

Elemental analysis

When conducting spectral analysis, the only actual *facts* available to chemists are the relative atomic masses of the elements (A_r), elemental composition, the relative molecular mass (M_r) and the exact measurements from the spectral data. All other analyses are interpretations, calculations and inferences from comparisons with other molecules. The most fundamental data is the elemental composition and the relative molecular mass (M_r). No spectral interpretations can be considered to have any validity without that basic and essential information.

The elemental analysis of a compound may appear to be boring and trivial but, in reality, it is an extremely skilled task given that the sample analysed is rarely of a mass greater than 0.5mg and is such a small quantity it can hardly be seen. Measuring such a small mass precisely is extremely difficult and consequently the elemental composition is measured a number of times and mean results calculated. This means that, occasionally, this means that the total elemental composition does not always total 100% and 99.95 – 100.05% is acceptable. Traditionally, organic compounds were analysed for their carbon, hydrogen and oxygen content via combustion analysis. The carbon was collected as carbon dioxide, hydrogen as water and oxygen was calculated by difference. Nitrogen was determined separately by the Kjeldahl technique whilst sulfur was oxidised to sulfur dioxide which, dissolved in water, could then be titrated, having formed sulfuric acid. Halogens were determined by methods involving fusion with a known mass of sodium metal and gravimetric (weighing) analysis of the product.

The original combustion analytical method was established by the renowned French chemist, Joseph Gay-Lussac (pictured below left), who used his method to establish the elemental composition and hence molecular



formula of water. Until then, although water was known to contain both hydrogen and oxygen, it was believed that the molecular formula of water was believed to be HO, not H_2O . Gay-Lussac's method was further developed by Justus von Liebig (pictured right) who was responsible for the design of much laboratory glassware, notably the essential and indispensable Liebig condenser used in every organic chemistry laboratory to this day. Liebig combined



Gay-Lussac's methods to form an '*analytic train*' of measurements enabling the determination of the C, H, O content of a molecule in one experiment. More modern instrumental methods still involve combustion of almost invisible quantities of a sample with detection by infrared methods but the essential principles remain unchanged.

It is a mistake to dismiss these methods as relatively unsophisticated when compared to modern instrumental techniques such as infrared and multinuclear nmr spectroscopy and mass spectrometry. Without precise, reliable and accurate elemental composition data all other measurements and interpretations have no validity whatsoever. It is also worth understanding the difference between spectroscopic and spectrometric measurements. Spectroscopy involves the measurement of the effects of electromagnetic waves e.g. light whilst metric is simply a measurement and *spectro* refers to a range and *metric* means a range. There are many excellent textbooks explaining the theory of all techniques and so the following pages simply describe the principles relevant to the analyses of the compounds investigated in this series.

Empirical and Molecular Formula Calculations

Although difficult to master initially, calculating the empirical formula and the molecular formula can become routine if a set procedure is followed. This will be demonstrated by calculating the empirical formula and the molecular formula of butanoic acid and then three other compounds (propanol, propanoic acid and cyclohexene) which are discussed later in the context of spectrometry and spectroscopy. It is worth giving a number of examples as the data is entirely fundamental to all other measurements.

As a reminder, the *empirical formula* is the number of atoms of each element present in their lowest possible ratio whilst the *molecular formula* states the exact number of atoms of each element present in the molecule. Since many compounds e.g. inorganic compounds are not molecules it is becoming more common to use the term *formula mass* but for organic compounds which we are exclusively dealing with the conventional term, relative molecular mass (M_r), is retained.

Calculating the empirical formula

Step 1: The elemental composition of butanoic acid is C: 54.50% H: 9.17% O: 36.33%

Step 2: Divide each percentage composition by the relative atomic mass of the element:

	C	H	O
	$\frac{54.50}{12.00}$	$\frac{9.17}{1.01}$	$\frac{36.33}{16.00}$
=	4.54	9.08	2.27

Step 3: Divide the results by the lowest number which in this case is 2.27 (oxygen):

	C	H	O
	$\frac{4.54}{2.27}$	$\frac{9.08}{2.27}$	$\frac{2.27}{2.27}$
=	2.00	4.00	1.00

This means that the empirical formula is C_2H_4O .

