

The nature and composition of water

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The nature and composition of water has intrigued scientists since the beginning of philosophical and scientific inquiries. From being a religious symbol and one of the primeval elements it had to wait until the end of the eighteenth century to elucidate that water was a compound material.

Keywords: Water, Cavendish, Lavoisier, Dumas, Morley

In spite of water being one of the most abundant substances, present everywhere, and indispensable for life, its nature and composition remained the subject of much discussion and argument until the very end of the eighteenth century.

The importance of water appears in many religious and mythological beliefs. In the Book of Genesis water is already mentioned in the second verse: "And the spirit of the Lord moved upon the face of the waters." The verses that follow describe the creation of the earth by drying part of the water, followed by the appearance of life on earth and water. The Babylonians were well accounted with traditions referring to the Creation; in one their tablets it is written that "There was a time in which there existed nothing but darkness, an abyss of waters, wherein resided most hideous things..." All this was an allegorical description of nature, for the whole universe consisting of moisture, and animals being continuously generated therein..." According to Smith, there is a strong correspondence between the statements in Assyrian inscriptions and in Genesis stating that a watery chaos preceded the creation, and formed, in fact, the origin and groundwork of the universe.¹ An extension of these traditions would later become reflected in Greek mythology where the Ocean is the father of all things.

Of the four elements of the ancients, water is the only one that is a pure chemical substance, although a compound and not an element. It should not be surprising, therefore, that it was the last of the four to be shown not to be elementary. This may well be due

to the fact that water is quite stable thermodynamically, and therefore rather difficult to decompose. In addition, it is so abundant that its formation in many processes would be quite easy to overlook, particularly if it was unforeseen or if other possible sources of moisture were present. As we will see, from the earliest dawn of scientific speculation to the last years of the eighteenth century, the simple, uncompounded, or elementary nature of water was regarded as an unquestionable fact.

Curiosity about the nature of cosmos occupied philosophers since ancient times. In the beginning the question asked was: What is the world made of? Early in Greece certain thinkers, particularly at Miletus, attempted to single out the common identical elements from the various processes in nature and thus arrive at a universal first principle to which all changes in diversity could be referred. This led to the conception of a World-Substance, something fundamental, which persisted throughout all change, which is the beginning of everything and whose transformations give rise to all the phenomena which man observes in the Universe. Both in Egypt and in Babylonia men speculated in the earliest periods on the divinity of water, but it was reserved for the more scientific intellect of the Greeks to recognize in it the possibility of forming a source of all other things. Thales, Anaximander, and Anaximenes recognized, respectively, water, the infinite, and air as the single underlying substance¹. Thales of Miletus (ca. 640-548 BCE), the first Greek philosopher, asserted that a physical element, water or moisture, was the first principle of things (all things come from water). He was probably led to this conclusion by the fact that water exhibits itself naturally to the senses, without

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any apparatus of scientific experiment, in the three forms solid, liquid and gaseous, as ice, water, and steam². According to Thales the primeval matter is water because seeds germinate in dampness and everything on which they nourish themselves is damp; it is water which gives rise to ice and which in the alluvial deposits of rivers consolidate itself into land; it is water which evaporating becomes air; and finally, it is water which comes forth from the earth in the streams and which falls in rain from the skies. And so water is the primeval element from which all other things originate³. Aristotle (348-322 BCE) believed that Thales got his ideas about water from seeing that “the nutriment of all things is moist and that heat itself is generated by the moist and kept alive by it...and that the semen of all creatures has a moist nature, and water is the origin of the nature of moist things.” He had observed, so Aristotle and the later commentators tell us, that the seed of all animals is wet, that even all vegetable life requires moisture, and that the very fire of the sun and stars appears to draw water from the sea.

We see that Thales is the first to have offered a general explanation of matter without invoking the aid of any power outside nature. Thales recognized three forms of “that which exists”, mist, water and earth, and he was of opinion that mist and earth are both forms of water. Adapting an idea found in Egyptian tradition, he taught that the universe is a mass of water in which our world forms a bubble with the earth floating in water at the bottom and the waters above, from which the rain comes, arched over it. The heavenly bodies, which he supposed to be watery exhalations in an incandescent state, float across the waters above just as the earth floats on the waters below, and the sun, moon, and stars, when they set do not pass under the earth but float round it out of sight until they come to their appointed places on the eastern horizon.

Being interested in physics, Thales was aware that the gaseous and solid water were so different from the surrounding liquid state that it was almost impossible to guess their origin without experience of the transformation. There was no need to strain the philosopher’s credulity or stretch his imagination to go one additional step and infer a further alteration of water into the multiple and diverse kinds of solid bodies and all the various degrees of vapour from the thick clouds verging on liquid rain, or solid hail and snow, to the thin bright blue of the sky, or even the

collected and focused luminousness of the sun and moon and stars. Thales regarded his World-Substance not as something in itself inert and in need of an outside force to move and direct it, but as something in which movement and life was always and naturally inherent.

