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HYDROGEN - SOME HISTORICAL HIGHLIGHTS

Abstract: The early history of experiments in which an inflammable air was prepared is outlined. Once hydrogen had been discovered by Cavendish in 1766, the world of science and technology was given a colossal impetus. Its scientific and social consequences form the main focus of this essay. Special attention is given to explain why experiments were done, and their aims. The many difficulties which confronted scientists in the interpretation of their results are discussed. Timelines have been used in order to facilitate an understanding of the evolution of ideas. A particular emphasis is given to the story of how, through spectral analysis of the hydrogen atom, our understanding of atomic structure developed. Experiments involving hydrogen constitute important teaching material in schools. Detailed instructions are given for making hydrogen in the laboratory and for demonstrating its lightness and flammability. Suggestions are made of how to use these reactions to teach a wide variety of chemical concepts and facts.

Keywords: hydrogen, gas, chemistry, atom, experiment

Introduction

There can be few better ways to introduce the subject of hydrogen to an audience, than to prepare it from a chemical reaction, fill a balloon with it and demonstrate its lightness, flammability and explosive combustion with oxygen. These effects can be achieved in simple demonstration experiments.

To prepare hydrogen and to fill a balloon with it, use high quality latex balloons of 30 cm (12") diameter. Apparatus and reagents: 500 cm³ plastic fizzy drink bottle, 150 cm³ 20 % (approx. 3.6M) sulphuric acid, 150 g granulated zinc (a great excess), 0.7 g copper sulphate pentahydrate, one 1 dm³ beaker, spatula. Method: The acid should be prepared 24 hours before the experiment, in order that it can cool down to room temperature. To make 1 dm³ of stock acid solution, carefully add 200 cm³ concentrated sulphuric acid to 800 cm³ water in a 2 dm³ beaker, stirring continuously. Since the reaction is strongly exothermic, the dilution should be done in a well ventilated room/fume cupboard. At the start of the experiment place the zinc and copper sulphate in the bottom of the plastic bottle, and place this in a 1 dm³ beaker containing about 500 cm³ cold water. This will serve to modify the speed of the reaction, which is exothermic. Carefully pour in 150 cm³ of the acid, and then stretch the neck of the balloon over the mouth of the bottle. The balloon will now take approximately 15 minutes to inflate, at an ambient temperature of 20 °C. After this period of time, carefully remove the balloon from the bottle, tie a knot in it and then tie it to a piece of thin string about 2 metres long, which is anchored with

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a weight e.g. a steel set screw, weighing 20 grams. The hydrogen in the balloon can be safely ignited, using a lighted wooden splint, which is attached to a 1 metre ruler.

To fill a balloon with a mixture of hydrogen and oxygen requires two stages - oxygen, followed by hydrogen. This experiment is more difficult to achieve and will require the assistance of a competent student or technician. A different colour of balloon is recommended. Apparatus and reagents: 500 cm³ fizzy drinks bottle, freshly prepared 3 % hydrogen peroxide solution, potassium permanganate, blue balloon. Method: Into a 500 cm³ plastic fizzy drinks bottle pour 300 cm³ of 3 % (10 vol.) hydrogen peroxide solution. Using a spatula, carefully insert about 0.1 g. potassium permanganate crystals. Immediately stretch the neck of the balloon over the top of the bottle, and swirl gently, to enable the permanganate to react with the peroxide. The mixture effervesces vigorously, and the balloon will start to inflate. With continued swirling, enabling the permanganate to react with more of the peroxide, the balloon should become partly filled (about 10-15 cm diameter) with oxygen. When the reaction has subsided (usually after 2-3 minutes), carefully remove the balloon from the bottle and keep its neck firmly pinched. Prepare another 500 cm³ fizzy drinks bottle for producing hydrogen, as described above, using the same quantities of reagents. Once the acid has been poured into the zinc and copper sulphate mixture, carefully attach the partially filled balloon to the mouth of this second hydrogen generator, and place this bottle into a 1 dm³ beaker containing 500 cm³ cold water, in order to modify the rate of reaction. This step must be carried out with the help of a second person. If the transfer of the balloon has been successful, and little oxygen has escaped, then this second balloon will become fully inflated with a mixture of hydrogen and oxygen, after some 15 minutes. It will rise when tied to an anchored string, but will be less buoyant than the balloon filled with pure hydrogen, on account of the greater density of oxygen. When ignited with a burning splint as described above, the mixture explodes with a loud report.

Figure 1 shows a balloon being filled with hydrogen gas from the reaction between zinc and sulphuric acid, using copper sulphate catalyst. Figure 2 shows the combustion, in air, of a balloon of hydrogen gas. Figure 3 shows the explosive combustion of a stoichiometric mixture of hydrogen and oxygen.

After the experiments have been completed, the hydrogen generators should be allowed to continue reacting overnight, during which time the acid will become fully neutralised and converted to zinc sulphate solution. This can be disposed of down the sink, and the remaining zinc rinsed thoroughly with water. It can then be re-used for about two more experiments. The residue from the oxygen generator, mainly water, can safely be washed down the sink.

There are several aspects of these experiment which lend themselves for teaching purposes: reactivity series of metals, acid plus metal reaction, displacement reaction, writing a word equation and balanced symbol equation, ionic equation, redox equation, catalytic activity, exothermic reaction, moles calculation involving concentration of solution and volume of gas produced, excess and limiting reagents. Once the hydrogen has burnt, there is more scope for teaching - writing word and balanced equations for the reaction of hydrogen with oxygen.

Experiments similar to these have been stalwarts of the repertoire of scientists, teachers and university lecturers, for over two centuries, even before Cavendish's notable achievement.



Fig. 1. A balloon being filled with hydrogen



Fig. 2. Hydrogen burning in air

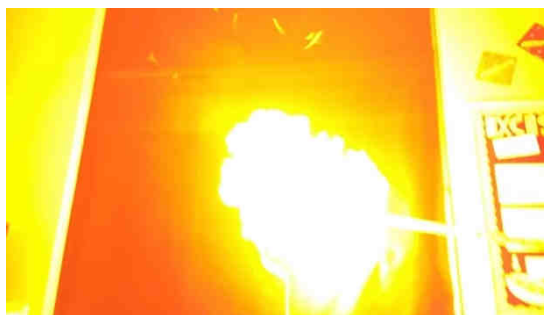


Fig. 3. Hydrogen/oxygen explosion

Prehistory

Hydrogen was discovered by Henry Cavendish [1731-1810] in 1766, yet several earlier accounts exist of the preparation of this flammable gas. This stands to reason because the mineral acids (sulphuric and hydrochloric) had been known since the Middle Ages, and metals such as iron, zinc and tin were known to the Ancients. Each of these metals reacts with acids to produce hydrogen as the principal aeriform product.

The first known written account of the formation of a foul smelling form of hydrogen (made from iron filings and oil of vitriol) is given by the Geneva born physician and iatrochemist Turquet de Mayerne [1573-1655]. Although the description of his experiment was not published until 1700, it is clear from manuscripts that he had performed it at some stage before his death. "I have taken 8 oz. of iron filings and in a deep glass cup I have added successively 8 oz. of oil of vitriol and a little later an equal quantity of warm water. There was produced an enormous agitation and a great ebullition and meteorism of matter easily quieted by stirring by a rod. There is also raised a most fetid sulphureous vapour very noxious to the brain, which (as happened to me not without danger) if brought near a candle takes fire, on account of which this operation should be made in the open air or under a chimney" [1].

In a work published in 1670 the Irish natural philosopher Robert Boyle [1627-1691] described the preparation and collection of hydrogen: "We took a clear glass bubble (capable of containing by guess about three ounces of water) with a neck somewhat long and wide, of a cylindrical form; this we filled with oil of vitriol and fair water, of each almost a like quantity, and casting in half a dozen small iron nails... and speedily inverting the phial, we put the neck of it into a small wide-mouthed glass... with more of the same liquor in it... soon after we perceived the bubbles produced by the action of the menstruum upon the metal, ascending copiously... the whole cavity of the glass bubble, and most of its neck, seemed to be possessed by air, since by its spring it was able... to hinder the... liquor from regaining its former place..." [1].

In a posthumously published work in 1700, Boyle described the combustion of hydrogen which he had prepared from "a very sharp and piercing saline spirit" (HCl) and iron filings. "Upon the approach of a lighted candle it would readily enough take fire and burn with a blueish and sometimes greenish flame at the mouth of the vial, for a good while" [1].

Nicholas Lemery [1645-1715] was a French chemist who formulated an early theory of acid/base reactions. He was an internationally renowned chemical demonstrator and author of one of the most important early chemical textbooks: *Cours de Chymie* which was first published in 1675, translated into several languages and republished in several editions. Holmyard notes that: the general impression left on the mind of the modern reader is that Lemery must have been one of the most acute and skilful experimenters that France has ever produced. Not the least interesting passage is that which describes the explosion of a mixture of air and hydrogen... "If 3 ounces of oil of vitriol be put into a middle-sized phial, with a long neck, and to it 12 ounces of water; then the mixture grows warm, if an ounce... of iron file dust be thrown into it... there will rise an ebullition,... which will produce white vapours that will rise and fill the neck of the phial. If one puts to the aperture a lighted wax candle, the vapour will immediately take fire, and at the same time occasion a violent and cracking noise" [2].

Since hydrogen has such a distinct and lengthy historical background prior to 1766, what was so special and different about Cavendish's discovery of it? In order to fully appreciate the significance of his discovery, it should be mentioned that during the second half of the 18th century two strands of chemistry were rapidly evolving: practical - the manipulation of gases (airs), theoretical - ideas about combustion.

