Extension 6: Case Studies from the History of Chemistry

Unit 6 in the book contains much of the chemistry we associate with chemistry laboratories: changes in colour, fizzing solutions, smelly gases and precipitation. The chemistry contained in the unit provides a good background to briefly look at a few pieces of the history of chemistry.

1. The history of chemistry in context

It is tempting to look back at chemistry over the last four centuries with a condescending eye. For example, why did our ancestors believe that the process we now call the oxidation of copper in air involved the loss of a material called phlogiston? Why did it take so long to accept that the simplest formula of water is H_2O? We will look at these examples in greater detail later, but for now it is worth emphasising that the raw intellectual capacity of humans has remained unchanged for thousands of years. Put another way, if hypothetically, one hundred children at birth were taken from their home in 1600 and placed in homes in the 21st century, the average intellectual and educational progress of the children would be indistinguishable from that of other children in other families. Our ancestors have included geniuses such as Isaac Newton and Gottfried *Leibniz*. What we should be aware of is the very different environment that we now live in: an environment that has stimulated an historically relatively recent explosion in scientific progress on an unprecedented scale. Science is a human activity and scientific activity does not occur in a vacuum. Modern society has given individuals, which we now call scientists, the time and resources to discover, invent – and crucially - to educate future generations and pass down knowledge, principles and practice.

A key stimulant to the development of science has been the growth of our communities. Thousands of years ago, humans lived in relatively small communities and many of their lives were dominated by the physical need for food and warmth. Many people had short lifespans. Being preoccupied with getting enough to eat, there was little opportunity for specialisation in science or anything else. Even towns did not possess the critical mass of experts to make much progress. It is not surprising then, that scientific progress and the increasing mastery and use of nature, has paralleled the development of agriculture and (later) industrialisation, all of which created larger centres of population. By the late 19th century, professional scientists, engineers and mathematicians emerged, replacing the small numbers of part-time or amateur scientists or the scientists of the royal courts of previous decades. The new breed of professional scientists and engineers worked in industry as well as in the universities. The scale of scientific activity in the modern era would be staggering to our ancestors, with scientific-related activity now part of every commercial, public and industrial venture.

Modern science uses well-developed processes to assess and validate scientific work and journals to communicate scientific progress throughout the world. Some indication of the growth of science over recent time may be gauged by noting the increasing volume of publications. For example, the journal index *Chemical Abstracts* provides a paragraph summarising each paper from thousands of other journals. In the year 1907, about 12,000 abstracts were included in Chemical Abstracts. It took 30 years for Chemical Abstracts to log its first million abstracts, but after one hundred years it had indexed over a million records in a single year and was now adding new entries at a rate of over 20,000 per week.

The scale, technical sophistication and specialisation of scientific endeavour in the 21st century dwarfs that of the 17th, 18th or 19th centuries. When the great pioneers of chemistry, such as Antoine Lavoisier (1743-1794) and Joseph Priestley (1733-1804), were carrying out their famous investigations, they worked alone or in small groups and only a relatively small number of researchers across the world eagerly followed their progress. Faced with these facts, the achievements of such scientists in their scientifically impoverished times is all the more remarkable.
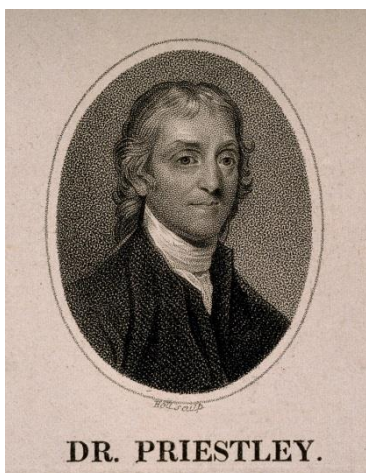
Fig. 6.1 Joseph Priestly. Credit: Wellcome Collection, CCBY

Fig. 6.2 Antoine Lavoisier and his wife Marie-Anne, who assisted him in his laboratory and edited and published his memoirs, painted by Ernest Board. Wellcome Collection, CCBY

We make two cautionary notes before proceeding. The first relates to the influence of religion on scientific thought. By 1750, the influence of the occult and the supernatural on western societies was weakening, but even so we must not make the mistake of imagining that we can put ourselves in the place of scientists of say 200 years ago and judge their lives and achievements on that basis. Their culture and environment was very different to our own, and religion often remained much more central to their interpretation of the world than it is for many scientists today. In other words, they saw the world through a different 'lens'.