Anaximander (ca. 610-ca. 545 BCE), a pupil of Thales, did not agree with his master that everything was originally water, since water does not generate fire, but destroys it. Apparently he found water too specific, too linked to its nature and ways, in a word, too essentially watery, to be transformed without dissent in fact and imagination into all the countless things, which water so manifestly is not. To him the substance of which all things are made must be something more versatile, more adaptable, more capable of throwing itself into its innumerable and absolutely roles and parts. However, Anaximander, refused to specify the nature of the World-Substance.

Anaximenes (ca. 545 BCE), a pupil of Anaximander, did not agree with either Thales or his master. He thought that the World-Substance was vapour or air. The process by which our world arose from the original World-Substance was one of condensation and rarefaction. When air is dilated and becomes rarefied, it becomes fire; while winds, on the other hand, is condensed air. Cloud is formed from air by compression and this, still further condensed, becomes water. Water condensed still more, turns to earth, and when condensed as much as it can be, to stones. Anaximenes arrived at the conclusion that air is the one, movable, infinite, first principle of all things. For he speaks as follows: “Air is the nearest to an immaterial thing; for since we are generated in the flow of air, it is necessary that it should be infinite and abundant, because it is never exhausted. Air is infinite in quantity but is defined by its qualities, and all things are generated by a certain condensation or rarefaction of it. And by compression of the air the earth was formed, and it is very broad; accordingly he says that this rests on air, and that the sun and the moon and the rest of the stars were formed from earth.”

Later philosophers started to move from a single primeval substance into more, primeval matter was now not unitary, it had different components and these were such that all known matter resulted from their mixing together in various proportions. Heraclitus of Ephesus (ca. 500 BCE) would add fire because he considered it to play a similar, though not

entirely equal role as water and air. Empedocles of Agrigento (490-430 BCE) claimed that four substances formed the root of everything: fire, air, earth, and water: "for these always remain and do not come to, except that they come to be more or fewer, being aggregated into one and segregated out of one." These four elements underlined all the various quantities found in the sensory world. The qualities were compounded of these elements, but the elements themselves were not subject to change or disintegration. The four elements combined and separated, and it was these combinations and separations that constituted the processes of the physical world. How Empedocles decided upon four substances, and these particular four, has been much discussed and never settled. He also distinguished them with the mythological titles Hera (Earth), Zeus (Water), Nestis (Air) and Aidoneus (Fire)⁴.

Empedocles' theory of matter remained the dominant one until the revival of atomism by Pierre Gassendi (1592-1655) and Robert Boyle (1627-1691) in the seventeenth century.

The complete equality of the four elements was for long an accepted fact. Plato (427-348 BCE) and Aristotle adopted it, although both philosophers postulated sub-elemental particles and allowed for transmutation. Then the obvious effect of thermal processes, combined with early theories about the power of fire, gradually gave a position of pre-eminence to this element. Next, air was added as a second active element on account of its elasticity and its closeness to the hot element. Hence, in the post-Aristotelian period we find the elements divided into active (fire and air), and passive (water and earth).

Aristotle adopted from Empedocles and Plato that all things in the sub-lunar world are constituted from four basic elements, earth, air, water, and fire, but he also maintained that heavenly bodies consist of quite a different substance, a fifth element, *aether*. He needed this argument to account for the eternal, unvarying, circular movements of the heavenly bodies. The natural movement of the four terrestrial elements is either up-wards or downwards, from or to the centre of the earth; fire and air naturally rise, water and earth naturally fall, when nothing impedes their movement. They can, of course, be moved in other directions as well, but such movement is not natural, but enforced. But the circular movement of the heavenly bodies, being eternal, cannot be enforced. An object that moves naturally in a circle

cannot hence be one of the terrestrial elements or a compound of them. So there must be something, a fifth element, which moves naturally and continuously in a circle. Bodies that fell naturally toward the earth's centre did so because their predominant element was heavy; those that rose naturally upward had a predominantly light element. Earth was considered to be absolutely heavy because it would fall toward the earth centre whenever it was above the natural place of earth, whether this was in water, air, or the fiery region above air. Fire was conceived as absolutely light, definitely weightless, and, if unhindered, would always rise from the regions below toward its natural place above air and below the lunar sphere. Water and air were intermediate elements possessing only relative heaviness and lightness. When below its natural place somewhere within the earth, water would naturally rise; but when above its natural place, in air or fire, it would fall⁴.