In 1727, the English clergyman and natural scientist Stephen Hales [1677-1761] published his celebrated *Vegetable Staticks*. In this work he described the collection and manipulation of gases over water and mercury. The word "gas" had been coined by the Flemish iatrochemist Johannes Baptista van Helmont [1579-1644] in 1624, and different gases in our sense of the word were still described by philosophers as different "airs". As a scientist, Hales was primarily interested in plants and how they transport water. But he also developed a technique for collecting samples of "airs" which were formed in certain chemical processes e.g. heating coal to red heat in a gun barrel, and reacting iron filings with dilute sulphuric acid. During this early part of the 18th century, natural philosophers were concerned not only with widening the scope of their experimental techniques and investigations, but they were also trying to explain exactly what was going on. Among topics of particular interest at this time, was combustion.

The phlogiston theory of combustion was the ingenious brainchild of the German natural philosopher Johann Joachim Becher [1635-1682]. It was published in its original form in 1677 and subsequently developed by Georg Ernst Stahl [1660-1734]. It was a theory which had its roots in alchemical speculations, and which explained the process of combustion - a chemical process which had puzzled people since time immemorial. Phlogiston was said to be "the matter and principle of fire, not fire itself". Substances which were flammable were said to be rich in phlogiston, which escaped from the substance when it burnt. This explanation was easily accepted for substances which seemed to disappear, or became lighter when burnt e.g. coal, wood, sulphur. However, as the quantitative combustion of metals (such as tin and iron) became increasingly investigated during the course of the 18th century, they were shown to gain in mass during combustion. The validity of the phlogiston theory thus became more open to question. Neither Becher nor Stahl had conducted combustion experiments gravimetrically, thus they had no evidence to support their theory. The phlogiston theory underwent many modifications, including the suggestion that phlogiston itself had negative mass. Throughout the 18th century it still provided a satisfactory explanation to combustion phenomena, and was widely accepted by the scientific community.

On the basis of a thorough quantitative analysis of combustion experiments, and his own interpretations, Antoine Laurent Lavoisier [1754-1794] formulated a theory of combustion which was experimentally beyond reproach, and which convincingly explained all the deficiencies of the phlogistonists. This theory was published in his *Traite Elementaire de Chymie* in 1789. It was to constitute the dawn of a new age - the age of modern chemistry. But in spite of the clear superiority of Lavoisier's ideas, there remained many adherents of the phlogiston theory who clung tenaciously to their beliefs. Among these were two brilliant English experimenters: Joseph Priestley [1733-1804] and Henry Cavendish.

Enter Cavendish

If hydrogen had been known for some centuries before Cavendish, and its method of preparation and its combustion were well known, how and why was his discovery such a great step forward and what effect did it have on (a) the uses of hydrogen and (b) the theory of chemical reactions?

Henry Cavendish was conducting experiments at a time when: (i) gases had relatively recently been recognised as unique chemical substances, (ii) the chemical composition of air and water were unknown or even unsuspected, (iii) combustion and calcination (burning) of metals were both regarded as processes of decomposition.

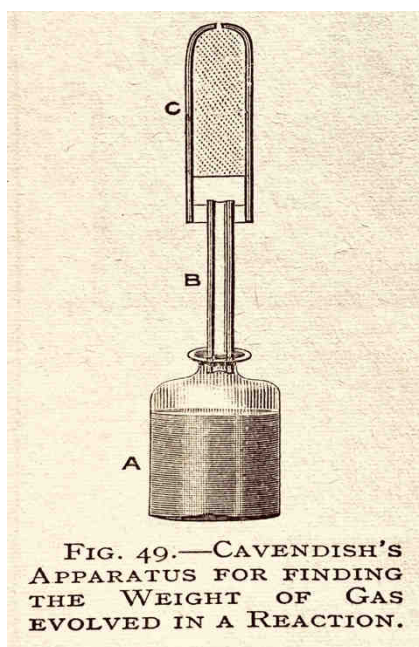


Fig. 4. Apparatus for measuring the weight of gas which is evolved during a chemical reaction [1]

Cavendish designed his own apparatus and had a profound insight into the nature of the chemical and physical processes which he investigated. Furthermore, he paid great attention to the importance of quantitative measurements. He studied inflammable air in the

context of identifying both its chemical and its physical characteristics. Cavendish prepared his inflammable gas from the reaction between a metal (zinc, iron or tin) and an acid (sulphuric or hydrochloric). He additionally called his inflammable gas phlogiston, believing it to be the essence of fires.

He published his results in the *Philosophical Transactions* in 1766 in his first chemical memoir, entitled: "Three papers containing experiments On Factitious Airs". The word factitious in this context means "obtained through an experiment from another substance". He measured the density of inflammable air in two ways: by weighing a known volume of the air in a bladder, or by measuring both the volume and weight of an air which was released from the same quantities of the same reagents, but with two independent experiments - one to measure volume and the other to measure mass. He then applied the equation: $\text{density} = \text{mass}/\text{volume}$. One of the items of apparatus which he used to establish the density of hydrogen is shown in Figure 4.

Flask A contains the acid. B is an upward delivery tube and C is a drying tube containing an absorbing agent e.g. pearl ash (anhydrous potassium carbonate). The top of the tube has an orifice to allow the gas to escape. The whole apparatus was weighed. The metal was weighed separately and then added to bottle A. The reaction was allowed to run to completion, and the whole apparatus and reagents were reweighed at the end. Thus, the mass of gas which was lost could be calculated. Its volume would be found by repeating the experiment under identical conditions, collecting the gas over water, marking off the level of the gas in the inverted collecting vessel, and measuring the volume of water which was needed to reach the mark. Figure 5 shows this arrangement.

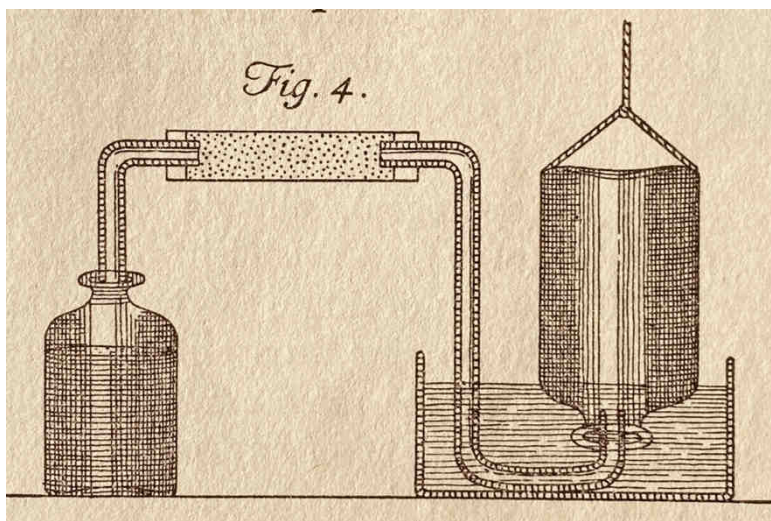
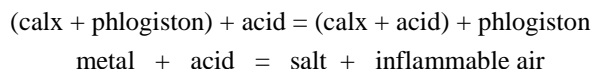


Fig. 5. Measuring the volume of gas by displacement of water [1]

Experiments similar to these are universally used in chemistry school teaching programmes today. Cavendish found that "the air is the same and of the same amount whichever acid is used to dissolve the same weight of any particular metal". He called it the inflammable air from metals. This seemed to make sense, since the metal disappeared, and

the inflammable air appeared. With hindsight, we can detect the fallacy of logic here - the acid was clearly the excess reagent so Cavendish could not be in a position to deduce that the gas had actually come from the acid and not the metal. This example illustrates to what extent the phlogiston theory had become embedded in people's minds. It shows just how complex these issues were to resolve. His scheme can be represented as follows:



A calx was the product formed when a metal burnt in air. Today we know that calxes are metal oxides. Cavendish also studied extensively, using his own specially constructed eudiometer, the explosive combustion of inflammable gas in air. He was particularly interested to see in what ratios hydrogen had to be mixed with air, in order to get the most violent explosion. During these experiments he noted that water was formed when inflammable air burns. Some of the main points of his researches into inflammable gas are summarized in Table 1.

Table 1

A summary of Cavendish's results

Name	Density compared to air	Ratio for most violent combustion	Method of preparation
Inflammable air = phlogiston	1 : 11	3 : 7 hydrogen : air	Iron, tin or zinc with hydrochloric or sulphuric acid

A dream come true

Cavendish had now clearly defined a new and unique aeriform substance. He had simultaneously and unwittingly defined a momentous and unstoppable new opportunity for exploration: manned flight.

Since the earliest times, people had been fascinated, even obsessed, with the possibility of flying. After all, birds make it look so simple and so effortless. And yet for all the extraordinary mental capacity of humans, their seemingly limitless ingenuity, the efforts of the greatest geniuses such as Leonardo da Vinci [1452-1519], all that had ever been achieved were hundreds of phantasmagorical designs of flying machines, failed attempts to fly, and thousands of bones of intrepid would-be hero adventurers, scattered over the bottoms of countless valleys.

Armed with the latest discovery, a "lighter than air gas", and sniffing that victory was in sight, a multitude of enthusiasts, engineers, scientists, fabric technologists, rope makers, instrument makers and entrepreneurs set about designing a machine which would finally fulfil the great challenge of flight. The design of a balloon that would fly people "high above the clouds" generated a level of excitement that had been unprecedented in the course of human history. There were many technical challenges to be overcome. The balloon had to be impermeable to hydrogen - it was made out of silk and coated with a solution of rubber in turpentine and enclosed in a light strong netting. The volume of hydrogen in the balloon had to be carefully varied in order to allow for expansion of the gas as the balloon ascended, a controllable gas valve thus had to be made in the top of the balloon in order to allow for the escape of excess hydrogen. An elongated wickerwork basket had to be constructed and suspended from the netting. The gas was generated from the reaction between iron and sulphuric acid. It took 4 days to inflate the early balloons.