Second, as a result of the need for simplification and brevity in introducing the history of science to students, eminent scientists have often be dramatically depicted (or even eulogised) as single discoverers with their own 'eureka moment'. This was often untrue: scientific progress is often slow and across a broad front with many stops, starts and reversals, and with many scientists contributing to the final development of a theory or new discovery even though some play a bigger part than others. It can also take decades for the full importance of a discovery (theoretical or practical) to be recognized. So, in summary, although we tend to concentrate on one or two key scientists in connection with a particular discovery, this is likely to be a simplification.

2. The legacy of alchemy

"*Alchemy involved seeing the extraordinary where the uninitiated saw nothing, because they stopped at the surface when they could have chosen to penetrate below it.*" – David Knight, Ideas in Chemistry.

Alchemy is often thought of as a set of philosophical and pre-scientific practices, centred on the manufacture of gold from less valuable metals and the search for the elixir of life. It covered many more subjects than this, yet, from a practical perspective, its historical importance lies in the

development of the techniques and equipment still used in the modern chemistry laboratory. These include flasks, distillation and the use of flames to bring about chemical change. For example, distillation led the way to chemical analysis and to the production of alcoholic drinks. Distilling a mixture of potassium nitrate and copper sulfate produced nitric acid ('aqua fortis' – 'strong water'). Mixing nitric acid with hydrochloric acid produced 'aqua regia' – 'royal water' – which even dissolved gold. Alkalis were known from the manufacture of soap, so that the range of laboratory reagents was gradually expanded.
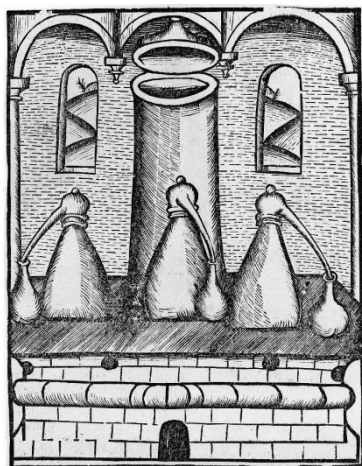

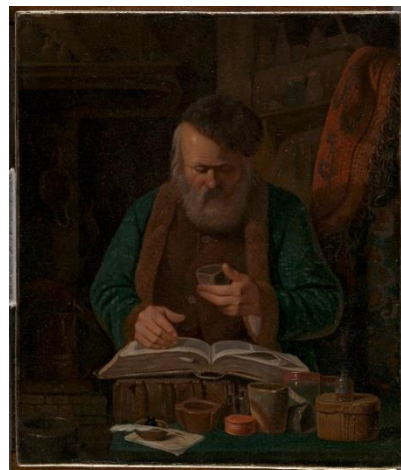Fig. 6.3 Distillation furnace. Credit: Wellcome Collection, CCBY

Fig. 6.4 Alchemist at work. Painted by Emile Francois. Credit: Wellcome Collection, CCBY

3. Phlogiston and oxidation

If copper metal is heated in air, a black powder (copper (II) oxide) forms on the surface of the metal:

$$2Cu(s) + O_2(g) \rightarrow 2CuO(s) \quad\quad\quad (1)$$

Imagine that 1 mol of copper is completely converted to copper(II) oxide. Since the oxide contains both copper and oxygen, 1 mol of copper oxide has a greater mass than 1 mol of copper metal. In other words, the copper metal has gained mass. This is our modern view of the oxidation of copper, but in centuries past a very different rationalisation of the experimental observations was made, one that involved a 'material' named phlogiston. This was at a time when the gaseous state was poorly understood, when heat was regarded as a substance ('caloric') in its own right, before the atomic theory was routinely used by chemists and when the idea of a metal like copper or gold being an element was not yet understood.