Calculating the molecular formula

Continuing the numbering from the previous steps above

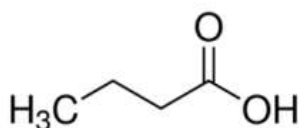
Step 4: The relative molecular mass (M_r) of butanoic acid is 88.08 g mol^{-1} .

Step 5: Calculate the relative molecular mass from the empirical formula.

The M_r of a fragment of empirical formula, C_2H_4O , is 44.04 g mol^{-1} .

The M_r of the actual molecule is exactly twice that value so the molecular formula is $C_4H_8O_2$.

Since the compound is a weak acid, this means that the structural formula must be:



Three further examples follow in order to build confidence and refer to molecules analysed later.

Propanol

Step 1: The elemental composition of propanol is C: 59.92%, H: 13.45%, O: 26.63% and the molecule has a relative molecular mass of 60.08 g mol⁻¹.

Step 2: Divide each percentage composition by the relative atomic mass of the element:

	C	H	O
	$\frac{59.92}{12.00}$	$\frac{13.45}{1.01}$	$\frac{26.63}{16.00}$
=	4.99	13.32	1.66

Step 3: Divide the results by the lowest number which in this case is 1.66 (oxygen):

	C	H	O
	$\frac{4.99}{1.66}$	$\frac{13.32}{1.66}$	$\frac{1.66}{1.66}$
=	3.01	8.02	1.00

This means that the empirical formula is C₃H₈O.

Calculating the molecular formula

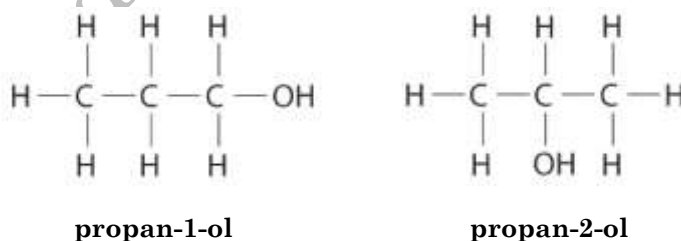
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Step 4: Note that the relative molecular mass (M_r) of propanol is 60.08 g mol⁻¹.

Step 5: Calculate the relative molecular mass from the empirical formula.

The M_r of a fragment of empirical formula, C₃H₈O, is 60.08 g mol⁻¹. This means that the molecular formula is the same as the empirical formula and so is C₃H₈O.

There are two possible structures for the molecule since the oxygen atom can sit on one of the terminal carbons or on the middle carbon atom.



Note that there is no such molecule as propan-3-ol as simple flipping over reveals it to be the same as propan-1-ol.

The instrumental, spectrometric and spectroscopic, methods can be used to distinguish between these two possible structures and since both molecules are small and very common they are extremely useful in developing and understanding the principles behind the analysis.

These isomers are used in deeper discussion later in this volume.

Propanoic acid

Step 1: The elemental composition of propanoic acid is C: 48.61%, H: 8.18%, O: 43.21% and the molecule has a relative molecular mass of 74.06 g mol^{-1} .

Step 2: Divide each percentage composition by the relative atomic mass of the element:

	C	H	O
	$\frac{48.61}{12.00}$	$\frac{8.18}{1.01}$	$\frac{43.21}{16.00}$
=	4.05	8.10	2.70

Step 3: Divide the results by the lowest number which in this case is 2.70 (oxygen):

	C	H	O
	$\frac{4.05}{2.70}$	$\frac{8.10}{2.70}$	$\frac{2.70}{2.70}$
=	1.50	3.00	1.00

Atoms only exist as whole numbers then multiplying by two means that the empirical formula is $\text{C}_3\text{H}_6\text{O}_2$.