The Romans simply followed the ideas developed by the Greeks. According to Pliny⁵: "As regards the elements also I observe that they are accepted as being four in number; topmost the element of fire, source of yonder eyes of all those blazing stars; next the vapour which the Greeks and our own nation call by the same name, air, this is the principle of life, and penetrates all the universe and is intertwined with the whole; suspended by its force in the centre of space is posed the earth, and with it the fourth element, that of the waters. Thus the mutual embrace of the unlike results in an interlacing, the light substances being prevented by the heavy ones from flying up, while on the contrary the heavy substances are held from crashing down by the upward tendency of the light ones".

The theory of primeval elements not only lasted well into the seventeenth century; it was supported in one way or another by some of the most famous scientists of the time. Obviously, this support included ignorance about the real nature of water. Isaac Newton (1642-1727), for example, believed that water could be changed into earth and that water vapours were closely related to air: "I know no Body less apt to shine than Water; and yet Water by frequent distillation changes into fixed Earth, as Mr. Boyle has tried...Nature seems delighted with Transmutations. Water, which is a very fluid tasteless Salt, she changes by Heat into Vapour, which is a sort of Air^{6a}." Newton admitted, the same as Boyle and

Gottfried Wilhelm Leibnitz (1646-1716), that rock crystal was simple crystallised water. According to Newton the transformation of water into quartz was due to the action of cold, the same as Diodoro Siculo (ca. 80-20 BCE) had explained it by the action of celestial fire. Georgius Agricola (1494-1555) had already criticized the theory in the sixteenth century, but Boyle and Andreas Sigmund Marggraff (1709-1782) still held to it until Antoine-Laurent Lavoisier (1743-1794) showed all the theories that claimed that pure water subjected to distillation, became earth were wrong. Interestingly enough, in the beginning of his career Lavoisier believed that water could not be decomposed and Pierre-Joseph Macquer (1718-1784) considered it to be an immutable and indestructible body.

The nature and composition of water could not be well understood until the nature of gases was understood and thus it is of interest to describe, in particular, the ideas of two distinguished scientists, Johannes Baptiste van Helmont (1579-1644) and Guillaume François Rouelle (1703-1770), who lived at the time when the stage was being set for the discoveries that would answer the riddle.

Van Helmont first used the name gas, and described carbon dioxide under the name of *gas sylvestre*: "Huc, spiritum, incognitum hactenus, novo nomine Gas voco, qui nec vasis cogi, nec in corpus visibile reduci, nisi extincto prius semine, potest" (I call this Spirit, unknown hitherto, by the new name of Gas, which can be neither constrained by vessels nor reduced into a visible form, without the seed being first extinguished⁷). According to van Helmont, a gas was composed of invisible particles, which could come together by intense cold and condense to minute drops⁸.

Van Helmont's views on primeval constituents are important. He rejected the theory of the four elements and three principles as taught by Paracelsus (1493-1541), and the "heathen" theory of a primary matter of Aristotle. As a result, he reduced the number of elements from four to two, air and water, with stress on the latter. He discarded fire and earth as elements since fire was not a form of matter and disappeared without leaving a trace and earth could be formed from water. In addition, neither of the two primary elements was convertible into the other nor an element could be reduced to a simpler state⁸. Most of his arguments against the basic elements were a

result of his deep religious ideas, he felt bound to reject the teachings of pagan philosophers.

Van Helmont's most famous experiment, named *Tree Experiment*, was as follows⁷: He planted a shoot of young willow tree in a weighed quantity of earth and watered it with rain for five years. Afterwards he compared the weights of the tree and the earth before and after and found that the shoot had increased in weight while the weight of the earth was unchanged. Since he had fed it nothing but water, the difference was due to water alone. The Book of Genesis taught him that water had played a vital role in the Creation, whence he concluded that water must be the material principle of all things, particularly since his willow experiment had shown him that water could transform itself into wood and hence into fire and ashes. At his time, of course, there was no knowledge about the part played by gases in assimilation, or about photosynthesis.

Van Helmont also believed that, with the help of a "seminal spirit" water could turn into metals. That spirit was not van Helmont's own invention, but had been used by the ancient chemists and especially by Paracelsus, who had attributed the natural evolution of metals to it. In spite of strong negative feelings, Helmont occasionally made use of the three principles of Paracelsus, as when he said that water contained salt, sulphur, and mercury, but it was only to meet the "weakness of our understanding⁷." The three principles were not bodies actually nor they were separated unchanged by fire, mercury was a simple actually existing body and not a constituent of things.