The phlogiston theory came from the work of Georg Stahl (1635-1682). He supposed that what we call metal was in reality 'calx' bonded to an elementary material known as phlogiston. The formation of calx in air resulted from the reaction:

$$(calx\text{-}phlogiston) \rightarrow calx \ + \ phlogiston \quad\quad\quad (2)$$
$$\text{(i.e. metal)}$$
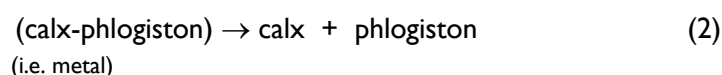
The phlogiston escaped from the metal and entered the air, leaving the non-metallic calx. The reaction had very little to do with the atmosphere (the air) which only served to receive the phlogiston. This meant, of course, that the metal lost mass (the loss in mass was equal to the mass of phlogiston lost) when heated in air and we will return to this shortly. A similar process was thought to occur in the combustion of a candle and again, phlogiston was released.

In modern terms, phlogiston might be described as 'minus (or negative) oxygen': whereas we now know that oxygen is *used up* in combustion, phlogiston was supposed to be *produced* in combustion.

If copper(II) oxide is heated with charcoal, metallic copper is formed. In modern terms - and with our knowledge of what is happening on the molecular scale – we would write:

$$2CuO + C \rightarrow 2Cu + CO_2 \qquad\qquad (3)$$
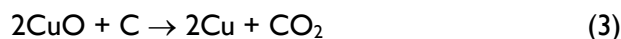
But Stahl's interpretation of this process was that the material we call charcoal *contained* phlogiston which was *transferred* to the black powder (copper(II) oxide) producing the material copper metal:

$$calx \ + \ phlogiston \rightarrow (calx\text{-}phlogiston)$$
$$\text{(i.e. metal)}$$
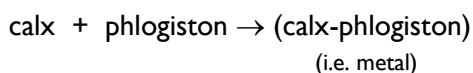
To someone of the 21st century, an explanation involving phlogiston appears implausible because we know that copper is an element and so copper metal does not contain phlogiston or anything else. Once it is realized that copper metal contains only copper atoms, the phlogiston idea falls, but this was not understood in Stahl's time and most chemists accepted the phlogiston theory until cracks appeared in the theory after about 1775.

The French civil servant Antoine Lavoisier (1743-1794) was one of the most important chemists in history, and he had an important part to play in the story of phlogiston. Lavoisier was familiar with the experiments of Louis-Bernard Guyton de Morveau (1737-1816) in which it had been shown that when metals were heated in air they gained mass: they did not lose mass. Lavoisier realized that this was difficult to explain using the phlogiston theory and that the gain in mass during reactions that we now call oxidations was likely to be because air was being 'fixed' in the metal. 'Fixed air' could be released when metal calx (oxide) was heated with charcoal. We now realize that the 'fixed air' being referred to in the reaction of metal with air is oxygen itself, whereas the 'fixed air' produced when oxides are heated with charcoal is carbon dioxide. To help reduce confusion, CO_2 is sometimes referred to as 'Black's fixed air' as it was the Scot Joseph Black (1728-1799) that was responsible for the experiments involving carbonates.

Although Lavoisier did not realize it, several 'airs' (i.e. gases) had already been studied. This included hydrogen, hydrogen chloride, carbon monoxide and oxygen itself, although these gases had other names in the 18th century. Evidence was also mounting that atmospheric air consisted of several gases. At first, Lavoisier proposed that the fixed air involved in the formation of the black coat of copper was Black's fixed air (CO_2), but a famous experiment involving mercury convinced him otherwise.

The experiment was as follows. When mercury is heated in air it also forms an orange material which we now understand to be mercury(II) oxide. The equation for the reaction is:

$$2Hg(l) + O_2(g) \rightarrow 2HgO(s)$$
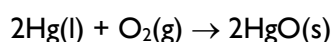
but unlike copper(II) oxide, it happens that mercury(II) oxide is easily decomposed by heating:
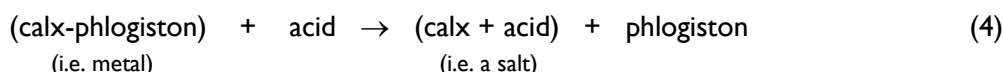
$$2HgO(s) \rightarrow 2Hg(l) + O_2(g)$$
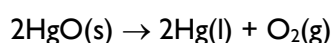
liberating oxygen gas. This experiment was famously carried out by Joseph Priestley in 1774. Priestley noted that the 'air' (i.e. gas) produced when mercury oxide was heated supported combustion much better than atmospheric air. The gas was, of course, oxygen itself, but Priestley

was a supporter of the phlogiston theory and so he called it 'dephlogisticated air'. It was later named 'oxygen', meaning 'acid producer', because carbon, sulfur, phosphorus produce acidic gases upon combustion.

