and find out more about how the type of bonding affects the properties of chemical substances, in other words a link between what’s happening on the atomic and molecular scale and the world we can see.

6 This session’s quiz

Check what you’ve learned by taking the end-of-session quiz.

Session 3 quiz

Open the quiz in a new window or tab (by holding ctrl [or cmd on a Mac] when you click the link), then return here when you have done it.

Summary of session 3

1. The chemical formulae of many substances can be understood by arguing that their atoms attain noble gas structures by chemical combination.
2. In ionic compounds, this is achieved by the transfer of electrons from one atom to another; in molecular substances, it happens through the sharing of electron pairs in covalent bonds. But in both cases, bonds between atoms consist of shared pairs of electrons. In covalent compounds the sharing is fairly equitable; in ionic compounds it is much less so.
3. In metals, the sharing takes a different form. An 'electron gas' is created by removing electrons from the atoms of the metallic elements. The result is an array of ions steeped in a pool of free electrons. The negatively charged electron gas occupies the space between the ions and pulls them together.

Session 4: More about chemical bonding

Introduction

In the last session study you focused on some elementary ideas about chemical bonding, specifically the electron pair bond, and the idea that many elements attain the electronic structures of noble gases when forming compounds. Now you will be taking these concepts further and looking at how they can provide a much more detailed insight into the *nature* of the bonding in molecules and hence account for some of their properties.

But first you'll be revisiting the important concept of valency and finding out more about what it can tell you about bonding.

Learning Outcomes

After studying Session 4 you should be able to:

- understand how the concept of valency can account for, and predict the formulas of compounds
- sketch Lewis structures of molecules and ions
- identify situations where and appreciation of dative bonding is required to account for the bonding in certain molecules and ions
- appreciate some molecules are not adequately represented by a single Lewis structure and seem to be a composite of two or more resonance structures.

1 More about chemical bonding

In the last session of study you focussed on some elementary ideas of chemical bonding, specifically the electron pair bond, and the idea that many elements attain the electronic structures of noble gases when forming compounds. In this session, you will be taking these concepts further and looking at how they can provide a much more detailed insight into the nature of the bonding in molecules and hence account for some of their properties.But first a look at what the concept of valency can reveal about bonding in molecules.

1 1Valency and the chemical bond

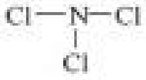
Up to this point you have simply treated valencies as just been numbers that are used to predict the formulae of compounds. But in the case of covalent substances they can tell us so much more.

In particular, they reveal how the atoms are linked together in a molecule. This information is obtained from a two-dimensional drawing of the **structural formula** of the molecule. (Note that structural formulae cannot be assumed to carry any implications about molecular shape.)

Consider, for example, the molecules H_2, Cl_2, NCl_3 and CH_4. Their structural formulas are shown here as Structures **4.1-4.4**. They can be drawn correctly by ensuring that the number of lines or bonds emerging from any atom is equal to its valency.

4.1

4.2



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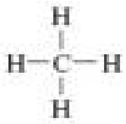


4.4

H_2 and Cl_2 are simply represented as a single line between the two atoms, both hydrogen and chlorine have a valency of one.

Recalling that nitrogen has a valency three, and chlorine a valency of one; NCl_3 is shown with three bonds emerging from the nitrogen atom and one from each chlorine atom.

■ Account for the structure of methane CH_4 (**4.4**) in terms of the valency of its atoms.

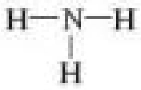
□ Carbon has a valency of four, so will form four bonds to hydrogen, which has a valency of one.

At this point, check that you are comfortable with these bonding ideas by attempting the following.

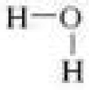
■ Draw structural formulas for the following molecular substances: hydrogen chloride (HCl), ammonia (NH_3), water (H_2O), oxygen (O_2), carbon dioxide (CO_2), ethane (C_2H_4), hydrogen cyanide (HCN), ethyne (C_2H_2) and ethanal (CH_3CHO).

□ The structural formulae are as shown below:

4.5



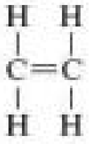
4.6



4.7

4.8

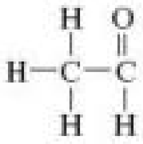
4.9



4.10

4.11

4.12



4.13

1.2 Lewis structures – the next step

You will recall Lewis structures, developed by American chemist G.N. Lewis in 1916, are essentially drawings of where the atoms comprising a molecule are, and where their valence electrons are located. And, later in this course you will find they are used to predict the shape of molecules and infer a lot about the chemical and physical properties of compounds.

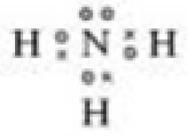
Essentially, when constructing a Lewis structure, the shared electron-pair bond is used to re-express structural formulas in an electronic form in which each atom has the shell structure of a noble gas.

Consider for example ammonia (NH_3). From the structural formula you know there is a central nitrogen atom to which is attached three hydrogen atoms.

- ■ How many electrons are there in the valence shell of nitrogen?
- □ Five ($2s^2$ $2p^3$)

So in order to achieve the shell structure of the nearest noble gas – neon, a nitrogen atom must gain three electrons. Likewise hydrogen attains the shell structure of helium, with 2 outer electrons.

Therefore, if nitrogen shared three of its valence electrons with hydrogen atoms, it can indeed acquire an octet in its valence shell. This is shown in structure 4.14.



4.14

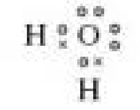
Note that the electron pairs in these Lewis structures are of two types.

The pairs shared between atoms represent chemical bonds and are called **bond pairs**. But there are also pairs that remain on just one atom and are unshared. These are called **non-bonded electron pairs** or **lone pairs**.

- ■ How many bond pairs and non-bonded electron pairs are there in the ammonia molecule?
- □ NH_3 contains three bond pairs and one non-bonded pair.

Now let's turn to another simple molecule, water (H_2O).

- ■ Draw the Lewis structure for the water molecule (H_2O). How many bond pairs and non-bonded pairs are there?
- □ Oxygen has six electrons in its valence shell, and so it can acquire an octet by sharing electrons with two hydrogen atoms, which in turn fills its valence shell, see structure 4.15 resulting in two bond pairs and two non-bonded pairs.



4.15

1.3 Multiple bonds

So far, any two atoms in the Lewis structures you have looked at have been held together by just one electron pair bond.

Logically this is called a **single bond**.

But sometimes two or even three shared pairs may be involved, two examples are shown in Figure 1, however the name of the game is still the attainment of eight outer electrons.

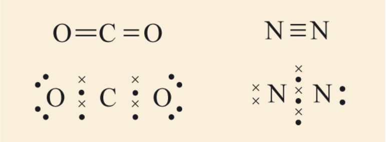


Figure 1 Lewis structures (bottom) and structural formulas (top) for CO_2 and N_2

In carbon dioxide, the *two* electron pairs between each oxygen atom and the central carbon atom represent each carbon-oxygen **double bond**.

Turning now to the Lewis structure of the nitrogen molecule, the *three* shared pairs in the nitrogen molecule are equivalent to a **triple bond.**

As an aside, it is worth adding that nitrogen, N_2, is chemically very unreactive, in fact almost as inert as the noble gases. This stems from the great strength of this triple bond. Indeed, gaseous nitrogen finds applications where inert atmospheres are required, including manufacture of air-sensitive chemicals, and in the liquid form when extreme cold is essential (Figure 2), such as the preservation of blood and semen, and rapid freezing of food.

Figure 2 Nitrogen finds many applications as a refrigerant in the liquid form

You can see some demonstrations involving liquid nitrogen in the following video.

Video content is not available in this format.

1.4 Linking Lewis structures with valency

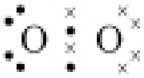
The Lewis structures that you have look at so far, tell you *why* carbon, hydrogen, nitrogen, oxygen and chlorine have the valencies they have.

When atoms are forming covalent bonds, the valency is the number of shared electron-pair bonds that the atom must form if it is to attain the electron arrangement of a noble gas.

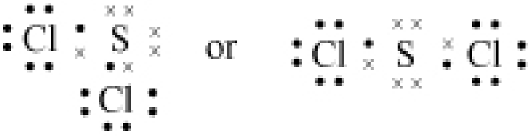
Thus hydrogen and oxygen form water, H_2O, rather than HO or HO_2, because H_2O enables *both* elements to attain the structure of a noble gas.

■ Oxygen gas and sulfur dichloride contain the molecules O_2 and SCl_2 respectively. Draw a Lewis structure for each molecule. Which noble gas structure is achieved by each atom in the molecules?

□ With six outer electrons each, the two oxygen atoms in the O_2 molecule must form a double bond (two shared electron pairs, structure **4.16)** with each other if each is to attain a noble gas configuration. SCl_2 contains single bonds (structure **4.17**).



4.16



4.17

In these Lewis structures, oxygen attains the neon configuration, and sulfur and chlorine the argon configuration. When drawing Lewis structures, shape is unimportant; the important point is to show the correct number of bonds (shared electron pairs) formed by each atom. As either form of structure **4.17** does the job, both are acceptable.

1.4.5 Lewis structures of ions

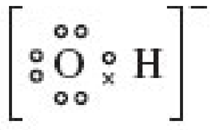
So far, you have only written Lewis structures for neutral molecules, but they can also be drawn for ions, such as the hydroxide ion, HO^- and the ammonium ion, NH_4^+.

However, to take the charges into account you need to begin by adding or subtracting electrons from particular atoms.

One way of giving chemically plausible structures is to add or subtract electrons from the atom of highest valency.

So as the hydroxide ion carries a single negative charge, you need to add one electron to the shell structure of the oxygen atom.

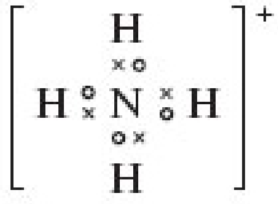
This means the Lewis structure for OH^- is written as shown in structure 4.18:



4.18

Note again, each atom possesses a noble gas structure.

- What shell structure in the ammonium ion is adjusted in order to write a Lewis structure?
- Nitrogen has a higher valency than hydrogen, so the single positive charge on the ammonium ion requires the removal of one electron from the nitrogen atom shell structure.

- Sketch a Lewis structure for the ammonium ion.
- 

4.20

Again each atom possesses a noble gas structure.

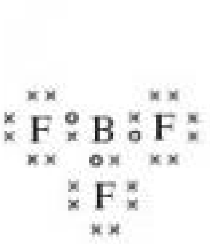
In fact it is remarkable how many molecules and ions can be represented by Lewis structures in which each atom has a noble gas shell structure.

Nevertheless, many exceptions do exist and you will look at a few examples in the next section.

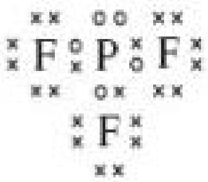
1.6 Noble gas configurations under stress

The elements phosphorus and boron form fluorides having formulas BF_3, PF_3 and PF_5.

- ■ Write the Lewis structures for BF_3, PF_3 and PF_5.
- □ As the valency of fluorine is one, each bond in BF_3, PF_3 and PF_5 is a shared electron pair, so the Lewis structures may be written:



4.21



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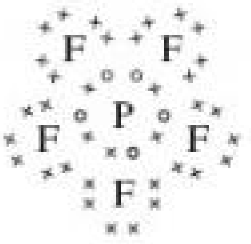


4.25

- ■ In how many of these Lewis structures do all the atoms have noble gas shell structures?
- □ In only one, namely PF_3.

Looking first at BF_3, you can see around the boron atom there are six electrons – it is two electrons short of the shell structure of neon. In contrast there are five electron pairs around the phosphorus atom in PF_5, which is two more than the shell structure of argon.

Clearly things aren't as neat and tidy as they first appeared.

1.7 Dative bonds

So far, the bonds in Lewis structures have been shared electron pairs made by taking one electron from each of the two bound atoms.

But this need not necessarily be the case.

To take an example, if you mix the colourless gases ammonia, NH_3 and boron trifluoride BF_3, a reaction occurs. This is shown in the following video.

Video content is not available in this format.
Video 4.1 : Reaction of ammonia and boron trifluoride

■ Describe the appearance of the product of the reaction of NH_3 and BF_3.

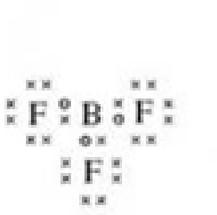
□ The product appears as a dense white smoke.

Now let’s try to explain this reaction using the Lewis structures of the reacting molecules.

As you have seen already, ammonia (NH_3) comprises three electron pair bonds to hydrogen atoms and one non-bonded pair being allocated to nitrogen (Structure 4.14). And in the last section you also saw that the Lewis structure of boron trifluoride left the boron atom two electrons short of a noble gas configuration Structure 4.21.

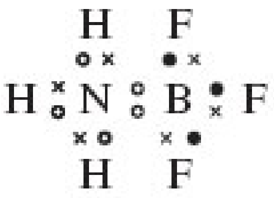
The Lewis structures of these two molecules are reproduced below.

4.14



4.21

If an electron-pair bond is created by allowing the non-bonded electron pair on nitrogen in the ammonia molecule to be shared between the nitrogen and boron atoms, the Lewis structure (Structure **4.26**) can be written in which all atoms, including boron, have a noble gas shell structure.

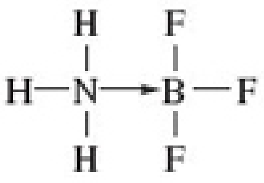


4.26

A bond in which the electron pair is provided by just one of the bonded atoms, as is the case here, is called a **dative bond (or coordinate bond)**.

Note that, in order to focus attention on the bonding electrons, the non-bonded electron pairs on the fluorine atoms have been omitted from Structure **4.26** - this is common practice.

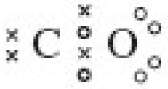
In order to differentiate dative bonds from the more familiar bonds in which *each* bound atom contributes an electron to the electron pair, dative bonds are represented as arrows running from the ‘donor’ atom (in this case nitrogen) to the 'receptor' atom (in this case boron) (**4.27**).



4.27

1.8 Some more examples of dative bonding

On the face of it the bonding in carbon monoxide, CO, the highly toxic gas formed by incomplete combustion of natural gas, is a bit of a puzzle.

- A student was asked to sketch the Lewis structure for CO, and came up with structure **4.28.**
- 

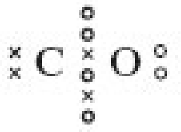
  4.28

- Why is the representation of CO as a double bond likely to be incorrect?
- The oxygen atom with two shared electron pairs and two non-bonded pairs, has an octet, but carbon is two electrons short of a noble gas state.

Suppose that in addition, a dative bond is formed by allowing one of the oxygen non-bonded pairs to become shared between oxygen and carbon, then carbon can achieve a filled shell configuration.

This is represented by structures **4.29** and **4.30**.

4.29

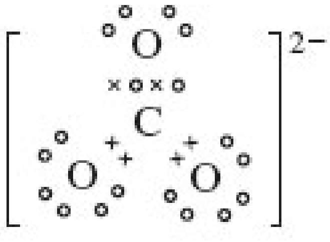


4.30

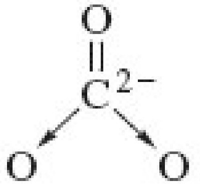
There are now three shared electron pairs between carbon and oxygen, so this is an example of a **triple bond**.

Note again the use of an arrow to denote the donation of a pair of electrons from oxygen to carbon.

Dative bonds are also useful when writing Lewis structures for ions such as carbonate, CO_3^{2-}. Beginning in the usual way by adding the overall charge to the atom with highest valency, namely carbon, this means adding two electrons to carbon, which gives the atom eight electrons in its outer shell. Formation of one C=O double bond and two C→O dative bonds then gives Lewis structure **4.31**, which is equivalent to structural formula **4.32**.



4.31



4.32

Before leaving dative bonds, consider now an alternative way you often see them represented.

Suppose that atom A forms a dative bond with atom B by donating a non-bonded electron pair to it, this is represented by A→B.

But consider atom A before the bond is formed.

■ If you were to remove one of the lone pair of electrons on atom A and put it on atom B, what would be the result?

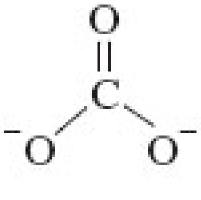
□ You would end up with the separate ions $[A^{\bullet}]^{+}$ and $[B^{\bullet}]^{-}$.

Suppose you now form a conventional shared electron-pair bond from the odd electrons on the two ions. The electrons are shared between the A and B sites in just the way as before, but the bond would now be written as .

Thus, A→B and are equivalent ways of writing the dative bond between A and B, and both are equally valid. The structures $H_3N{\rightarrow}BF_3$ and CO can therefore also be written as H_3 $-F_3$ and respectively.

■ Transform Structure **4.32** for the carbonate ion into this new dative bond representation.