The first flight (unmanned) of a balloon took place on 27th August 1783. It had a diameter of 10 feet (3 metres) and used 225 kg sulphuric acid and 500 kg of scrap iron. The quantities of reagents were determined purely from a trial and error approach. Chemistry and the chemical industry were still an art at this stage - but this was all about to change during the next few decades. Figure 6 shows an artist's impression of an early balloon being filled with hydrogen - it is reproduced from a school science book from 1857.

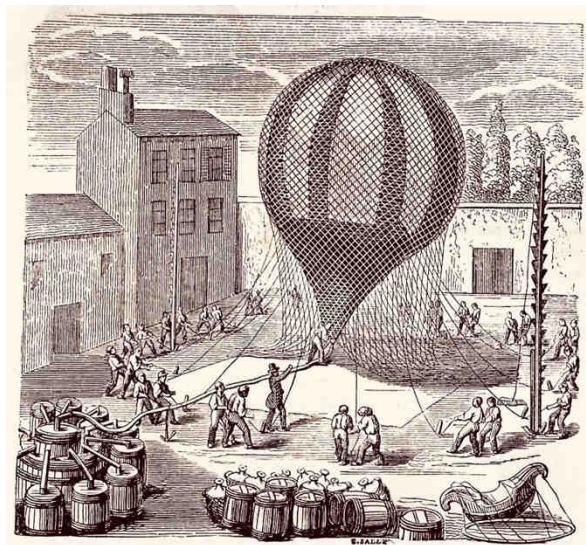


Fig. 6. Filling a balloon with hydrogen [3]

How extraordinary to see barrels full of sulphuric acid! These would have been lined with lead and would have been very awkward to handle. Furthermore, the hydrogen was contaminated with small amounts of the most obnoxious and smelly gaseous impurities. But the excitement of watching this giant contraption inflate and rise in the air, was far too great to dampen the enthusiasm of the balloon crew. The passenger gondola can be seen on the bottom right hand corner of the illustration.

In front of an audience of an estimated 300,000 people, the first successful manned flight, from Paris, occurred on 1st December 1783. The balloon carried three people: the physicist Jacques Cesar Charles [1746-1823] and the brothers Anne-Jean Robert [1758-1820] and Nicholas Louis Robert [1760-1820]. They were both mechanical engineers. The flight lasted for two hours and carried them a distance of 24 km (15 miles). The euphoria of the event was indescribable [4]. A similar level of excitement was generated by hot air balloons, whose tradition stems back to Ancient China. On 21 November 1783 the first of these, made out of linen fabric lined with a specially treated paper (with alum to render it fireproof), was successfully flown by Jacques-Etienne Montgolfier [1745-1799]. But hydrogen filled balloons gained the upper hand at this stage and they came to dominate the world of manned flight.

Scientific instruments such as a mercury barometer, thermometer, hygrometer, compass and telescope were taken up on the pioneering flights. Thus, a whole new range of

information about the earth's atmosphere became available: variation of pressure, temperature and humidity with height, the chemical composition of the air - this was still not fully understood as a mixture - and the observation and classification of different types of cloud. Figure 7 gives an impression of the tranquillity which can be experienced high above the clouds. No wonder then that some early aeronauts, such as Charles Green [1785-1870], made as many as 1400 ascents in his long life.

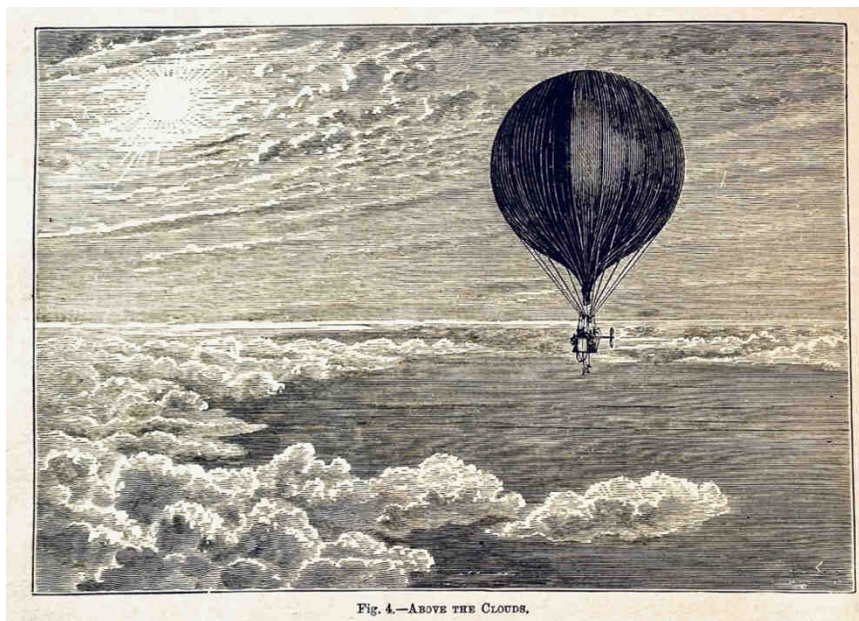


Fig. 7. Above the clouds [5]

Throughout the nineteenth century, balloon flying together with two other scientific and technological advances - photography (from 1822) and steam railway travel (from 1812) - transfixed Europeans on an hitherto unprecedented scale. Balloons became bigger and bigger. An example of such a construction was the gigantic captive balloon that was built by the French engineer Henri Giffard [1825-1882] for the Paris exhibition of 1878. This had a diameter of 36 metres (118 feet) and when filled with hydrogen it had a lifting capacity of 27 tonnes (Mg) and was able to carry 52 passengers. It was made of 7 layers of muslin, India rubber and canvas, put in alternate layers. To make the required amount of hydrogen required 190 tonnes of sulphuric acid and 80 tonnes of iron [6].

As time progressed new and novel uses for balloons were developed, especially for military purposes. These had disastrous consequences. Writing about German losses during the first world war, Egon Larsen notes that: "the 480 German airmen who died in their Zeppelins must have gone through terrible suffering, knowing that there was little chance of survival. It was one of the most inefficient as well as costly and inhuman instruments of war ever employed" [7].

During the latter decades of the 19th century, power units were developed for the balloons (the first one was in 1852, invented by Giffard). Initially these were steam engines

which proved to be extremely inefficient and dangerous. Following these, the newly invented internal combustion engines rapidly came into use. Navigable balloons became known as dirigibles or airships. They grew in size (the R34, the first British airship to cross the Atlantic and back in 1919 was 200 metres long) and were able to carry dozens of passengers on transatlantic trips, as a luxury form of transport.

Unfortunately, the “inflammable air” of Cavendish was to have the last say: after hundreds of accidents during the preceding 150 years, involving thousands of fatalities, the Hindenburg disaster of 6th May 1937 temporarily laid to rest the era of “lighter than air” transport.

The composition of water

For thousands of years, people had considered water and air to be fundamental substances in Nature. They had constituted part of the Aristotelian 4 element system, of which the other two were earth and fire. With the development of experimental science from the seventeenth century onwards, the concepts of air and water as elements or “building blocks” of Nature became more and more open to question. Countless experiments were conducted which, with hindsight, would appear to change or instantly alter our perception of the Universe. And yet it took decades, if not centuries, for new ideas to gain acceptance. The idea that air is a mixture of gases, of variable composition, and that water is a compound of two elements hydrogen and oxygen with a fixed chemical formula H_2O , are two examples of this phenomenon of the slow acceptance of a new order.

One of the important pieces of apparatus which Cavendish employed was a eudiometer. This is a laboratory device which measures change in volume of a gas mixture, following a physical or chemical action. Eudiometers were first used during the last 3 decades of the 18th century, and had been invented by the Italian chemist, physicist and meteorologist Marsilio Landriani [1751-1815]. His fellow countryman Alessandro Volta [1745-1827], natural philosopher and electric battery pioneer, had the brainwave of fitting eudiometers with spark wires in order to initiate the combustion of gaseous mixtures [8]. In the interpretation of eudiometer combustion experiments it is important to note that gases were referred to as elastic fluids whereas liquids were said to be inelastic fluids. This important distinction between the two types of fluid underpins the science in today’s universally used technologies of hydraulics and pneumatics.

Cavendish had noted that inflammable air (elastic fluid) burns in ordinary air to produce water (inelastic fluid). Using his eudiometer, he conducted several quantitative experiments, working to several significant figures of accuracy, whose aim was to establish the proportions of inflammable air and normal air, which would result in the greatest contraction of volume. Yet in spite of these experiments, he did not reach the conclusion that water is a compound of hydrogen and oxygen. As it became increasingly clear that water was not a simple substance (element), two important types of experiments came to dominate research: synthesis of water, by combining hydrogen with oxygen, decomposition of water into hydrogen and oxygen.

Further developments in the water story can be summarized by a timeline which draws attention to some keystone experiments. It is clear from this, that exploding mixtures of hydrogen with air or oxygen consumed a great deal of research time, and surely generated much entertainment as well.

- 1781 - Priestley observed that a mixture of dephlogistigated air (oxygen) and inflammable air (hydrogen) explodes violently when ignited.
- 1781 - Cavendish noted that water was formed as a product when inflammable air was burnt with dephlogistigated air (this of course, was Priestley's name for oxygen). A great rivalry existed between French and English chemists, as to priority for advances in research on water, and this was echoed in contemporary accounts: "This great philosopher (Cavendish) ... may be considered as the true discoverer of the composition of water", wrote Nicholson in 1808 [9].