Rouelle is probably the most famous French teacher of chemistry of the second half of the eighteenth century. At one time or another almost all the French eminent names of the second half of the eighteenth century in science, philosophy, and letters studied chemistry with him, the most important being Pierre-Simon Lavoisier (1743-1794). His chemistry notes⁹ became very famous and popular and were translated into many languages. The entry about water is very enlightening because it gives an excellent picture of the ideas prevalent at his time. According to Rouelle "There is almost nothing more difficult to know than water, it is everywhere, it permeates all bodies and can be separated from them only with difficulty. In its normal state of aggregation it is a fluid body, odourless, insipid, transparent, colourless, and at a certain degree of cold it becomes hard and looks like glass. Water contains fire; the movement of

this principle makes water fluid because when this movement decreases to a certain point, water becomes ice. But ice still contains fire because it transmits light and evaporates. Fluidity enters by accident into water because solidity seems to be its natural state. Its primitive molecules, if could be seen, appear under the form of an earth and it is this earth that allows them to enter in combination with concrete bodies. Fluidity is only a phenomenon of aggregation.”

“Water contains a large amount of air intimately mixed with its parts and deprived of its elasticity. Water is not elastic by itself and not because of the air it contains. Its parts are more subtle than those of air, they are immutable; they rarefy and separate one from the other by the action of heat. The last state of dilation of water is boiling...as much as water is dilatable it is not compressible. It is important to distinguish between the expansibility of water and the elasticity of air. The latter assumes a perfect aggregation while the former is accompanied by a destruction of this aggregation. The molecules of water separate as the molecules of fire do. In this state the molecules have the appearance of air, particularly when they move inside a fluid. They appear as bubbles. Water can expand only when it is in contact with air. If the joints of a distillation flask are well sealed, it is impossible to distil it. Isn't it necessary that in order to ascend that it has to dissolve in air, which will in this case serve as vehicle?¹⁰

Ice floats in water because the molecules of air in it want to disengage but cannot escape; freezing begins on the surface, the molecules of air agglomerate in the centre where they recover their elasticity and become the bubbles that increase the volume of the ice and make it lighter than water. This result has been confirmed by the experiments of Hombert who has frozen water completely purged of air and shown that it sinks in water¹⁰.”

In the following statements Rouelle talked about the solvent power of water, its presence in certain bodies like acids and oils, to which it communicated their fluidity; its role in crystallization, and its participation in the formation of animals and vegetables, in which “this water is but an instrument that is not part of this mixture of entities since one can take it out without perturbing the mixture¹⁰.”

Rouelle is considered to be the one who introduced the phlogiston theory in France, Lavoisier, his most famous student, is credited with putting this

theory to rest, and in doing so he also demonstrated that water was a compound.

Lavoisier, in his book *Elements of Chemistry*¹¹ described the development of knowledge about the nature and composition of water in the following words: “It will, no doubt, be a matter of surprise, that in a treatise upon the elements of chemistry there should be no chapter on the constituent and elementary parts of matter; but I shall take occasion, in this place, to remark that the fondness for reducing all the bodies in nature to three or four elements proceeds from a prejudice which has descended to us from the Greeks. The notion of four elements, which by the varieties of their proportions compose all known substances in nature, is a mere hypothesis assumed long before the first principles of experimental philosophy or of chemistry had any existence. In those days, without possessing facts, they framed systems, while we, who have collected facts, seem determined to reject them when they do not agree with our prejudices. The authority of these fathers of human philosophy still carries great weight and there is reason to fear that it will even bear hard upon generations yet to come.

It is very remarkable that, notwithstanding the number of philosophical chemists who have supported the doctrine of the four elements, there is not one who has not been led by the evidence of facts to admit a greater number of elements into their theory. The first chemists that wrote after the revival of letters considered sulphur and salt elementary substances watering into the composition of a great number of substances; hence, instead of four, they admitted the existence of six elements. Joachim Becher (1635-1682) assumed the existence of three kinds of earth, from the combination of which, in different proportions, he supposed all the varieties of metallic substances to be produced. George Ernst Stahl (1660-1734) gave a new modification to this system; and succeeding chemists took the liberty to make or imagine changes and additions of a similar nature...All that can be said upon the number and nature of elements is, in my opinion, confined to discussions entirely of a metaphysical nature. The subject only furnishes us with indefinite problems, which may be solved in a thousand different ways, no one of which, in all probability, is consistent with nature. I shall therefore only add upon this subject that if by the term *elements* we mean to express those simple and indivisible atoms of which matter is

composed, it is extremely probable we know nothing at all about them; but if we apply the term *elements*, or *principles of bodies*, to express our idea of the last point which analysis is capable of reaching, we must admit, as elements all the substances into which we are capable, by any means to reduce bodies by decomposition. Not that we are entitled to affirm that these substances we consider as simple may not be compounded of two, or even a greater number of principles; but since these principles cannot be separated, or rather since we have no hitherto discovered the means of separating them, they act with regard to us as simple substances, and we ought never to suppose them compounded until experiment and observation has proved them to be so¹¹.”

In a very short time air was shown to be of two other airs or gases. Then, water was shown also to contain two other airs, one identical with the constituent of common air, the other different.