Lavoisier realized that the production of (what we now call) oxygen by heating mercury was a very significant experiment since the mercury metal was regenerated simply by heating. No charcoal was needed and so there was no obvious way in which phlogiston could be introduced into the mercury oxide. This, along with the loss in mass when metals are oxidised in air, served to severely undermine the phlogiston theory.

However, Lavoisier remained cautious as phlogiston appeared to explain why hydrogen was produced when some metals react with acid. The phlogiston theory easily explains this by assuming that the salt produced is a combination of calx (oxide) and acid:

$$(calx\text{-}phlogiston) \quad + \quad acid \quad \rightarrow \quad (calx + acid) \quad + \quad phlogiston \qquad (4)$$
$$\text{(i.e. metal)} \qquad\qquad\qquad\qquad \text{(i.e. a salt)}$$

Lavoisier finally provided an alternative explanation for the production of hydrogen from acid and metal after learning of the work of Henry Cavendish (1731-1810). Cavendish had shown that when inflammable air (hydrogen) and 'dephlogisticated air' (oxygen) react, water is made. This suggested that water was not an element. In this reaction, which we now depict by the equation:

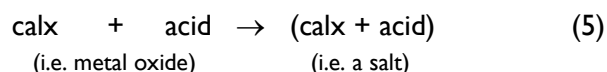$$H_2(g) \ + \ O_2(g) \ \rightarrow \ 2H_2O(l)$$
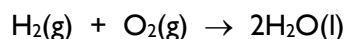
hydrogen gas has made a new substance (water). This raises the possibility that hydrogen itself could also come from a substance which was not an element. Taking the reaction of zinc and sulfuric acid as our example, the modern version of Lavoisier's explanation becomes clear from the chemical equation:

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) \ + \ H_2(g)$$
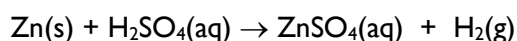
This shows that the hydrogen gas originates from the acid itself and there is no need to invoke phlogiston in our explanation.

Metal oxides do not produce hydrogen gas when reacted with acid. The phlogiston theory explained the lack of hydrogen by supposing that this reaction involved calc (oxide) and acid to produce a salt:

$$calx \quad + \quad acid \quad \rightarrow \quad (calx + acid) \qquad (5)$$
$$\text{(i.e. metal oxide)} \qquad\qquad \text{(i.e. a salt)}$$

The non-phlogiston explanation for the fact that hydrogen was not produced when metal oxides react with acid was only possible after it was realized that water was produced as one of the products. For example:

$$CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) \ + \ H_2O(l)$$
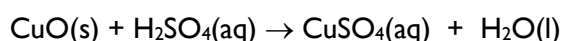
Historically, the water was not easily identified in this reaction as a product because the reaction took place using aqueous acid in the first place and the additional water produced in the reaction was therefore largely concealed. Using the language of modern chemistry, the fact that hydrogen gas is not produced in this reaction has a simple explanation: the hydrogen of the acid appears in the product water and not as hydrogen gas. Once more there is no need to invoke phlogiston in our explanation.

As to the gain in mass when metals oxidise in air, this does not appear to have greatly perplexed the defenders of phlogiston and it was even suggested that phlogiston is sometimes without mass! The proposed nature of phlogiston itself changed over the years. Initially, in the 'Old Phlogiston' theory, phlogiston was regarded as what we might nowadays call 'minus oxygen': but as early as 1766 phlogiston was considered identical to 'inflammable air', produced by reacting metals with acid, and now known as hydrogen gas, H_2. Looked at with our knowledge from the 21st century, it is difficult to see how hydrogen would be involved in the oxidation of metals in air, but the realization that metals react with the oxygen of the air only came later.

Eventually the idea of phlogiston changed again and it became strongly connected with the heat and light associated with chemical reactions but by then the credibility of the phlogiston idea was much weakened in the eyes of many chemists, and by 1785 Lavoisier was able to write with both confidence and authority that: 'Chemists have made phlogiston a vague principle which is not strictly defined and which consequently fits all the explanations demanded of it. Sometimes it has weight, sometimes it has not…' It [the phlogiston theory] is a veritable Proteus that changes its form every instance'.

Despite this, the eminent Joseph Priestley never rejected the role of phlogiston and even Sir Humphry Davy referred to phlogiston in his writings of 1807. The idea of phlogiston slowly faded: there was no revolution overnight.