Cavendish also noted that the water thus formed was acidic. Repeated sparking of the residual gaseous mixture (which would have been a mixture of atmospheric nitrogen and oxygen) caused a gradual increase in the acidity of the product, and he recognised this as nitric acid. He also recognised that the acid was formed by the reaction between phlogistigated air (nitrogen) and dephlogistigated air. When further sparking gave no further reaction i.e. no further diminution on volume of the gaseous mixture, there remained a small bubble of gas whose presence Cavendish was unable to satisfactorily explain. This bubble was shown to be argon by William Ramsay [1852-1916] and Lord Rayleigh [1842-1919] in 1894. Oxides of nitrogen are generated on an everyday basis today, in internal combustion engines, in exactly the same manner that Cavendish generated them 250 years ago.

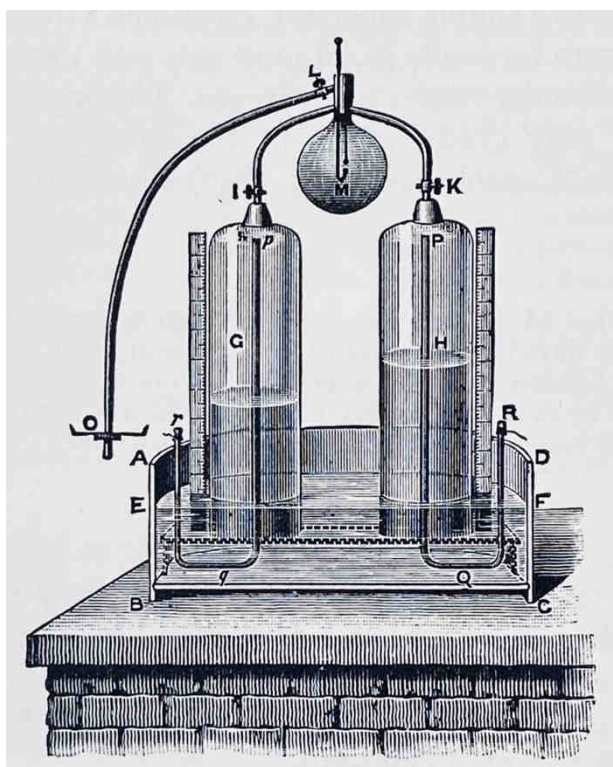


Fig. 8. Monge's apparatus for the synthesis of water [1]

- 1783 - The French mathematician Gaspard Monge [1746-1818] synthesized water by sparking a mixture of dephlogistigated air (obtained from the decomposition of red calx of mercury) with inflammable air, which was obtained from pure iron wire in dilute sulphuric acid. He published his result in a memoir entitled "On the result of the inflammation of inflammable gas and dephlogistigated air in closed vessels." This was published in the *Mémoires de l'Académie des sciences* for 1783. To initiate the combustion reactions, Monge used an electric spark, as had been suggested earlier by Volta. Figure 8 shows his apparatus.

The gases were introduced into cylinders G and H via the siphon tubes PR. They passed through stopcocks I and K to the globe M. This had previously been exhausted via tap L, which leads to a vacuum pump at O. The gas mixture is then exploded by an electric spark at M, and the process was repeated.

- 1784 - Antoine Lavoisier and the mathematician/engineer Jean Baptiste Meusnier [1754-1793] decomposed water by passing steam over iron filings in a red hot gun barrel. This was the first experiment in which water was chemically decomposed. It was subsequently employed, alongside the "acid plus metal" reaction, to generate hydrogen in laboratories, and also for filling balloons. Figure 9 shows the arrangement of an apparatus for a school experiment which illustrates this reaction.

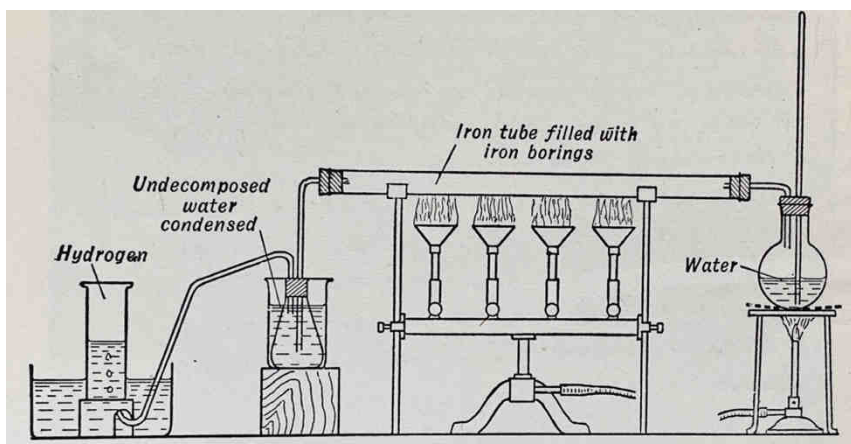


Fig. 9. Lavoisier's "gun barrel" experiment, showing the decomposition of water [10]

- 1788 - The Scottish inventor, mechanical engineer and chemist James Watt [1736-1819] drew attention to Priestley's experiments on the explosive reactions of dephlogistigated air and inflammable air, which produced water.
- 1788 - Antoine Lavoisier, whose theory of combustion was rapidly bringing about the rejection of the phlogiston theory, gave hydrogen its modern name. This was derived from two Ancient Greek words - hudro (water) and genes (born). Lavoisier stated clearly: "Water is nothing but oxygenated hydrogen, or the immediate product of the combustion of oxygen gas with hydrogen gas."
- 1789 - During the late 18th century, static electricity machines had been invented, which were capable of delivering sparks with great energy. One of these was employed

- by the Dutch chemists Johann Deiman [1743-1808] and Adrien Paets van Trootswijk [1752-1837], who used gold wire electrodes to decompose water into “small bubbles”.
- 1790 - The continued enthusiasm for research into the exact nature of water, was boundless: a grand experiment on the composition of water by the French chemists Antoine Fourcroy [1755-1809], Louis Vauquelin [1763-1829] and Armand Seguin [1767-1835] was “begun on Wednesday May 18th 1790 and was finished on Friday, the 22nd of the same month. The combustion was kept up for 185 hours with little interruptions, during which time the machine was not quitted for a moment. These experimenters alternately refreshed themselves when fatigued, by lying for a few hours on matrasses in the laboratory” [9].
 - 1800 - The English polymath, chemist, author and natural philosopher William Nicholson [1753-1815] and the surgeon Anthony Carlisle [1768-1840] decomposed water into hydrogen and oxygen by the use of electrolysis. This experiment was undertaken in the same year that Volta had, in his epoch making work on electric cells, initiated the new science of electrochemistry.
 - 1805 - The French natural scientist Joseph Gay Lussac [1778 - 1850] and the Prussian naturalist and geographer Alexander von Humboldt [1754-1845] eudiometrically demonstrated that water is composed of two volumes of hydrogen combined with one volume of oxygen.



Fig. 10. Humphry Davy with hydrogen and oxygen [from an original print in the author's collection]

- 1806 - The Cornish chemist and inventor Humphry Davy [1778-1829] electrolytically decomposed pure water into hydrogen and oxygen, and showed that these two gases are combined in water in the volumetric ratio 2:1. A modified version of this experiment, the “Hofmann Voltameter”, is popular and important in today’s school teaching programmes. Figure 11 shows a small fragment of an original print of a cartoon by the celebrated caricaturist James Gillray [1756-1815]. It depicts the impish expression on Humphry Davy’s face, who is clearly anticipating some fun with hydrogen and oxygen. The whole cartoon shows a scene from one of Davy’s acclaimed public lectures at the Royal Institution of Great Britain - they inspired generations of future scientists.
- 1842 - The French chemist Jean-Baptiste Dumas [1800-1884] devised a complex apparatus to accurately establish the gravimetric composition of water.
- 1915 - The English chemists F.P. Burt [died in 1939] and E.C. Edgar, both based at Manchester University, and using a complex apparatus, published a paper entitled “The combining volumes of hydrogen and oxygen” in the Philosophical Transactions of the Royal Society.

These highlights show just what an extraordinarily complex historical background there is, to one of the most well-known facts of science - the formula for water is H_2O .

Theories of matter, the laws of chemical combination and diffusion

Theories of matter

Theories that matter is composed of tiny particles have their origins in Ancient Egypt and in India. The Greek philosopher Democritus [c.460-c.370 BC] first formulated a coherent atomic theory. The word atom is derived from the Ancient Greek “atomos”, meaning “uncuttable”. Arguments which were put forward by the Greek philosopher Aristotle [385-322 BC] suggested that matter was not composed of particles, but was continuous. It was considered to fill all space. An important consequence of this philosophy was the tenet that “Nature abhors a vacuum”. This philosophy of Nature was accepted by leading scholars, and for several centuries it underpinned the practical art of alchemy. Yet on account of its many failings to explain experimental results, the Aristotelian world view gradually became more and more open to question. Leading intellectuals, including the French philosopher Pierre Gassendi [1592-1655], Robert Boyle, and the English natural philosopher, alchemist, theologian and mathematician Isaac Newton [1643-1727] were ardent atomists. With the experimental demonstration of the vacuum by the Italian physicist and mathematician Evangelista Torricelli [1608-1647] in 1643, the idea that matter was ultimately composed of tiny inanimate particles was given a huge new impetus.