□ See Structure **4.33**; each C→O bond is replaced by −, and as the carbon atom forms two dative bonds, a charge of +2 must be added to the double negative charge on carbon in Structure **4.32**. This gives zero charge on carbon in the new version, but as there is now a single negative charge on each of the two singly bonded oxygens, the total charge on the ion is −2 as before.



4.33

2 Resonance Structures

Gaseous oxygen occurs as O_2 molecules. But ultraviolet light or an electric discharge converts some of the oxygen to ozone, this is a naturally occurring **allotrope** of oxygen with the molecular formula O_3.

For ozone, a Lewis structure can be written which gives each atom a noble gas shell structure. This is shown in Figure 3 along with a corresponding structural formula.

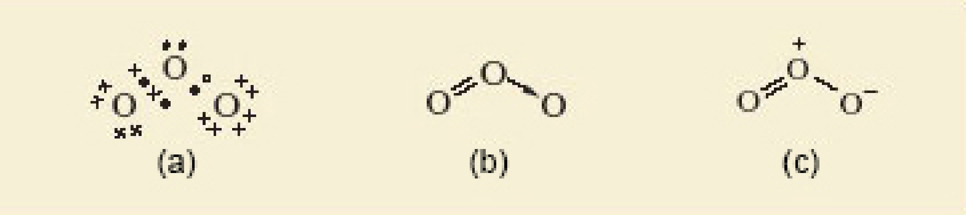


Figure 3 The ozone molecule: (a) a Lewis structure, (b) and (c) show structural formulas with alternative representations of the dative bond

- Do the representations shown in Figure 3 suggest that the lengths of the two bonds in the ozone molecule should be equal or unequal?
- Unequal; one is a double bond and the other a single dative bond. It would be expected this difference would impact on their lengths.

But experimental measurement shows that both bonds have the same length (127.8 pm).

To account for this, you need to realise that the structures shown in Figure 3 have counterparts in which the double and single bonds have simply been exchanged.

The real structure of the molecule with its equal bond lengths is a sort of average of the two. In situations like this, where a molecule is not adequately represented by a single Lewis structure and seems to be a composite of two or more, the competing structures are written down and linked by a double-headed arrow.

The two structures are called **resonance structures**, and the real structure of ozone is said to be a **resonance hybrid** of the two. This is shown in Figure 4.

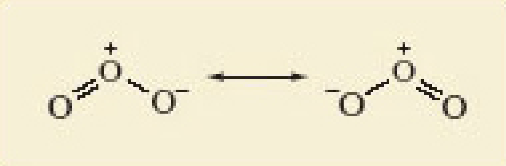
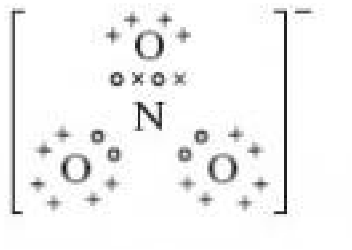


Figure 4 The two resonance structures of ozone

The significance of the representations in Figure 4 is that in ozone, each bond is a mixture of one-half of a double bond and one-half of a single dative bond.

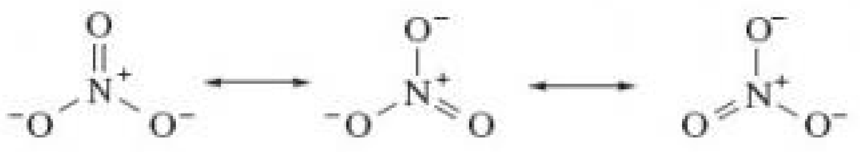
An analogy (which often crops up in chemistry textbooks) is with a mule- a hybrid of a horse and a donkey. Mules do not oscillate between a horse and a donkey. Likewise a resonance hybrid is a combination of a number of contributing resonance structures for a particular molecule. Figure 4 is not meant to imply that the molecule is constantly changing from one resonance structure to the other.

- ■ In the nitrate ion, NO_3^-, all three nitrogen-oxygen bonds are of equal length. Is this consistent with the Lewis representation of this molecule?
- □ No, this contains one double bond and two single bonds (Structure 4.34). The atom of highest valency is nitrogen, so the single negative charge on the NO_3^- ion is assigned to nitrogen, giving it a full outer shell. All atoms gain the shell structure of neon if nitrogen forms one double bond and two single dative bonds to oxygen.



4.34

- ■ In the light of your answer to the previous question, account for the fact that in the nitrate ion, NO_3^-, all three nitrogen-oxygen bonds are actually of equal length.
- □ The nitrate ion can be represented as a resonance hybrid (**4.35**)



4.35

To develop this discussion of resonance structures further, an example from the world or organic chemistry will be considered in the next section.

2.1 Bonding in benzene

Benzene, a hydrocarbon is a one of the products of fractional distillation of crude oil, and the starting point for the preparation of many important chemical compounds. Superficially its molecular structure comprises six carbon atoms joined in a ring, but a closer look reveals some interesting points.

Benzene, like ozone, can be represented as a resonance hybrid of two resonance structures in which all atoms have noble gas configurations (Figure 5).

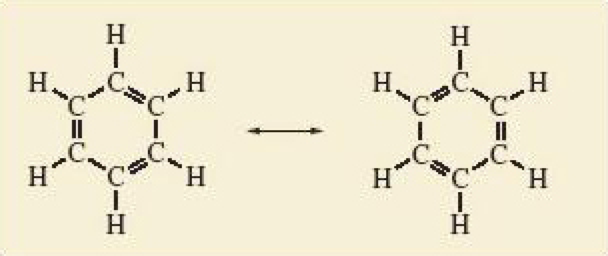
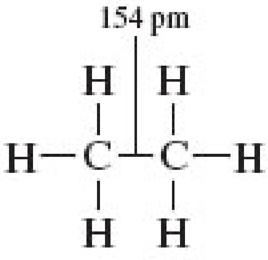


Figure 5 The two resonance structures of benzene

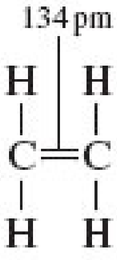
To dig deeper into the nature of the bonding in this molecule, let’s look at some simpler molecules.

Ethane has the formula C_2H_6 and comprises solely single bonds (C-C and C-H), whereas ethene (C_2H_4) contains a double bond between the two carbon atoms, and four C-H single bonds.

A typical C—C single bond length in ethane, (Structure **4.36**), is 154 pm; in contrast, a typical C—C bond length in ethene, (Structure **4.37**), is 134 pm. The *individual* resonance structures in Figure 5 therefore suggest that the carbon-carbon bond lengths in benzene should alternate between about 134 pm and 154 pm around the ring.



4.36



4.37

- ■ But what does the whole of Figure 5 suggest?
- □ The real structure of benzene is a hybrid of the individual structures, and each carbon-carbon bond will be a mixture of one-half single and one-half double bonds; all carbon-carbon bond lengths should be equal and lie *between* 134 and 154 pm.

This is precisely the case: all carbon—carbon bond lengths in benzene are 140 pm!

Number the carbon—carbon bonds in a benzene ring of Figure 5 clockwise from 1 – 6. All bonds contain at least one pair of electrons. However, in one of the resonance structures, bonds 1, 3 and 5 are double bonds, each containing a second electron pair; in the other resonance structure, the double bonds and extra pair of electrons are found at bonds 2, 4 and 6.

The implication of Figure 5 is that in the resonance hybrid these three extra pairs of electrons are not confined to, or *localised* within, just half of the bonds in the ring. Instead, they are **delocalised** around the ring and equally shared within all six bonds.

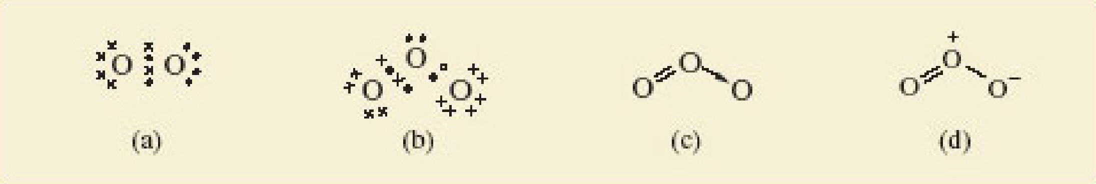
3 When Lewis structures don't work

Lewis structures provide a convenient, relatively straightforward and by and large successful of representing the bonding in molecules.

But they don't always tell the whole story.

Consider the oxygen molecule (O_2).

- Sketch a Lewis structure for oxygen (O_2)
- This is shown below (**4.38**).



If you take the Lewis structure of the oxygen molecule at face value, then it looks like all the bonding electrons are arranged in pairs, and there is a double bond between the two oxygen atoms. However, the following video suggests otherwise.

Video content is not available in this format.
Paramagnetic properties of oxygen

Note: the term paramagnetism won't be discussed in detail here, suffice to say this is a weak form of magnetism as opposed to the effect you experience in magnetic materials made of iron, or rare-earth elements for example.

- What were your observations of the behaviour of liquid oxygen in a magnetic field?
- Liquid oxygen was attracted to the poles of the magnet (in contrast to liquid nitrogen which passed straight through).

Without going into details here, the implication of the above result is that the oxygen molecule contains one or more unpaired electrons.

The Lewis structure indicates all electrons are paired, so clearly is not an adequate representation of the bonding in O_2.

So although they are very useful (in fact later in this course you will see how drawing a Lewis structure is the basis for predicting the shape of molecules) and routinely used, chemists often have to use more sophisticated theories to provide a more detailed and refined picture of the bonding in molecules.

In the next session you will start to look at the principles underpinning reactions and the reactivity of substances.

4 This session's quiz

Now it's time to complete the Week 4 badge quiz. It is similar to previous quizzes, but this time instead of answering 5 questions there will be 15.

Session 4 quiz

Remember, this quiz counts towards your badge. If you're not successful the first time, you can attempt the quiz again in 24 hours.

Open the quiz in a new window or tab, then return here when you have done it.

Summary of session 4

1. In Lewis structures, each covalent bond is represented by a shared electron pair. Double bonds require two shared pairs; a triple bond requires three. These allocations often leave some atoms with non-bonded electron pairs.
2. Generally this operation provides each atom with a noble gas shell structure, especially if dative bonds in which both electrons are contributed by one atom are introduced. But in some cases, such as PF_5, it does not.
3. Sometimes the bond lengths in a molecule are such that it cannot be represented by a single Lewis structure or structural formula. It is better described as a resonance hybrid-an average or superposition of two or more structural formulae called 'resonance structures'.

You are now half way through the course. The Open University would really appreciate your feedback and suggestions for future improvement in our optional end-of-course survey, which you will also have an opportunity to complete at the end of Week 8. Participation will be completely confidential and we will not pass on your details to others.

Session 5: Chemical reactions

Introduction

At the heart of chemistry is the chemical reaction, the transformation of one type of matter into another – a chemical change.

The ancient alchemists were obsessed with the transformation of base metals into gold, and the synthesis of an elixir of immortality. Today chemists carry out reactions, less rooted in the realms of fantasy to produce useful substances such as new drugs, electronic materials and fabrics.

So far in this course you have seen a number of examples of how chemists convert one substance to another.

In this session you will be looking at several facets of reactions and reactivity, and meet another example of the chemist's language, the chemical equation. Finally, building on what you already know about molecular structure you will look at how reactivity is focussed at particular parts of molecules.

To set this topic in context a running theme will be the chemistry of what you might consider to be the archetypal reactive chemicals – explosives.

Learning Outcomes

After studying Session 5 you should be able to:

- understand what is meant by a chemical reaction
- construct balanced chemical equations to represent reactions
- be aware that the reactivity of molecules is, generally speaking, focused at certain parts of a molecule.

1 Chemical reactions

A chemical reaction produces some sort of change in a substance.

The substances you start out with are called **reactants** and the new substance or substances formed following reaction, are called **products**.

For example, a classic demonstration you might have seen at school is burning magnesium ribbon in air. The silvery strip of metal burns with an intense white flame to leave you with a powdery white solid, this is magnesium oxide.

All very impressive, but the point to remember is the physical and chemical properties of the product are very different from the material you started out with. For example, in addition to the obvious change in appearance; magnesium metal conducts electricity, magnesium oxide does not.

But what reaction is taking place?

The air in which the magnesium burns is a mixture of gases. (Table 1).

Table 1 The components of air

Substance	Content by volume
Nitrogen	78%
Oxygen	21%
Argon	0.9%
Carbon dioxide	0.03%
Other gases	0.003%
Water	variable

However the component of air that reacts with magnesium, is oxygen (in fact to be absolutely precise there will be some reaction with nitrogen too, but to keep things simple we will ignore this).

If you were to carry this reaction out in a sealed container with exactly the right amount of oxygen present to react with the amount of magnesium used, then there would be no oxygen left over afterwards. In other words you would get complete conversion to magnesium oxide.

In fact this is telling you what chemical reactions are all about.

Chemical reactions simply involve the rearrangement of atoms, in this case magnesium atoms are combining with oxygen atoms, to form magnesium cations and oxide anions, which form an ionic solid, magnesium oxide (note the link with your study of chemical compounds in Session 2).

This means there is no change in the total mass from that present before reaction – this is the **Law of conservation of mass** which is the cornerstone of any chemical reaction.

The mass of reactant(s) you start with must equal the mass of product(s) you end up with.

1.1 Chemical reactions – a first-hand experience

This is an account from around 150 years ago when American chemist Ira Remsen discovered, in no uncertain terms, what chemical substances combining to form new substances – a chemical reaction – can mean in practice.

> *While reading a textbook of chemistry, I came upon the statement, nitric acid acts upon copper, and I was determined to see what this meant. Having located some nitric acid, I had only to learn what the words act upon meant. In the interests of knowledge, I was even willing to sacrifice one of the few copper*

> *cents then in my possession. I put one of them on the table, opened the bottle marked “nitric acid”, poured some of the liquid on the copper, and I prepared to make an observation. But what was this wonderful thing which I beheld? The cent was already changed, and it was no small change either. A greenish-yellow liquid formed and fumed over the cent on the table. The air became coloured dark-red. How could I stop this? I tried by picking up the cent and throwing it out of the window. I learned another fact: nitric acid acts on fingers. The pain led to another unpremeditated experiment. I drew my hands across my trousers and discovered nitric acid acts on trousers. This was the most impressive experiment I have ever performed. I tell of it even now with interest. It was a revelation to me. Plainly the only way to learn about such remarkable kinds of action is to see the results, to experiment, to work in a laboratory.*

Chemists represent reactions by writing equations, and for Ira Remsen’s reaction this is as follows:

(5.1)

At first sight this may appear unintelligible, something akin to a foreign language, and that is essentially what it is. A chemical equation is written in a different language from that used for everyday communication. However the basic tools to enable you to unravel equations such as these are covered in Section 2.

2 Chemical equations

Chemical equations are representations of chemical reactions.

At this point you do have some experience of the use of numbers and symbols to represent elements and compounds (chemical formulas), chemical equations use these as a starting point.

Let's begin by writing an equation for a simple reaction, one which is crucial to our everyday lives; the combustion of natural gas in air. Natural gas is almost pure methane whose molecules are made up of carbon and hydrogen atoms (i.e. it is hydrocarbon). And, methane burns in (reacts with) oxygen to yield the molecules carbon dioxide and water along with the production of heat.

In writing a chemical equation to represent this process, the first step is to identify the reactants and the products.

The reactants are written on the left and the products on the right to give, initially, a word 'equation':

> methane *and* oxygen *go to* carbon dioxide *and* water

Even this simple word equation carries a lot of useful information in a relatively concise form, but you can go further. You know already that a formula reveals much more about a particular substance than does a name.

The molecular formula of methane is CH_4.

■ What does the formula CH_4 tell you about the methane molecule?

□ CH_4 indicates that the methane molecule comprises one carbon atom and four hydrogen atoms.

So the next step is to replace the names of the compounds in the equation with appropriate formulas.

■ What other formulas do you need to write the equation for the combustion of methane?

□ You also need oxygen O_2, and carbon dioxide CO_2 and water H_2O.

So now you could write:

The word *and* can be replaced by the plus sign, +, and the reaction representation becomes:

Even at this early stage of development of the equation, there is useful information about the chemistry going on.

■ What has happened to the hydrogen atoms in the methane molecule?

□ Hydrogen atoms of the methane molecules in the reaction end up as part of the product water molecules

■ What has happened to the carbon atom in methane?

□ The carbon atoms end up as part of the product carbon dioxide molecules.

It is important to note that the relationship provides information about the overall reaction. It does not say anything about how the reaction actually occurs, such as the way in which bonds are broken and formed to give the final products. Essentially it provides a summary of the reaction.

2.1 Balancing the equation

In writing an equation for the combustion of methane, the formulas of the reactants and products are now in place.

Can you see a problem with the equation?

On the left, there is one molecule of methane with four hydrogen atoms. Hydrogen appears on the right of the equation in the water molecule but the one water molecule contains just two hydrogen atoms. There are different numbers of oxygen atoms on each side: two on the left and three on the right.

So in going from the left to the right, there is a change in the numbers of atoms.

This can’t happen.