Calculating the molecular formula

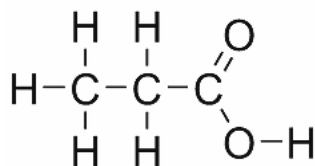
Continuing the numbering from the previous steps above

Step 4: Note that the relative molecular mass (M_r) of propanoic acid is 74.06 g mol^{-1} .

Step 5: Calculate the relative molecular mass from the empirical formula.

The M_r of a fragment of empirical formula, $\text{C}_3\text{H}_6\text{O}_2$, is 74.06 g mol^{-1} . This means that the molecular formula is the same as the empirical formula and so is $\text{C}_3\text{H}_6\text{O}_2$.

The only plausible structure of the molecule is



and this is confirmed by the instrumental, spectrometric and spectroscopic, methods discussed later in this volume.

It also reinforces the chemical data such as that the crystalline solid dissolves in water and creates an acidic solution and reacts with, neutralising, alkaline solutions.

Cyclohexene

Step 1: The elemental composition of cyclohexene acid is C: 87.70%, H: 12.30% and the molecule has a relative molecular mass of 82.10 g mol^{-1} .

Step 2: Divide each percentage composition by the relative atomic mass of the element:

	C	H
	$\frac{87.70}{12.00}$	$\frac{12.30}{1.01}$
=	7.31	12.18

Step 3: Divide the results by the lowest number which in this case is 7.31 (carbon):

	C	H
	$\frac{7.31}{7.31}$	$\frac{12.18}{7.31}$
=	1.00	1.66

Atoms can only exist as whole numbers so this means that we have to multiply the proportions:

Multiplying by

gives us

	C	H
2	2.00	3.32
3	3.00	4.98

Rounding up gives us the empirical formula C_3H_5 .

Calculating the molecular formula

Step 4: Note that the relative molecular mass (M_r) of propanoic acid is 82.10 g mol^{-1} .

Step 5: Calculate the relative molecular mass from the empirical formula.

The M_r of a fragment of empirical formula, C_3H_5 , is 42.05 g mol^{-1} .

Since this is half of the relative molecular mass of the molecule, this leads to the obvious conclusion that whilst the empirical formula is C_3H_5 , this means that the molecular formula is C_6H_{10} .

The only plausible structure of the molecule is



and this is confirmed by the instrumental, spectrometric and spectroscopic, methods discussed later in this volume. Note that it is irrelevant where the $\text{C}=\text{C}$ bond is drawn as a simple rotation makes all possible structures chemically and magnetically equivalent.

Definitions

It is very important that scientists know exactly what each is referring to, for two reasons, clarity and brevity. It is, sometimes, said that scientists want people to be *blinded by the science*. This is not correct and it is not a deliberate attempt to exclude anybody. It is merely an attempt to refer to certain concepts which then require no further explanation.

There can be confusion about terms which have very precise meanings in science, again for clarity, but which have multiple meanings in every day usage. Four examples are **work**, **energy**, **charge** and **magnetism**.

Work

We all know that **Work** can mean, in everyday English language, paid work, classwork, homework etc;

In physics, though, **Work** has a very precise definition:-

Work is performed when something is made to move by something else.

There is no reference to how the **something** is made to move or even what the **something** is and it can, therefore, cover movement due to impact of particles (*mechanics*) such as the collision of the white ball with other balls on a pool table and also action at a distance by *fields* (magnetic and/or electric) which is demonstrated by the repulsion or attraction between two bar magnets depending on the orientation of the magnets and hence their poles.

Energy

Given the above definition of **work** we can now define the term **energy** which does sound a bit vague but is actually very precise. Again, we all know the everyday meaning such as when tired but asked to do something we say “*Oh, I don't have the energy . . .*”

However, in physics:- **Energy is the ability to perform work.** In other words, possession of **energy** is the possession of the ability of *something* to move *something else*. Again the *something* and *something else* are undefined.