Solving the riddle

Newton had some mixed ideas about water; we have mentioned already that in his book *Optiks*^{6a} he first assumed that liquid water was a very fluid tasteless salt, water vapour was some kind of air and that quartz was solid water. Further on the book, he used the optical properties of water to infer that water was a compound postulated that water, which were unlike each other, one of them (or one class of them) inflammable. Thus, conclusion is often referred to as if Newton had predicted in so many words, that water would be found to consist of two gases, one of them inflammable. His own words, however, do not guarantee any such conjecture. In the course of his investigations on the refractive indexes of various bodies, Newton noticed that while transparent, non inflammable substances refracted light more powerfully the denser they were, there was an exception in favour of combustibles, such as camphor, the oils, turpentine, etc., whose refractive indexes were much air than their density could account for: “Water has a refractive power in a middle degree between those two sorts of substance, which consist as well of sulphurous fat, and inflammable parts as of earthy, lean, and alkalizate one^{6b}.” It is impossible to understand from such a general statement what Newton’s precise opinion really believed about the nature of water, and though we may look back at it as a prediction that one of the constituents of that liquid would prove to be inflammable¹².

The beginning of the events, which led to the discovery of the composition of water may be considered the observation made by several chemists during the second half of the eighteenth century that the burning of inflammable air (or inflammable gas, today hydrogen) deposited dew on the walls of the vessel. Thus, in 1766 Macquer while studying the possibility that a flame of inflammable gas evolved smoke or soot, observed that whenever a glass vessel was held over the burning jet, moisture formed inside the vessel, which he assumed to be water¹³. In the same year, and independently of Macquer, John Warltire performed some experiments to determine whether heat has weight or not¹⁴. To do so he used an electric spark to fire a mixture of inflammable gas and air in a closed copper vessel (to avoid the risk of injury from explosions) holding about three pints. He weighted the vessel before and after the explosion and to his surprise he found that a loss of weight of about two grains always occurred, although the vessel was hermetically closed so that no air could escape by the explosion. He repeated his experiments under a bell jar made of glass and again he found the same loss in weight but now he also noticed that the inside of the glass, though clean and dry before, rapidly became dewy. In his words: “immediately after the flame is extinguished there appeared through almost the whole of the receiver a fine powdery substance like a whitish cloud, and the air in the glass is left perfectly noxious.” Warltire believed that the gases contained some water diffused through them, and that that this, being condensed, appeared in drops on the sides of the containing vessel. He paid little attention to this result because, as mentioned before, he was interested in demonstrating the ponderability of heat. To Joseph Priestley (1733-1804), these results confirmed his opinion that common air deposits its moisture by phlogistication¹⁴.

Shortly thereafter Priestley made some astonishing claims regarding the properties of water. On December 8, 1782, he wrote to James Watt (1736-1819) that he could “readily convert water into permanent air by first combining it with quicklime and then exposing it to a red heat”, and on the same day he reported his discovery to Josiah Wedgwood (1730-1795), adding that the air was “little worse than that of the atmosphere”, though it contained a small proportion of fixed air (carbon dioxide)¹⁵. Richard Kirwan (1733-1812), another famous British scientist, was extremely sceptical about this result and

expressed his opinion very bluntly in a letter to Torbern Olof Bergman (1735-1784) on January 20, 1783: "Doctor Priestley believes he has changed water into air. I believe none of it"¹⁶. To confirm his suspicions Kirwan wrote to the French chemist Louis-Bernard Guyton de Morveau (1737-1816) describing Priestley's claims and requesting his help in repeating the experiments and confronting the results. Guyton answered accepting the request and remarking cautiously that Priestley's results departed far from generally accepted ideas and that it would be necessary to be very careful before admitting them to be true. Only experiment could provide the proper answer¹⁷.

In a first series of experiments Guyton confirmed that large amounts of air were produced when water combined with quicklime was heated to redness in an earthenware retort. From two ounces of quicklime and one ounce of water he collected 252.67 in³ of water, 14.67 in³ of which was fixed air (accidentally present in the lime) and the remainder was very similar to common air. Guyton also agreed with Priestley that there was no evolution of air when an ordinary glass retort was used. Priestley had also found that air was produced in a glass retort that had lost its polish. To prepare such a glass Guyton heated a mixture of fluorspar and sulphuric acid in the retort. From four ounces of lime and two of water he obtained only 51.25 in³ of air, less than the volume of the retort and attributable to thermal expansion. The last result contradicted Priestley's and gave Guyton the clue to what was happening: atmospheric air was penetrating the equipment. He now repeated his experiments this time using an ordinary retort completely coated with an opaque and heat resistant clay covered with powdered glass and borax. This time he obtained an amount of air which was smaller than the volume of the retort, however strongly he heated it. In other words, whenever Priestley found a large volume of air, it had entered from the outside the retort; earthenware was always porous and Priestley's roughened glass must have been treated mechanically, not chemically, with an abrasive that formed minute cracks, which, although invisible, were large enough to let air pass through the pores or cracks whenever the retort ceased to be filled with a fluid capable of resisting it¹⁷. Guyton reported his findings to Kirwan and his conclusion that Priestley's results were due to faulty experimentation and not to a deviation from known chemical principles.