Recall, the Law of Conservation of Mass says that mass is neither lost nor gained in chemical reactions – the total mass of products at the end of a reaction is identical to the total mass of reactants at the beginning. Reactions are all about rearranging atoms on going from reactants to products.

When writing an equation this law must be accommodated– the equation must be *balanced*.

To write a balanced equation, the relative number ofeach of the formula units that is required is written immediately in front of that formula in the equation:

(5.2)

To represent two water molecules, the number 2 is placed immediately before the formula for water. This number indicates there is two of everything that comes after the number. So above there are two water molecules, i.e. two H_2O units. Where a number is not shown (such as in front of CH_4), you should assume (as with formulas) that a number 1 is implied.

Now a final check on the numbers of atoms: on the left (before the *go to*), there are 4 hydrogen atoms, 4 oxygen atoms and 1 carbon atom.

On the right, there are 4 hydrogen atoms, 4 oxygen atoms and 1 carbon atom.

There is a balance in the numbers of atoms of each type on each side – which is as it should be.

Finally, the words ‘go to’ can be replaced with an equals sign to give:

(5.2)

The equals sign indicates that the representation is a balanced chemical equation. This is why the words *go to* were retained earlier because, at that point, the reaction representation was not balanced. Note, instead of an equals sign you will often find an arrow (à) used.

It’s also important to realise that you cannot balance equations by changing chemical formulas. For example, methane molecules always contain one carbon atom and four hydrogen atoms, CH_4. It is only the relative numbers of formula units in the equation that are changed in the balancing process.

An additional piece of information that is often included in chemical equations is an indication of the physical states of the species.

Gas is represented by (g) coming immediately after the species, (l) represents liquid and (s) solid. These are called state symbols. You'll also frequently come across (aq) short for aqueous – this is used to indicate species that are dissolved in water.

At 25 °C, methane, oxygen and carbon dioxide are gases and water is a liquid.

So following all these steps, you end up with the following balanced chemical equation:

(5.3)

2.2 Some further examples of chemical equations

In this section you will get some practice constructing chemical equations.

■ If you watched the 'trailer' for this module, you will have seen a young chemist combining hydrogen (H_2) and oxygen (O_2) to form water (with a bang!). Write a balanced chemical equation for this reaction.

□ (5.3)

Next, a chemical equation to represent a reaction on which our very existence depends.

The reaction of the simple sugar glucose is vital to the generation of energy within the body. Glucose has a complicated molecular structure but it can be represented by the formula $C_6 H_{12}O_6$.

■ The chemical equation for the reaction between glucose and oxygen to give carbon dioxide and water is:

(5.4)

Show that this equation is balanced.

□ On the left of the equation, there are 6 carbon atoms, 12 hydrogen atoms and 6 oxygen atoms from glucose and a further 12 oxygen atoms from oxygen molecules, a total of 6C, 12H and 18O. On the right, there are 6 carbon and 12 oxygen atoms from carbon dioxide plus 12 hydrogen atoms and 6 oxygen atoms from water, a total of 6C, 12H and 18O. This is a balanced chemical equation. And, as ever, the atoms have simply been rearranged in the reaction.

So, up to this point, you have seen how a balanced chemical equation can encompass a lot of information about a reaction.

It not only identifies the reactants and products and their respective formulas but also indicates the relative numbers of each reactant molecule and the relative numbers of each product molecule. It also shows, in the example above, that carbon from the glucose molecules ends up in carbon dioxide molecules, the hydrogen produces water and the oxygen in the product molecules comes both from the glucose molecules and from molecular oxygen.

Now for some more practice.

■ Write balanced equations for the reactions represented in (a)–(d).

$FeO + H_2$ *go to* $Fe + H_2O$

$Fe_2O_3 + H_2$ *go to* $Fe + H_2O$

$CH_4 + Cl_2$ *go to* $CH_2Cl_2 + HCl$

☐ The balanced equations are as follows.

$FeO + H_2 = Fe + H_2O$ (5.5)

$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O$ (5.6)

$N_2 + 3H_2 = 2NH_3$ (5.7)

$CH_4 + 2Cl_2 = CH_2Cl_2 + 2HCl$ (5.8)

As promised in the introduction, in this part of the module you will be making a few excursions into the word of explosive materials and looking at the chemical reactions involved. Your starting point, in the next section is gunpowder.

3 Gunpowder – the explosive reaction of charcoal, sulfur and potassium nitrate

An explosive is a material that releases large quantities of hot gas extremely rapidly, and very violently.

Indeed, the following quote is attributed to Roger Bacon (Figure 1), a Franciscan monk who introduced gunpowder (also known as blackpowder) to Europe in the 13th century:

> ‘By the flash and combustion of fires, and by the horror of sounds, wonders can be wrought, and at any distance that we wish, so that a man can hardly protect himself or endure it.’

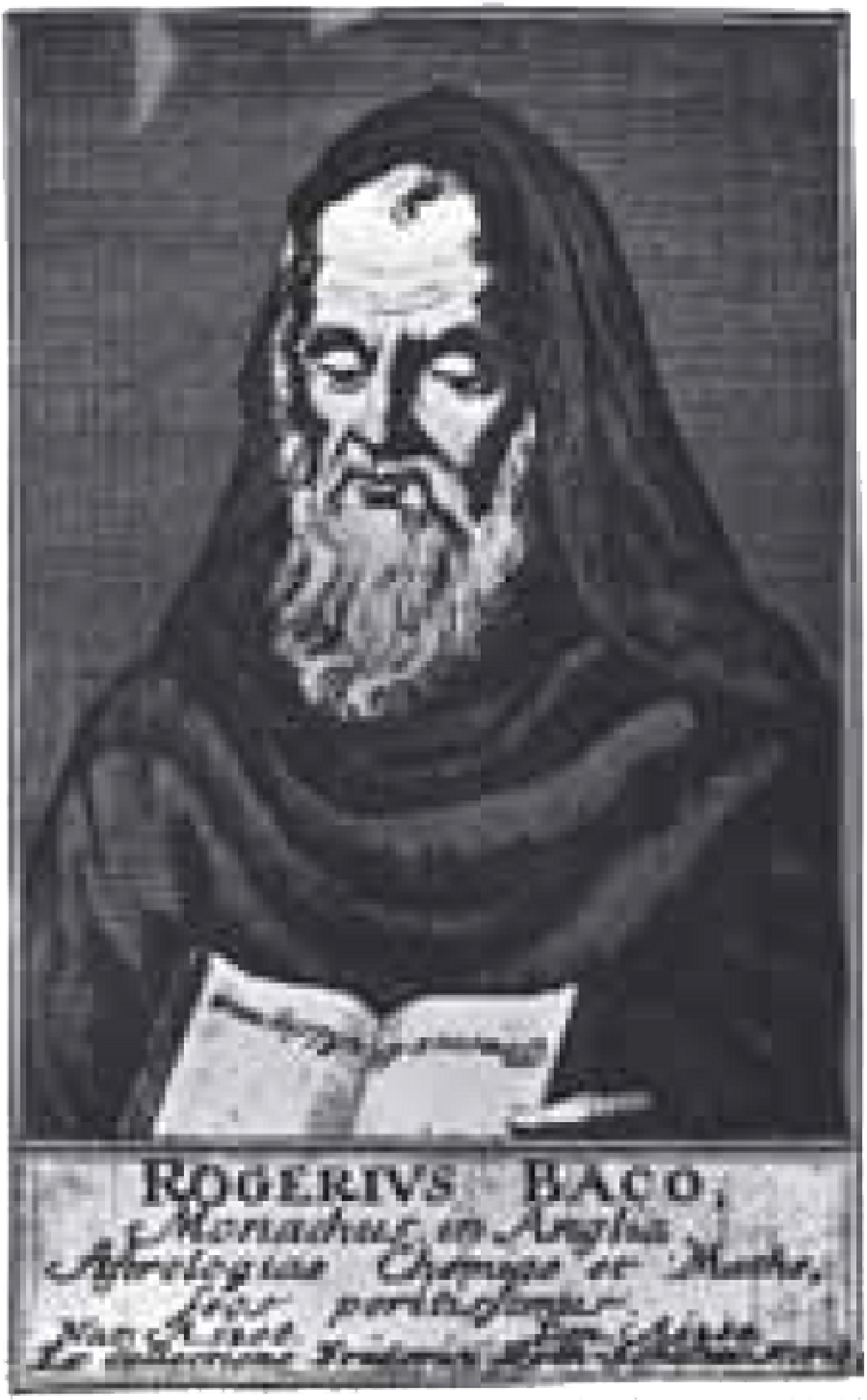


Figure 1 Roger Bacon

Gunpowder consists of sulfur and charcoal (fuels), mixed with potassium nitrate (an oxidiser – a type of chemical which a fuel requires in order to burn).

The basic mixture was, in fact, originally discovered by eighth century Chinese alchemists. However, Bacon experimented with the relative proportions and undertook a detailed scholarly investigation into the explosive. As a consequence he incurred the wrath of the Church, and suffered long term imprisonment for his efforts. However he did manage to preserve his recipe for blackpowder in the form of an anagram (Figure 2).

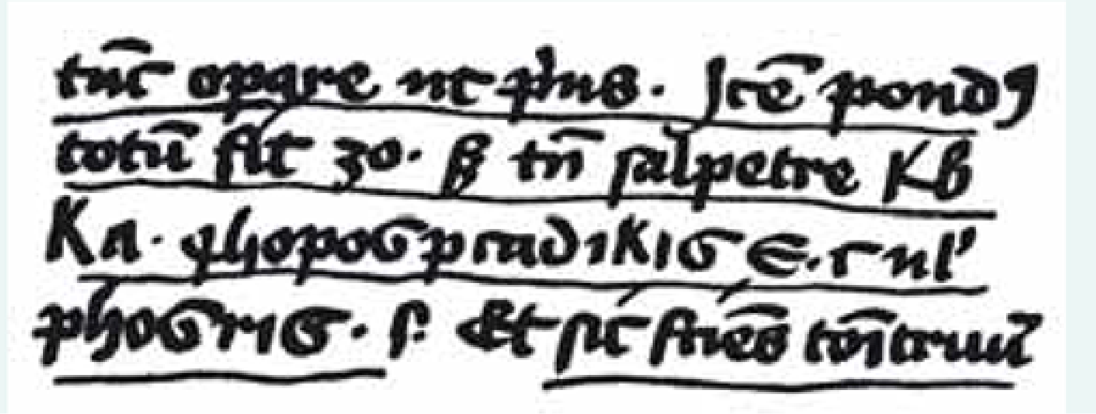


Figure 2 Bacon's anagram for the composition of gunpowder

In fact on line two, you can make out the word ‘saltpetre’, the old fashioned name for potassium nitrate.

- A simplified (unbalanced) equation for the deflagration (a self-propagating burning surface reaction) of gunpowder is shown below – re-write this in balanced form.

  $KNO_3 + S + C = K_2S + CO_2 + N_2$ (5.9)

- $2KNO_3 + S + 3C = K_2S + 3CO_2 + N_2$ (5.10)

4 Chemical equations involving ions

Many reactions involve charged species – ions.

The rules for balancing equations representing reactions involving ions are exactly the same as they are for the reactions of neutral species.

When the gas sulfur trioxide, SO_3, dissolves in water, hydrogen ions, H^+(hydrogen atoms that have lost an electron) and the sulfate anions, SO_4^{2-}, are produced. The sulfate anion comprises four oxygen atoms covalently bonded to a sulfur atom and the whole unit has two negative charges from two additional electrons represented by the superscript 2−.

The balanced chemical equation for the reaction is:

$SO_3\ (aq) + H_2O(l) = 2H^+(aq) + SO_4^{2-}\ (aq)$ (5.11)

There are equal numbers of atoms of each type on both sides of the equation: 1 sulfur, 4 oxygen and 2 hydrogen atoms.

For **ionic equations** such as this, there is one more test that must be applied to ensure the equation *really is* balanced: the total charge on each side of the equation must be the same.

In this case, there are only uncharged species on the left.

On the right, there are two hydrogen ions each with a single positive charge and a sulfate anion with a double negative charge.

So the total charge on the right is 2 − 2 = 0.

And the total charge on each side is zero.

To be clear, the total charge on each side of an ionic equation doesn’t have to be zero; it is just that it must be the *same* on each side.

So, at this point you are equipped with the tools required to communicate information about chemical reactions in the everyday language of the chemist. In the next section you will look further at reactions themselves, and the properties of molecules which impact on their reactions.

5 Reactivity of molecules

Reactivity is not spread evenly over a molecule; it tends to be concentrated at particular sites within its structure.

The consequences of this idea are particularly apparent in the chemistry of carbon and its compounds (known as organic chemistry), and has proved so valuable that it receives specific recognition through the concept of the **functional group**.

5.1 Functional groups and reactivity

Structure 5.1 is an abbreviated structural formula for hexan-1-ol, an alcohol. As mentioned earlier, don't worry about the naming of the compounds at this point.

CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—OH 5.1

The functional group here is the **—**OH fragment of the molecule, often referred to as 'the alcohol group'.

The reactivity of this molecule is concentrated at the —OH site; and it is possible through an informed choice of other chemical reactants, to change that site (and sometimes the atoms immediately adjacent to it) into something else *while leaving the rest of the molecule unchanged.*

For example, the liquid thionyl chloride, $SOCl_2$, will convert hexan-1-ol into 1-chlorohexane:

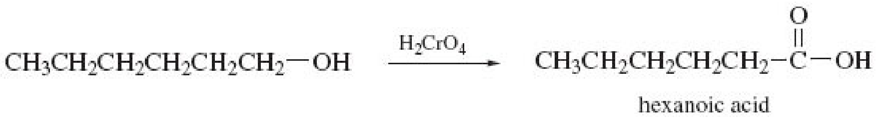
5.12

(5.12)

(Note that in the formulas in this equation all the bonds apart from the ones connecting the functional groups to the rest of the molecule have been omitted; these are known as ***condensed structural formulae***.)

- ■ What has happened to the —OH group in this reaction?
- □ The —OH group has been replaced by —Cl.

An example of a change in both the functional group *and* its adjacent atoms is the reaction of hexan-1-ol with chromic acid, H_2CrO_4, which yields hexanoic acid:



$$CH_3CH_2CH_2CH_2CH_2CH_2{-}OH \xrightarrow{H_2CrO_4} CH_3CH_2CH_2CH_2CH_2{-}\overset{\overset{\Large O}{\|}}{C}{-}OH \qquad (5.13)$$

hexanoic acid

Here, the —CH_2OH fragment of the original molecule has been converted into —COOH. So this molecule now has a different functional group. This is now the carboxylic acid functional group.

- ■ What bond types are contained within the carboxylic acid functional group?
- □ Note, in addition to a single bond attaching it to the chain of five carbon atoms, there is one carbon oxygen double bond, and a single bond to an –OH group.

Now look again at the reaction equation.

Note that an arrow has been used, rather than an equals sign.

This type of equation allows you to concentrate attention on the way in which one molecular fragment, in this case—CH_2OH, is transformed into another, —COOH.

Organic chemists often write equations of this sort, the reagent that brings about the change is written above the arrow.

■ Based on what you've seen so far, organic molecules can be divided into three parts – what are these?

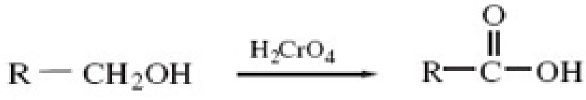
□ (i) functional groups, (ii) the immediate environment of the functional group, and (iii) the rest of the molecule.

To a first approximation, the functional group and its immediate environment would be expected to respond to a reactant in exactly the same way whatever the rest of the molecule is like.

Thus, if you write the many molecules containing an alcohol functional group as R—OH, the general form of Reaction 5.12 becomes:

$$\text{R—OH} \xrightarrow{SOCl_2} \text{R—Cl} \qquad (5.14)$$

Likewise, if we write the many molecules that terminate in the unit —CH_2OH as R—CH_2OH, then the general form of Reaction 5.13 becomes:



$$\text{R}-CH_2OH \xrightarrow{H_2CrO_4} \text{R}-\overset{\overset{\displaystyle O}{\|}}{C}-OH \qquad (5.15)$$

In principle therefore, Reactions 5.14 and 5.15 allow us to predict the response of many very different molecules to thionyl chloride and chromic acid.