By the beginning of the 19th century, with a rapidly increasing body of chemical knowledge and reactions which included not only combustion but also acid/base and the then relatively recently discovered electrochemical processes, natural philosophers were more urgently seeking an explanation as to why do reactions occur at all, and how do chemical particles interact? By now, Robert Boyle’s definition of an element as a simple substance which could not be chemically broken down, had gained wide recognition. Chemists started to construct tables of different substances and trying to classify them e.g. metals, simple earths. Figure 11, taken from an early (1808) dictionary of chemistry, shows a “table of characters to be made use of in chemistry, by Messrs Haffenfratz and Adet”. “Hydrogen” is included in the list of “combustible simple substances commonly

called inflammable substances". Others in this list included carbon, sulphur and phosphorus. (Pierre Adet [1763-1834] worked with Lavoisier on a new chemical notation system, whereas Jean Hassenfratz [1755-1827] was a French chemist, physics professor, and mine inspector).

Figure 12 shows part of the entry for hydrogen. Its role as a lifting agent was already widely recognised in 1808. Incidentally, there is in this dictionary, a most interesting article on water. This is not surprising since its author, William Nicholson, had first electrolysed water in 1800, as mentioned above.

Table I.
of the Characters to be made use of in
Chemistry.
By Mess.^{rs} Hassenfratz and Adet.








Simple Substances, which can exist in the aeriform state in the ordinary temperature of the Atmosphere, and which, entering into the composition of an infinity of substances, demand a great simplicity of their Characters.		Light
		Caloric
		Oxygen
		Nitrogen
		Characters to express such new and simple Substances as may be discovered.
Alkalis considered as simple Substances.		Potash
		Soda
		Barytes
Simple Earths.		Lime
		Magnesia
		Alumine
		Silica
		Silica
Combustible Simple Substances commonly called Inflammable Substances.		Hydrogen
		Carbon
		Sulphur
		Phosphorus

Fig. 11. Table of characters [9]

Two important newly evolving theoretical strands are relevant to the fact that hydrogen had such a low density: ideas of atomic weight (relative mass of particles) and diffusion (movement of particles).

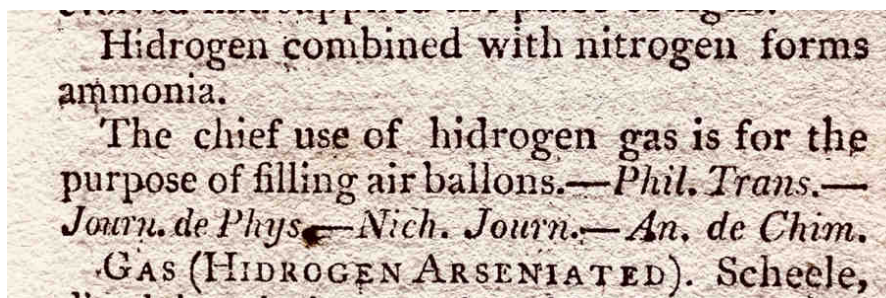


Fig. 12. Uses of hydrogen [9]

The laws of chemical combination

The English natural scientist and meteorologist John Dalton [1766-1844] had, since his early years, been a firm believer in the idea that matter is particulate. The genius of his atomic theory was that it was a chemical theory, which explained the way in which particles react to form new substances. His theory had a huge impact on our understanding of chemical reactions, and on their quantitative aspects. The main points of his Atomic Theory, first conceived in 1803, and published in 1808 (in his book *A New System of Chemical Philosophy*), are:

1. Elements consist of atoms which for any particular element are all identical in all respects including weight
2. Atoms of all different elements differ in weight
3. Atoms are very minute particles which are indivisible and indestructible
4. Atoms of different elements combine together in simple numerical proportions to form compound atoms (molecules)
5. Compound atoms (molecules) of the same compound are identical i.e. they are made up of the same atoms combined in the same numbers

In 1803 Dalton published the first table of atomic weights. Some of his values are: hydrogen 1, oxygen 5.66, azote 4, carbon 4.5, water 6.66, ammonia 5, nitrous gas 9.66. Dalton did not, at this stage, distinguish between atoms and molecules.

His theory formed the basis for establishing the Laws of Chemical Combination, which were experimentally determined by various chemists, within a few years of the publication of his atomic theory. These are stated below. They underpin today's chemical industry and their application marked a shift in the change of the chemical industry, from an ART, which it had been from time immemorial (Ancient Egypt, China, India), to an EXACT SCIENCE, which it is today.

1. Law of conservation of mass, otherwise known as the Law of indestructibility of matter. Although this had always been assumed by experimenters, it was the Russian polymath and natural philosopher Mikhail Lomonosov [1711-1765] who first proved this on the basis of experimental evidence, in the years 1753-1756 [11]. Subsequently Lavoisier stated this in 1789. Many chemists (including the Swiss chemist Hans Landolt [1824-1910]) went to extraordinary lengths to find just one example of a reaction which did not obey the law. Landolt did not succeed, therefore, by default, the Law was verified.
2. Law of constant composition

3. Law of multiple proportions
4. Law of reciprocal proportions

Although these laws are not formally learnt in schools today, they underpin all “moles calculations” topics. The elucidation of these laws was made possible by means of the acceptance of two important principles - Gay Lussac’s Law of combining gas volumes (1808): “When gases react, they combine in simple numerical proportions by volume, to produce simple volume proportions of products (where gaseous), all measurements being made at the same conditions of temperature and pressure”, and the Italian scientist Amedeo Avogadro’s [1776-1856] hypothesis (1812): “Under equal conditions of temperature and pressure, equal volumes of different gases contain equal numbers of molecules”. This seemingly far-fetched idea (there was no way in which Avogadro could count molecules) initially encountered much opposition and hostility in scientific circles, but its application gradually served to enable chemists to make significant progress in our understanding of the ratios in which molecules combine.

The English physician William Prout [1785-1850] published an anonymous paper in 1815 in which he suggested that ultimately all elements were derived from hydrogen. His views were based on the rather inaccurate values of atomic weights, which approximated to whole numbers. Prout’s hypothesis, as it became known, was rapidly rejected by the Swedish chemist Jons Jacob Berzelius [1779-1848], who established the first comprehensive table of atomic weights, and by other chemists. The fact that such an hypothesis was published at all, reflected the ancient belief that ultimately there is a prime matter from which all other matter is derived. For Prout, this was hydrogen.

Diffusion

The idea of a tiny particle called a molecule, which is not necessarily the smallest part of an element, had its origins in the late 18th century and was first probably used by Avogadro. Our understanding of matter being able to exist in one of three states: gas, liquid or solid, dates back to the beginning of the 19th century. With an increased understanding of the concept of energy, we can now explain the behaviour of particles in the three states of matter. Diffusion, which can occur in gases and liquids, is defined as the random movement of particles in a manner which is independent of external gravitational forces. Particles always diffuse from an area of high concentration to an area of lower concentration.

Thomas Graham [1805-1869] was a Scottish chemist who was working at a time when explanations of the behaviour of substances in terms of the movement of small particles, was very much in fashion. He is considered today to be the founder of a most important branch of chemistry - colloid chemistry. Whilst working with the German chemist Johann Dobereiner [1780-1849], Graham noticed that hydrogen escapes more rapidly from a fissure in a metal vessel than the air can get in to replace it. He investigated this phenomenon carefully, and in 1829 he published the first version of his law of gaseous diffusion [12]. This can be stated as: “The rate at which a gas diffuses is inversely proportional to the square root of its density”.

An experiment in which the rapid diffusion of hydrogen is exploited to cause a spectacular effect, was demonstrated by the Irish physicist and populariser of science, John Tyndall [1820-1876], at the Royal Institution of Great Britain in London in the summer of 1874. A diagram of his experiment is reproduced in Figure 13. A bell jar containing hydrogen is lowered over a porous pot which is connected by means of a delivery tube, to a Woulfe bottle containing water and a glass tube with a nozzle.

On account of the much more rapid movement of hydrogen molecules than nitrogen and oxygen molecules in the air, the hydrogen diffuses rapidly into the porous pot, causing a pressure build-up inside the flask resulting in a fountain of water.

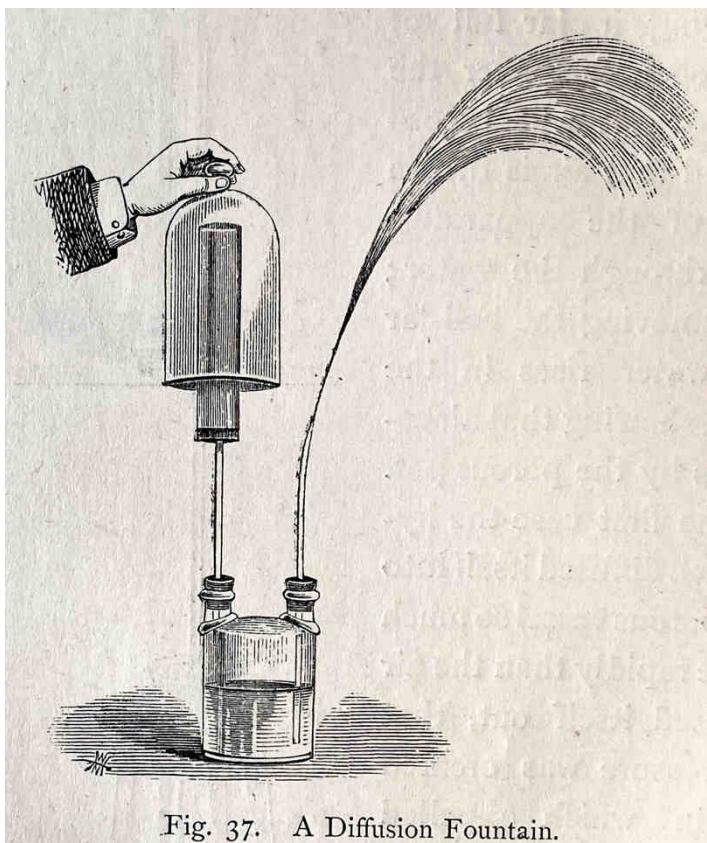


Fig. 13. A diffusion fountain, using hydrogen [13]

Thomas Graham also did a noteworthy research [1866-1869] on the absorption of hydrogen by two metals - palladium and rhodium. These metals are today used in hydrogen storage research for powering cars and other machinery.