Energy is the basis of everything and, whatever pupils learn in school, there are only two forms of energy:

- There is energy associated with movement which is known as **kinetic energy**;
- All other forms of energy are stored and provide bodies with the *potential* to perform work and are traditionally known as **potential energy**. These types are now more commonly described as *stored energy* and include chemical energy, nuclear energy, the energy stored in a compressed spring or a taut rubber band (elastic energy), the energy we obtain from food (also chemical energy) etc; but the clearest example is *gravitational potential energy* (G.P.E.) which explains why a ball will drop down a staircase or a ball kicked over a cliff will fall to the ground.

We also have magnetic and electrical energy which brings us on to electromagnetic radiation which is a means of transferring energy from one location to another, remote, location and is highly significant for the rest of this series. Later pages discuss the movement of electrons between energy levels and require either the input of energy to allow transition from one level to a higher one, ultimately leading to ionisation, or releasing energy when transitioning from a higher to a lower energy level.

Charge

The concept of charge has been described since at least the time of the ancient Greeks who knew the effect of rubbing amber on a material and then attracting or repelling other materials. This is replicated in every schoolchild's experience of rubbing a plastic ruler on a sleeve and picking up small pieces of paper, repelling another charged ruler, made of different material, and also diverting a stream of water from a tap.

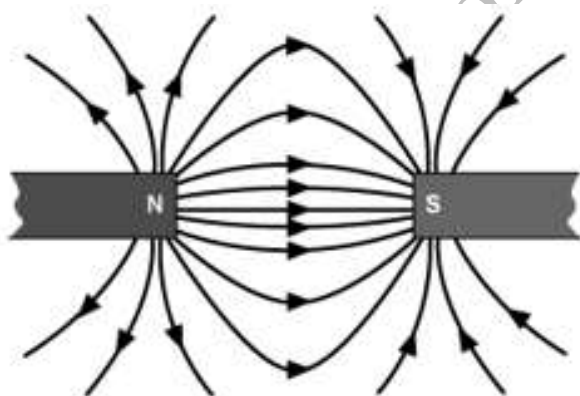
Scientists use the term **charge** so often that it is easy to forget exactly what the term means and why there are two forms of charge.

Put simply, and as the ancient Greeks described it,

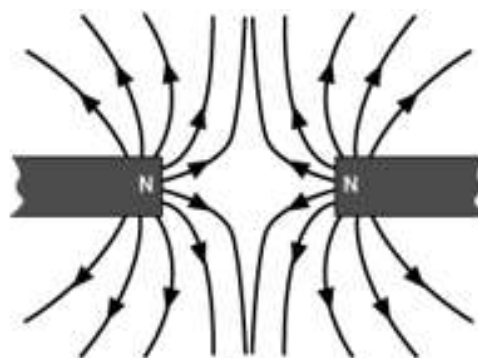
Charge is the ability of a material to **attract** or **repel** another material

Since there are two actions of **charge**: *attraction* and *repulsion* they became referred to both as North & South and positive & negative. This is now understood to be due to *static* electricity.

Charge has a special property however and that is its ability to perform work at a distance i.e. to make another object move. This *work* is to attract or repel another charged substance but at a distance without any contact as in bar magnets whose N – N and S – S poles repel each other but N – S poles attract. This led to the concept of fields where the invisible *lines of force* are drawn with an arrow as in the familiar pictures of bar magnets attracting or repelling each other depending on their arrangements. All school children are familiar with visualisation of the field using a bar magnet and iron filings which reveals the lines of force as shown below.



Unlike poles attract



Like poles repel

This also leads us to the definition of a *neutral* material which is one which is unaffected by a charged object.

As an aside, when *current* electricity was discovered and it was determined that it constituted a flow of these charges, circuit diagrams were drawn as if the flow of the current was from positive to negative and hence was described as a flow of positive charges.