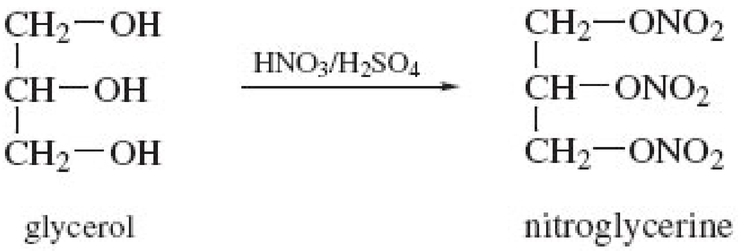
6 The reaction of alcohols with nitric acid – more explosives

As you saw in the last section, to a first approximation, the behaviour of organic functional groups is unaffected by the larger environment of the molecules in which those groups are set. A good example is the reaction of some alcohols with nitric acid, HNO_3 (or $HONO_2$), to give so-called nitrate esters (once again focus on the principles being discussed and don't worry about the names of the compounds):

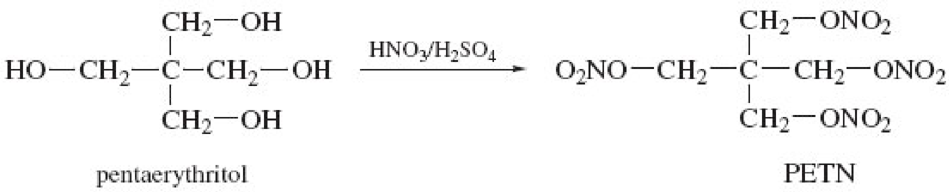
(5.16)

Thus, hexan-1-ol (Structure **5.1**) yields hexyl nitrate, $CH_3CH_2CH_2CH_2CH_2CH_2—O—NO_2$.

Two organic molecules that contain more than one alcohol functional group are glycerol (Reaction 5.17), made by heating natural fats or oils with sodium hydroxide, and pentaerythritol (Reaction 5.18).



$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} \xrightarrow{HNO_3/H_2SO_4} \begin{array}{l} CH_2-ONO_2 \\ | \\ CH-ONO_2 \\ | \\ CH_2-ONO_2 \end{array} \quad (5.17)$$



$$HO-CH_2-\overset{\overset{\displaystyle CH_2-OH}{|}}{\underset{\underset{\displaystyle CH_2-OH}{|}}{C}}-CH_2-OH \xrightarrow{HNO_3/H_2SO_4} O_2NO-CH_2-\overset{\overset{\displaystyle CH_2-ONO_2}{|}}{\underset{\underset{\displaystyle CH_2-ONO_2}{|}}{C}}-CH_2-ONO_2 \quad (5.18)$$

These reactions show how a mixture of concentrated nitric and sulfuric acid replaces all of the —OH groups with $—O—NO_2$ groups, leaving the rest of the molecules unchanged. Thus reinforcing the point made earlier, that reactivity tends to be concentrated at specific sites in a molecule.

Finally, consider cotton, whose fibres consist of the polymer cellulose – a polymer being a very large molecule made up of many repeated building blocks.

Cellulose is made of glucose molecules linked via oxygen atoms to form long chains. Two molecules joined this way are shown in brackets on the left hand side of Figure 3 and this unit repeats many times. The linking together of these groupings into long chains is indicated by *n,* the value of which varies, but may be as large as 2000.

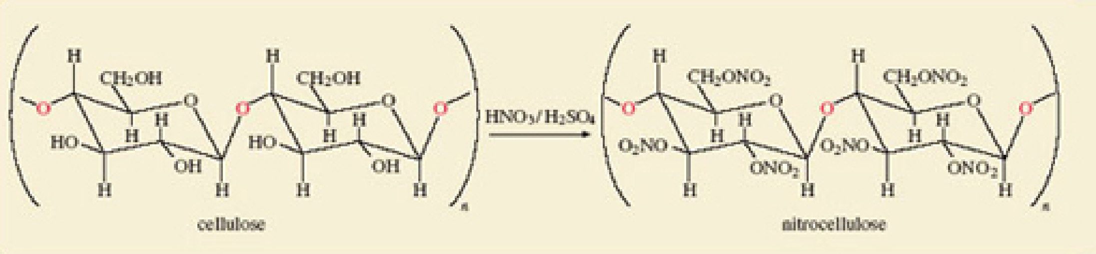


Figure 3 The nitration of cotton

Figure 3 shows that despite this polymeric situation, all of the —OH groups can still be replaced by —O—NO_2 groups through a reaction with mixed nitric and sulfuric acids.

The products of Reactions 5.17, 5.18 and Figure 3 are called nitroglycerine, pentaerythritol tetranitrate (PETN) and nitrocellulose (also known as guncotton), respectively. They are three important explosives, and the synthesis of each serves to illustrate the reactivity of functional groups relative to the rest of the reactant molecule.

Alfred Nobel (1833-1896) made his fortune through the manufacture of high explosives. Nobel appears here at the controls of the equipment that he invented for the manufacture of nitroglycerine. As shown in Figure 4, the dangerous nature of the work is revealed by the one-legged stool on which he sits. It protects the operator from the mortal dangers of falling asleep on the job!

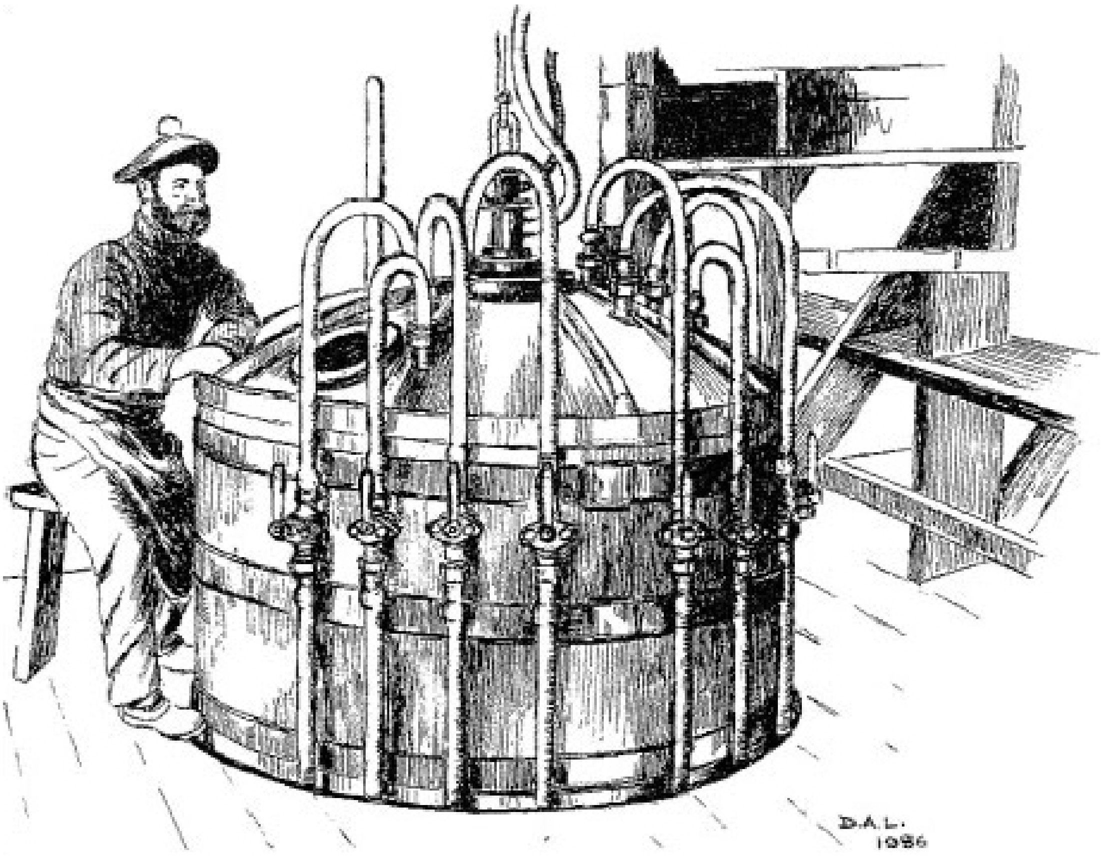


Figure 4 Nitroglycerine manufacture – a hazardous job!

But what makes functional groups such as —OH so much more reactive than the carbon-hydrogen skeleton to which they are attached? This is considered in the final section.

7 A closer look at functional groups

In order to probe further the enhanced reactivity of functional groups, take a look again at Structure **5.1** (hexan-1-ol).

$\mathbf{CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—OH}$ 5.1

- ■ Which of the 21 atoms in hexan-1-ol have non-bonded electron pairs?
- □ Only one; the oxygen atom of the functional group has two non-bonded electron pairs.

Chemical reactions often occur in steps; in each step, groups of atoms attach themselves to the molecule, undergo change, and then depart. Attractive points of attachment in a molecule will therefore make a reaction more likely.

- ■ Why are non-bonded electron pairs possible points of attachment?
- □ They allow formation of dative bonds.

Such bonds cannot be formed by carbon and hydrogen atoms in hexan-1-ol, because all their outer electrons are used to form strong C—H and C—C bonds. This, then, is one reason why the —OH functional group in **5.1** is the most probable site for a reaction.

Another arises from the fact that functional groups often introduce electronegativity differences into an organic system.

- ■ What is meant by electronegativity?
- □ This is the ability of an atom in a bond to attract bonding electrons towards itself.

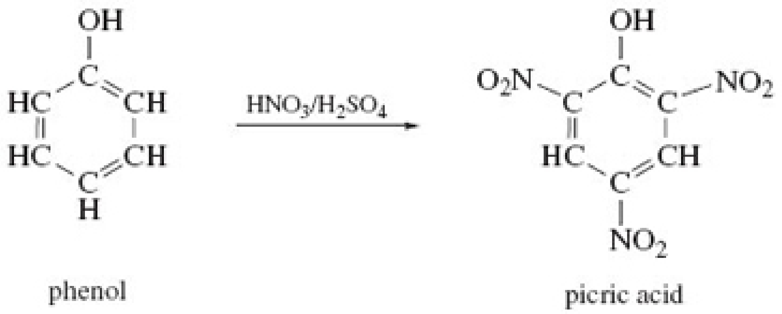
For example, the oxygen atom is very electronegative.

Thus, in the C—O—H sequence of bonds in any alcohol, the oxygen atom attracts electrons from the adjacent carbon and hydrogen atoms (carbon and hydrogen have similar electronegativities). The oxygen atom of an alcohol therefore carries a fractional negative charge, and the carbon and hydrogen atoms carry fractional positive charges. Any one of the three atoms then becomes a possible point of attachment for the atom of a reagent that carries a fractional charge of opposite sign.

Finally, a reminder of a reservation made earlier about functional groups: the idea that their reactions are unaffected by the rest of the molecule is only an approximation.

This can be conveniently illustrated with reference to another powerful explosive.

Consider reaction 5.19.



(5.9)

In phenol, on the left of Reaction 5.19, an —OH group is attached to a benzene ring. Here if you react it with a mixture of concentrated nitric and sulfuric acid, in complete contrast to the examples you looked at earlier, the —OH group is untouched, and hydrogen atoms at three points on the benzene ring are replaced by the nitro group, $—NO_2$.

The product is a yellow crystalline solid known as 2, 4, 6-trinitrophenol or picric acid, whose explosive power exceeds that of TNT.

Clearly expectations about the nitration of —OH functional groups were worked up from cases where the hydrocarbon skeleton is **saturated**; that is, all carbon valencies in the skeleton are used to form *single* bonds to either hydrogen or other carbon atoms. Evidently, the benzene ring, which is not saturated, enhances the reactivity of the hydrogen atoms attached to it, and simultaneously diminishes that of the attached —OH group. So the behaviour of a functional group can in actual fact be affected by its immediate environment.

In the next session you will be developing some ideas around molecular shape you met earlier, and finding out how the arrangement of atoms in three dimensions plays a key role in understanding chemical reactions.

8 This session’s quiz

Check what you’ve learned by taking the end-of-session quiz.

Session 5 quiz

Open the quiz in a new window or tab (by holding ctrl [or cmd on a Mac] when you click the link), then return here when you have done it.

Summary of session 5

- In a chemical reaction, the total mass of the reactants equals the total mass of the products.
- Balanced chemical equations are used to concisely represent chemical reactions.
- The structural formulas of organic molecules can be divided into the carbon-hydrogen framework or skeleton, and the functional group(s). In the first approximation, the functional groups are the sites where reaction occurs, the framework remaining unreactive.
- The above approximation works best when the framework consists of saturated carbon atoms.

Session 6: Exploring the shapes of molecules

Introduction

You have looked at the structural formulas of a number of molecules so far in this course. For example, Figure 1 is a structural formula for hexan-1-ol, which shows you the immediate neighbours of any particular atom. It is a simply a two-dimensional drawing. But in studying the structures obtained by the technique of X-ray crystallography, it can be shown that the atoms in a substance have a definite three-dimensional arrangement in space.

$\mathbf{CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—OH}$

Figure 1 The structural formula for hexan-1-ol

An understanding of the shapes of molecules is often the key to an understanding of chemical reactions, and this is the main focus of your study in this session.

Learning Outcomes

After studying Session 6 you should be able to:

- appreciate the link between molecular shape and chemical reactivity
- understand what steric effects are
- predict the shapes of simple molecules.

1 Molecular shape affects molecular reactivity

To start your exploration of the effect of the shape of molecules on how they react, let us start with two simple examples: methane, CH_4, and bromomethane, CH_3Br.

In both cases, the carbon atoms form four single bonds and it turns out that these are directed towards the corners of a tetrahedron (you will see why this is later).

The resulting molecular shapes are shown in Figure 2 as ball-and-stick representations. The grey sphere is the carbon atom, the white spheres represent the hydrogen atoms and the red sphere is bromine.

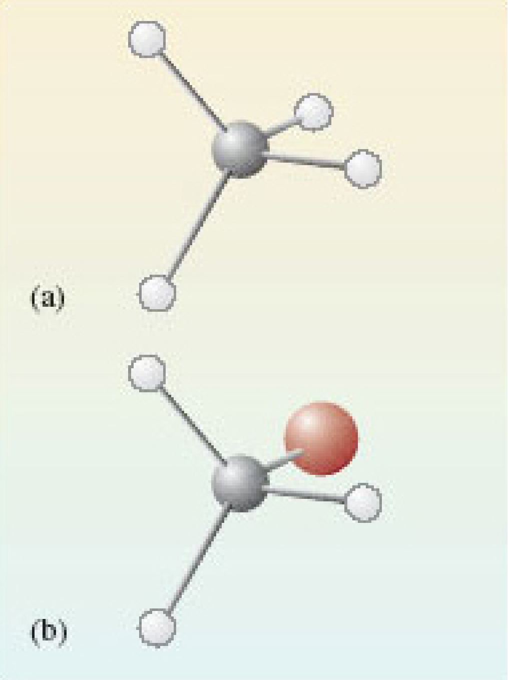


Figure 2 The structures of (a) methane, CH_4; (b) bromomethane, CH_3Br

- If you take bromomethane (Figure 2b) and successively replace each hydrogen atom by a methyl group, CH_3, what are the formulas of the resulting molecules?
- ☐ CH_3CH_2Br, $(CH_3)_2CHBr$ and $(CH_3)_3CBr$.

Ball-and-stick representations of each of these molecules are shown at the top of Figure 3. Again at each carbon atom, there are four bonds directed towards the corners of a tetrahedron, and the complexity of the molecular shape increases from left to right, in line with an increase in the number of carbon atoms.

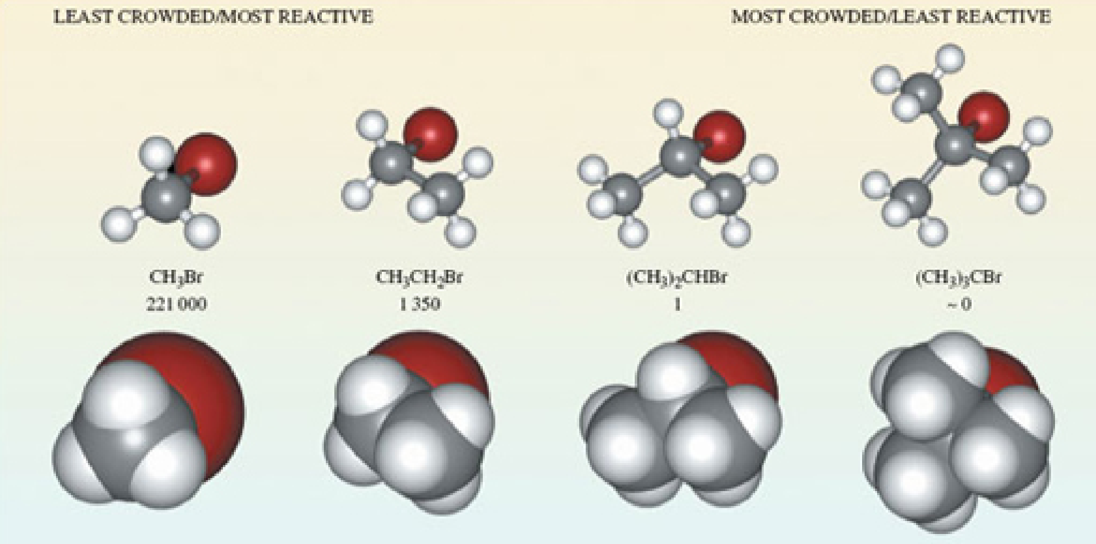


Figure 3 The molecules (a) bromomethane, CH_3Br; (b) bromoethane, CH_3CH_2Br; (c) 2-

bromopropane, $(CH_3)_2CHBr$; (d) 2-bromo-2-methylpropane, $(CH_3)_3CBr$, shown in both ball-and-stick (top) and space-filling representations (bottom)

Ball-and-stick representations are a natural three-dimensional development of structural formulae, and they show the disposition of the atoms in space. But by emphasising the bonds, they fail to reveal the subtleties of the molecular shape created by the different sizes of atoms. In this respect, so-called **space-filling** models are better. These appear at the bottom of Figure 3. In each case, the viewing direction is the same as the ball-and-stick model above.