Hydrogen and electrical phenomena

At the beginning of the 19th century, great advances were made in our understanding of electrical phenomena. These can broadly be split into two categories: electrochemical - first described by Volta in 1800, and electromagnetic - first described in 1819 by the Danish physicist Hans Christian Oersted [1777-1851]. Hydrogen was to become an important player in each of these two theatres of science.

Volta's discovery concerning the generation of an electric current from two dissimilar metals, simultaneously initiated a huge field of research, which can broadly be split into:

chemical electricity (the construction of voltaic cells) and electrolysis (the use of an electric current to decompose substances). Accompanying these two rapidly evolving fields of research were theories which tried to explain them. A novel idea was consequently invented - electrically charged particles. The English natural philosopher and founder of electromagnetic induction, Michael Faraday [1791-1867] conducted significant research into the field of electrolysis. He introduced the words: electrode, ion, anode and cathode into the chemical terminology during the early 1820's. They had been suggested to him by his friend, the English scientist, historian of science, Anglican priest, philosopher and theologian William Whewell [1794-1866].

The idea that electrically charged particles exist, with opposite charges attracting one another and like charges repelling one another became necessary to explain electrochemical phenomena. However, they raised the important fundamental question: how is it possible for atoms to change to ions? The observations were quite clear: metallic sodium (composed of sodium atoms) is quite different from electrically charged sodium particles (ions), which are found in common salt (sodium chloride). This observation seemed to directly contradict the postulates of Dalton's Atomic Theory, which had stated that atoms are indivisible and unchangeable for any given element.

Throughout the 19th century, various explanations were put forward to try and explain this situation. None were entirely satisfactory. The idea that hydrogen could exist in the form of electrically charged particles naturally arose from the results of early experiments on the electrolysis of water. Furthermore, in the debate on the exact cause of acidity, for which Lavoisier had suggested that all acids contain oxygen (the word is derived from the Ancient Greek words meaning "acid maker"), Humphry Davy proposed in 1815 that all acids contain hydrogen. This was because he had shown that muriatic acid, also known as spirits of salt or hydrochloric acid, does not contain oxygen. This idea was further developed by the German chemist Justus von Liebig [1803-1878] in 1838, who "assumed that acids were compounds of hydrogen, and that this hydrogen could be replaced by metals" [14].

In 1884 the Swedish physical chemist Svante Arrhenius [1859-1927] defended his doctoral thesis, in which he proposed an early version of the ionic theory. In his thesis, Arrhenius made the avant garde suggestion that the particles (molecules) of certain substances (electrolytes) could be split into electrically charged particles, ions, immediately when the substance dissolved in water. These ions were always present in a solution, regardless of whether a current flowed or not. He furthermore proposed that all acids furnish hydrogen ions. His ideas were subsequently developed by the German physical chemists Walter Nernst [1864-1941] and Wilhelm Ostwald [1853-1932]. Arrhenius was awarded the Nobel Prize for chemistry in 1903 for his work in this field. Figure 14 gives a summary of the fields of chemistry which were influenced by Arrhenius' theory.

In 1909 the Danish chemist Søren Sørensen [1868-1939] invented the pH scale. pH is defined as the logarithm to base 10 of the reciprocal of the hydrogen ion concentration in an aqueous solution. Today universal indicator is widely used in school teaching programs, to introduce children to ideas on acidity and alkalinity, and to the concept of pH. The indicator was invented by chemists, and consists of four indicators: thymol blue, methyl red, bromothymol blue and phenolphthalein, in carefully measured proportions. Figure 15 shows the full range of universal indicator colours, which remarkably and coincidentally are ordered in the same sequence as in a rainbow.

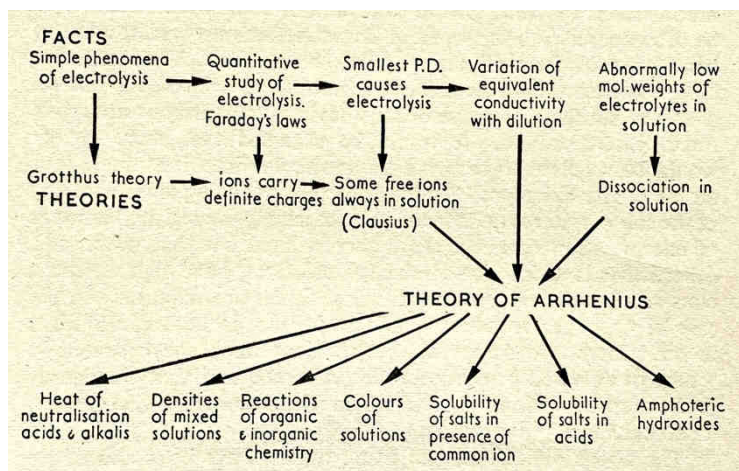


Fig. 14. The theory of Arrhenius [15]



Fig. 15. Colours of universal indicator

From Rainbows to Atomic Structure

Towards the end of the 18th century, our understanding of two invisible, but nevertheless increasingly tangible, phenomena - gases and electricity, had greatly improved. The visible, yet quite intangible phenomenon of light however, remained a mystery. And what more fascinating natural optical phenomenon exists than the rainbow?

In the latter half of the 17th century, two theories were postulated, concerning the nature of light. The first was the corpuscular theory, published in 1672, based on Isaac Newton's observations concerning the splitting of white light into a mixture of 7 colours, by means of a prism. The second theory, published in 1678 by the Dutch physicist, mathematician and astronomer Christian Huygens [1629-1695] postulated that light consists of waves. The Dutchman's theory was accepted as the more logical one, since it satisfactorily explained the phenomenon of diffraction, which had been noted in the 1660's, whereas Newton's theory was unable to do so.

It was not until the beginning of the 19th century that significant progress was made with the analysis of spectra. Having constructed an elementary type of spectroscope using

a prism in conjunction with a slit, in 1802 the English chemist William Hyde Wollaston [1786-1828] noted that dark gaps were present in the solar spectrum. In that same year the English polymath Thomas Young [1773-1829] had demonstrated the wave nature of light, through the analysis of interference patterns when a coherent monochromatic light source was shone through two narrow slits in a thin sheet of metal. It is likely that he obtained a monochromatic light source by using white light (sunlight) with a suitable coloured filter. Importantly, he was able to determine the different wavelengths of the colours in white light.

Investigations concerning the nature of light continued to evolve during the first few years of the 19th century. In 1814 the German physicist Joseph von Fraunhofer [1787-1826] invented a device which would measure the wavelength of light in a more satisfactory manner - this was the diffraction grating, which consisted of many lines which were ruled parallel to one another, on a piece of smoked glass. Using the diffraction grating, Fraunhofer was able to carefully catalogue all of the black lines of the solar spectrum, which had earlier been shown to exist by Wollaston. Figure 16 shows some of these lines.

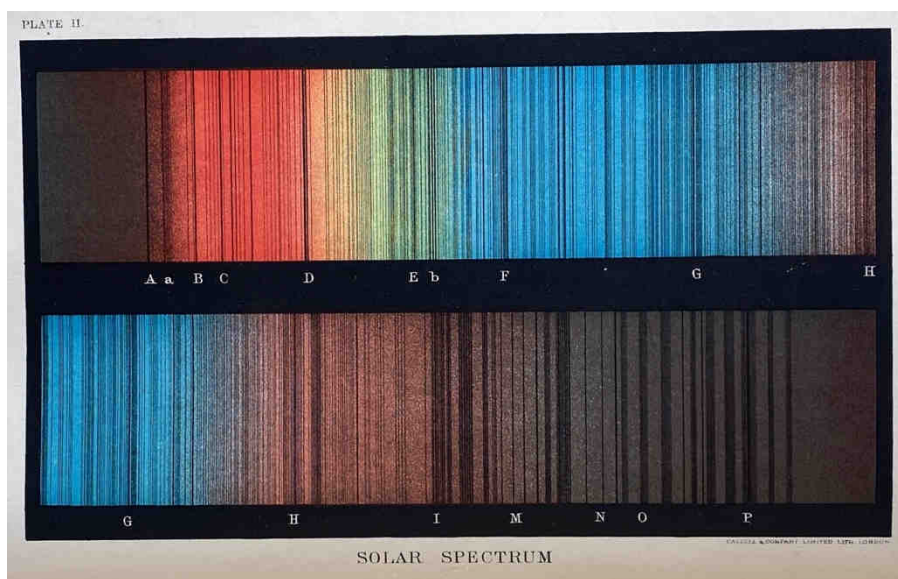


Fig. 16. The Fraunhofer lines of the solar spectrum [16]

Fraunhofer found over 570 of these lines and was of course, able to calculate the wavelengths of the light that caused them. One significant question remained unanswered: what caused these black lines?

During the middle decades of the 19th century, more attention was being given to the spectral analysis of coloured flames which were produced by different compounds. These coloured flames had been known and used for many centuries in fireworks, but scant attention had been paid to the origins of the colours. Figure 17 shows the coloured flames of lithium, sodium and copper. When spectroscopically analysed, they are seen to consist of a series of lines i.e. discrete wavelengths.