Eventually, Priestley repeated his experiments and confirmed that the air he had found previously had entered the retort through pores in the earthenware and was not a result of the decomposition of water¹⁸.

The formation of dew reported by Warltire was neglected as an irrelevant effect by all except Cavendish, who thought that perhaps the dew was what was left behind as phlogiston was released from inflammable air. Cavendish's own statement is, that it was the appearance of moisture casually observed by Priestley and Warltire, which seemed to him "likely to throw great light on the subject he had in view", and, accordingly, "he thought it well worth examining more closely." He also believed that "if there was no mistake in the alleged weight loss it would be very extraordinary and curious." Consequently, he designed his experiments to follow as close as possible those of Warltire and accordingly test the possible loss of weight during the explosion of inflammable gas, as well as Priestley's statement that the detonation was followed by a deposition of moisture. The only difference was the use of a larger vessel to ensure that the weight loss was not caused by errors in weighing. His results contradicted those of Warltire: "The experiment did not succeed with me; for though the vessel I used held more than Mr. Warltire's, namely 24,000 grains of water (1 lb = 7000 grains), and though the experiment was repeated several times with different proportions of common and inflammable air, I could never perceive a loss of weight of more than one-fifth of grain, and commonly none at all...In all the experiments the inside of the glass globe became dewy, as observed by Mr. Warltire." Cavendish analysed his results and concluded that "423 measures of inflammable air are nearly sufficient to completely phlogisticate 1000 of common air; and that the bulk of the air remaining after the explosion is then very little more than four-fifths of the common air employed, so that we can safely conclude that when they are mixed in this proportion and exploded, almost all of the inflammable air and about one-fifth of the common air lose their elasticity, and are condensed into the dew which lines the glass"¹⁹.

Additional experiments to identify the nature of the liquid phase led Cavendish to conclude: "by this experiments with the globe it appears that this dew is plain water, and consequently that almost all the inflammable air, and about one-fifth of the common

air are turned into pure water.” The air has disappeared in the ratio two to one (at that time the term *airs* was applied to any substance present as a gas)^{20,21}. An additional observation was, that, in some of the experiments the resulting liquor had an acid taste and contained nitric acids, a phenomenon that Cavendish showed to result from the oxidation of the nitrogen of atmospheric air, not entirely removed by the air pump when the globe was exhausted. If excess of oxygen were used, the liquid was acid, but if this gas was in a proportion as exactly, or nearly exactly, to oxidise all the hydrogen, then “the condensed liquor is not at all acid, but seems pure water, without any addition whatever; and as when they are mixed in that proportion, very little air remains after the explosion, almost the whole being condensed, it follows that almost the whole of the inflammable and dephlogisticated air is converted into pure water.” Cavendish’s most comprehensive conclusion is summed up in the following sentence: I think we must allow that dephlogisticated air is in reality nothing but dephlogisticated water, or water deprived of its phlogiston; or in other words, that water consists of dephlogisticated air united to phlogiston; and that inflammable air is either pure phlogiston, as Dr. Priestley and Mr. Kirwan suppose, or else water united to phlogiston; since according to this supposition these two substances united together to form pure water²⁰.”

Shortly after Cavendish made public his findings about the burning of inflammable air and the formation of water, Watt²² came forward with the claim that he had announced the same result on a previous date, and afterwards, Lavoisier declared that he had discovered the compound nature of water before, and independently of either²³. A controversy accordingly arose in which Cavendish and Watt disputed with each other the priority of the discovery while at the same time they rejected Lavoisier’s arguments regarding the identification of the composition of water. This dispute, to be called later *the water controversy*, not only was settled during the lifetime of the claimants, every so often it continues to flare again in the literature^{24,25}.