Note: also shown in Figure 3 are the relative rates of reaction of the four compounds when they are treated with lithium iodide in acetone (propanone) solution – you will be looking at this in the next section.

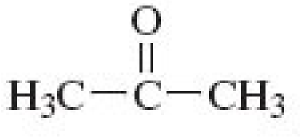
1.1 Reactivity of R-Br

Now consider a reaction of the four molecules shown in Figure 3.

- ■ Identify the functional group common to these molecules.
- □ —Br (known as the bromo group).

So the molecules are of the general type, RBr, where R is the framework to which the functional group is attached.

When such bromo compounds are treated with a solution of lithium iodide (LiI) in the solvent propanone (acetone, Structure **6.1**), they often undergo a reaction in which the bromo group is replaced by an iodo group (equation 1)



$H_3C-C(=O)-CH_3$

6.1

RBr + I^- = RI + Br^- (1)

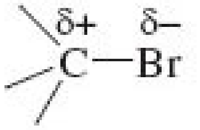
- ■ What is the role of lithium iodide in the reaction?
- □ It is a source of I^- ions.

What happens in this reaction at the molecular level?

As Figure 2 shows, the reactant R—Br contains a carbon-bromine bond, C—Br.

This bond is polar.

- ■ Why is the R-Br bond polar? (*Hint*: think back to what you know about electronegativity)
- □ Bromine is more electronegative than carbon, so the carbon atom in this bond carries a partial positive charge, written δ+, and the bromine atom a partial negative charge, written δ− (Structure **6.2**).



6.2

Given the polarity of the bond, the negatively charged iodide ion will then tend to approach, and become attached to, the positive carbon. As a carbon-iodine bond is formed, the carbon-bromine bond breaks and a bromide ion is ejected. The reaction is therefore a good illustration of an important point made in Session 5; electronegativity differences often contribute to the reactivity of functional groups.

What is interesting however, is that in this case, the four bromo compounds react at very different speeds.

- ■ Figure 3 gives the relative rates of reaction of the four bromo compounds with iodide, what does this tell you?
- □ The rate of reaction decreases from left to right. For example, CH_3Br reacts 221 000 times as quickly as $(CH_3)_2CHBr$, and the reaction of $(CH_3)_3CBr$ is so slow that it appears not to take place at all.

In order to find a reasonable explanation for this, take another look at the space-filling depiction of these molecules in Figure 2.

The reaction involves an iodide ion approaching and attaching to the carbon atom that is bound to the bromine atom.

Logically there must be room for this to happen.

There is most room for such an approach on the side of the carbon atom that is opposite to the bulky bromine atom – in other words, according to the direction of view depicted in Figure 3.

- ■ Why do you think the reaction with iodide should be easier for CH_3Br than for $(CH_3)_3CBr$?
- □ In CH_3Br, the carbon atom is very exposed to the incoming iodide, because hydrogen atoms are small. But if they are replaced by bulkier methyl groups, this exposure diminishes, until at $(CH_3)_3CBr$ the carbon atom attached to bromine lies at the bottom of a small cavity created by the three surrounding methyl groups. The iodide cannot reach this carbon atom, so effectively, no reaction occurs.

The “blocking” effect that an organic group produces by virtue of its bulk is described as **steric or steric hindrance**. This chosen example is a crude one, but it illustrates an important idea.

In the next section you will see how these same ideas can be extended to more complex molecules.

2 Steric effects in enzymes

Enzymes are protein molecules that facilitate vital biological reactions.

They can do this because their molecular surfaces contain ***active sites*** to which the molecules participating in the reaction (known as ***substrates***) can become temporarily bound.

The active sites are crevices in the enzyme surface, often of a complicated shape. The substrate has the precise shape required to fit the opening, and potential competitors that lack this shape are excluded (Figure 4). The need for the substrate to bind to the enzyme surface will often weaken other bonds within the substrate itself, encouraging the changes that the enzyme facilitates.

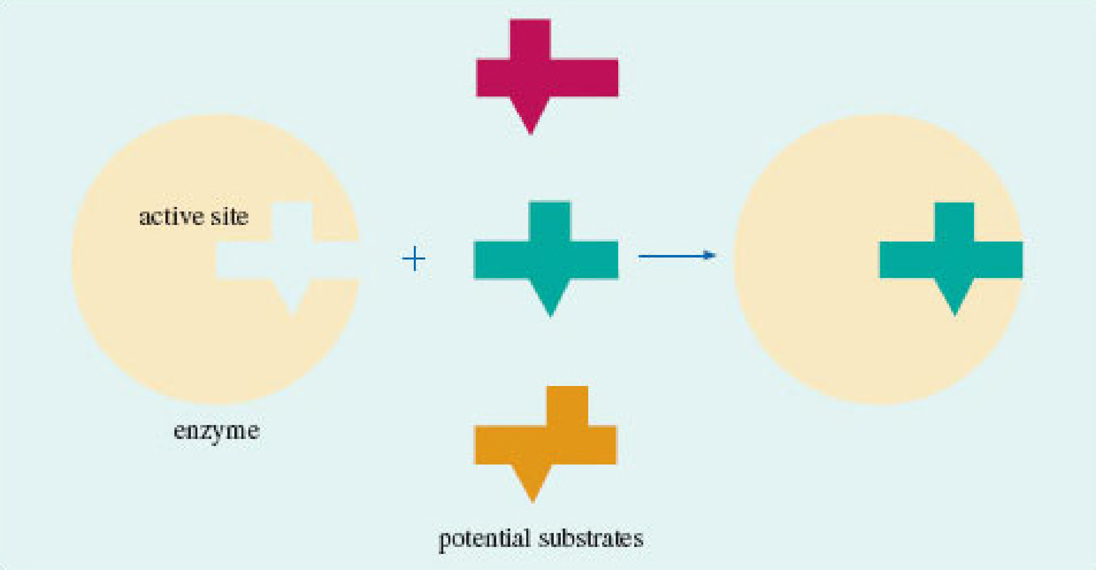


Figure 4 A model for enzyme action: only one of the three molecules has the shape required to fit the cavity on the enzyme surface; the other two are excluded

3 The shapes of some molecules

Let’s now look at the shapes of some simple molecules.

Again consider methane, CH_4 (Figure 5)

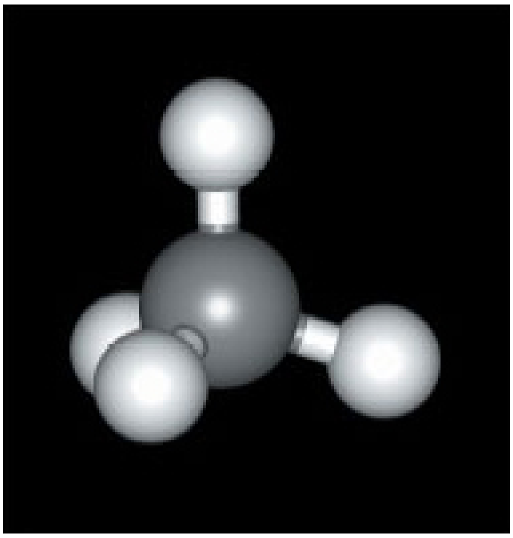


Figure 5 A ball and stick model of methane (CH_4)

As an alternative, methane can be represented using so-called '**flying-wedge notation**', which is one way of addressing the challenge of representing three-dimensional shapes in two-dimensions either on-screen or on paper.

A flying-wedge representation of the methane molecule is shown in Figure 6.

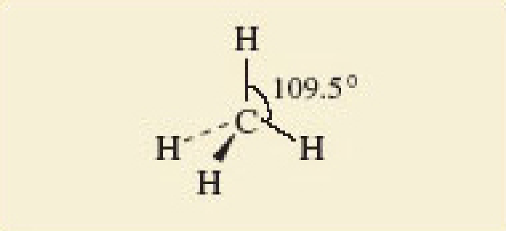


Figure 6 A flying-wedge representation of methane

The atom at the pointed or thin end of the wedge is assumed to be in the plane of the paper, and the atom at the thick end is in front of the plane (this is sticking out towards you). A continuous line (—) joins two atoms that both lie in the plane of the paper. A dashed line (- -) joins together two atoms, one of which is in the plane of the paper, whereas the other is behind it (pointing away from you).

Look back at the ball and stick representation (Figure 5) and compare the two.

You will be seeing the flying wedge approach used to depict the shapes of other molecules in the sections that follow.

3.1 The shapes of some simple fluorides.

In this section you will be looking at the geometries adopted by some fluorides of several elements.

The examples you will be looking at are: BeF_2, BF_3, CF_4, PF_5, SF_6 and IF_7; their shapes, which have been experimentally determined, are shown in Figure 7.

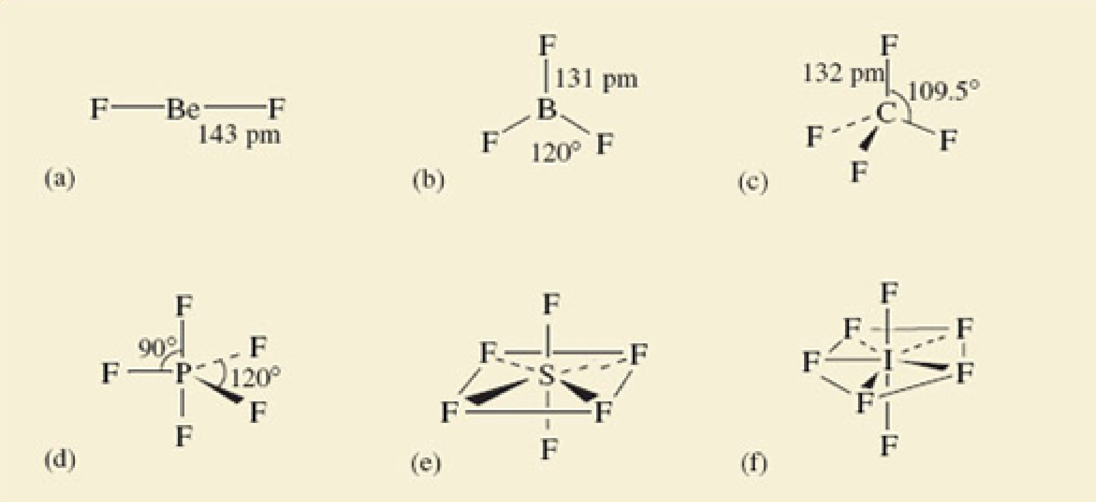


Figure 7 The shapes of some fluoride molecules: (a) BeF_2; (b) BF_3; (c) CF_4; (d) PF_5; (e) SF_6; (f) IF_7 (Note the “flying wedge” notation is used here)

Beryllium difluoride (BeF_2) is a glassy non-molecular solid at room temperature, but the BeF_2 molecule (Figure 7a) is obtained when the solid is vaporised by heating it to 1 200 ° C. It is **linear**; that is, the sequence of atoms F—Be—F lies on a straight line. The spatial arrangement of the neighbouring atoms around a particular atom is said to be the **coordination** of that atom.

At 25 °C, BF_3, CF_4, PF_5, SF_6 and IF_7 are all gases containing molecules with the shapes shown in Figure 7b-f.

In BF_3, all four atoms lie in the same plane, the boron atom forming three B—F bonds to three fluorine atoms at the corners of an equilateral triangle This arrangement of fluorines around boron is called **trigonal planar**.

In CF_4 there is **tetrahedral coordination** of the four fluorine atoms around carbon. This is the situation which you have already met in the methane molecule.

The coordination in PF_5, SF_6 and IF_7 is a little more complicated and perhaps best described by starting with the horizontal planes containing the central atom of these molecules.

In PF_5, this plane contains three P—F bonds directed towards the corners of an equilateral triangle as in BF_3; in SF_6, it contains the sulfur atom with four surrounding fluorines at the corners of a square.

- What does the horizontal plane contain in IF_7?
- The iodine atom, and five I—F bonds directed towards five fluorine atoms at the corners of a regular pentagon.

In all three cases, the coordination is then completed by two other bonds to fluorine at 90° to those in the horizontal plane, one pointing up, and the other pointing down. These arrangements in PF_5, SF_6 and IF_7 are called **trigonal bipyramidal, octahedral** and **pentagonal bipyramidal**, respectively.

In the octahedral molecule SF_6, all the fluorine atoms are equivalent. From each of the fluorine atoms, the “view of the rest of the molecule” looks the same. But in PF_5 and IF_7, this is not so. There are two kinds of fluorine position: *equatorial positions* in the horizontal plane, and *axial positions* at right-angles to it. In Figure 8, these two kinds of position are labelled for the trigonal-bipyramidal arrangement in PF_5.

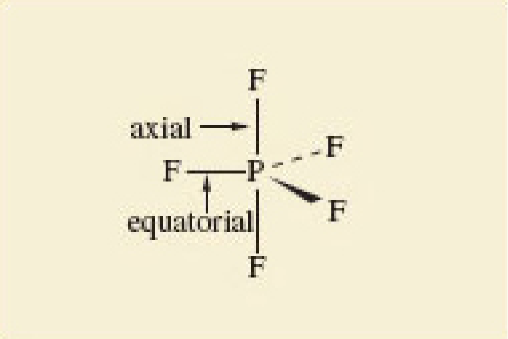


Figure 8 Axial and equatorial positions in PF_5

All this begs a rather obvious question, why do molecules adopt the shapes they do? This will be addressed in the next section.

3.2 Explaining molecular geometry?

To answer the question posed at the end of the last section,think about what you know about a chemical bond.

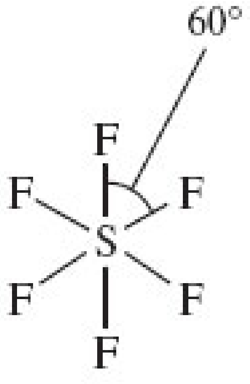
- In a single sentence describe a covalent bond.
- A shared pair of electrons holding together two atoms.

As bonds comprise negatively charged electrons, and two negatively charged objects will repel each other, logically you would expect bonds to repel each other.

As a result they adopt positions where they are as far apart in space as possible.

Consider now the molecule SF^6 – sulfur hexafluoride, a potent ‘greenhouse gas’.

Looking simply at its forumula, you *might* expect SF_6 would have the shape shown in Structure **6.3**. The sulfur atom has six S—F bonds directed towards the corners of a regular hexagon, and all seven atoms are in the same plane. However experiment shows this isn’t the case and the actual shape is the octahedral one shown in Figure 7e.



6.3

But, of course, you are aware of the nature of electrostatic repulsion so,

- Suggest why SF_6 is octahedral?
- The S—F bonds repel one another, so that they get as far apart in space as possible. In Structure **6.3**, they are confined to a single plane and the angle between them is only 60°. By adopting octahedral coordination, the greatest possible separation of the S—F bonds is achieved, the angle being increased to 90°.

All the shapes shown in Figure 7 conform to this principle by enforcing a good separation of the bonds in space. The principle looks even more reasonable if you recall that bonds comprise pairs of electrons; the like charges of these electron pairs lead to an expectation that one pair will repel another.

However, two very common molecules will soon dispel the notion that repulsion between bonding pairs of electrons is the *sole* determinant of molecular shape. These are water, H_2O, and ammonia, NH_3 and will be considered in the next section.

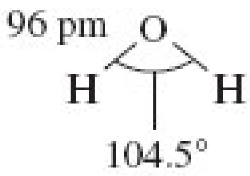
3.3 The geometry of the water and ammonia molecules

To start with apply the logic introduced in section 3.2, and think about *possible structures* for H_2O and NH_3.

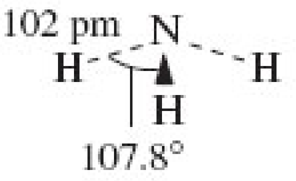
- What would be the shapes of the H_2O and NH_3 molecules *if* they were dictated *only* by bond-bond repulsions?
- The two O—H bonds of H_2O and the three N—H bonds of NH_3 would get as far apart as possible: H_2O would be linear like BeF_2, and NH_3 would be trigonal planar like BF_3 (see Figure 7).

The observed (experimentally determined) shapes are shown in Structures **6.4** and **6.5**.

H_2O is V-shaped and NH_3 is pyramidal. In both cases the inter-bond angle is much closer to the tetrahedral angle of 109.5° than to the *possible value* of 180° and 120°, respectively.



6.4



6.5

■ What is present in H_2O and NH_3 that might explain these differences?