We now know that the flow of charges is actually the movement of negatively charged electrons and the current flows in the opposite direction but, for consistency with the many decades of drawn circuit diagrams, circuit diagrams are still drawn in that way.

Magnetism

Magnetism is a physical phenomenon which results in attractive and repulsive forces between objects. All materials possess magnetic properties. There are three types of magnetism: *paramagnetism*, *diamagnetism* and *ferromagnetism* and the phenomenon arises from the electrons surrounding the nucleus which as a spinning charge create a magnetic field.

Diamagnetism occurs in all materials and is caused by the tendency of a material to oppose, and hence be repelled by, an applied magnetic field. Diamagnetism occurs in materials which contain no unpaired electrons. *Spin pairing* of electrons is discussed later in this volume.

Paramagnetism is exhibited by substances that resonate with, and strengthen, an applied external magnetic field. They are materials which contain an unpaired electron in each atom and create their own field which cannot be cancelled out by the non-existent fellow electron and creates a *magnetic moment*. This unpaired electron is free to align its magnetic moment in any direction and does exactly that in the absence of an applied external magnetic field. The magnetic field of the Earth is far too weak to have any effect however, in the presence of an applied external magnetic field, these magnetic moments will tend to align themselves in the same direction as the applied field and hence reinforce and strengthen it.

Ferromagnetism is exhibited by the common metals iron, cobalt and nickel as well as by a handful of the rare earth metals and some alloys. This phenomenon is caused by the presence of an unpaired electron but in these materials there is also a tendency for these electrons' magnetic moments to align themselves permanently to create a lower energy state.

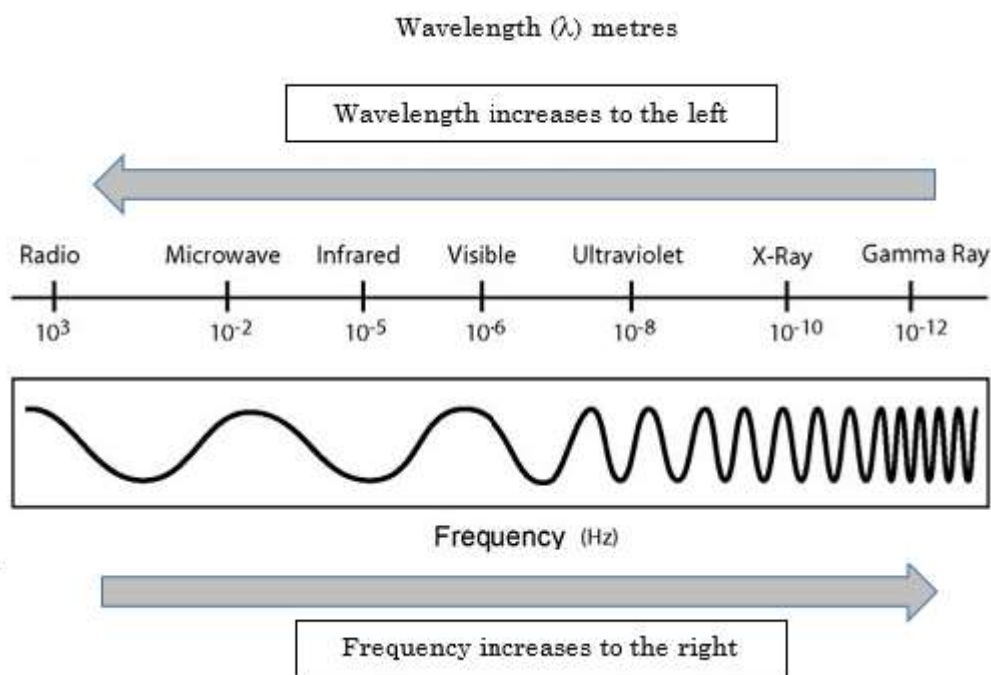
The specific details of the movement of an electric charge is of extreme importance:

- We now know that charged materials possess a surplus or a deficit of electrons and this means that they are, respectively, negatively or positively charged;
- An electric current is the movement of a stream of electrons which by their very movement create a magnetic field.
- An electric field is created by the presence of two different metals which are of different electronegativity which is discussed later;
- A charged particle can be moving whether changing its location or merely rotating (*spinning*) and nuclear spin is also discussed later in this volume;
- All particles rotate, *spin*, at even the lowest temperatures so magnetic fields are always created;
- In most cases the magnetic fields cancel each other out;
- There is a deep connection between electric charges and magnetic fields since the magnetism is created by the movement of the charge;
- The combination of electric fields and magnetic fields lead to the formation of electromagnetic radiation e.g. light.

All of this is highly relevant to the discoveries we discuss and investigate later in this volume and so it is worthwhile refreshing our ideas about the electromagnetic spectrum which is highly pertinent to our investigations.

The Electromagnetic Spectrum

It is worthwhile, briefly reconsidering the electromagnetic spectrum and when particular wavelengths of light can impact on chemical compounds and inform us about their structures. Just as all countries put their nation in the centre of a world map, we place the visible portion of the electromagnetic spectrum in the centre which is not mathematically correct but all regions are important and of use, as demonstrated below.



Applications of the electromagnetic spectrum and an approximation of the size of the wavelengths

Region	Scale	General Applications	Scientific Applications
<i>Radio</i>	Buildings	Radio and TV transmissions	Multinuclear NMR spectroscopy
<i>Microwave</i>	Humans	Radar, mobile signals & heating food	Rotational analysis of molecules and air pollution analysis
<i>Infrared</i>	Butterflies	Remote controls and thermal imaging	Determination of functional groups and elemental composition
<i>Visible</i>	A fine needle point	Human Vision	Colours and the discovery of optical activity
<i>Ultra violet</i>	Bacteria and viruses	Suntans, Vitamin D production	Electronic transitions within metals, determination of oxidation states and water pollution analysis
<i>X-Ray</i>	Atoms	Medical assessments	Determination of the impurities in metals
<i>Gamma ray</i>	Atomic nuclei	Radiotherapy	Nuclear chemistry, astrophysics and geochemical analysis

Later in this volume we will investigate describe the application of infrared radiation, radio waves and visible light as well as, in some cases, the use of electric and magnetic fields. In the following pages we will investigate three techniques, infra red spectroscopy; mass spectrometry and nuclear magnetic resonance spectroscopy.

Infrared spectroscopy is a technique for the determination of the presence or absence of functional groups.

A *functional group* is an atom or group of atoms within a molecule that behave similarly wherever they appear in different compounds. This means that even when other parts of the molecule are quite different, certain functional groups tend to react in certain ways. For our purposes these include O – H, C = C and C = O and C – O bonds which can all be detected by infrared spectroscopic analysis, enabling the confirmation of the structures of alcohols, alkenes, aldehydes and ketones as well as carboxylic acids and esters. Quite often it is not capable of distinguishing between isomers (molecules of the same molecular formula but different structures e.g. the isomers propan-1-ol and propan-2-ol) and this is where mass spectrometry and nuclear magnetic resonance spectroscopy become invaluable.

Mass spectrometry involves the application of electric fields to accelerate ions and magnetic fields to deflect them i.e. make the charged particles slightly change direction in order to separate them and determine their relative mass/charge ratio.

Nuclear magnetic resonance spectroscopy is the most powerful technique of all as it allows the determination of the precise arrangements of hydrogen and carbon atoms in a molecule.

To make use of the information all these techniques provide we need to understand the structure of the atom.

The following chapter discusses the various experiments and calculations that led from the concept of the atom being a hard and indivisible particle about which nothing could, apparently be known, to the determination that all matter has an associated wave and all waves can be associated with matter and some high energy waves can, indeed, produce matter. The concept of the wave – particle duality of matter is discussed in the next chapter and is a hard concept to accept and understand by all of us including the physicists who discovered it.