Lavoisier's status in the history of chemistry is such that he is often referred to as 'the Father of Modern Chemistry'. In addition to his work on combustion and oxidation and on the destruction of the phlogiston theory, he pioneered the belief that mass is conserved in chemical reactions and along with others, he built up a list of substances which could not be broken into simpler substances – the forerunner of the list of elements we take for granted today. Lavoisier's work set the scene for the next revolution in chemistry - the use of the atomic theory of matter led by John Dalton. Lavoisier did not believe that 'atomism' would ever be practically important to chemists and so it is doubly unfortunate that Lavoisier didn't live to see the impact of Dalton's work. Lavoisier was executed in 1794 (at the age of 50) in the French Revolution for being a tax inspector.

4. Electrolysis and the formula of water

Every school pupil knows that the formula of water is H_2O? But what is the reasoning for believing that the formula is H_2O? What is the proof that 'water is H_2O?' This is not nearly as straightforward as it might at first appear!

The electrolysis of water is sometimes thought to be the proof needed. The equipment usually used is called a Hofmann voltameter. It consists of two tubes each connected to a source of direct current (DC) by a platinum wire electrode (see Fig 6.5). Since water is poor conductor of electricity, a few drops of dilute sulphuric acid is added. Upon turning on the current, hydrogen gas collects at

the negative electrode (the cathode) and oxygen collects at the anode. More hydrogen is produced than oxygen. The ratio of the volume of the gases is: 2:1.
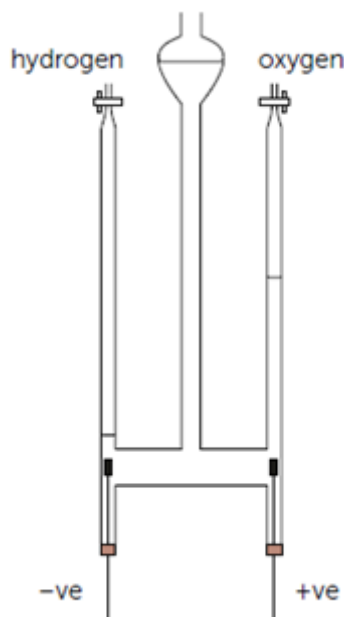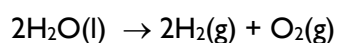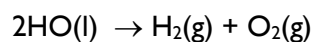

Fig. 6.5 Hofmann voltameter

According to Avogadro's Law, volumes of gases at the same temperature and pressure may be equated with numbers of molecules. The fact that twice the volume of hydrogen is produced as oxygen means that twice as many hydrogen molecules are produced from electrolysis as oxygen molecules. This may induce us to regard this as proof that the formula of the water molecule is H_2O, since it also contains the 2 to 1 ratio of H to O as observed in electrolysis, but such a step is unjustified and the next section examines this in greater detail.

Knowing that the formula of water is H_2O, and that of hydrogen H_2 and oxygen is O_2, the electrolysis of liquid water may be summarized as:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

It is interesting to note that if water had the formula HO then the equation for electrolysis would be:

$$2HO(l) \rightarrow H_2(g) + O_2(g)$$

In that case, the volumes in each limb of the Hofmann voltameter would be equal. If hydrogen gas were monoatomic (i.e. H not H_2) and oxygen diatomic and water was HO, the volume ratio would be two to one:

$$2HO(l) \rightarrow 2H(g) + O_2(g)$$
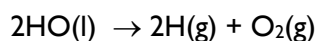
This is, of course, the observed ratio.

The two to one ratio of hydrogen and oxygen gas (and therefore of gaseous volumes) would also be obtained if the formula of water was H_4O_2:

$$H_4O_2(l) \rightarrow 2H_2(g) + O_2(g)$$
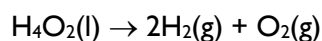
A summary of the position is at follows. Only if we take for granted that both hydrogen and oxygen gases are diatomic does the two to one volume observed from the electrolysis of water confirm the formula of water is in the simple ratio H_2O. Even then, its true molecular formula might be a multiple of the 2:1 ratio e.g. H_4O_2. Historically of course, the molecular formula of hydrogen and oxygen gases (now known to be H_2 and O_2) were as unknown as the molecular formula of water itself. Historically then, electrolysis did not prove that the formula of water is H_2O.