□ In H_2O and NH_3, the O and N, carry non-bonded electron pairs.

You have previously looked at the Lewis structures for these molecules, and noted that in order to make up an octet of electrons around the central atoms you had ‘left over’ non-bonded electrons.

Specifically, for H_2O around the oxygen atom there are two bonding pairs of electrons and two non-bonded pairs. And in NH_3 there are three bonding pairs and one non-bonded pair.

Thus, both central atoms are surrounded by four pairs of electrons, and if these four pairs repel one another, they will be directed towards the corners of a tetrahedron like the four C—F bonds of CF_4 in Figure 7c. The resulting arrangements are shown in Figure 9, both consistent with the idea that the four pairs of electrons around the central atoms try to get as far apart as possible. The non-bonded pairs as well as the bonding pairs are involved in this repulsion

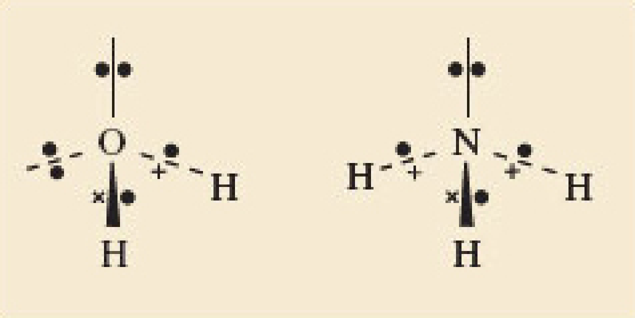


Figure 9 The shapes of the H_2O (left) and NH_3 (right) molecules

Overall the prediction is for a V-shaped H_2O and a pyramidal NH_3 molecule, with inter-bond angles close to the tetrahedral angle.

4 This session’s quiz

Check what you’ve learned by taking the end-of-session quiz.

Session 6 quiz

Open the quiz in a new window or tab (by holding ctrl [or cmd on a Mac] when you click the link), then return here when you have done it.

Summary of session 6

1. Molecules have a three-dimensional shape which plays a crucial role in the way it reacts.
2. Bulky irregularities in the shape of a molecule around a reactive site can exclude a potential reactant. Such effects are described as steric.
3. A sufficient refinement of the molecular shape in the region of the reactive site can make that site specific to just one particular reactant. Many enzymes operate in this way.
4. The shapes of simple molecules can be predicted by taking into account the repulsions between electron pairs surrounding a central atom.
5. So far you have seen there is a link between the shapes of molecules and chemical reactivity. Indeed this course concludes with a look in more detail at reactions in general. However to carry out a reaction in the laboratory it is important to mix reactants in the correct proportions, and this entails having some means of doing this on the basis of the number of atoms or molecules of the substances reacting. You will be exploring this requirement in more detail in the next session.

Session 7: Counting atoms and molecules

Introduction

Atoms are small, they have incredibly small masses. Therefore weighing them out, if you want to carry out a chemical reaction or analytical procedure is not realistic. For example, you may wish to make up a solution having a particular concentration, in theory this involves measuring out billions and billions of molecules at a time so you know how many molecules of a substance it contains.

Alternatively you may wish to calculate the weights of reactants for a reaction in a ratio that matches the ratio of reactants in its chemical equation. For a general equation: X + Y = Z, you cannot simply take one gram of X, and one gram of Y, as they will contain different numbers of particles (be they atoms, molecules and ions).

This is where the concept of the mole is so important to the chemist, and as you will see one mole of any substance contains the same number of particles. However, as you will be dealing with quantities such as mass and volume throughout this section, your starting point is a look at how these are measured.

Learning Outcomes

After studying Session 7 you should be able to:

- appreciate how mass and volume are measured in the laboratory
- understand the concept of the mole and its link to chemical equations
- understand what is meant by a solution, and how concentration is measured.

1 Units of measurement

The international system of units (*Le Système International d'Unites*, abbreviated to SI) was developed in France during the 18th century in an effort to create a unified and rational system of weights and measures. The SI system was adopted as the world standard in 1960.

Mass and volume (of liquids) are the quantities chemists most often work with and later in this session you will look at how these are determined in the laboratory, but first a look at their SI units.

1.1 Units of volume

The SI unit of volume is the cubic metre (m^3), but this is too large for the types of volumes laboratory chemists generally work with; litres, l (or cubic decimetres, dm^3) are used instead, where 1 l = 1 dm^3.

But what does 1 litre (or 1 dm^3) of fluid look like? What about a millilitre (ml, one thousandth of a litre) or a microlitre (μl, one millionth of a litre)?

A litre is the volume of liquid (or gas) that would fit into a cube measuring 10 cm (or 1 dm) on each side: 10 cm × 10 cm × 10 cm = 1000 cubic centimetres (cm^3) = 1 litre.

A millilitre is the volume of a cube measuring 1 cm on each side:
1 cm × 1 cm × 1 cm = 1 cm^3 = 1 ml.

A microlitre is the volume of a cube measuring 1 mm on each side:
1 mm × 1 mm × 1 mm = 1 mm^3 = 1 μl.

To help you visualise these volumes, consider the following:

A typical carton of fruit juice has a capacity of 1 litre.

A teaspoon holds about 5 ml of liquid.

One raindrop is about 30 μl.

■ Express 2 μl in litres.

□ 2 μl = 2×10^{-6} l

1.2 Units of mass

You will have noticed that the term mass in the title of this section. **Mass** is a measure of how much matter an object contains, and is the correct term to use rather than weight. However the terms weigh and weight are used in general day to day parlance.

Weight is actually the gravitational force experienced by an object (measured in newtons):

Weight = mass × acceleration due to gravity

Mass is measured in kilograms (kg), which again is not the most appropriate unit for laboratory use; chemists tend to weigh in grams (g, one thousandth of a kilogram) or milligrams (mg, one thousandth of a gram).

To help you visualise these masses, consider the following:

- A litre of water weighs 1 kg.
- A £20 note weighs about 1 g.
- A UK pound coin weighs around 10 g.

Originally a ‘pound’ was the monetary value given to a pound mass of sterling silver (an alloy of 92.5% silver and 7.5% copper), hence ‘pound sterling’.

■ Express 120 mg in grams

□ 120 mg = 0.120 g

In practice, the most commonly used units differ from each other by a factor of 1000. For example, in Figure 1 you can see how the units of mass – tonne (t), kilogram (kg), gram (g), milligram (mg) and microgram (μg) – differ from each other by a factor of 1000.

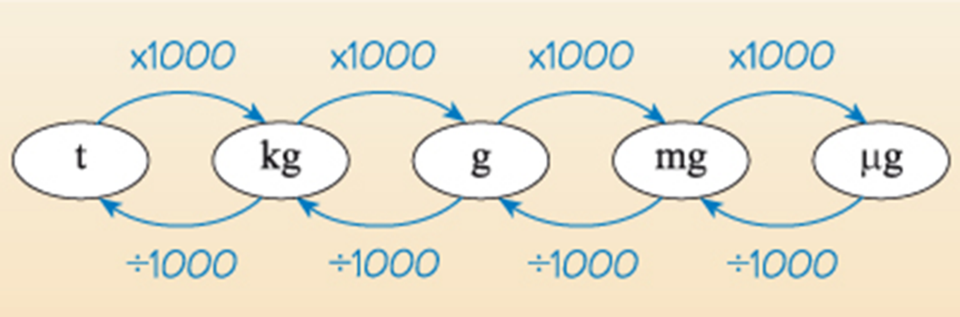


Figure 1 Common units of measurement of weight

2 Weighing and measuring volume in the laboratory

Up to this point you have looked at *what* chemists measure in the laboratory, in the next two sections you will be looking at *how* they do it.

2.1 Weighing solids and liquids in the laboratory

It is probably fair to say that if you made a list of the most frequent operations carried out by a laboratory chemists, weighing samples in one form or other would be at, or at least near, the top.

Examples of different types of laboratory balance are shown in Figure 2.

There are two types of balance: the general-purpose (or top pan) balance (Figure 2a) and the analytical balance (Figure 2b), of which the microbalance (Figure 2c) is a specific type.

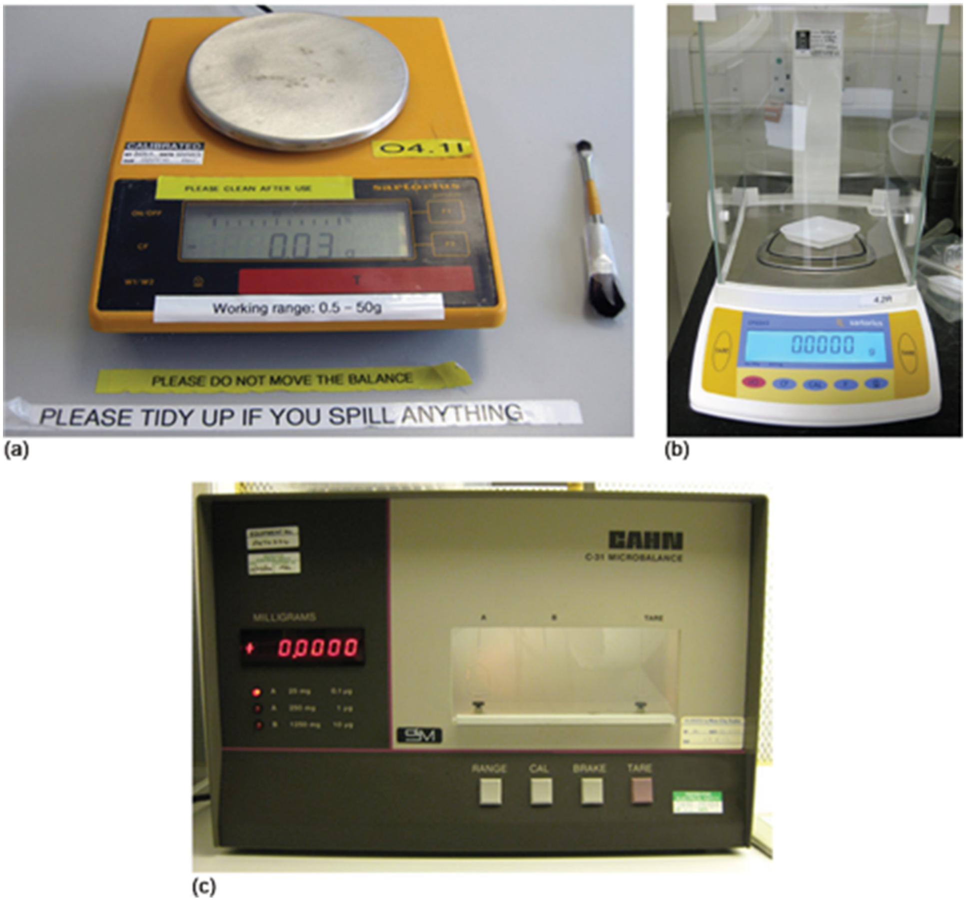


Figure 2 (a) A general-purpose (or top pan) balance; (b) an analytical balance; (c) a microbalance

Simply looking at the external appearance of both main types reveals a very obvious difference: the analytical balance has an enclosed weighing compartment, the general-purpose balance does not. However, the operational difference lies in the accuracy you require.

General-purpose balances read to two or three **decimal places** in grams, i.e. their zeroed display will show 0.00 g or 0.000 g respectively. You may come across the terms two-place or three-place used in this context.

However, an analytical balance is far more accurate and reads to four or five decimal places. Microbalances that measure to six decimal places are also quite common (Figure 2c).

- ■ What will be the zero reading on four-place and five-place analytical balances?
- □ The readings will be 0.0000 g and 0.00000 g respectively.

The correct choice of balance for the job you are required to carry out is essential.

For example, if you were asked to weigh a 5 g sample of a substance to ±0.01g then a general-purpose balance measuring to two decimal places would be ideal. Alternatively, if you were asked to weigh a sample to a much higher degree of accuracy, say 0.5 g of a substance to 0.0001 g, you would need to use an analytical balance measuring to four decimal places.

2.2 Measuring volumes of liquids in the laboratory

A range of apparatus is used for handling liquids in the laboratory, each item appropriate for a specific application and differing in the accuracy with which they can deliver required volumes.

2.2.1 Where an approximate volume is required

Where accuracy is not essential you will generally use a measuring cylinder (Figure 3), having a volume scale etched into the glass, or a dispenser (Figure 4). The latter fits onto a container of liquid and is used for the repeated delivery of known volumes.

Figure 3 A selection of measuring cylinders

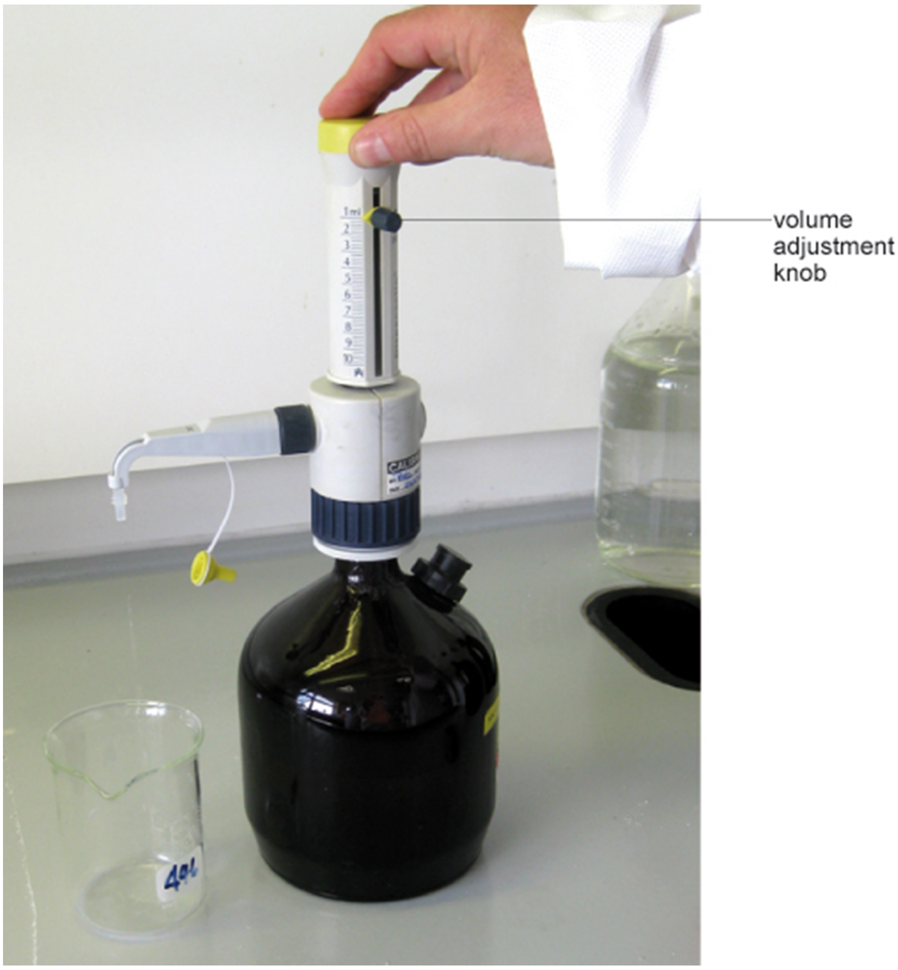


Figure 4 A dispenser being used to deliver a known volume of liquid

In addition, the humble Pasteur pipette (Figure 5) is probably one of the most commonly used items in the laboratory. These are used for the transfer of liquids (often dropwise) where accuracy is not required.

Figure 5 A Pasteur pipette

2.2.2 Where an accurate volume is required

For more accurate work, volumetric glassware is used, these include pipettes, burettes and volumetric flasks. A pipette is shown in Figure 6.

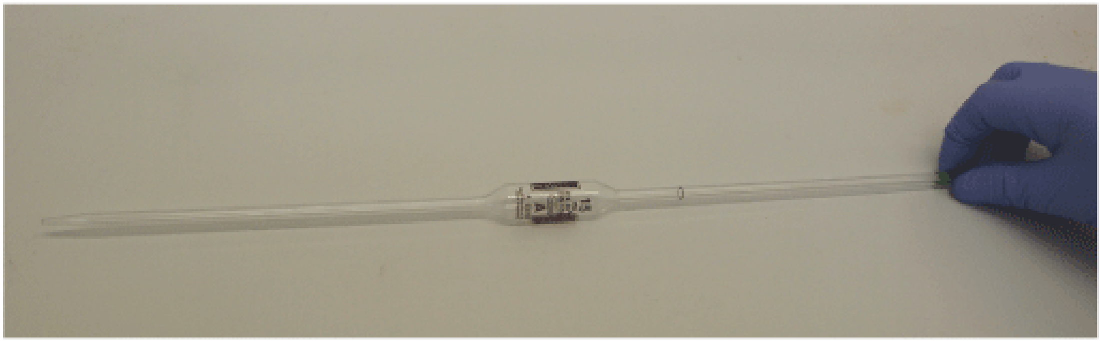


Figure 6 A volumetric pipette

Volumetric glassware is calibrated with graduation lines; there may be a scale, or just one line indicating a specific volume. Either way, the key point is measurements must always be read from the lowest point of the meniscus (the concave curvature on top of an aqueous solution), and shown in Figure 7.