Fig. 17. Lithium, sodium and copper flame colours

Figure 18 shows some examples of spectra. Sodium, shown above as a bright orange flame, has a particularly strong line (actually two lines very close together, known as the sodium D lines, with wavelengths 588.9950 and 589.5924 nm respectively) is reproduced from a school physics book from 1934.

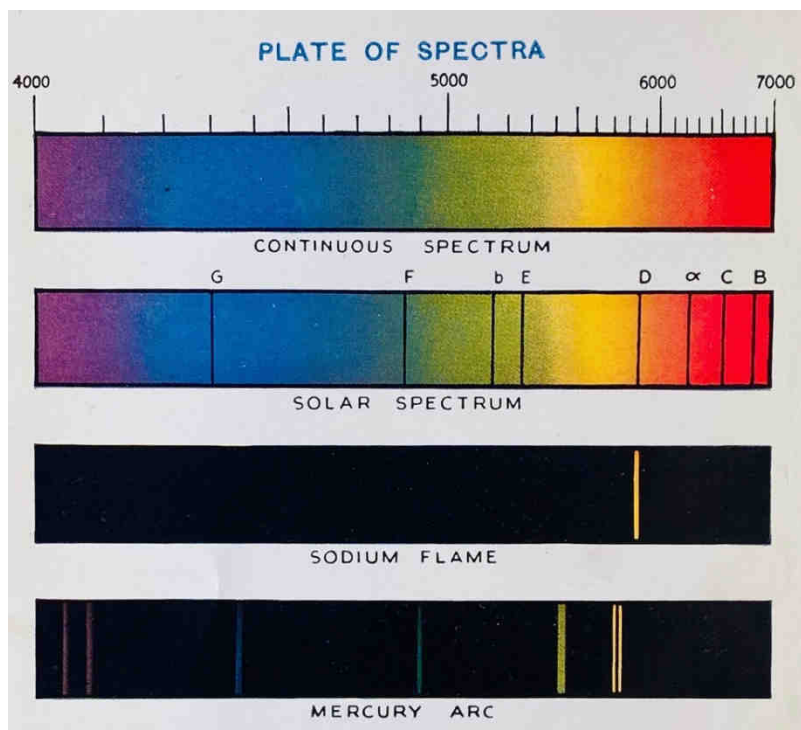


Fig. 18. Some spectra [17]

In 1861 the German physicist Gustav Kirchhoff [1824-1887] made the sensational discovery that the black Fraunhofer lines of the solar spectrum coincided with the wavelengths of metallic compound vapours, which he had analysed. The lines themselves, which constitute an absorption spectrum, were caused by metal vapours in the sun's corona. Together with his colleague and compatriot chemist Robert Wilhelm Bunsen [1812-1899], they established a most important principle: every element, when suitably energised, will emanate a radiation which when analysed, will give an emission spectrum that is characteristic of that element only. Thus was born one of the most important analytical tools of the chemist and physicist - spectroscopy. The instrument itself consisted of beautifully constructed brass tubes (collimator, micrometer and telescope) with prisms and lenses, set up on a circular brass table. Various scales were engraved, from which accurate measurements of distances and angles could be made. A diagram which shows the principle of operation of a spectrometer is shown in Figure 19.

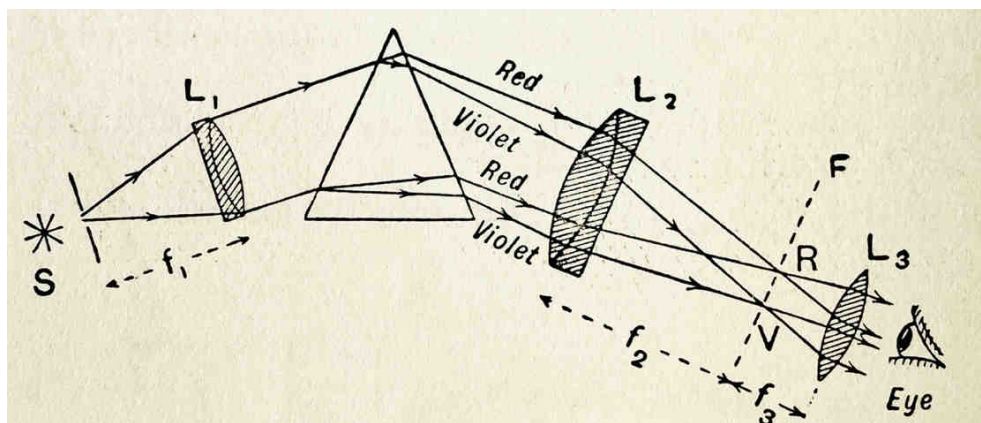


Fig. 19. Principle of the spectrometer [17]

In 1871 the French astronomer Pierre Janssen [1824-1907] who had conducted detailed spectroscopic and photographic studies of the Sun, first discovered the presence of the spectral lines of hydrogen in the sun's corona. In 1925 the British born American astronomer and astrophysicist Cecilia Payne-Gaposchkin [1900-1979] as part of her doctoral thesis, made the controversial suggestion that the sun and stars were composed primarily of hydrogen and helium. She was subsequently shown to be correct, and thus hydrogen assumed a new "prima inter pares" status in the Universe.

Mathematics and the hydrogen spectrum

In trying to understand the origin of spectra of the elements, it made good sense to investigate the spectrum of the lightest element hydrogen. A simplified diagram of part of the hydrogen spectrum is given in Figure 20. It occurs in the visible region of the spectrum, and was the first to be subjected to analysis, by the Swiss schoolteacher of descriptive geometry, Johann Jacob Balmer [1825-1898] in 1885. He elucidated an empirical mathematical relationship which involved the wave numbers of the spectral lines.

$$\bar{\nu} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

where $\bar{\nu}$ is the wave number (reciprocal of wavelength) of a given line, R_H is a constant ($109677.76 \text{ cm}^{-1}$), now called the Rydberg constant, and n is an integer which assumes the values 3,4,5,6... for successive lines of the series.

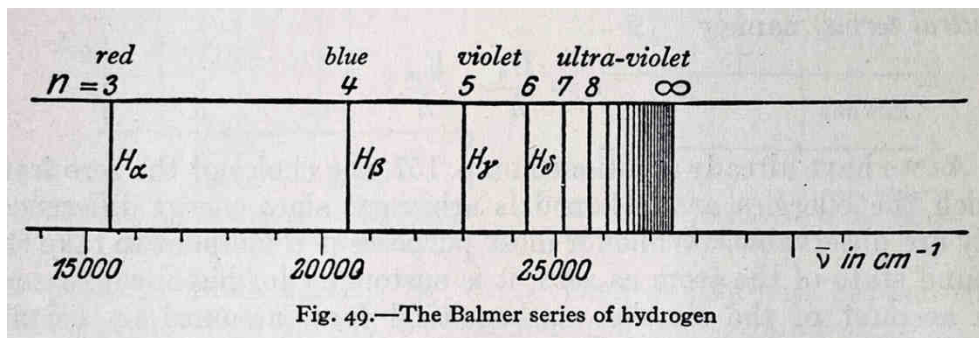


Fig. 49.—The Balmer series of hydrogen

Fig. 20. Part of the hydrogen spectrum [18]

The complete spectrum of hydrogen consists of several sets of lines, which were subsequently denoted by the names of the scientists who investigated them. The German physicist Friedrich Paschen [1865-1947] in 1908, the American physicists and spectroscopists Theodore Lyman [1874-1954] in 1916, Frederick Brackett [1896-1988] in 1922 and August Pfund [1879-1949] in 1924.

In 1888 the Swedish spectroscopist Johannes Rydberg [1854-1919] formulated a general expression, based on the equation above, to include wave numbers of all the series. This subsequently became known as the Rydberg equation.

Although the spectral lines of hydrogen were now shown to fit into an elegant mathematical relationship, their origin remained unexplained. In this respect, a major breakthrough was made by the Danish physicist Neils Bohr [1885-1962] in 1913 who answered some fundamental questions concerning the structure of atoms. Before explaining his contribution and the rationale behind it we should look back at the evolution of ideas concerning atomic structure in the 19th century.

From the publication of Dalton's atomic theory in 1808 until the end of the 19th century, the idea of an atom being indivisible was clearly becoming untenable, due to the existence of ions and to its failure to explain the concepts of chemical affinity and chemical combination. On account of the extremely small size of atoms, evidence for a new model could only be gained from the increasingly sophisticated apparatus, both electrical and optical, which was being developed by physicists. In 1896, the English physicist Joseph John Thomson [1856-1940] experimentally verified the existence of a new type of subatomic particle - the electron. In a revolutionary step, he proposed a new model for the atom, which became known as the plum pudding model. Atoms were spheres of positive charge with tiny negatively charged particles - electrons - distributed within the sphere rather like plums in a plum pudding.

A further improvement to this model was made in 1913 by the New Zealand born nuclear physicist, Edward Rutherford [1871-1937]. On the basis of an experiment which

yielded extraordinary results, he postulated that the entire mass of the atom was to be found in its tiny centre, or nucleus, and that electrons were to be found at the periphery of the atom. The experiment had involved the firing of alpha particles at a very thin sheets of metal foils in order to see how they were deflected. A small number of these bounced back. Rutherford was so surprised that he wrote: "It was almost as incredible as if you fired a 15 inch shell at a piece of tissue paper and it came back and hit you". Although the Rutherfordian model provided a much improved picture of atoms, a significant problem remained. The model failed to explain why negatively charged electrons on the periphery of the atom did not spontaneously spiral into the positively charged very dense nucleus, and continuously emit energy as they do so.