This “paternity” controversy caused a series of fortuitous events. Cavendish reported his findings to Priestley, who repeated the experiments and reported them to Watt. In a letter written to Joseph Black (1728-1799) in June 1788, Watt refers to some experiments of Priestley in which the dephlogisticated

and inflammable airs were exploded in a copper vessel, producing water, which always contained nitric acid: “It appears, however, that more than 9 tenths of the liquor thus produced is water, which probably in its own form constitutes the greater part of the mass of all sorts of air. I think it highly probable that the acid proceeds from the inflammable air, and the dephlogisticated air acts the same part that it does on the burning of sulphur and phosphorus.” It is clear that Watt regarded water as constituting “the greater part of the mass of all sorts of air” and it seems that he regarded it as pre-existing in the two gases⁸. In May or June of 1783, nearly a year before the publication of Cavendish’s paper, but two years after he began his experiments, Charles Blagden (1748-1820) visited Paris and told Lavoisier of Cavendish’s discovery. This information, together with the one reported by Watt, led Lavoisier to the correct explanation of both sets of experimental evidence. Lavoisier had been searching for the acid, which he thought must be formed by the union of hydrogen and oxygen, the “principle of acidity.” On June 24, he and Blagden repeated Cavendish’s experiment of burning hydrogen and oxygen and producing water, and the next day Lavoisier sent a memoir on the subject to the Académie des Sciences. With this explanation he had the key for the difference between the reaction of a metal or its calx with an acid, by admitting that water participated in the reaction. In the first reaction, water decomposed and released its inflammable gas and dephlogisticated air (oxygen). The latter combined with the metal to yield the metallic calx (the term ‘oxide’ had not been defined yet). The second reaction was simply the combination of the acid with the calx to give the pertinent salt.

In spite of Lavoisier’s claim to the discovery, it is clear that Cavendish had anticipated him in the experiments, of whose work he was fully apprised by Blagden⁸.

As noted by Wilson¹² although the original claims were founded on similar experiments, Cavendish, Watt, and Lavoisier arrived at their conclusions while performing them for different purposes. Cavendish was investigating the products of combustion; Watt was studying the changes that a vapour may undergo, if all its latent heat became sensible; and Lavoisier was seeking in the combustion of inflammable gases for additional proofs of the truth of his view that oxygen is the great acidifying agent.

Lavoisier's hypothesis about the composition of water was further demonstrated by its decomposition²⁷. The experiments were witnessed and controlled by a commission appointed by the Académie des Sciences, which included, among others, Claude-Louis Berthollet (1748-1822) and Gaspard Monge (1746-1818). Water was contacted with hot iron filings, which rusted giving off inflammable air. The weight of the inflammable air plus the weight gain of the rusted filings was shown to be equal to the weight of the water consumed. The commission's report included the following statements: "One of the parts of the modern doctrine the most solidly established, is the formation, decomposition, and recomposition of water. And how can we doubt it, when we see that in burning together fifteen grains of inflammable air and eighty-five of vital air, we obtain exactly one hundred grains of water, in which, by decomposition, we find again the same principles and in the same proportions. If we doubt of a truth established by experiments so simple and palpable, there would be nothing certain in natural philosophy."

According to Lavoisier, the results show that "100 grains of water have been decomposed; 85 grams of oxygen have united with the iron to constitute it in the state of black oxide, and there are disengaged 16 (a mistake for 15) grains of a peculiar inflammable gas, thus water is composed of oxygen and of the base of the an inflammable gas, in the proportion of 85 parts to 15. Thus water, independently of the oxygen, which is one of its principles, and which is common to many other substances, contains another which is peculiar to it, and for which we have been compelled to find a name. Nothing seems better than hydrogen, that is to say, "generative principle of water", from *νδωρ*, water, and *γεινομαι*, I produce. We call it hydrogen gas the compound of this principle with caloric, and the word hydrogen alone expresses the base of this same gas, the radical of water^{23,24}."

Lavoisier's interpretation was accepted gradually but it was, however, powerless to convince Priestley, who remained faithful to the phlogiston theory until his death. The phlogiston theory was now on its way out to be replaced by Lavoisier's new chemistry.

All these results led to intensive research on the composition of water. In the winter of 1804-1805 Gay-Lussac collaborated with Alexander von Humboldt (1769-1859) in researching the use of hydrogen as a way of estimating oxygen²³. This

method had not been universally appreciated but Gay-Lussac and Humboldt by careful quantitative work were able to show that when properly used, it was capable of considerable precision. One reason for Gay-Lussac for championing volumes as opposed to weights was that he had come to consider it a method of greater intrinsic accuracy. In his research with Humboldt, Gay-Lussac claimed that the relative volumes (but not the relative weights) of hydrogen and oxygen, which combined to form water, were independent of water vapour present. Greater precision was therefore possible, if one dealt with volumes rather than weights. The Gay-Lussac-Humboldt, experiment consisted in exploding measured volumes of air with hydrogen. The mean result of twelve experiments gave them than 100 parts oxygen, supposedly pure, required 98.7 of hydrogen. By putting the oxygen gas over potassium sulphide, as used by Carl Wilhelm Scheele (1742-1786) for absorbing oxygen from air, they found that it was absorbed to 0.004. From this result, they came to the conclusion that 100 parts of oxygen required for saturation of 200 parts of hydrogen.