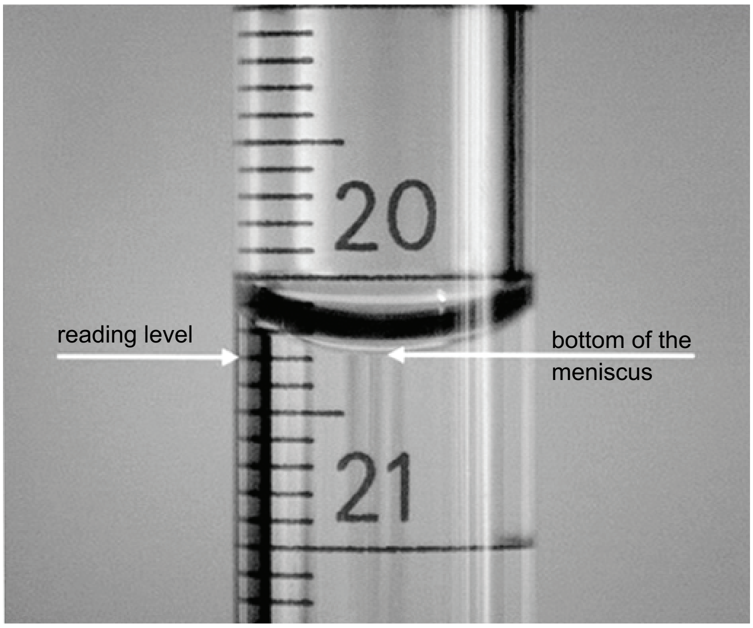


Figure 7 Reading the level of a meniscus

- ■ What is the volume of liquid shown in Figure 7?
- □ 20.30ml

So having had a glimpse inside the laboratory, in the next section you will return to the problem posed at the start of this session, how do chemists quantify amounts of atoms and molecules?

3 Introducing the mole

The **mole** is a measure of **amount of substance.**

Before exploring what this means this in more detail, recall what you learned about 'weighing' atoms in session 1.

The relative atomic mass (RAM) of an element is the average mass of an atom of the element relative to one-twelfth the mass of an isotope of carbon-12.

This leads you on to the concept of **relative molecular mass (RMM)** which is simply the sum of the relative atomic masses of the atoms in a molecule. As this term can only be strictly applied to molecules, you will often find the term **relative formula mass (RFM)** used instead, which covers ionic substances like sodium chloride (NaCl) and calcium oxide (CaO).

■ Calculate the relative molecular mass of water, given the relative atomic masses of hydrogen and oxygen are, 1.01 and 16.0 respectively.

□ RMM (H_2O) = [2 x RAM(H)] + RAM (O)]
= (2 x 1.01) + 16.0
= 18.02.

■ What is the relative formula mass of sodium chloride (NaCl), given the relative atomic masses of sodium and chlorine are 23.0 and 35.5 respectively.

□ RFM (NaCl)= (23.0 + 35.5) = 58.5.

Now back to the mole.

One mole of an element or compound has a mass equal to its relative atomic mass, its relative molecular mass or its relative formula mass expressed in grams.

Also, the number of formula units (which may be atoms, molecules, groups of ions etc) in a mole is 6.022×10^{23} mol^{-1}, this is known as **Avogadro's constant**.

For example if you had one mole of sodium metal it would weigh 23g, and in those 23 grams you would find 6.022×10^{23} atoms.

The point is that one mole of any substance, whether it comprises, atoms, molecules or ions, contains this number of particles (whether they be atoms, molecules or ions).

3.1 Molar mass

The mass of one mole of a substance is the relative mass of that substance expressed in grams. This is true whether you are talking about relative atomic masses for elements, relative molecular masses for covalent compounds, or relative formula masses for ionic compounds.

The mass of one mole of a substance is called the **molar mass**; it has units of grams per mole (g mol^{-1}).

■ What is the difference between a molar mass and the relative mass?

□ The former has units, the latter does not.

However the actual number *is* the same.

Thus helium has a relative mass of 4 (no units), meaning the helium atom is, relatively speaking, 4 times heavier than a hydrogen atom. Helium has a molar mass of 4 g mol^{-1}, meaning that each mole of helium atoms has a mass of 4 g.

- ■ What is the molar mass of water (H_2O)?
- □ The RMM of H_2O is 18.02 so, Molar mass of H_2O = 18.0 g mol^{-1}

The definition of molar mass leads to two simple mathematical equations which help in performing calculations involving moles (they are in fact two forms of the same equation):

> Mass of a substance = (number of moles of substance) × (molar mass of substance) **(1)**
>
> Number of moles of a substance = mass of substance /molar mass of substance **(2)**

If you were asked to find the number of moles of water in 100 g, this is one way you might go about it.

Choose which form of the equation you need to use.

As you want to find the number of moles, you should use equation **2**:

You have previously worked out the molar mass of H_2O = 18.0 g mol $^{-1}$, so putting the numbers and units in the equation you get:

Number of moles of water = 100 g/18.0 g mol−1 = 5.56 mol

- ■ Account for the unit mol in the above calculation?
- □ The units can be found using the following sequence:

  g /g mol^{-1}= 1 mol^{-1}= mol

Now have a go at the following calculations.

- ■ How many moles are there in 0.769 g of CaF_2, given RAM (Ca) = 40.08 and RAM (F) = 19.00?
- □

  RFM CaF_2 = 40.08 + (19.00 x 2)

  = 78.08

  Molar Mass CaF_2 = 78.08 g mol^{-1}

  Number of moles of CaF_2

  = 0.769/78.08

  = 0.01 mol.

- ■ What is the mass of 0.140 mol of $C_6H_{12}O_6$ (glucose)?

  RAMs: C (12.01), H(1.01) and O (15.99).
- □

  RFM $C_6H_{12}O_6$ = (12.01 x 6) + (1.01 x 12) + (15.99 x 6)

  = 72.06 + 12.12 + 95.94

  = 180.12

  Mass of $C_6H_{12}O_6$ = 0.140 x 180.12

  = 25.21 g

3.2 Moles and chemical equations

The concept of the mole gives an alternative interpretation of the chemical equation.

Look again at the following equation for the combustion of methane:

CH_4 (g) + $2O_2$ (g) = CO_2 (g) + $2H_2O$(l)

- Explain in a single sentence what this equation means to you.
- ☐ This equation represents an overview of a chemical change in which molecules of methane and oxygen are converted to molecules of carbon dioxide and water.

This is the molecular interpretation of the equation, but you could also view it somewhat differently.

The equation can also represent a process in which one mole of methane molecules and two moles of oxygen molecules react together to form one mole of carbon dioxide and two moles of water.

This is a molar interpretation of the equation.

Using the mole, it is possible to calculate quantities of reactants and products from a chemical equation.

Methane is the major component of natural gas. The average house in the UK burns about 1000 kg of methane each year. How much carbon dioxide enters the atmosphere from this source?

The relative molecular mass of methane is 16.0 and that of carbon dioxide is 44.0.

So the mass of one mole of methane molecules is 16.0 g and the mass of one mole of carbon dioxide molecules is 44.0 g.

One mole CH_4 is converted to one mole CO_2.

So 16.0 g CH_4 are converted to 44.0 g CO_2.

1.00 g CH_4 is converted to 44.0/16.0 g CO_2

And

1.00 kg CH_4 is converted to 44.0/16.0 kg CO_2

1000 kg CH_4 is converted to 1000 × 44.0/16.0 kg CO_2= 2.75×10^3 kg

So on average, each house adds 2750 kg of carbon dioxide to the atmosphere each year.

So have seen that using the concept of the mole in conjunction with balanced chemical equations allows the masses of reactants and products to be calculated. However much of the work carried out by chemists take place in solution, and as such there is a need to be able to quantify *how much* of a particular substance is dissolved in a liquid – to this end, being able to work in moles is crucial. This is the focus of the next section.

3.3 Working with solutions: concentration

In making a solution, the chemicals involved are dissolved in a liquid which is referred to as the **solvent**.

The substance that dissolves is called the **solute**.

The most common solvent is water, but in the laboratory a chemist may choose to work with any one of a number of others. Different substances dissolve more easily or less easily in a particular solvent i.e. they have different **solubilities**. Here the **solubility** of a substance is defined as the maximum amount of **solute** that will dissolve in a given amount of solvent.

For example, when common salt (sodium chloride, the solute) is dissolved in water (the solvent) this gives a solution of sodium chloride. The solubility of a substance varies with temperature and is usually expressed as the maximum amount of a substance that will dissolve in 100 g of water at a particular temperature. However, it is often more usual (and more useful) to express the amount of solute that is dissolved in a *specific volume of solution* at a particular temperature.

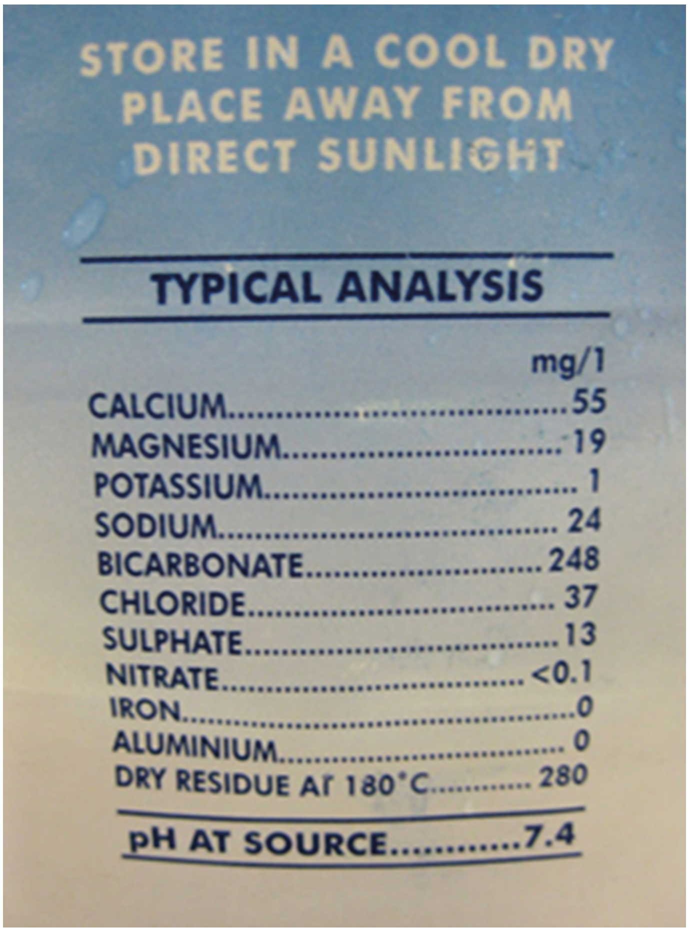
This is known as the **concentration** of a solution, which is expressed as the amount of solute in 1dm^3.

Thus, if 10.0 g of sodium chloride is dissolved in water to give 1 dm^3 of solution, the concentration would be 10.0 g per dm^3 and so we would write 10.0 g dm^{-3}.

One important point: it is essential to define concentration as the amount of solute in exactly 1 dm^3, that is in 1 dm^3 of the final solution rather than the amount of solute dissolved in 1 dm^3 of water. If you did dissolve 10.0 g of sodium chloride in 1 dm^3 of water then the final volume would in effect be greater than 1 dm^3. Therefore to make up a solution with a particular concentration of a solute, the required amount of solute is firstly dissolved fully in a suitable amount of water (less than 1 dm^3) and then sufficient water is added to achieve the correct final volume of 1 dm^3 .

Note 1dm^3 = 1 litre

This is a label from a bottle of mineral water. It shows the concentration of each of the solutes expressed as mg/l.



STORE IN A COOL DRY
PLACE AWAY FROM
DIRECT SUNLIGHT

TYPICAL ANALYSIS

	mg/1
CALCIUM	55
MAGNESIUM	19
POTASSIUM	1
SODIUM	24
BICARBONATE	248
CHLORIDE	37
SULPHATE	13
NITRATE	<0.1
IRON	0
ALUMINIUM	0
DRY RESIDUE AT 180°C	280

pH AT SOURCE............7.4

Figure 8 Label from a bottle of mineral water

3.4 Expressing concentration in moles

In the last section concentration was described in terms of a mass of solute dissolved in a defined volume. However, it is often more practical to express concentrations as the number of *moles* of solute is dissolved in a specific volume (1 dm^3) at a given temperature.

Thus, if you have 10.0 g of sodium chloride dissolved in 1.00 dm^3 of water, you can calculate the concentration of that solution in moles per dm^3 (mol dm^{-3}).

First, you need to calculate the molar mass of sodium chloride (NaCl).

■ So….what is the molar mass of sodium chloride?

□ The relative atomic masses of Na and Cl are 23.0 and 35.5, respectively, so: relative mass of 1 mole of NaCl = (23.0 + 35.5) g = 58.5 g

Thus the molar mass of NaCl is 58.5 g mol^{-1}.

Second, you need to calculate the number of moles of NaCl.

How many moles are there in 10.0 g of NaCl?

Number of moles of NaCl = mass of NaCl/molar mass of NaCl

= 10.0/58.5 = 0.171 mol

Therefore, 0.171 mol of NaCl is dissolved in 1.00 dm ^{3} of water, so the concentration of the solution is 0.171 mol dm^{-3} .

■ What happens to a crystalline structure of sodium chloride when it is added to water?

□ You know sodium chloride dissolves to form a solution, the crystalline structure which comprises an array of equal numbers of sodium cations (Na^+) and chloride anions (Cl^-), breaks up and the ions become surrounded by water molecules.

So when sodium chloride dissolves in water, the resulting solution will contain equal numbers of sodium and chloride ions:

■ Write a chemical equation for this process.

□ $NaCl(s) = Na^+(aq) + Cl^-(aq)$

Thus, if 1.0 mole of sodium chloride is dissolved in water to form 1 dm ^{3}, giving a 1 mol dm $^{-3}$ solution, the solution will contain 1.0 mol dm^{-3} of $Na^+(aq)$ ions and 1.0 mol dm^{-3} $Cl^-(aq)$ ions.

Next consider what would happen if you dissolved calcium chloride ($CaCl_2$) in water.

■ Write a chemical equation for this process.

□ $CaCl_2(s) = Ca^{2+}(aq) + 2Cl^-(aq)$

The resulting solution has two chloride ions for every calcium ion. So if you have a 1 mol dm^{-3} solution of calcium chloride, this means there is a concentration of 1 mol dm^{-3} of $Ca^{2+}(aq)$ ions and 2 mol dm^{-3} of $Cl^-(aq)$ ions. In this example, you would multiply the concentration by 2 for the chloride ions as there are twice as many.

Finally, having been introduced to the mole, and how it can be used to “count” atoms, molecules and ions; in the next section you will see how you can take this concept and answer a question posed at the very start of the course.

4 How small is an atom?

At this point you are going to look again at the basic building blocks of matter introduced in Session 1 – atoms, and using the concept of the mole, and the Avogadro constant, attempt to get an idea of the size of their size..

Let’s use gold as an example.

The relative atomic mass of gold is 197, so, rounding things up a little one mole of gold has a mass of about 200g. Now gold is a dense metal: each cubic centimetre has a mass of about 20g, so one mole of gold occupies a volume of about 10 cm^3, which is 1 x 10^{-5} . This volume, therefore contains 6 x 10^{23} gold atoms.

So 6 x 10^{23} gold atoms occupy 1 x 10^{-5} .

This means 1 gold atom occupies 1 x 10^{-5} / 6 x 10^{23} m^3 = 1.7 x 10^{-29} m^3.

Let’s think of this tiny volume as a cube.

- ■ What is the length of its side?
- □ It is the length which when multiplied by itself, and then by itself again, gives the volume of 1.7 x 10^{-29} m^3. This length is 2.6 x 10^{-10} m.

So using the Avogadro constant you arrive at an atomic size (2.6 x 10^{-10} m) in line with what was given in Session 1, and if you want to visualise how small this number is; you could set about 30 million gold atoms in a line across your fingernail!

5 This session’s quiz

Check what you’ve learned by taking the end-of-week quiz.

Session 7 quiz

Open the quiz in a new window or tab (by holding ctrl [or cmd on a Mac] when you click the link), then return here when you have done it.

Summary of session 7

1. The mole is used to quantify the number of atoms or formula units involved in a reaction or contained in a volume of gas or solution.
2. The mole is the amount of substance containing the number of particles equal to Avogadro's constant, 6.02×10^{23}.
3. To calculate quantities of reactants and products, it is essential to start with a balanced chemical equation that is viewed from a molar rather than a molecular perspective. The relative molecular mass values for the substances involved must be calculated and, from this information, the masses of the substances involved in the reaction can be determined.
4. Concentration is a measure of the amount of solute dissolved in a solution and is measured in mol dm^{-3}.