It was at this stage, in conjunction with two more ideas, that Bohr stepped in. The first, proposed in 1865 by the Scottish physicist James Clerk Maxwell [1831-1879], was that light is a form of electromagnetic radiation. The second, made by the German theoretical physicist Max Planck [1858-1947] in 1900, was that at the subatomic level, energy comes in discrete packets, which he called quanta. With this assertion was born a new era in our understanding of matter - the era of quantum mechanics, which today underpins the entire world of information technology.

Bohr accepted two further ideas which had been advanced: a single electron is responsible for each spectral line; quantum laws apply to jumps between different states of an electron. His two distinctly new principles were:

(1) Of the infinite number of orbits of electrons about an atomic nucleus, which are possible according to classical mechanics, only certain discrete orbits actually occur. The orbits correspond to specific energy states. These states are characterized by specific values of angular momentum. In classical mechanics theory, the angular momentum L , of a body of mass m , moving around the periphery of a circle of radius r , with a constant velocity v is given by the expression $L = m \cdot v \cdot r$. According to the Bohr model, in which only certain energy states are possible, the angular momentum is an integral multiple of Planck's constant divided by 2π . This is expressed by the equation:

$$m \cdot v \cdot r = nh/2\pi$$

where: m - mass of electron, v - velocity of electron, h - Planck's constant, r - radius of electron orbit, n is an integer.

The electron is held in the orbit by the electrostatic force that attracts it to the nucleus, which is given in turn by the expression: force = $m \cdot v^2/r$. By using the above expression for a given stationary energy state, and balancing it against the electrostatic force exerted by the nucleus (using Coulomb's law), Bohr was able to calculate the actual radii for "permissible" electron energy states. The first Bohr orbit was calculated to have a radius of 0.05292 nm.

(2) Radiation is emitted or absorbed by a transition of the electron from one quantum state to another - by a quantum jump. The energy difference between the two states is given by the equation:

$$E_1 - E_2 = h \cdot \nu$$

where E_1 and E_2 are the energy states at two different quantum levels, h is Planck's constant, and ν is the frequency corresponding to a given spectral line. When an electron jumps from one energy level to a higher one, it absorbs a quantum of energy, and when the electron goes from a higher energy level to a lower one, it emits the same quantum of energy.

While Bohr's theory was able to explain and predict many phenomena relating to atomic structure it was limited to one type of system: hydrogenic particles i.e. one electron atoms or one electron ions e.g. H, He^+ , Li^{2+} , O^{7+} . Whilst the study of many electron systems introduced a whole new range of issues, the historical role of hydrogen was quite unique.

Figure 21 shows what is superficially recognisable to every school child as a Bohr model of an atom with all its electron shells. It is in fact an ingenious version of the Periodic Table of the elements, which is exceptionally informative.

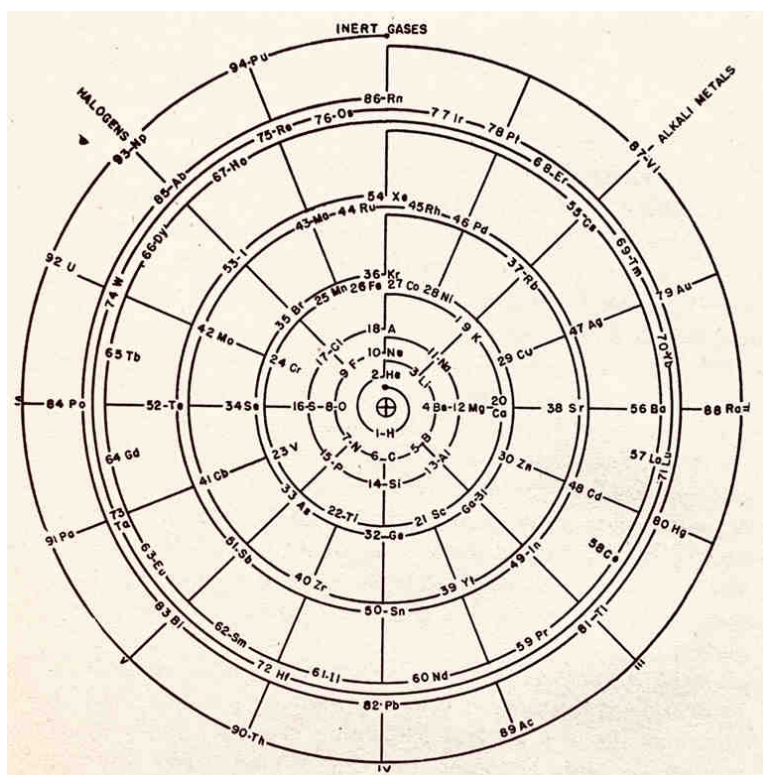


Fig. 21. Periodic chart of the elements [19]

The table is arranged spirally to show:

1. Atomic numbers in consecutive order
2. Theoretical structure of each atom
3. Shell arrangements (periods)
4. The numbers of electrons in the outer shell
5. Oxidation states (Roman numerals)
6. Groups, showing chemical relationships (radial positions)

Hydrogen bonds

Hydrogen bonds are the particularly powerful secondary forces (intermolecular attractions) which exist between certain molecules. They are caused by strong attractions

between lone pairs of electrons on one type of atom in a molecule, and covalently bonded hydrogen atoms in neighbouring molecules. They were first described by the American chemists Wendell Latimer [1893-1955] and Worth Rodebush [1887-1959] in 1920. Water owes many of its extraordinary physical properties to these bonds. These properties include high surface tension, high dielectric constant, in its solid state (ice) it is less dense than liquid water. Furthermore, water has high boiling and melting points compared to molecules of similar relative molecular mass such as methane, CH_4 , which do not have hydrogen bonds. Figure 22 shows the open structure of ice, caused by hydrogen bonds, which are shown with dotted lines.

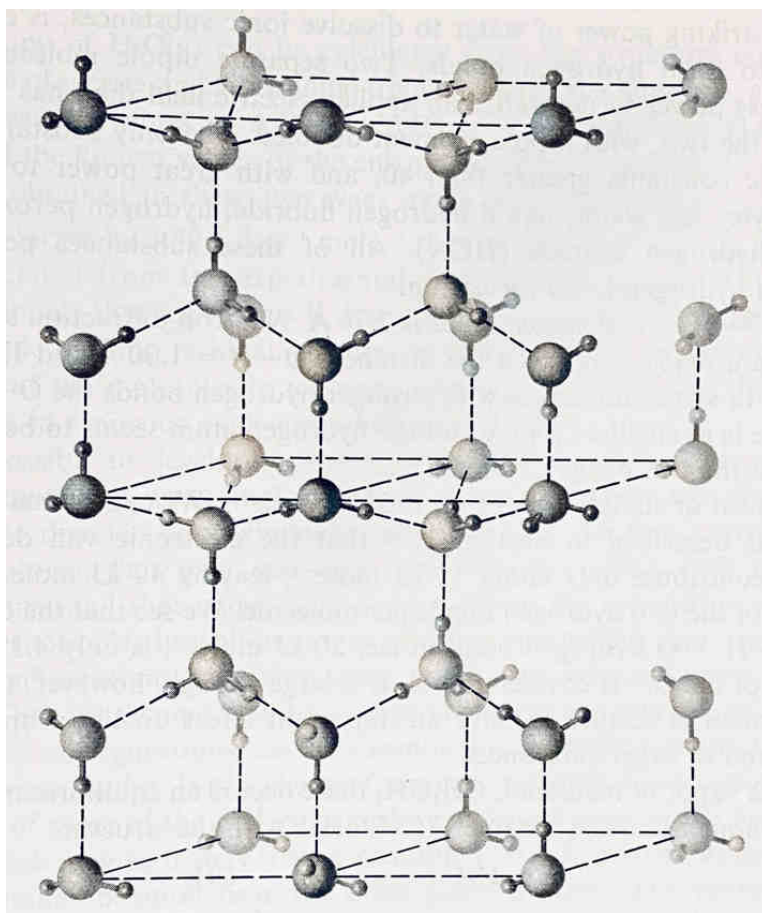


Fig. 22. The structure of ice [20]

Figure 23 shows the result of the high strength of hydrogen bonds in water, which have split a beaker of water. Liquid nitrogen was used to rapidly freeze the water. The same effect, with much more serious consequences, can occur in the cylinder blocks (made of brittle cast iron) in motor car engines, and in lead water pipes in old houses.



Fig. 23. Hydrogen bonding in action

Conclusion

Another important episode from the history of science has been sketched (see also the article on the history of combustion [21]), and some of the scientific achievements of the pantheon of 80 performers in the grand theatre of hydrogen presented. A description of details of their lives, circumstances and personalities has been carefully avoided. The reason is simple: the story behind each of these scientists that is so utterly captivating that it would require another eighty 5000 word essays on each of them, to give a fuller picture of hydrogen and its history. A short paragraph taken from page 250 of a school textbook of physics from 1934, illustrates just one example:

“Joseph Fraunhofer [1787-1826] was born in Bavaria and when quite young was left an orphan. He became apprenticed to a glass manufacturer and spent his nights in searching for knowledge in old books which he borrowed. In 1801 the house in which he lived fell down and killed everyone in it except the boy, who was only released after four hours, badly hurt” [16]. Two further examples of the remarkable lives and achievements of the two English chemists Read and Partington have recently been described in greater detail by the present author [22].

The continued study of hydrogen and the possibilities which it opens, will undoubtedly yield a plethora of beneficial results.

A quote from one of today’s leading textbook authors, Professor Peter Atkins, elegantly summarizes the importance of element ONE:

“An understanding of the structure of the hydrogen atom is central to the understanding of all other atoms, the periodic table, and bonding. All accounts of the structure of molecules are based on the language and concepts it introduces” [23].

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