5. Relative combining masses and the formula of water

We have failed to prove the formula of water by electrolysis and now we turn to the masses of hydrogen and oxygen gases that react to produce water. If we write the equation for the formation of water as:

$$\text{hydrogen gas} + \text{oxygen gas} \rightarrow \text{water}$$
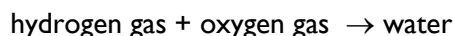
our question is, 'what mass of hydrogen and oxygen gases are required to produce 1.00 g of water?'

Fortunately, the reaction of hydrogen and oxygen goes to completion, and by ensuring we start with two volumes of hydrogen to one of oxygen we can ensure that at the end of the reaction only water is present and that there is no oxygen or hydrogen left over. It is found that 1.00 g of hydrogen gas reacts with 8.00 g of oxygen gas to produce 9.00 g of water. Provided we know the atomic masses of hydrogen and oxygen:

$$m(H) = 1.00 \text{ u}; \qquad m(O) = 16.0 \text{ u}$$

we can work out the number of moles of hydrogen and oxygen atoms reacting:

$$\text{moles of H} = 1.00/1.00 = 1.00 \text{ H}; \quad \text{and} \quad \text{moles of O} = 8.00/16.0 = 0.50 \text{ O}_2$$

The relative number of moles of atoms reacting to make water is therefore 1.0 : 0.50 = 2:1. This means that the simplest formula of water is H_2O. This is only the *ratio* of the number of hydrogen and oxygen atoms, so that the formula might be H_4O_2 or H_8O_4.

Measuring the masses of reacting hydrogen and oxygen has confirmed the simplest formula of water as H_2O, but historically there was an obstacle to those seeking this conclusion. How do we know the atomic masses ('atomic weights') of hydrogen and oxygen? Without those masses, we cannot calculate the number of moles of H and O atoms and so we cannot determine the simplest of water.

One response to this difficulty might be to argue that since there are twice as many hydrogen atoms as oxygen atoms in the water molecule (H_2O) and we know (from experiment) that 1.00 g of hydrogen reacts with 8.00 g of oxygen, the atomic mass of an atom of oxygen must be 16 times that of an oxygen atom. In this way the proposal goes, we have established the relative atomic masses of H and O. Of course, this is nonsense, since we still have to ask the question 'how do we know the simplest formula of water to be H_2O?' We are stuck and going around in circles. **We cannot find the formula of water without the atomic masses of H and O and we cannot find the atomic masses of H and O without knowing the formula of water is H_2O.** This kind of difficulty is called 'circularity' and historically, the atomic theory of chemistry struggled to make progress because of circularity.

Atomic mass of H and O?
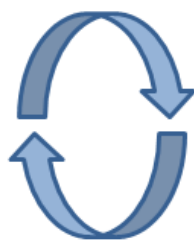
Formula of water?

Fig. 6.6 Circularity: the early 19th century dilemma. We cannot find the formula of water without knowing the atomic masses of hydrogen and oxygen, and we cannot find the atomic masses without knowing the formula of water.

Circularity was not only an obstacle to further progress in a matter which was fundamental to chemistry but also an embarrassment to the scientific community. In the mid-1960s an anonymous writer, identifying himself as a certified lunatic at Hanwell asylum London, sent satirical letters to the publication 'Chemical News' mocking the inability of chemists to agree on something as apparently simple as the formula of water. Indeed, the period 1820-1850 is sometimes described as chaos in the world of chemistry, and at its heart was the difficulty in determining the relative masses of atoms themselves.

John Dalton (1766-1844) realized the difficulty caused by circularity. To break the difficulty, he assumed that nature would prefer a one-to-one combination of atoms. The formula of water would therefore be HO. Dalton rationalised this approach in the belief that similar atoms would repel each other so that H_2O (with two H atoms repelling each other) or HO_2 (two oxygen atoms repelling each other) would be more unstable than HO. Similarly, hydrogen gas was H and oxygen was O. Dalton's 'rule of simplicity' was, of course, wrong and it was the work of Joseph Gay-Lussac (1778-1850) and Amedeo Avogadro (1776-1856) that began the assault on Dalton's formula of HO. Gay-Lussac established that when water is formed as a gas, two volumes of water are produced from exactly one volume of oxygen gas. Avogadro established that at the same temperature and pressure equal volumes of all gases contain the same number of molecules. According to Dalton, the formation of water should be represented by the equation:

$$H(g) + O(g) \rightarrow HO(g)$$
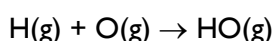
But following Gay-Lussac, if the volume ratio of oxygen to water is 2:1, as observed experimentally, then this means that the reaction is better represented as:

$$H(g) + \tfrac{1}{2}O(g) \rightarrow HO(g)$$
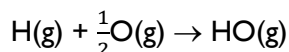
on the molecular scale. Whatever the formula of water, it was universally agreed that atoms are indivisible, so that half atoms of oxygen ($\tfrac{1}{2}O$) were impossible. (This indivisibility of atoms in chemical reactions holds good today). This suggested that oxygen *molecules* consisted of more than one atom: this might be true of hydrogen too.

What was required were ways to find the atomic masses of elements without having to know the formula of the molecules they contained and it took about fifty years, until about 1850, for the values of atomic masses of common elements (and therefore the formula of water) to be agreed. The idea of valency (the combining power of atoms) was developed at about the same time.

The determination of atomic masses of elements is strongly associated with the Swedish chemist Jacob Berzelius (1779-1848) who, along with Joseph Priestley, Robert Boyle, John Dalton and Antoine Lavoisier, is regarded as one of the 'Fathers of Chemistry' (see book, p. 27). Berzelius accepted the principles of Dalton's atomic theory but realized that Dalton's atomic masses of elements were insufficiently accurate to be of use in assigning molecular formulae. Berzelius assigned atomic masses by applying remarkably insight and by considering experimental facts, such as work done by others on the density of gases and on the heat capacity of elements. The details of this work are involved and need not detain us here[1]. Berzelius published a table of atomic masses in 1826, many of which are fairly close to the values that are accepted today.

The determination of atomic masses – which we take for granted today - broke the chaos of chemistry and allowed the science of chemistry to develop into its modern form. It also allowed the simplest formulae of many compounds, including water, to be established with confidence.

6. Finding the formula of water using mass spectrometry

Nowadays, the easiest way to find the molecular formula of water today is to use a mass spectrometer to analyse water vapour. The strongest (parent) peak is observed at m/z = 18, corresponding to the ion H_2O^+. The peak at m/z = 17 is caused by the ion HO^+, produced by fragmentation. Scientists of previous centuries would have much appreciated the elegance and simplicity of this proof for the formula of water, for not only does it provide the simplest ratio of H to O atoms (**2**H to **1**O) but it allows a determination of the true molecular formula of the water molecule.
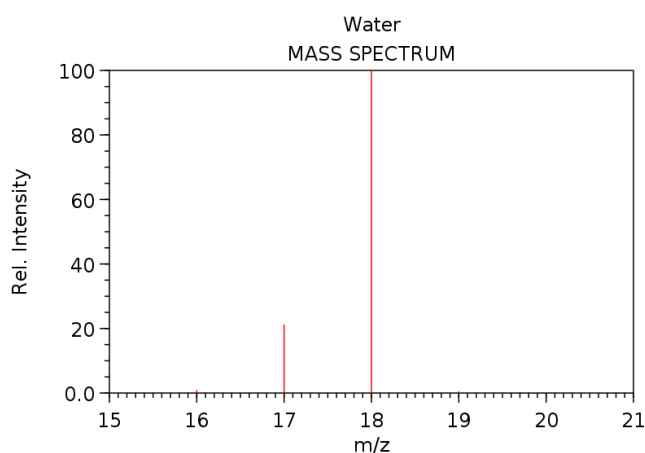

Fig. 6.7 Mass spectrum of water vapour. Source: NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard.

Further reading

1. The History of Chemistry, A Very Short Introduction, by William H Brock. Oxford University Press, 2016.
2. https://pubs.acs.org/subscribe/archive/tcaw/13/i12/pdf/1204chronicles.pdf An article on the importance of Jacob Berzelius' work.

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[1] A gentle introduction to how vapour density and heat capacity ('specific heat') were used to determine the atomic mass of elements and the molecular formulae of compounds will be found in either the first, second, third or fourth edition of an old school textbook, A New Certificate Chemistry, by A Holderness and J Lambert, published by Heinemann. It is sobering to realize that this subject formed part of the curriculum for those under sixteen year olds in past decades!