In 1783, Monge investigated the nature of the product yielded by the combustion of inflammable air and oxygen²⁹. The inflammable gas was prepared by dissolving clean iron filings in diluted sulphuric acid and the oxygen by heating red oxide of mercury, and taking many precautions to secure the purity of both gases from admixture with atmospheric air. Monge transferred portions of each gas into the detonation globe (one twelfth of oxygen and eleven of inflammable gas) and after explosion he added another twelfth of oxygen, followed by a second sparking, and so on. The total amount of water produced by the combustion of the gases was determined by weighing the globe, first with the liquid it contained and then after it had been emptied and dried. The liquid collected was perfectly transparent and faintly acid, as shown by a slight reddening of blue turnsole paper. Monge attributed this acidity to the sulphuric acid that was carried over by hydrogen from the solution of iron that yielded it. His main conclusion was: "It follows from this experiment that when inflammable gas and dephlogisticated gas, both considered pure are exploded, there is no other result than pure water, the matter of heat and that of light."

Berzelius and Dulong were the first to determine the composition of water by weight with tolerable

accuracy³⁰. They passed a stream of hydrogen over a weighed amount of copper oxide, absorbed the water produced in drying tubes and weighed it, and deduced the weight of oxygen used from the loss in weight of the tube, which had contained the copper oxide when the latter was reduced to metallic copper. In 1842, Jean-Baptiste André Dumas (1800-1884) repeated this experiment more carefully and showed that “water formed by weight of 1000 parts of hydrogen to 8000 of oxygen, that is to say, that these bodies combine in the simple ratio of 1 to 8.” This was in accordance with the hypothesis of Joseph-Louis Proust (1754-1826) that the combining weights of the elements were simple multiples of that of hydrogen. “Whatever it may be, the atomic weight of hydrogen can hardly be below 12.50 when oxygen is represented by 100. My experiments place it between 12.50 and 12.56⁷.”

By the end of the nineteenth century Alexander Morley performed one of the most comprehensive researches on the properties of oxygen and hydrogen, as well as on the synthesis of water from weighed quantities⁸. The first two parts of the work deal with an exhaustive series of measurements of the densities of highly pure oxygen and hydrogen, which were weighed in large glass globes, and led to values 1.42900 ± 0.000034 g/L for oxygen and 0.089873 ± 0.0000027 g/L for hydrogen. The third part of the work deals with the volumetric composition of water. In these experiments Morley used a Bunsen eudiometer, a graduated glass tube, with platinum wires above in the sealed end for exploding the gas contained in it. The ratio of the volumes of hydrogen and oxygen combining was found to be 2.00269. In the fourth part of the memoir, Morley described the synthesis of water from weighed quantities of hydrogen and oxygen. The hydrogen was weighed adsorbed in palladium and the oxygen in a large globe. Both were combined in a special apparatus and the water formed also weighed. Twelve experiments were performed in which the ratio 2 (oxygen/hydrogen) varied from 15.8787 to 15.882, and the ratio of water/hydrogen varied from 17.877 to 17.883. The atomic weight of oxygen compared with that of hydrogen as unity is thus very nearly 15.897, or in other words, one gram of hydrogen combined with half this quantity of oxygen to form water⁸.

Partington closes his monograph about the water controversy with a timetable of the main events that led from the ancient concept of water being a

primeval element, to the determination of its composition⁸:

- (i) Thales of Miletus (600 BCE) assumed water to be the constituent of all things. Later Greek philosophers added fire, earth, and air to the primeval elements.
- (ii) In 1648 van Helmont reported his Tree Experiment, which he considered demonstrated Thales' hypothesis.
- (iii) Around the seventeenth century Boyle described the preparation and combustibility of inflammable air (hydrogen).
- (iv) Between 1766 and 1785 Cavendish published his three memoirs describing his Experiments of Factitious Air, which he reported his experiments with inflammable gas, carbonic acid (CO₂), and the gases evolved during fermentation and putrefaction. He established that the combustion of inflammable gas with air or oxygen led to the production of water, and that the water formed is acid. His results indicated that water was formed by one volume of oxygen and 2.02 volumes of hydrogen.
- (v) In 1784 Lavoisier gave for the first time the correct composition of water. He proved his hypothesis by realizing the synthesis and analysis of water.
- (vi) In 1805 Gay-Lussac and Humboldt found that almost two volumes of hydrogen combined with one volume of oxygen to form water.
- (vii) In 1842 Dumas determined the composition of water by weight and found that two parts (by weight) of hydrogen combined with 15.96 parts of oxygen. Later experiments changed the ratio to 2 to 15.88.
- (viii) In 1895 Morley obtained the composition of water by weight, as 2 parts of hydrogen to 15.879 of oxygen.

And thus the saga came to its end. After much water went from heaven to earth and back, its nature and composition were unravelled and water moved from the privileged status of primeval element to that of all chemical compounds.

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