Session 8. Chemical reactions and why they happen

Introduction

So far, you have been largely concerned with atoms, molecules and their electronic and spatial structures, you have not looked in much detail up to this point at chemical reactions themselves and why they happen at all. This will be the topic of this session.

Rather than just discuss this in theoretical terms, to put some of the ideas you will be presented with in context, you will concentrate on one particular reaction which occurs in the modern motor car.

Learning Outcomes

After studying Session 8 you should be able to:

- appreciate the concept of chemical equilibrium and equilibrium constant
- recognise that at equilibrium the amounts of reactants and products are constant but not necessarily the same
- appreciate that at equilibrium the rate of the forward reaction is the same as the rate of the reverse reaction
- understand what is meant by rate of reaction and the influence of catalysts.

1 Petrol engine emissions

In a world where electric and hybrid cars are becoming commonplace, your focus will be on the ‘old fashioned’ petrol engine and one reaction in particular, which is in part responsible for the move towards this new generation of ‘cleaner’ vehicles. This is a chemical process which leads to gaseous emissions thought to be detrimental to the environment, and human health.

Table 1 shows typical percentages of the main constituents of the exhaust gas that emerges from a modern car engine.

Table 1 The percentage by volume of the different gases in a typical car exhaust stream

Gas	Volume per cent
nitrogen and argon	71.00
carbon dioxide	13.50
water vapour	12.50
carbon monoxide	00.68
oxygen	00.51
hydrogen	00.23
nitric oxide	00.11
hydrocarbons	00.05

Looking at Table 1, the main concern stems from the release of carbon monoxide, CO, and nitric oxide (strictly known as *nitrogen monoxide*), NO into the environment. Both are very poisonous gases.

For example, when nitric oxide emerges from the exhaust into the open air and cools down, it reacts with oxygen to form nitrogen dioxide, NO_2. This causes respiratory problems even at very low concentrations .You may recall (from Session 3) that NO_2 is a product of the reaction of copper with concentrated nitric acid (Figure 1).

Figure 1 Brown nitrogen dioxide gas being produced, in this case, by the reaction of copper with concentrated nitric acid

However these dangers apart, there is a reaction that could be very beneficial:

$2NO(g) + 2CO(g) = N_2(g) + 2CO_2(g)$ (1)

If NO and CO reacted like this, then the nitric oxide in the exhaust would disappear, and take a substantial amount of poisonous carbon monoxide with it. Unfortunately, the reaction does not seem to happen in practice. To understand why, you need to be introduced to a concept fundamental to an appreciation of chemical reactions - **chemical equilibrium**.

2 Chemical equilibrium

By and large chemical reactions do not go to completion, and they are reversible.

This means they take place in two ways; reactant(s) going to product(s), and product(s) going to reactant(s). The forward and reverse reactions occur at the same time, and never stop.

When the rate of the forward reaction is equal to the rate of the reverse reaction, the reaction is said to have reached **equilibrium**.

In general, a chemical reaction that proceeds to equilibrium, can be represented by:

Here the symbol indicates that the reaction is reversible.

To reiterate; at equilibrium the forward reaction (by convention, the one going from left to right as written) and the reverse reaction (the one going from right to left) occur at the same rate. This means there is *no further change* in the relative amounts of products and reactants present in the reaction mixture. So at equilibrium, the concentrations of the reactants and products are constant, however they are not necessarily equal.

But chemists are mostly interested in the product.

The proportion of a reaction product in an equilibrium mixture is known as the

equilibrium yield of that substance.

In the next section you will consider how the position of equilibrium may impact on reaction (1).

2.1 Is the equilibrium position unfavourable?

The first possibility is that the reaction system has been able to reach chemical equilibrium, but the equilibrium position is not favourable.

How does this come about?

Look again at Reaction (1).

$2NO(g) + 2CO(g)\ N_2(g) + 2CO_{2(g)}$ (1)

This indicates that both the forward reaction:

$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$ (3)

and the backward reaction:

$N_2(g) + 2CO_2(g) \rightarrow 2NO(g) + 2CO(g)$ (4)

are taking place: at the microscopic, molecular level there is continuous change in both directions.

However, at equilibrium, the reaction system then *seems* static because, at the macroscopic level where measurements are made, there is no apparent change in the amounts or concentrations of any of the four gases involved.

Suppose that Reaction (1) appears not to occur because, although it has reached equilibrium, the equilibrium position is unfavourable. Then it must be that the rates of the forward and backward reactions become equal when the concentrations of the reactants (NO and CO) are very high, and those of the products (N_2 and CO_2) are very small, so small as to be undetectable.

This possibility can be tested by examining the *equilibrium constant, K*, for the reaction.

2.2 The equilibrium constant

An expression for the equilibrium constant of a reaction can be put together from the concentrations of the reactants and products at equilibrium.

Chemists represent theconcentration of a reactant or product by enclosing its chemical formula in square brackets.

Thus, the concentration of NO(g) is written [NO(g)].

To write down the equilibrium constant of a reaction, you need to start with the concentrations of the products. Each one is raised to the power of the number that precedes it in the reaction equation, and the corresponding terms for each product are then multiplied together.

■ Do this now for the products of the equilibrium system (2)

□ The result is $[N_2(g)] \times [CO_2\ (g)]^2$, or, taking the multiplication sign as read, $[N_2(g)][CO_2(g)]^2$. In Equation (1), CO_2 (g) is preceded by a two, so its concentration is squared.

So that's the products dealt with, now for the reactants.

■ Repeat the operation for the reactants in Equation (2)

□ The result is $[NO(g)]^2[CO(g)]^2$, both NO(g) and CO(g) are preceded by a two.

The equilibrium constant, *K*, is obtained by dividing the result for the products by the result for the reactants:

(1)

So returning to the earlier question, is the equilibrium position unfavourable?

In other words Reaction (1) does not happen because the equilibrium position for equilibrium system (2) lies well over to the left. As stated above, at equilibrium, the concentrations of NO(g) and CO(g) are very high, and those of N_2 (g) and CO_2(g) are so small as to be undetectable.

■ If so, will *K* be large or small

□ It will be very small because the large quantities ([NO(g)] and [CO(g)]) occur on the bottom of Equation (1), and the small quantities ($[N_2(g)]$ and $[CO_2(g)]$) occur on the top.

Actally, the value of *K* can be determined experimentally. Assuming a typical temperature in a car exhaust system is 525 °C. At this temperature, *K* turns out to be 10^{40} mol^{-1} litre.

■ Given this information, does the equilibrium position lie to the left or right of Equation (2)?

□ *K* is immense, so at equilibrium, the concentrations of the products must be much greater than those of the reactants (which appear on the bottom). The equilibrium position for Reaction 7.2 at 525 °C therefore lies well over to the right.

Note: the units here are mol^{-1} litre for this equilibrium, mol is shorthand for moles, which as you know is a measure of an amount of substance**.**

So up to this point, the issue of why the polluting gases NO and CO predominate hasn't been addressed, as the equilibrium is in fact favourable.

Another factor must be coming into play.

This is considered in the next section.

2.3 Is the rate of reaction very slow?

If the equilibrium position is very favourable, then the reason why Reaction (1) fails to occur at 525 °C must be that its rate is very slow.

Usually, a reasonable response would be to increase the temperature further, but the structure and economy of the car provides little scope to do this. The alternative is to use a **catalyst**, which leaves the equilibrium constant unchanged, while speeding the reaction up.

Internal energy is the sum of the kinetic and potential energies of the component particles of the system being considered. If you look at the changes that take place in the internal energy as reactants change progressively into products. Figure 2 shows a simplified version. The internal energies of the reactants (2NO + 2CO) and products (N_2 + $2CO_2$) are marked by two 'platforms'. The platform for the products lies lower than that for the reactants. This shows that the internal energy change during the reaction is negative.

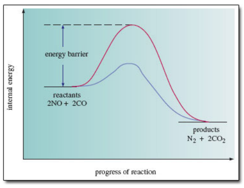


Figure 2 A simplified version of the change that takes place in the internal energy of the molecules as nitric oxide and carbon monoxide change into nitrogen and carbon dioxide. The upper (red) curve shows the change in the absence of a catalyst; the lower (blue) curve, the change when a catalyst is present

Between the reactants and products, the internal energy does not decrease gradually as the reaction progresses; instead, it rises initially, reaches a maximum, and then declines. The upper curve shows the situation in the absence of a catalyst. The internal energy of the reacting molecules must first increase by an amount marked 'energy barrier' in Figure 2.

■ How might the reactants, NO and CO, acquire this additional energy?

□ One possible source is the kinetic energy of other molecules. Lucky collisions may provide some NO and CO molecules with unusually high energies. If these high-energy molecules then chance to collide with each other, they might be able to surmount the energy barrier and react together.

This also explains why an increase in temperature increases the rate of a reaction: a temperature rise increases the speed of the molecules, and the required increase in internal energy following collisions then becomes more probable.

But as we have seen, in this case the rate is not great even at 525 °C, the energy barrier must be very high.

- The main reason is a property of nitric oxide, looking at Reaction 1, can you suggest what this might be?
- In Reaction 1, the nitrogen and oxygen atoms in NO must be separated at some point, this involves breaking the bond between the two atoms, a reasonable thought is that this bond is strong.

Indeed the bond that holds the nitrogen and oxygen atoms together is very strong – it is a triple bond. A large input of energy is therefore needed to bring the separation about, so the energy barrier is high and the reaction is slow.

The solution to the high energy barrier for Reaction 1 is to involve a third party – a catalyst. What happens at the molecular level, and how the catalyst is considered, is covered in the next section.

2.4 The three-way catalytic converter

Catalysts are substances that speed up reactions without being used up in the reaction. They tend to be very specific and will only change the rate of a particular reaction.

As far as Reaction 1 is concerned, a suitable catalytic material is the metal rhodium.

When NO and CO molecules enter a catalytic converter, they become bound to rhodium surfaces. The attachment of NO to rhodium weakens the bond between the N and O atoms in the molecule, and the NO unit becomes more vulnerable to change.

For example, it is believed that in some cases, the bond is so weakened that the N and O atoms separate completely, and move about on the rhodium surface. Pairs of nitrogen atoms can then meet, combine and leave the surface as $N_2(g)$; oxygen atoms can meet and combine with CO molecules on the surface, leaving as $CO_2(g)$.

Obviously, this type of reaction pathway is very different from one that takes place entirely in the gas phase with no catalyst present. Most particularly, because the catalyst surface assists the breaking of the bond in the NO molecule, it has a lower energy barrier (see Figure 2) and is much faster.

In a *three-way catalytic converter*, some 90 per cent of the nitric oxide in the exhaust stream is converted to nitrogen and carbon dioxide. Figure 3 shows an example. The catalyst actually contains rhodium and platinum. The platinum catalyses the reactions of both carbon monoxide and unburnt hydrocarbons (from the petrol) with oxygen, giving carbon dioxide and steam.

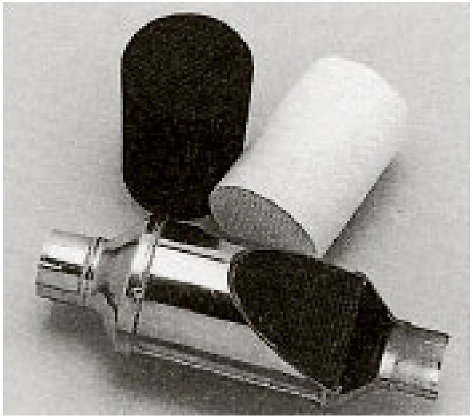


Figure 3 A three-way catalytic converter; the metal shell has been partially cut away, exposing a gauze lining, inside which is the cylindrical grid of exhaust channels. A

separate grid of this type is shown above and to the left. It is black because the platinum-rhodium catalyst has been dispersed over its surfaces. Before the catalyst is spread over it, the ceramic grid is white, as shown above and to the right

The converter is called 'three way' because it removes all three main types of pollutant: nitrogen oxides, carbon monoxide plus unburnt hydrocarbons.

3 Catalysts in action

Catalysts are widely used in the industrial manufacture of bulk commodity chemicals.

One example is in the preparation of nitric acid, a chemical which has many uses, but most is combined with ammonia to produce ammonium nitrate a widely used fertilizer.

Nitric acid, HNO_3, is made on a huge industrial scale by the **Ostwald process** in which gaseous ammonia is converted first to NO and then to NO_2 over a catalyst made from platinum metal. This reaction, where combination with oxygen is occurring is known as **oxidation**, and is demonstrated on the laboratory scale in the following video.

Video content is not available in this format.
The oxidation of ammonia.

- ■ In the video, what evidence was there that a catalytic reaction (involving the spiral of platinum metal) was occurring?
- □ The platinum wire was initially heated in a flame until red-hot. On lowering it into the flask of ammonia (through which oxygen was bubbling) it continued to glow red (accompanied by the occasional explosion!)

The NO_2 is then dissolved in water to give a concentrated aqueous solution of the acid, and the NO produced in this step is recycled back into earlier stages.

Now attempt the following question.

- ■ The combination of sulfur dioxide with oxygen, and the decomposition of steam into hydrogen and oxygen are both reactions of great potential value. These reactions and their equilibrium constants at 427°C (700K) are as follows.

  i. Write expressions for the equilibrium constants of the two reactions.
  ii. When the two reactions are attempted at 700K, neither seems to occur. Which of the two might be ‘persuaded’ to proceed at this temperature, and what form might your persuasion take?
- □ The equilibrium constant of the first reaction, K_1, is given by

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The data show that K_2 is tiny: at equilibrium, the concentrations of the hydrogen and oxygen in the numerator (the top line of the fraction) are minute in comparison with the concentration of steam in the denominator (the bottom line of the fraction). So in a closed system at 700 K, significant amounts of hydrogen and oxygen will never be formed from steam.

By contrast, K_1 is large, so the equilibrium position at 700 K lies well over to the right of the equation, and conversion of sulfur dioxide and oxygen to sulfur trioxide is favourable. The fact that the reaction does not occur must be due to a slow rate of reaction. We may therefore be able to obtain sulfur trioxide in this way if we can find a suitable catalyst to speed up the reaction. A suitable catalyst is vanadium pentoxide, V_2O_5, and at 700 K, this reaction is the key step in the manufacture of sulfuric acid from sulfur, oxygen and water.

4 Equilibrium positions and rates of reaction – an overview

So far you have seen that if a chemical reaction is to occur at a particular temperature, two conditions must be fulfilled.

- ■ What are these conditions?
- □ The equilibrium constant must be sufficiently large, and reaction rate sufficiently great.

So there is a crucial distinction between the equilibrium constant and the rate and this reveals itself in Figure 2.

The figure shows two different pathways by which the reactants can change into the products, but both routes begin at the *same* reactant energy level, and finish at the *same* product energy level. Regardless of reaction pathway, the energy difference between reactants and products is the same.

It is an energy difference between reactants and products that determines the equilibrium constant of a reaction, and therefore the equilibrium position. The fact that both pathways have the same energy difference, and therefore the same equilibrium constant, shows that the equilibrium constant in a reaction is not affected by *how* reactants change into products. With equilibrium constants, the nature and energies of the initial and final states are everything; what happens in between is immaterial.

When we turn to reaction rates, this is not so. In Figure 2, both routes start with the same reactants, and end with the same products, but the intervening stages along each pathway are very different. Such sequences of intervening stages are called **reaction mechanisms**, and the mechanism in the presence of a catalyst delivers a smaller energy barrier and a faster rate than the one that pertains when the catalyst is absent. With rates of reaction, therefore, the mechanism is crucial.

5 This session’s quiz

Now it’s time to complete the Week 8 badge quiz. It is similar to the badged quiz that you took at the end of Week 4, with 15 questions in total.

Session 8 quiz

Remember, this quiz counts towards your badge. If you’re not successful the first time, you can attempt the quiz again in 24 hours.

Open the quiz in a new window or tab, then return here when you have done it.

Summary of session 8

1. The equilibrium constant of a reaction is fixed at any particular temperature. It depends only on the natures of the initial reactants and the final products; what happens as reactants change into products has no effect on the equilibrium constant or position of equilibrium.
2. The rate of a chemical reaction is affected both by the temperature and by the pathway (reaction mechanism) through which reactants change into products. This pathway can sometimes be altered, for example by the introduction of a catalyst.
3. The catalyst causes a change in the reaction mechanism which leads to a lowering of the energy barrier and to a greater rate of reaction.

Additional resources

You may be interested in exploring OpenLearn's **Elements of the periodic table** interactive. You'll also find more science related content on the Science, Maths & Technology pages.

Tell us what you think

Now you've come to the end of the course, we would appreciate a few minutes of your time to complete this short end-of-course survey (you may have already completed this survey at the end of Week 4). We'd like to find out a bit about your experience of studying the course and what you plan to do next. We will use this information to provide better online experiences for all our learners and to share our findings with others. Participation will be completely confidential and we will not pass on your details to others.

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